Isobenzofuran–Aryne Cycloadducts: Formation and Regioselective Conversion to Anthrones and Substituted Polycyclic Aromatics[1]

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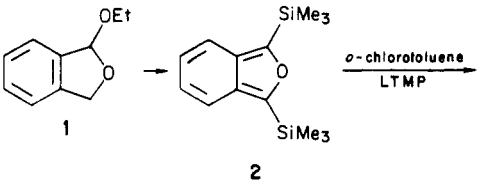
Several substituted anthracenes, benz[*a*]anthracenes, dibenz[*a*,*c*]anthracene, and more complex ring system derivatives are formed by the cycloaddition of 1,3-bis(trimethylsilyl)isobenzofuran (**2**) with arynes generated by LTMP-induced dehydrohalogenation of readily accessible haloaromatics. The cycloadducts undergo a novel acid-induced conversion to anthracenones. For several substrates this reaction is highly regioselective, allowing position specific introduction of another substituent at this stage. Reduction/dehydration of the anthrones provides an expeditious route to various polycyclic aromatic hydrocarbons.

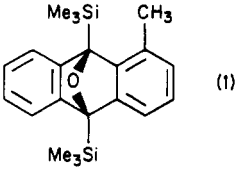
The recently reported[2] one-flask procedure for conversion of the acetal **1** to 1,3-bis(trimethylsilyl)isobenzofuran (**2**), followed by the in situ generation/cycloaddition of arynes, has been extended to encompass several new methyl-, bromo-, and benzo-substituted examples. Treatment of many of these cycloadducts with trifluoroacetic acid causes the formation of anthrones (anthracenones); this novel reaction exhibits high regioselectivity, allowing the formation of polycyclic aromatics with certain specific substitution patterns.

Results and Discussion

(a) Formation of Cycloadducts. The general procedure used is outlined in eq 1, which illustrates the preparation of the 1-methylanthracene derivative **3**. The conversion of **1** to **2** was accomplished as described previously,[2] with 3 equiv of RLi (usually *n*-butyllithium) and a catalytic amount (2–5 mol %) of lithium tetramethylpiperidide (LTMP), followed by addition of trimethylsilyl chloride (Me_3SiCl). To the same flask, the aryl halide



1 2



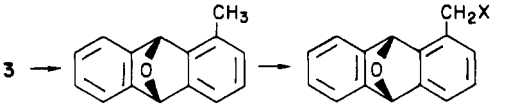
(1)

3(90%)

(usually 1–2 equiv) was added, followed by LTMP, and the mixture stirred at ambient temperature with monitoring by TLC (usually several hours). Isolation of the cycloadducts was done either by chromatography or direct recrystallization of crude products. Yields have not been optimized; in some instances comparison of material before and after chromatography indicated that losses occurred in this step. This problem was especially acute with bromoanthracene derivatives, which we were unable to retrieve from several attempts to chromatograph with different column packings and solvents.

Compound **3** was isolated in 90% yield (based on acetal **1**) by chromatography, when 1.5 equiv of *o*-chlorotoluene and 2.0 equiv of LTMP were used. The efficiency of aryne trapping by **2** is noteworthy, since similar reactions with, e.g., furans typically involve a large excess of the diene.

Some potential applications of this procedure would require functionalization of the alkyl substituent, and to examine feasibility the sequence depicted in eq 2 was carried out. The KOH/Me_2SO protiodesilylation method described previously[2] was used to convert **3** to **4** (quantitative). Radical bromination with *N*-bromosuccinimide

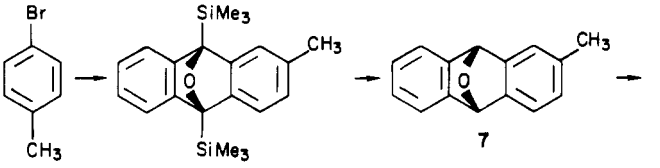


(2)

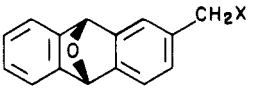
4 5a, X = Br b, X = OAc

(NBS) proceeded smoothly to give **5a**, with no indication of interfering reactions at the bridgehead positions (this was of concern in part because of the very facile carbanion processes, e.g., **3** to **4**, which occur at these sites). Bromide **5a** was in turn converted to the acetate **5b** to establish that nucleophilic displacement reactions can also be employed with such substrates.

The same sequence was employed starting with **2** and *p*-bromotoluene to generate the 2-methylanthracene analogue **6**. Protiodesilylation to **7**, NBS bromination to **8a**, and displacement by NaOAc in DMF to form **8b** again took place cleanly (eq 3).



6(77%)



(3)

8a, X = Br b, X = OAc

Previous work[2] demonstrated that **2** efficiently adds to 1,2-naphthalyne (from 1-bromonaphthalene) to form the benz[*a*]anthracene skeleton. Similar use of readily available 1-bromo-4-methylnaphthalene gave the 5-methyl analogue **9**.

