as determined by infrared spectroscopy.

X-ray Data Collection and Structure Determination.
Yellow-orange platelike crystals of ferrocenesulfonyl azide,[4] mp
42–43 °C, were obtained from petroleum ether (bp 30–60 °C).
Weissenberg, oscillation and precision photographs showed the
crystals to be monoclinic. Space group $P2_1/n$ was indicated by
the systematic absence of reflections $0k0$ with k odd and $h0l$ with
$h + l$ odd. An appropriate single crystal was mounted on a glass
fiber, with the c axis of the crystal slightly inclined to the fiber
axis. Final lattice parameters as determined from 12 high-angle
reflections carefully centered on an Enral-Nonius CAD-4 are as
follows: mol wt 291.12; $D_{calcd} = 1.699$ g cm^{-3}; space group $P2_1/n$;
molecules/unit cell, 8; Mo Kα radiation ($\lambda = 0.71069$ Å); cell
constants $a = 5.993$ (4) Å, $b = 35.185$ (6) Å, $c = 10.797$ (6) Å, p
$= 92.28$ Å^3; cell volume = 2274.9 Å^3. Intensity data were recorded
on the diffractometer in the usual manner.[12] All reflections in
one independent quadrant out to $2\theta = 18°$ were measured. Two
reference reflections (the 010 and the 104) were monitored every
25 reflections. Severe loss in intensity of the reference reflections
(20%) occurred during the course of data collection. The intensity
of each reference reflection was linear with respect to time, and
the intensity data were corrected for decomposition, Lorentz, and
polarization effects, but not for absorption. The MULTAN-74
system of programs was used to locate the two pairs of iron and
sulfur atoms in the asymmetric unit. Difference Fourier maps
phased on the positions of these atoms revealed the location of
the remaining non-hydrogen atoms. The atomic coordinates and
isotropic thermal parameters were refined by full-matrix least
squares using the SHELX (2) system of programs. The hydrogen
atoms were placed at calculated positions 1.00 Å from the bonded
carbon atom. The hydrogen atoms were given fixed isotropic
thermal parameters of the carbon atom to which it was bonded.
In the final stages of refinement the cyclopentadienyl rings were
restrained to ideal geometry and refined as rigid groups using the
SHELX system. The final reliability index ($R = \sum(|F_o| - |F_c|)/|F_o|$)
is 0.078.

Supplementary Material Available: Tables IV (intramo-
lecular distances and angles for FSA) and V (fractional coordinates
and isothermal parameters for FSA) and a drawing (Figure 3) of
the unit cell (5 pages). Ordering information is given on any
current masthead page.

Preparation of Isobenzofuran–Aryne Cycloadducts

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A one-pot procedure is described for carrying out the sequence 1,4-elimination of acetal 1 to form isobenzofuran;
the formation of 1,3-dilithioisobenzofuran; the conversion to 1,3-bis(trimethylsilyl)isobenzofuran (**5**); the generation
of arynes and cycloaddition to **5**. This method allows the use of lithium tetramethylpiperidide induced dehy-
drohalogenation of haloaromatics to generate the arynes, a procedure which fails with unsilylated isobenzofuran
due to the acidity of the 1,3-protons. The protiodesilylation of the cycloadducts occurs with surprising ease,
upon treatment with either tetraalkylammonium fluoride/THF or base (potassium *tert*-butoxide or KOH) in
Me$_2$SO, to furnish the novel unsubstituted isobenzofuran–aryne adducts. Three examples are given, utilizing
benzyne, 1-naphthalyne, and 3-pyridine. Procedures for subsequent deoxygenation of the cycloadducts to
anthracene, benz[a]anthracene, and benz[g]isoquinoline, respectively, are described. The cycloadduct precursor
of benz[a]anthracene is shown to undergo highly regioselective reduction on treatment with lithium tri-*tert*-
butoxyaluminohydride/triethylborane, with preferential attack occurring at the more accessible 7-position.

The cycloaddition of benzyne with furan constituted one
of Wittig's proofs of the formation of this reactive inter-
mediate,[1] generated from an *o*-dihalobenzene. Fieser[2]
subsequently used the anthranilic acid route[3] to develop
the same reaction on a preparative scale. These two
methods of generating benzyne have been used to form
adducts with various substituted furans.[4] From the
viewpoint of availability of starting materials, the more
general procedure for generating arynes is base-induced
dehydrohalogenation.[5] A frequently observed side reac-
tion, addition of the base to the benzyne, has been cir-
cumvented by the use of bulky lithium dialkylamide bases,[6]
e.g., lithium tetramethylpiperidide (LTMP). However,
application of this approach with furan failed to give cy-
cloadduct,[6,7] although both 2,5-dimethylfuran and 1,3-
diphenylisobenzofuran gave the expected products.[7]
Shepard has suggested that the failure to isolate furan
cycloadduct may be due to subsequent reaction of this
product, and he has pointed out that phenols, which ap-
pear to be derived from cycloadducts, have occasionally
been observed in these attempts. It is also of interest that
the dehydrohalogenation route to some arynes has been
successfully used to form cycloadducts of furan when
weaker bases were employed.[8]