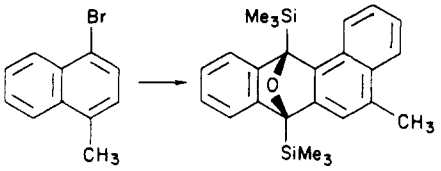
Several other cycloadducts were prepared in this way, as illustrated in the following equations. Commercial

† Recipient of the Robert H. DeWolfe, College of Creative Studies Summer, and President's Undergraduate Fellowships.

(1) Portions of this work were presented at the 10th International Congress on Heterocycles, Waterloo, Canada, August 1985.

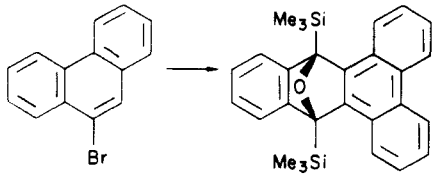
(2) Crump, S. L.; Netka, J.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 2746.

0022-3263/86/1951-1189$01.50/0



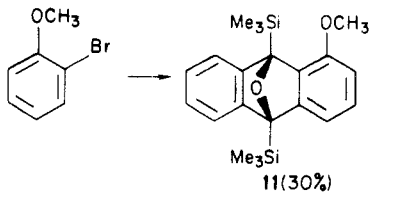
9 (67%) (4)

9-bromophenanthrene served as the starting material for the dibenz[*a*,*c*]anthracene derivative **10**; although the yield was modest (possibly due to losses on chromatography), this provides a very simple and direct route to this ring system.



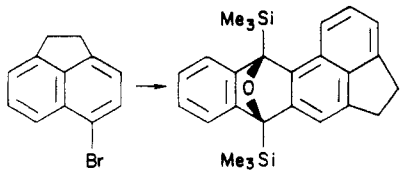
10 (27%) (5)

The reaction of *o*-bromoanisole gave cycloadduct **11** in good yield (NMR) as a crude oil. Chromatography caused extensive decomposition of this material, and difficulties in recrystallization resulted in modest recovery of pure product.

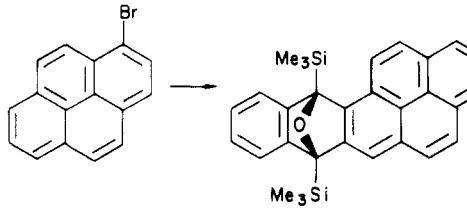


11 (30%) (6)

Two unusual ring systems were constructed through the use of 5-bromoacenaphthene and 1-bromopyrene as aryne precursors, illustrated in eq 7 and 8.

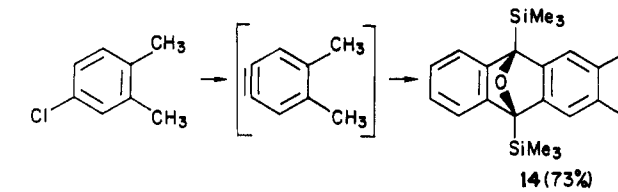


12 (26%) (7)



13 (47%) (8)

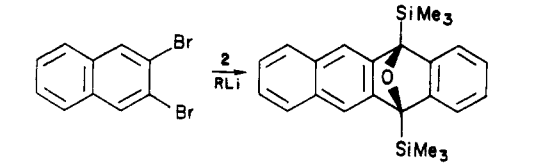
The dehydrohalogenation of 4-chloro-1,2-dimethylbenzene could in principle give two different arynes, but only one cycloadduct was observed in the crude product and isolated from this reaction. This product (**14**) is derived from the symmetrical aryne depicted in eq 9. The results shown in eq 1 and 3 suggest that if the alternative aryne had been generated, cycloaddition would have occurred without difficulty, and therefore it appears that this dehydrohalogenation is regiospecific as shown. This conclusion is reinforced by the observation that 2-bromo-1,4-dimethylbenzene is very resistant to reaction.[3] This



14 (73%) (9)

and a related example of regioselective aryne formation discussed below are potentially useful for linear annulation procedures.

An alternative method is required for generation of 2,3-naphthalyne, since dehydrohalogenation of, e.g., 2-bromonaphthalene is expected[5] to give mainly or exclusively 1,2-naphthalyne. We utilized the alkyllithium-induced dehalogenation of 2,3-dibromonaphthalene to form this reactive intermediate in the presence of **2**, leading to the tetracene (naphthacene) system **15**. It is also possible



15 (78%) (10)

to construct this ring system (with protons in place of the bridgehead Me_3Si groups) by taking advantage of the very rapid dehalogenation reaction to effect cycloaddition with unprotected isobenzofuran (as had been shown for the simple anthracene analogue[2]), but the yield in the one attempt to do so was lower (20% recrystallized 5,12-dihydro-5,12-epoxynaphthacene obtained); since **15** itself was of interest for the work described in the next section of this paper, no efforts to improve this alternative route were undertaken.

Although it has been known for some time that dehydrohalogenation of aryl dihalides could be used to generate haloarynes,[5] these intermediates have seen few synthetic applications.[6] We were especially interested in the possibility of preparing bromoanthracenes and other brominated polycyclic aromatics in this manner. Since the product of cycloaddition of a haloaryne would itself be a potential aryne precursor, it was encouraging to note that dihalides should have significantly higher reactivity toward base than monohalides, based on Huisgen's early observations.[5] This has indeed proven to be true in the systems we have examined in this work, making it possible to obtain cycloadducts in modest to good yields without re-

(3) No cycloadduct was observed when 2-bromo-1,4-dimethylbenzene was used with LTMP and **2**; the NMR spectrum of crude product indicated that both **2** and the halide were recovered unchanged. An attempt to use $NaNH_2$ for this elimination was similarly unsuccessful. It should be noted that 1,4-dibromo-2,5-dimethoxybenzene has served as an aryne precursor ($NaNH_2$).[4]

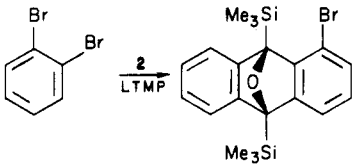
(4) Cragg, G. M. L.; Giles, R. G. F.; Roos, G. H. P. *J. Chem. Soc. Perkin Trans. 1* **1975**, 1339.

(5) Huisgen, R.; Mack, W.; Herbig, K.; Ott, N.; Anneser, E. *Chem. Ber.* **1960**, *93*, 412. This paper reports relative rate constants for dehydrohalogenation of various aromatic bromides by lithium piperidide in ether/piperidine solvent. Nearly exclusive 1,2-elimination was found for 2-bromonaphthalene under these conditions. Interestingly, 3-bromotoluene is reported to undergo elimination in both directions with very similar rates (cf. ref 3 above).

(6) In addition to ref 4, see: (a) Anderson, P. S.; Christy, M. E.; Colton, C. D.; Halczenko, W.; Ponticello, G. S.; Shepard, K. L. *J. Org. Chem.* **1979**, *44*, 1519. This paper reports the first application of LTMP with aryl dihalides to generate haloarynes. (b) Stringer, M. B.; Wege, D. *Tetrahedron Lett.* **1980**, 3831.

sorting to the use of large excesses of the (often expensive) dihalide.

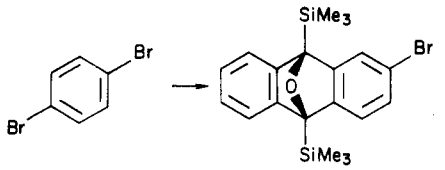
The reaction of *o*-dibromobenzene with LTMP in the presence of **2** affords the 1-bromoanthracene derivative **16** in good yield. It is necessary to isolate **16** by direct recrystallization, since all efforts to retrieve this material from column chromatography have failed; this instability is not understood (even methanol washing of the column gives only a small amount of undecipherable material).



(11)

16 (71%)

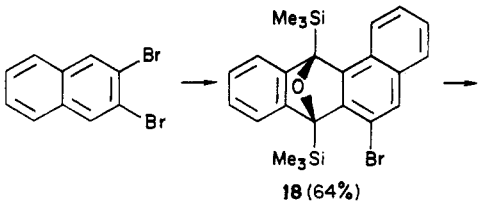
The 2-bromoanthracene derivative **17** was similarly prepared from *p*-dibromobenzene and again isolated, in modest yield, by recrystallization.



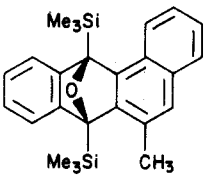
(12)

17 (23%)

LTMP treatment of 2,3-dibromonaphthalene was used to generate 3-bromo-1,2-naphthalyne, which reacted with **2** to give the 6-bromobenz[*a*]anthracene derivative **18**. A portion of this material in THF solvent was treated with methyllithium followed by methyl iodide to provide the 6-methyl analogue **19**. This result is significant in demonstrating that metal/halogen exchange and alkylation can take place at a site "peri" to a bridgehead Me_3Si group, without cleavage of the latter function.



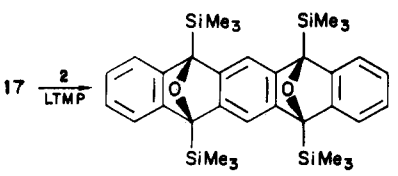
18 (64%)



(13)

19

The 2-bromoanthracene derivative **17**, although isolable as indicated in eq 12, can indeed serve as an aryne precursor, as demonstrated by treatment with LTMP in the presence of **2**. The same cycloadduct is obtained when 1 equiv of *p*-dibromobenzene is treated with 2 equiv of **2** and excess LTMP. The striking feature of this reaction is that it appears to be highly regioselective, giving only the linearly annulated pentacene derivative **20**. The modest