(1) Wittig, G.; Pohmer, L. *Angew. Chem.* **1955**, *67*, 348.
(2) Fieser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599.
(3) Stiles, M.; Miller, R. G. *J. Am. Chem. Soc.* **1960**, *82*, 3802.
(4) For two recent interesting examples, see: (a) Barlett, P. D.; Combs,
G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625. (b) LeHoullier, C. S.; Gribble, G.
W. *J. Org. Chem.* **1983**, *48*, 2364. The latter illustrates the ortho dihalide
approach to 2,3-naphthalyne, and use with both furan and isoindole for
the preparation of polycyclic aromatics.
(5) Hoffmann, R. W. "Dehydrobenzene and Cycloalkynes"; Academic
Press: New York, 1967.

(6) Olofson, R. W.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 582.
(7) Shepard, K. L. *Tetrahedron Lett.* **1975**, 3371.
(8) For example: (a) cyclopropabenzynes, NaNH$_2$/*tert*-butyl alcohol
(5/1) (Halton, B.; Randall, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 6310), this
procedure involves a large excess of base and furan and has also been
successfully used with bromobenzene (personal communication from Dr.
Halton). (b) 3,5-dimethoxybenzyne, NaNH$_2$ (Cragg, G.M.L.; Giles, R. G.
F.; Roos, G. H. P. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1339.

Cycloaddition of arynes with isobenzofurans could in principle lead to novel polycyclic systems. The base-induced formation of isobenzofuran (IBF)[9,10] appeared to offer a simple one-pot method to effect these reactions. However, several attempts to obtain cycloadduct from IBF and benzyne, generated by lithium dialkylamide treatment of bromobenzene, gave no material with the expected NMR features. Although the products of these reactions have not been characterized,[11] these failures are attributed to lithiation of IBF, which has been shown[10] to be a stronger acid than R$_2$NH. Similar deprotonation could account for the failure of furan[7] to give cycloadduct under these conditions and represents a limitation for the use of any furan containing an acidic α-proton.[12]

In this paper we describe IBF–aryne cycloadditions involving both the o-dihalobenzene method for generating benzyne and the use of trimethylsilyl protecting group chemistry which allows extension to the more general dehydrohalogenation route to arynes.

Results and Discussion

The recently devised[10] method to convert acetal 1 to IBF (2) by treatment with RLi and catalytic (5 mol %) lithium dialkylamide allows the isolation of 2 in solutions containing only a small amount of the amide base, without having to resort to aqueous washes. Subsequent addition
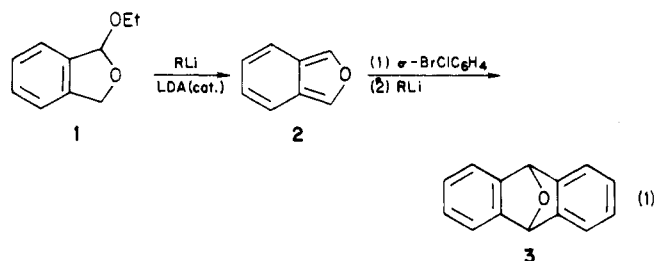
of 1 equiv (based on 1) of o-bromochlorobenzene followed by alkyllithium afforded 68% of the previously unreported 9,10-dihydro-9,10-epoxyanthracene (3), as outlined in eq 1. The success of this approach is attributed to very fast lithium–bromine exchange, followed by loss of lithium chloride, with both steps occurring more rapidly than deprotonation of 2.

The structure of 3 was evident from its NMR symmetry features and was also shown by deoxygenation to anthracene (90%), employing the Fe$_2$(CO)$_9$ procedure developed by Wege.[14] In addition, the mixed hydride reagent, (LiAlH(O-t-Bu)$_3$/Et$_3$B), described by Brown and co-workers,[15] was used to reduce 3 to 9,10-dihydro-9-anthracenol (4); this useful reaction has recently been
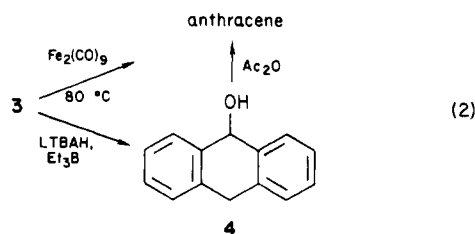
(9) Naito, K.; Rickborn, B. *J. Org. Chem.* **1980**, *45*, 4061.
(10) Crump, S. L.; Rickborn, B. *J. Org. Chem.* **1984**, *49*, 304.
(11) Nucleophilic addition of 1,3-dilithio-IBF to benzyne could lead to 1,3-diphenyl-IBF, but none was detected by TLC.
(12) Shepard and co-workers[13] have shown that N-alkylisoindoles are suitable substrates for cycloaddition to arynes, with the latter generated in different ways including LTMP-induced dehydrohalogenation.
(13) Anderson, P. S.; Christy, M. E.; Colton, C. D.; Halczenko, W.; Ponticello, G. S.; Shepard, K. L. *J. Org. Chem.* **1979**, *44*, 1519.
(14) Best, W. M.; Collins, P. A.; McCulloch, R. K.; Wege, D. *Aust. J. Chem.* **1982**, *35*, 843.
(15) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1979**, *44*, 3678.

shown with other 7-oxabicyclo[2.2.1]heptanes to occur with inversion at the cleaved center.[16] When 4 was allowed to stand overnight in CDCl$_3$ containing acetic anhydride, it was completely dehydrated to anthracene.