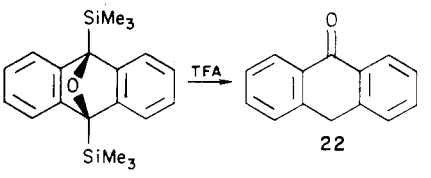
(14)

20 (39%)

yield of cycloadduct obtained in this reaction (39% starting with either **17** or the alternative route using *p*-dibromobenzene directly) prevents a definitive conclusion about the step that determines this selectivity, although we suspect that it is the dehydrohalogenation (rather than the trapping reaction) which imparts the regioselectivity (cf. eq 9).[7] Compound **20** is formed as a mixture (ca. 1:1) of cis and trans isomers. Although these have been tentatively identified, complete elucidation of these interesting structures requires further work. For purposes of the present study, the mixture has been utilized as described in part b.

To summarize this portion of the work, the LTMP induced dehydrohalogenation of aryl halides appears to have wide applicability, and efficient trapping of the resultant arynes by **2** leads to a variety of novel polycyclic systems. Interesting regioselectivity is observed, which allows linear annulation of the anthracene skeleton. Although the present study does not focus on these products, all of the cycloadducts examined to date readily undergo protiodesilylation in essentially quantitative yield. Some common functional group interconversions have been carried out without interference by the oxabicyclic substructure (in fact some processes may be enhanced by removing the reactive 9,10-positions of anthracenes from the substrates). It is also worth noting that these epoxides have generally much higher solubility in common organic solvents than the corresponding polycyclic aromatic hydrocarbons, a feature which may be advantageous in carrying out reactions that might be common to both substrates.

(b) Acid-Induced Reactions of Cycloadducts. The aryne–isobenzofuran cycloaddition reaction provides a very direct and convenient route to the carbon skeleton of various polycyclic aromatic hydrocarbons, but the deoxygenation required to prepare the actual hydrocarbons presents problems in some instances.[2] We have found that the $Fe_2(CO)_9$ method devised by Wege[8] for some related materials is quite effective for the preparation of anthracene itself from the (protiodesilylated) 9,10-epoxide, although other substrates have given poorer yields[2] or no desired product. Another procedure, reduction by $LiAlH(OtBu)_3/Et_3B$ in tetrahydropyran (followed by acid-catalyzed elimination of water), has been effective in the few cases examined[2,9] but requires some uncommon reagents, and its wider generality remains to be determined. In searching for simpler alternatives, we had occasion to examine the reaction of **21** with trifluoroacetic acid (TFA) in $CDCl_3$ solvent. A rapid reaction occurred



(15)

22

21

which, within the time required to obtain an NMR spectrum, gave 9(10*H*)-anthracenone (9-anthrone, **22**) and presumably (not isolated) the known volatile (bp 89 °C)

(7) Preliminary efforts to generate bis adducts by treating **16** and **18** with LTMP/**2** have been unsuccessful. Models show that severe steric problems would be associated with two "bay region" Me_3Si substituents in, e.g., the naphtho[*a*]anthracene derivative that would result from reaction of **16**, and this may preclude cycloadduct formation. It also appears, however, that **16** and **18** are more stable than **17** to LTMP, and aryne generation may be prevented for reasons which are not obvious. Further work is planned with these materials.

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

(9) Moss, R. J.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 1381.

trimethylsilyl trifluoroactate. No indication of a possible intermediate silylated species was observed in this or other examples discussed below, and integration of the spectrum indicated that the product was entirely in the keto form. The mechanistic details of this reaction are not known, but the absence of aryltrimethylsilanes and 9-anthracenol (the enol form of **22**) may be a consequence of facile acid-induced protiodesilylation and acid-catalyzed equilibration, respectively. Although the keto/enol tautomeric equilibrium of 9-anthrone has been recognized for many years, only the recent definitive work of Mills and Beak[10] has established that the keto form is very strongly favored (>99.9%) in solvents such as those employed in this study.

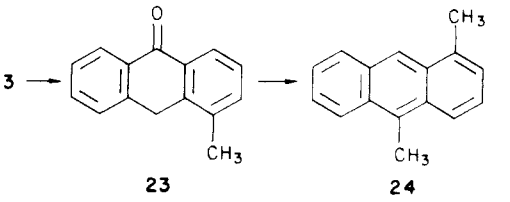
In further discussion, we will refer to all ketones of this general class as "anthrones", even though the parent ring system might call for another name. Before outlining our results, some further features of these materials require comment. The position of keto/enol equilibrium has apparently not been examined by modern methods for *substituted* anthrones. Beak[10] has commented on the difficulty of obtaining accurate equilibrium measurements because of slow interconversion of tautomers in nonpolar solvents and sensitivity to oxidation. In all of the cases we have examined in this study, the NMR spectra indicate that the product is formed exclusively or nearly so in the keto form (as shown by integration of the methylene absorption in the 4–5 ppm region vs. total aromatic protons). As noted above, this may be the result of rapid acid-catalyzed equilibration, although this point has not been confirmed. We also find that the anthrones are generally unstable to (air) oxidation, and oxidation products almost invariably develop as contaminants, in some cases more rapidly than others. These products include quinones (as observed by Mills and Beak[10]) and in at least some instances, bianthronyls.[11] The latter materials can be especially confusing contaminants in viewing NMR spectra, since their benzylic protons typically have chemical shifts similar to the precursor anthrones. A further complication in analysis arises because of the (not unexpected for such polycyclic aromatics) concentration dependence of chemical shifts. Problems due to oxidation are particularly acute when small samples or dilute solutions (slower desired reaction) are employed, and these features must be kept in mind when using the procedures described below. We recommend that anthrones generally be treated as unstable materials and used soon after preparation if further manipulations are needed. With very few exceptions, the oxidation processes have resulted in isolation of yellow-tinged solids, and these colors deepen on standing in solution or for some substances, in the solid form.

The bridgehead protonated (protiodesilylated) analogue of **21** also rearranges to 9-anthrone on treatment with TFA, but the reaction is much slower than that of **21** itself. For example, a competitive kinetics examination of the two materials (equimolar) with TFA (ca. 1 equiv) in a stoppered NMR tube indicated that all of **21** had been consumed within 30 h (slowed by dilution), while most of the bridgehead protonated material remained after 90 h. This and other examples indicate that the Me_3Si substituents are still present in the rate-controlling step (i.e., the reaction does not proceed by protiodesilylation followed by rearrangement) and that the Me_3Si group(s) substantially accelerates the rate. This is in keeping with the rate-determining step being cleavage of the (protonated) oxa bridge to generate a carbenium ion. Although the effect is much less pronounced than the well-known carbenium ion stabilizing influence of β-silicon, a recent report shows that α-carbocations are indeed also stabilized by a Me_3Si group (relative to H).[13]

Conversion to the anthrone followed by lithium aluminum hydride (LAH) reduction and elimination of water provides a convenient method for converting the cycloadducts to the corresponding polycyclic aromatics. The keto function can also be used to introduce another substituent, e.g., by addition of Grignard reagent with subsequent elimination of water. Both processes are illustrated in some examples discussed below.

The most interesting aspect of the TFA reaction is that *the conversion to anthrones is regioselective*, in several cases leading to a single isomer.

When **3** was subjected to TFA (usually 3–4 mol equiv used) in CCl_4, a very rapid reaction ensued, leading exclusively to 4-methyl-9(10*H*)-anthracenone **23**. The product was obtained as a sharp melting (127–128.5 °C)[14] colorless solid, simply by vacuum evaporation of the solvent and byproducts from TFA. Both ^1H and ^{13}C NMR



(16)

23 **24**

analysis support the conclusion that a single isomer had been formed, and integration of the aromatic region indicated two downfield protons, attributed to those peri to the carbonyl group. Addition of a sample of **23** to excess CH_3MgBr in ether gave, after acidic workup (dehydration), the known 1,10-dimethylanthracene[16] (**24**) in 52% yield.[17]

The conversion of **3** to **23** is nicely accommodated by simple carbenium ion stabilization arguments; i.e., this anthrone is the predicted product from consideration of the ortho, para-directing influence of the methyl group as encountered in typical eletrophilic aromatic substitution reactions.

Similar treatment of the 2-methylanthracene derivative **7** gave initially confusing and difficult to reproduce results, suggesting selective but not regiospecific conversion to anthrone(s). These were carried out with small amounts of material, and NMR analysis was complicated by the oxidation processes noted above, which appear to be quite

(10) Mills, S. G.; Beak, P. *J. Org. Chem.* **1985**, *50*, 1216. The *K*-(enol/keto) for 9(10*H*)-anthracenone in CCl_4, $CHCl_3$, and CH_2Cl_2 was found to be <0.001.

(11) The classical method for preparing bianthronyls involves treatment of anthrone solutions, usually in HOAC or EtOH, with $FeCl_3$. Substituted anthrones give diastereomeric (meso and +/−) mixtures of bianthronyls. For a recent paper that illustrates earlier methods of forming anthrones, bianthronyls, and bianthrones and some of the interesting stereochemical features of these materials, see ref 12.

(12) Agranat, I.; Tapuhi, Y. *J. Org. Chem.* **1979**, *44*, 1941.

(13) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

(14) The mp similarity suggests that this may be identical with the "α-methylanthrone", mp 126–127 °C, obtained by v. Braun and Bayer in 1926, by reduction of 1-methylanthraquinone.[15] Anthrone **23** has also been prepared via phthalic anhydride and the Grignard reagent of *o*-bromotoluene, followed by reduction and acylation, to give material of mp 128–129.5 °C (see ref 27).