With cycloadduct 3 in hand, it was possible to examine its stability to strong base, and thus probe one possible reason for the earlier failures to effect benzyne–furan (IBF) reactions. Although we have previously used the base-induced method of generating IBFs to obtain cycloadducts with e.g. norbornene (excess base employed, but yields were markedly better when the base was added to a mixture of 1 and olefin), it appeared possible that the multiple inductive effects associated with 3 might make it more reactive to base. Treatment of 3 with excess LTMP in ether, 25 °C, did cause color to develop (orange turning green over time). However, when the mixture was quenched with D$_2$O after 16 h, crude material (110%) was judged by ^{1}H NMR to be >80% starting material. The ^{2}H NMR spectrum of this crude product showed that no measurable deuterium had been incorporated. While a small amount of degradation of 3 may have taken place, it appears that subsequent reaction of this adduct with base does not account for the failure to obtain any 3 from IBF and bromobenzene/LTMP. An alternative explanation for these failures is that 1-lithio-IBF undergoes facile Diels–Alder reaction, with the lithiated species formed in this manner rapidly decomposing (perhaps to phenolic materials).[17]

Extension to the more general aryne method (strong base induced dehydrohalogenation) required masking the acidic sites of IBF. It had been shown that trimethylsilylation of 1-lithio-IBF occurs readily,[10] and therefore the analogous reaction of 1,3-dilithio-IBF with Me$_3$SiCl (eq 3)
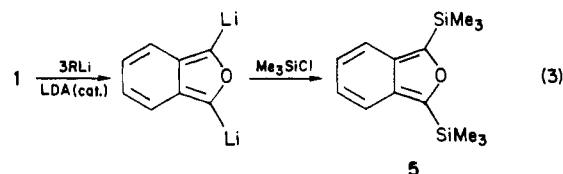
was examined. The formation of 1,3-bis(trimethylsilyl)-IBF in good yield was demonstrated by NMR and cycloadduct formation as described below. It was possible to isolate 5 as an oil (pale yellow), and it survived rapid chromatography on neutral alumina. However, on standing in stoppered flasks the neat material darkened and resinified, in the process losing the symmetrical AA'BB' aromatic proton pattern characteristic of 5. Solutions of 5 in ether (ca. 0.1 M) appear to be stable for at least several days, resembling the parent IBFs in this regard.

Solutions of 5 prepared without any workup were used to examine the reaction with benzyne generated from bromobenzene. The bromide was added, followed by a solution of LTMP in ether. After several hours at room temperature, aqueous washing and chromatography afforded the expected adduct 6 as a solid (57%). We had
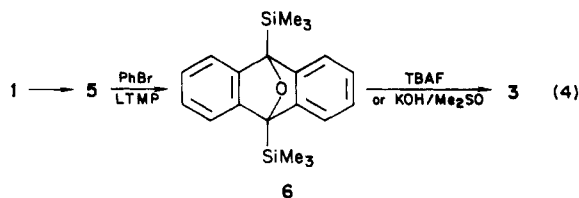

(16) Moss, R. J.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 1381.
(17) Since attempted reactions with furan usually involve an excess of this inexpensive material, this explanation would require that 2-lithiofuran be a much more reactive diene than furan in cycloaddition reactions.

anticipated that fluoride-induced desilylation of 6 might occur with opening of the strained oxa ring (if indeed any reaction took place) but were pleased to find that treatment with excess tetrabutylammonium fluoride (TBAF) in THF at ambient temperature caused quantitative conversion to 3 in a facile reaction. Presumably the water that is invariably associated with TBAF serves as the proton source for this reaction. Although the Me_3Si group is formally doubly benzylic, its bonding geometry and bridgehead location preclude any aromatic π stabilization; to the extent that negative charge develops on the bridgehead carbon in this cleavage, stabilization must be attributed to inductive effects of the oxygen and the two aromatic rings. The closests analogue for this protio-desilylation appears in the work of Chan,[18] who found that $1\text{-}R_3Si$ epoxides are readily cleaved by similar reagents/conditions, with retention of both stereochemistry and the oxirane ring.