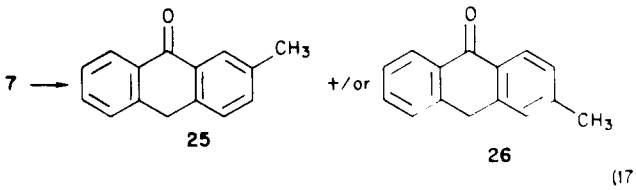
(15) v. Braun, J.; Bayer, O. *Chem. Ber.* **1926**, *59B*, 914.

(16) Two syntheses of **24**, involving very different routes, have been reported: (a) Boues-Laurent, H.; Moulines, F. *C. R. Hebd. Seances Acad. Sci.* **1964**, *258*, 3317. (b) Burgstahler, A. W.; Kulier, C. P. *J. Org. Chem.* **1965**, *30*, 4384. The possible alternative isomer 1,9-dimethylanthracene, although mentioned in the context of UV studies by the Boues-Laurent group, has apparently never been fully described (synthesis, physical properties).

(17) Literature reports of the addition of Grignard reagents to anthrones give yields ranging from negligible to ca. 60%. Excess Grignard reagent is commonly employed, and in one study this was found necessary to form product.[18] Typically a 3–4-fold excess is used.

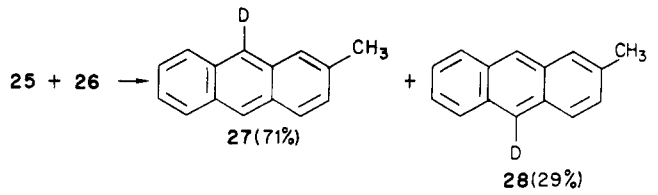
(18) Sieglitz, A.; Marx, R. *Chem. Ber.* **1923**, *56*, 1619.

facile with this system. This made it difficult to distinguish the two structures **25** and **26** (eq 17). This problem was



(17)

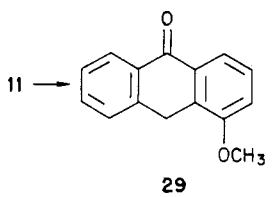
addressed by carrying out the reaction on a larger scale and then rapidly subjecting the anthrone to lithium aluminum deuteride (LAD) reduction followed by dehydration to form deuterated 2-methylanthracene. Fortunately, the 9,10-protons of 2-methylanthracene are sufficiently separated (300 MHz) from each other to allow identification. A difference NOE experiment was performed on an authentic sample of 2-methylanthracene; presaturation of H-1 singlet at 7.42 ppm caused enhancement (13%) of the singlet at 8.31 ppm (H-9), and a negligible effect on the singlet at 8.37 ppm (H-10). Integration of the ^{1}H NMR spectrum of the deuterated 2-methylanthracene showed that the deuterium was located mainly at C-9 (**27**), with the minor component being **28**; within integration error,



(18)

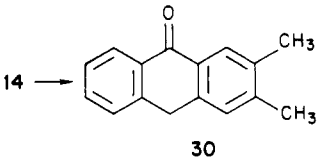
the mixture contained a total of 1 D/mol. Since **27** arises from **25** (and **28** from **26**), it is clear that the TFA reaction of **7** regioselectively forms **25** (71%). Note that this is the product expected from consideration of methyl group stabilization of an intermediate cation. It is not clear why the TFA conversion of **7** is less selective than that of **3**, i.e., whether there is higher selectivity imparted by a peri substituent for some reason, or if the carbenium ion stabilizing influence simply falls off with distance from the initially formed cationic center.

The 1-methoxyanthracene derivative **11** reacts with TFA quite rapidly, cleanly affording the single product 4-methoxy-9(10*H*)-anthracenone **29**, as outlined in eq 19. This anthrone was identified by NMR analysis, and its mp was identical with that reported by Yamamoto and Oki for this material.[19] The regiospecificity of this reaction parallels that of **3**, in keeping with the strong cation stabilizing influence expected for the alkoxy group.



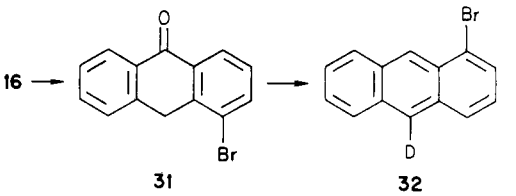
(19)

The symmetrical 2,3-dimethylanthracene derivative **14** on treatment with TFA gave essentially pure anthrone **30**, identified by comparison (mp, NMR) with the literature report.[21] In an NMR tube experiment, **30** was formed rapidly, but after standing for 2 days (stoppered), partial oxidation to 2,3-dimethylanthraquinone (15%) and the corresponding bianthronyl diastereomers (73%, both in equal amount) was observed, as shown by peak for peak correspondence with the literature chemical shift values for these materials.[21]



(20)