After the work involving TBAF reactions of the silylated materials described in this paper was completed, a report[19] describing facile protio-desilylation of benzylic silanes by potassium *tert*-butoxide in Me_2SO was noted. Interestingly, this base/solvent combination is also very effective for conversion of 6 to 3 (15 min, ambient temperature). Encouraged by this observation, we next examined the use of KOH pellets in Me_2SO, and again facile conversion to 3 (91%) was observed. The well-known ability of Me_2SO to enhance the reactivity of bases and nucleophiles may be important for the protio-desilylation reaction, since KOH in methanol (68 h, ambient temperature) failed to effect the reaction (the limited solubility of 6 in this solvent may also play a role.) The simplicity and low cost of the KOH/Me_2SO procedure, coupled with easy workup and isolation, makes this a method of choice for these protio-desilylations. Regardless of the mechanistic details, these procedures for protection followed by protio-desilylation are very encouraging for broader use of IBFs (and furans) with arynes.

To illustrate further the applicability of the silylation route, the sequence described above was carried out with 1-bromonaphthalene as the source of 1-naphthalyne. The bis(trimethylsilyl) adduct 7 was obtained in slightly impure form as an oil (70%) by column chromatography. Again,
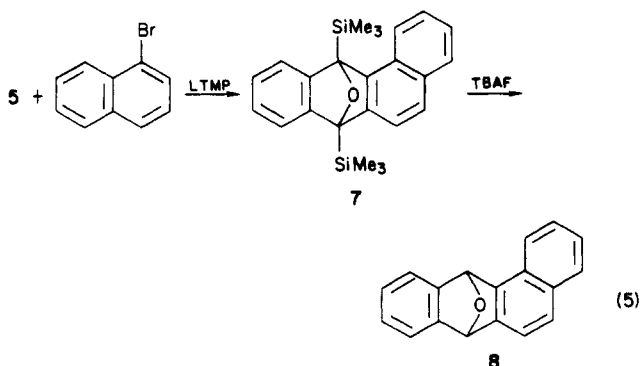

protio-desilylation with excess TBAF in THF at ambient temperature was complete within a short time, forming crystalline 8 in excellent yield. The precursor 7 exhibited two distinct equal-area singlets for the Me_3Si groups; these were replaced by singlets at 6.12 and 6.45 ppm (bridgehead protons), with the latter absorption attributed to the "bay region" site.

The LTBAH/Et_3B reduction of 8 was also examined, with the expectation that the reaction might exhibit regioselectivity. This reduction proved to be rather slow, and excess reducing agent was employed. After the usual workup, vacuum evaporation gave no alcohol but instead the dehydration product benz[*a*]anthracene (10). TLC examination of the reaction mixture prior to workup showed that 10 was not present. The reaction was repeated using the deuterated analogue (LTBAD); again the reaction proved sluggish, and a mixture containing starting material and reduction product (ca. 40%) was obtained. The NMR spectrum of this crude product after rotary evaporation, when it still contained some solvent THP, indicated that it contained no 10. Vacuum evaporation (ambient temperature) resulted in a pale yellow solid, which exhibited (NMR) the singlet at 9.2 ppm characteristic of 10; this absorption is attributed to the bay region H(12).[20] The H(7) singlet at 8.4 ppm was also evident but only constituted a fourth the area of the H(12) peak, showing that deuterium had been preferentially introduced at the C(7) position. The 300-MHz proton spectrum allowed a more quantitative evaluation, by comparison of the H(12) singlet with the H(1) doublet at 8.9 ppm; these areas were identical within measurement error, showing that the amount of deuterium incorporated at C(12) was 0–5%. Confirmation was obtained by examination of the ^2H NMR spectrum, which showed a sizeable absorption at 8.4 ppm, and a barely detectable (<2%) peak at 9.2 ppm. Therefore the reduction is nearly regiospecific, forming 9 as shown in eq 6. This strong preference for
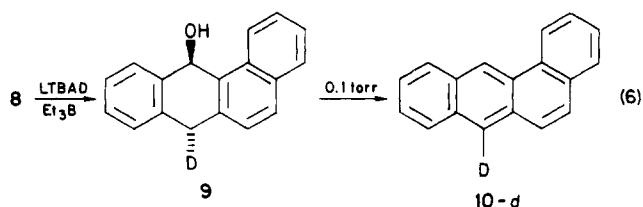
attack at the nonbay site is most easily explained as a reflection of the steric requirements of the reducing species, as demonstrated earlier by Krishnamurthy and Brown.[15] The especially facile dehydration of 9 may be attributed to the crowded steric environment of this alcohol, while the retention of ca. 75% deuterium in 10-d is presumably due to a kinetic isotope effect in the deprotonation step.

Heteroarynes can also be used to form cycloadducts with 5, as illustrated by the reaction of 3-bromopyridine. This material is known[13] to generate 3-pyridyne selectively on treatment with LTMP, and cycloaddition with 5 occurs to form 11. In this instance separation from tetra-


methylpiperidine was accomplished by column chromatography, and 11 was isolated as a solid (37%). The TBAF-induced protio-desilylation of 11 occurred rapidly,
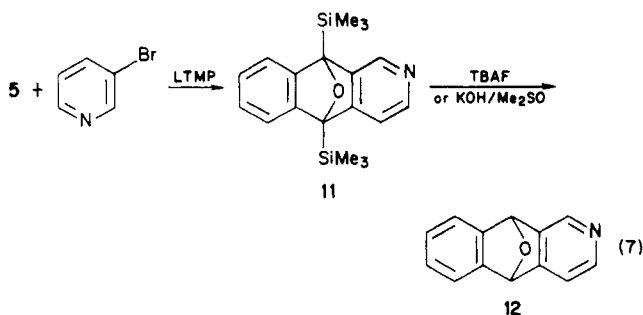
(18) Chan, T. H.; Lau, P. W. K.; Li, M. P. *Tetrahedron Lett.* 1976, 2667.

(19) Janssen, C. G. M.; Godefroi, E. F. *J. Org. Chem.* 1984, *49*, 3600.

(20) Memory, J. D.; Parker, G. W.; Halsey, J. C. *J. Chem. Phys.* 1966, *45*, 3567.

affording the novel benz[*g*]isoquinoline epoxide **12**. In a separate experiment, use of KOH/Me$_2$SO on crude **11** (isolated but not chromatographed) also gave **12**, in 20% overall yield (based on the acetal **1**).

Several different methods[21] were employed in attempts to deoxygenate **12** to form benz[*g*]isoquinoline (**13**). These efforts were initially hampered by the lack of correspondence of the properties of our materials with literature melting point and NMR data.[22] However, we conclude

$$12 \xrightarrow[\text{80 °C}]{\text{Fe}_2(\text{CO})_9} \qquad \qquad (8)$$

13
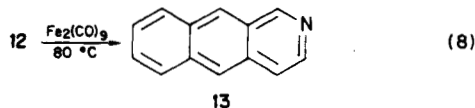
that the latter are erroneous, and the mp discrepancies may be due to impurities in earlier preparations. Our NMR data for **13**, mp 179–180 °C, fit those expected for this structure, as do other analytical data. Although the overall yield of **13** obtained as shown in eq 7 and 8 is modest (20–40%), the method avoids the pyrolysis needed in earlier approaches and provides a rational route to this material, apparently in higher purity than previously attained.

Experimental Section

Commercial halides and alkyllithium reagents were employed as received. Bromobenzene was vacuum distilled, and trimethylsilyl chloride was distilled from dimethylaniline and stored under nitrogen. The acetal **1** was prepared in 50–75-g batches by using the NaBH$_4$ method described previously.[25] Tetrahydropyran (THP) was vacuum distilled from sodium and then from LiAlH$_4$. ^{1}H NMR spectra were recorded on Varian EM-360 or NT-300 instruments, in CDCl$_3$ solvent. Tetramethylsilane was the internal standard, except for silylated products, where methylene chloride was used for this purpose. MS(EI) and MS-CI (chemically induced ionization, methane) spectra were taken on a VG ZAB-2F. Melting points were obtained in open capillary tubes on a Mel-Temp apparatus and are uncorrected. Anhydrous solvents were employed, and reactions were carried out under nitrogen.

9,10-Dihydro-9,10-epoxyanthracene (3). The acetal **1** (6.7 mmol, 0.92 mL) was taken up in 20 mL of ether in a flask equipped with a magnetic stir bar and a rubber septum. Diisopropylamine (0.34 mmol, 47 µL) was added, followed by methyllithium (6.7 mmol in 4.3 mL of ether). The mixture was stirred at room temperature for 3 h, at which point conversion to isobenzofuran

was judged to be complete by examination of the aromatic region of the NMR spectrum, taken directly of the reaction mixture. *o*-Bromochlorobenzene (6.0 mmol, 0.70 mL) was added, the mixture was brought to reflux,[26] and methyllithium (6.0 mmol) was added over 0.5 h. The mixture was then taken up in additional ether, washed with water and brine, dried over K$_2$CO$_3$, and evaporated to give crude product in high yield. Chromatography (silica gel, Skelly-solv/10% ether) gave 68% of colorless solid, pure by NMR. Recrystallization from methanol gave 54% of pure **3**: mp 158–159 °C; ^{1}H NMR δ 6.03 (s, 2 H), 6.9–7.4 (2 m, symmetrical AA′BB′ pattern, 8 H); MS-CI, calcd for C$_{16}$H$_{15}$O (P + C$_2$H$_5$) 223.1121, found 223.1125. Anal. Calcd for C$_{14}$H$_{10}$O: C, 86.57; H, 5.19. Found: C, 86.29; H, 5.08.

Deoxygenation of 3. *In a well-vented hood*, a mixture of 200 mg of **3** and 400 mg of Fe$_2$(CO)$_9$ in 10 mL of benzene was slowly heated in an oil bath. At ca. 60 °C the mixture turned black. The bath was held at this temperature for 1 h, and then the temperature was increased to reflux, which was continued overnight. After cooling and filtration through Celite, the solution was evaporated to dryness on a steam bath with a stream of nitrogen to remove any residual Fe(CO)$_5$. Column chromatography of the residue (silica gel, 1:1 Skelly-solv/CH$_2$Cl$_2$) gave 165 mg (90%) of anthracene, mp 212–215 °C (NMR identical with commercial material). Continued elution (CH$_2$Cl$_2$) gave a solid (9%), mp 254–258 °C; after recrystallization from CHCl$_3$/hexane; this material was identified as bianthronyl by comparison with Aldrich Chemical Co. catalog properties (mp 256–258 °C, NMR).