The 1-bromoanthracene derivative **16** proved to be much less reactive toward TFA than any of the other substrates discussed to this point. Competition kinetics runs carried out as described above showed that **16** reacted faster than its protiodesilylated analogue, but the rate-depressing effect of bromine was clearly evidenced by the observation that **16** reacted more slowly than either **21** (as expected) or its protiodesilylated analogue; i.e., the rate enhancement due to Me_3Si substitution is more than offset by introduction of the bromine. Nonetheless, the reaction of **16** proved to be highly regioselective, leading to 4-bromo-9-(10*H*)-anthracenone **31**. This structural assignment is based in part on the ^{1}H NMR spectrum of **31**, which exhibited two downfield (peri) protons. The degree of selectivity was established by LAD reduction followed by dehyration, which gave 1-bromo-10-deuterioanthracene (**32**) as outlined in eq 21. The ^{1}H NMR spectrum exhibited a peak at 8.78 ppm (H-9, integrating for ca. one proton) and a minor absorption (ca. 6%) at 8.43 ppm (the position of H-10); the ^{2}H spectrum was too broad for unambiguous interpretation, but a shoulder at 8.8 ppm on the major peak at 8.4 ppm suggests that the conversion of **16** to **31** indeed occurs with ca. 94% regioselectivity, supporting the ^{1}H NMR interpretation.



(21)

Analogous treatment of another sample of **31** with LAH gave 1-bromoanthracene, with mp and NMR spectrum in accord with those of material reported by Boyd and coworkers.[22] It is worth noting that this simple appearing material cannot be made by trivial extension of classical

(19) Yamamoto, G.; Oki, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 473. **29** was formed in high yield by sodium dithionite selective reduction of 1-methoxyanthraquinone. The possible alternative isomer (1-methoxy-9(10*H*)-anthracenone) has also been prepared, but because of intramolecular hydrogen bonding, it strongly prefers the enol form.[20]

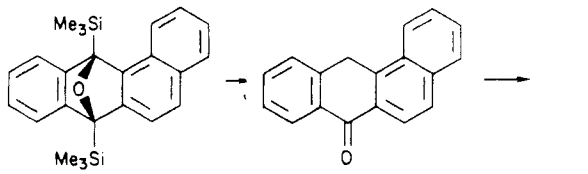
(20) Yamamoto, G.; Oki, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 481. Selective copper/aqueous acid reduction of 1-methoxyanthraquinone was used to obtain this material in modest yield.

(21) Cameron, D. W.; Edmonds, J. S.; Feutrill, G. I.; Hoy, A. E. *Aust. J. Chem.* **1976**, *29*, 2257. Our NMR data correspond peak for peak with those given in this paper, with all our chemical shifts larger by ca. 0.1 ppm (concentration or temperature effect), except for the peak assigned to H-1. The value given in this reference (δ 8.83) is clearly too large based on comparisons with other anthrones and related quinones. This appears to be a typographical error (the number appears out of order in an otherwise ascending sequence), and to be compatible with our spectrum (and that of 2,3-dimethylanthraquinone given in this reference) it should have appeared as δ 8.03.

(22) Akhtar, M. N.; Hamilton, J. G.; Boyd, D. R.; Braunstein, A.; Seifried, H. E.; Jerina, D. M. *J. Chem. Soc. Perkin Trans. 1* **1979**, 1442. We thank Prof. Boyd for providing a copy of the NMR spectrum of 1-bromoanthracene for comparison purposes.

anthracene preparative methods, and the one synthesis described in the literature involves several steps to provide material in modest overall yield.[22] The isobenzofuran–aryne route described here thus appears to be the method of choice for making 1-bromoanthracene and related materials which (in principle) can be formed from it by standard reactions.

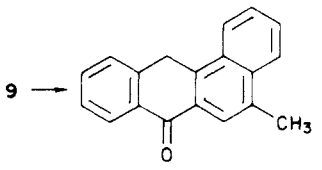
The benz[*a*]anthracene derivative **33** also reacted regiospecifically with TFA to give 7(12*H*)anthracenone **34**. None of the alternative 12-one isomer could be detected by NMR, as determined by the absence of the H-1 absorption characteristic of such materials in the 9.5–9.9 ppm region.[23] This conclusion was substantiated by LAD re-



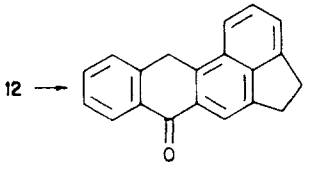
33 **34** **35** (22)

duction/dehydration, which gave 7-deuteriobenz[*a*]anthracene **35** with >97% isotope incorporation, as measured by ^{1}H NMR. No deuterium was detected at C-12, as signified by the 1:1 integrals for H-1 and H-12.

The related cycloadducts **9** and **12** were examined briefly in small-scale experiments with TFA in $CDCl_3$ solvent, giving spectra consistent with the structures **36** and **37**, respectively. These products (which were not isolated or examined further) are expected since both the benz[*a*] ring (cf. eq 22) and the methyl substituent (cf. eq 17) effects are working in concert to lead to this regiochemistry.