9,10-Dihydro-9-anthracenol (4). A mixture of 0.50 g (2.5 mmol) of **3** and 2.62 g (10 mmol) of LiAlH(O-*t*-Bu)$_3$ in 11 mL of THP was cooled in an ice bath, and 1.5 mmol of triethylborane (1 M in THF, Aldrich Chemical Co.) was added in two portions over 1.3 h. After 2 h 3 mL of 3 M aqueous NaOH was added, followed by 1 mL of 30% H$_2$O$_2$. Filtration gave a solution which was taken up in ether, washed with water and brine, dried over K$_2$CO$_3$, and vacuum evaporated to give a pale yellow solid (70%), which appeared to be nearly pure **4** by NMR. This material did not contain anthracene. Recrystallization from hexane gave 0.26 g of colorless fibrous needles; the NMR spectrum indicated that ca. 5% of anthracene had been formed in the recrystallization process.

Although some references to use of **4** appear in recent literature, these fail to state the source or properties. Our material, on slow heating in an open capillary, undergoes a sharp transformation (shrinkage) at 80–81 °C and then melts over a broad range (112–175 °C).[27] The melting point is higher on remelting, approaching that of anthracene. A sample in CDCl$_3$ to which a few drops of acetic anhydride had been added was cleanly dehydrated to anthracene on standing overnight.

4: ^{1}H NMR (300 MHz) δ 2.02 (d, OH, *J* = 7 Hz), 3.93 (d, 1 H, *J* = 18.5 Hz, further broadened by long range coupling), 4.15 (d, 1 H, *J* = 18.5 Hz), 5.65 (d, C*H*OH, *J* = 7 Hz, broadened by long range coupling), 7.3–7.5 (m, 6 H), 7.63 (br, d, 2 H, *J* = 9 Hz), aromatic protons ortho to carbinol group); IR (dilute in CCl$_4$) 3600 cm^{-1}.

9,10-Bis(trimethylsilyl)-9,10-dihydro-9,10-epoxyanthracene (6). A mixture of 6.1 mmol of **1** and 0.30 mmol of diisopropylamine in 15 mL of ether was cooled in an ice bath, and 18.9 mmol of *n*-butyllithium in 11.8 mL of hexane was added. After the mixture was stirred for 2 h at room temperature, it was cooled in a dry ice bath, and 12.3 mmol of trimethylsilyl chloride was added. After the resulting mixture warmed to room temperature, 6.1 mmol of bromobenzene (0.65 mL) was added. LTMP (6.1

(21) The reagents employed were: (a) LTBAH/Et$_3$B; (b) NaBH$_4$, trifluoroacetic acid, THF (Gribble, G. W.; Kelly, W. J.; Sibi, M. P. *Synthesis* **1982**, *1*, 143); (c) 6% Na·Hg, THF, methanol (this attempt was based on a report that Li·Hg effected the deoxygenation of a lower homologue; Kauffmann, T.; Boettcher, F. *Chem. Ber.* **1962**, *95*, 949); (d) lithium naphthalenide (Polovsky, S. B.; Franck, R. W. *J. Org. Chem.* **1974**, *39*, 3010); (e) TiCl$_4$, LiAlH$_4$, Et$_3$N, THF (Xing, Y. O.; Huang, N. Z. *J. Org. Chem.* **1982**, *47*, 140); (f) Fe$_2$(CO)$_9$ (see ref 14; our best results were obtained when the reactants were mixed in benzene and immediately brought to reflux.) Procedures (a) and (b) gave no **13** (by NMR). The others gave partial or complete loss of **12**, with evidence of formation of **13**, but with the exception of (f), mixtures were obtained.

(22) The preparations of **13** in the literature involve high-temperature (500–600 °C) copper-catalyzed dehydrocyclizations of methyl-substituted benzylpyridines; usually mixtures result, with **13** reportedly isolated by recrystallization. Melting points of 169–171 °C[23] and 166–168 °C[24] have been reported. An obviously incomplete listing of ^{1}H NMR peaks[24] identifies H(1) as the most downfield singlet at 9.08 ppm (CDCl$_3$). Our material has H(1) as a slightly broadened (meta coupling) singlet at 9.47 ppm (compare isoquinoline, which has the analogous adsorption at 9.34 ppm). Given the disparity between the melting point for our sample and the literature values and the very different NMR features, it is tempting to suggest that the earlier work led to some other material. However, the UV spectra[24] of both materials are similar, and both contain the multiple maxima characteristic of isoquinolines.

(23) von Braun, J.; Nelles, J. *Chem. Ber. Dtsch. Chem. Ges. B* **1937**, *70B*, 1760.

(24) Prostakov, N. S.; Kuznetsov, V. I.; Rai, C. D. *Khim. Geterotsikl. Soedin.* **1980**, *5*, 673; *Chem. Heterocycl. Cmpd. (Engl. Transl.)* **1980**, *5*, 525.

(25) Moss, R. J.; Rickborn, B. *J. Org. Chem.* **1982**, *47*, 5391.

(26) Addition of *n*-butyllithium (hexane) or methyllithium at −40 °C, followed by warming to room temperature, gave **3** in yields of 29% and 42% (after purification). In some other applications of this method of generating benzyne, we have found improved yields when the addition is carried out in refluxing ether (unpublished work of Russell White.)

(27) The original preparation of 9,10-dihydro-9-anthracenol was reported by H. R. von Prager (von Prager, H. R. *J. Prakt. Chem.* **1881**, *23* (2), 137) who gave mp 76 °C, while noting that the material was readily dehydrated to anthracene. Secondary references (Beilstein, Rodd) quote this melting point and reference, and the Chemical Rubber Handbook in turn refers to Beilstein. When prepared by NaBH$_4$ reduction of 9-anthrone, material of mp 78 °C has been obtained.[28] We suspect that the melting behavior of this substance is dependent on its history and the almost unavoidable contamination by anthracene.

(28) Miller, B. University of Massachusetts, personal communication.

mmol), prepared in a separate flask in ether/hexane, was transferred to the reaction vessel, and stirring was continued for 14 h. The ether solution was washed with water, 5% aqueous HCl, and brine, then dried (K_2CO_3), and evaporated. Chromatography of the residue (silica gel, Skelly-solv) gave 59% of colorless crystalline 6. Recrystallization from aqueous methanol gave over 90% recovery of pure 6: mp 154–154.5 °C; ^{1}H NMR$_1$ δ 0.42 (s, 18 H), 6.99 and 7.28 (2 m, symmetrical AA'BB' pattern, 8 H); MS-Cl; calcd for $C_{20}H_{26}OSi_2$ 338.1532, found 338.1530.

Conversion of 6 to 3. (a) With TBAF. To a solution of 6 (0.10 g, 0.25 mmol) in 4 mL of THF was added 1.25 mmol (1.25 mL of 1 M) of tetrabutylammonium fluoride in THF. The reaction was complete in less than 3 h (TLC). The mixture was taken up in ether, washed with water and brine, dried, and evaporated to give crude solid product. This was chromatographed as described above to give 3, mp 158–159 °C, in quantitative yield.

(b) In Me$_2$SO. Several samples of 6 were protio-desilylated to 3, all in greater than 90% yield, by addition of 6 to a solution of potassium *tert*-butoxide in Me$_2$SO or to Me$_2$SO containing KOH (either undissolved pellets or pulverized material), under a nitrogen atmosphere. The reactions developed a pink or red color of unknown origin. The starting material 6 has limited solubility in these solutions, whereas the product dissolves. The reactions were complete within a few minutes (TLC), paralleling the disappearance of undissolved 6. The solutions were added to excess water, extracted with ether, dried, and evaporated to give nearly colorless and essentially pure 3.

7,12-Bis(trimethylsilyl)-7,12-dihydro-7,12-epoxybenz[a]-anthracene (7). The procedure and scale used for formation of 3 was employed, with 6.1 mmol (0.85 mL) of 1-bromonaphthalene. Chromatography (graded elution, Skelly-solv to ether) gave 7 as a pale yellow oil, which darkened on standing (70%): ^{1}H NMR (300 MHz) δ 0.45 (s, 9 H), 0.50 (s, 9 H), 6.88 (m, 2 H), 7.25 (m, 1 H), 7.36 (m, 2 H), 7.46 (m, 1 H), 7.54 (s, 2 H), 7.80 (d, 1 H, J = 8.2 Hz), 8.02 (d, 1 H, J = 8.5 Hz); MS, calcd for $C_{24}H_{28}OSi_2$ 388.1679, found 388.1681.

7,12-Dihydro-7,12-epoxybenz[a]anthracene (8). Excess TBAF (9.0 mmol in 9.0 mL of THF) was added to 0.696 g (1.8 mmol) of 7 dissolved in 7 mL of THF. The reaction was complete (TLC) within 2 h at room temperature. The usual workup gave off-white solid (107%), which was recrystallized from petroleum ether after hot filtration. Pure 8 was recovered in 43% yield, mp 140–141.5° C; ^{1}H NMR (300 MHz) δ 6.12 (s, 1 H), 6.45 (s, 1 H), 6.83 (m, 2 H), 7.14–7.5 (m, 6 H), 7.69 (d, 1 H, J = 8.1 Hz), 7.79 (d, 1 H, J = 8.4 Hz); MS-Cl, calcd for $C_{20}H_{17}O$ (P + C_2H_5) 273.1278, found 273.1282. Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.26; H, 4.78.

Reduction of 8 to Benz[a]anthracene (10). A sample (50 mg) of 8 was taken up in 3 mL of THP containing excess (15 equiv) of lithium tri-*tert*-butoxyaluminohydride, and 3 equiv of triethylborane solution was added. After the mixture was stirred overnight, the usual workup and rotary evaporation (water aspirator) gave a residue, which contained neither 8 nor 10 (NMR). Vacuum evaporation (10 min, 0.2 torr) gave yellow 10, isolated in 90% yield after column chromatography, mp 156–159 °C; the ^{1}H NMR spectrum was identical with that shown in the "Aldrich Spectra Catalog".

The reaction was repeated on the same scale using LiAlD(O-*tert*-butyl)$_3$ (8 equiv) and 1.8 equiv of triethylborane, with quenching after 12 h. After workup as above and oil pump evaporation, the product was obtained as a yellowish solid, which by NMR consisted of 8 and 10 (partially deuterated) in approximately equal amounts. Further analysis to locate the position of deuterium incorporation was done as described in the text.

5,10-Bis(trimethylsilyl)-5,10-dihydro-5,10-epoxybenz[g]-isoquinoline (11). The procedure and scale described above was used, with 6.1 mmol (0.59 mL) of 3-bromopyridine. Workup after 11 h gave a dark oil, which was chromatographed (silica gel, graded elution Skelly-solv to ether) to give 0.75 g (37%) of 11. Recrystallization from aqueous methanol gave pure 11: mp 149–150 °C; ^{1}H NMR (300 MHz) δ 0.39 (s, 9 H), 0.41 (s, 9 H), 6.98 (m, 2 H), 7.21 (d, 1 H, J = 5.4 Hz), 7.32 (m, 2 H), 8.24 (d, 1 H, J = 5.4 Hz), 8.46 (s, 1 H); MS-Cl, calcd for $C_{19}H_{26}NOSi_2$ (P + H) 340.1551, found 340.1553.

5,10-Dihydro-5,10-epoxybenz[g]isoquinoline (12). Treatment of 0.35 mmol of 11 with 3 mmol of TBAF caused immediate darkening of the solution, and the starting material was consumed (TLC) within 15 min. The usual workup gave crude yellow solid 12 in quantitative yield. Chromatography (silica gel, ether) gave 53 mg (78%) of off-white material; recrystallization was effected by dissolving in a minimal amount of methylene chloride, adding hexane, and evaporating until turbidity was observed. Pure 12: mp 137.5–139 °C; ^{1}H NMR (300 MHz) δ 6.12 (s, 1 H), 6.20 (s, 1 H), 7.10 (m, 2 H), 7.32 (d, 1 H, J = 4.5 Hz), 7.41 (m, 2 H), 8.36 (d, 1 H, J = 4.5 Hz), 8.59 (s, 1 H); MS-Cl, calcd for $C_{13}H_{10}NO$ (P + H) 196.0761, found 196.0769. Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65. Found: C, 79.98; H, 4.63.

A similar overall yield of 12 was obtained when chromatographic isolation of 11 was omitted. Thus 12.2 mmol of 1 was converted in the usual way to 5, which was treated with 3-bromopyridine (12.2 mmol) and LTMP (12.2 mmol) for 20 h at room temperature. The solution was taken up in ether, washed with water and brine, dried, and evaporated to give a dark brown oil, consisting mainly of 11 and tetramethylpiperidine (by NMR). This mixture was treated directly with TBAF. Chromatography as above gave 0.77 g of discolored 12. Taking this material up in 5% aqueous HCl and washing with CH_2Cl_2 removed most of the color. The aqueous solution was made basic and extracted; the usual drying and evaporation gave 0.58 g of tan 12.

When this sequence was repeated using KOH/Me$_2$SO for the protio-desilylation step, 12 was again isolated in similar yield.

Benz[g]isoquinoline (13). To a solution of 12 (300 mg, 1.54 mmol) in 10 mL of dry benzene was added 1.12 g (3.08 mmol) of Fe$_2$(CO)$_9$; reflux was initiated immediately and continued for 6 h. Volatiles were removed on a steam bath (hood!) under a stream of nitrogen. The black solid residue was mulled with ether and filtered through Celite. Evaporation gave 120 mg (43%) of crude 13, which was recrystallized by dissolving in a minimal amount of methylene chloride, adding high-boiling petroleum ether, and evaporating to slight cloudiness. Pure 13 was obtained as pale yellow plates: mp 179–180 °C; ^{1}H NMR (300 MHz) δ 7.5–7.65 (m, 2 H, H(7) and H(8)), 7.75 (d, 1 H, J = 6 Hz, H(4)), 8.0–8.17 (m, 2 H, H(6) and (9)), 8.36 (s, 1 H, H(5) or H(10)), 8.43 (d, 1 H, J = 6 Hz, H(3)), 8.58 (s, 1 H, H(5) or H(10)), 9.47 (broadened s, 1 H, H(1)), IR(CCl$_4$) 3059, 1632 (sh), 1620, 1398, 1317, 1276, 1195 cm^{-1}; UV (CHCl$_3$) λ_{max} (log ϵ) 253 (4.48), 268 (3.85), 309 (3.36), 325 (3.51), 346 (3.57), 371 (3.73), 390 (3.65); MS, calcd for $C_{13}H_9N$ 179.0734, found 179.0729; m/e 179 (100), 178 (12), 152 (12), 151 (13), 76 (12).