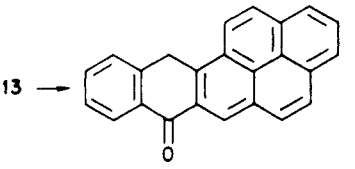
36 (23)



37 (24)

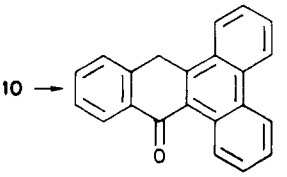
The naphtho[2,1,8a,8-*qra*]naphthacene derivative **13** also reacted readily with TFA in $CDCl_3$, but in this instance a pale yellow solid precipitated from solution. We were unable to obtain a sufficiently concentrated solution in various solvents for an NMR spectrum of this material, but the MS is appropriate for the anthrone **38**, with the regiochemistry shown based on analogy with the preceding examples.

The dibenz[*a*,*c*]anthracene derivative **10** is an interesting case, since the TFA reaction necessarily results in the "bay



38 (25)

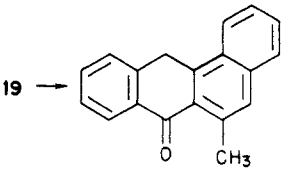
region" ketone **39**. This reaction indeed proceeds as shown in eq 26, but it is significantly slower than, e.g., the reactions of the unsubstituted anthracene system **21** or the benz[*a*]anthracene derivative **33**. Although the factor(s) causing this has not been identified, structural features which force the formation of a bay region ketone suppress the rate of the TFA reaction.



39 (26)

This aspect is especially pronounced for the 6-bromobenz[*a*]anthracene derivative **18**, in which the bromo substituent has the opposite directing influence from the benz[*a*] ring. In fact, **18** fails to react with TFA under our usual conditions and also in refluxing $CHCl_3$ (2 days). Even methanesulfonic acid does not cause reaction with this substrate, and to date we have been unable to effect the desired conversion to an anthrone with **18**, alone among all the compounds examined (it is recovered unchanged).

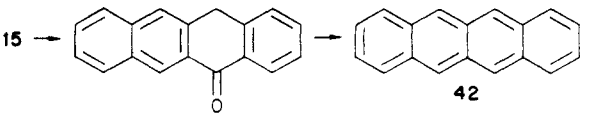
The same opposing regiochemical features, but without the rate suppression caused by the bromo substituent, are found in the 6-methylbenz[*a*]anthracene derivative **19**. In this instance, the conversion to anthrone also proved to be very sluggish with TFA, and this led to the examination of methanesulfonic acid as a stronger alternative. Slow reaction occurred, leading to 6-methyl-7(12*H*)-benz[*a*]anthracenone (**40**) as shown in eq 27. This structure



40 (27)

assignment is based on the NMR spectrum, which exhibits only one methylene singlet at 4.7 ppm, and more significantly, the absence of any absorption downfield of 8.4 ppm (a doublet for H-1 is expected downfield of 9 ppm for the alternative bay region ketone). It is not clear why **19** opens (exclusively) in this direction, particularly in view of the reaction of **10** (eq 26), which shows that it is possible to form a bay region ketone, and the strong selectivity of **3** (eq 16) for carbonyl formation distal from the methyl group. Clearly some step in the formation of a bay region ketone is kinetically disfavored.

The tetracene derivative **15** reacted readily with TFA to give 5(12*H*)-naphthacenone **41**; LAH reduction/dehydration of **41** was carried out to form the bright orange hydrocarbon naphthacene (tetracene, **42**). Gribble and

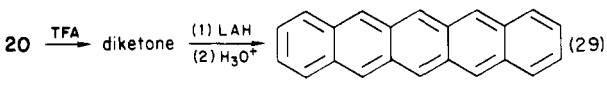


41 (28)

(23) For discussion of this point, see ref 12. Partially oxidized samples of **34** show absorptions in this downfield region, indicative of quinone formation.

co-workers have recently reported a novel alternative synthesis of **42**, involving a (formal) bis aryne cycloaddition with furan.[24]

Interestingly, the pentacene bis 1,4-epoxide **20** also reacts with TFA, generating a pink precipitate which had very low solubility characteristics and was characterized only by MS and IR (1660 cm^{-1}). This is presumably either the cis or trans diketone (or a mixture of the two), since addition of excess LAH to a slurry of this material in THF caused a reaction (slow, presumably limited by the rate of dissolution) which, after acidic workup, allowed the isolation by filtration of the dark purple-blue hydrocarbon pentacene **43**. This notoriously insoluble substance was characterized by MS and UV. Its pale blue (very dilute) solutions are rapidly photooxidized on exposure to air, in accord with the known properties of pentacene.[25]



(29)

43

The cycloaddition of arynes with 1,3-bis(trimethylsilyl)isobenzofuran thus provides a convenient method to construct the carbon ring skeleton of the various materials described here, affording some specific substitution patterns from readily available starting materials. The TFA-induced conversion of the cycloadducts to anthrones is highly regioselective for several of the substrates examined, allowing the selective introduction of another substituent at this stage. The (successful) TFA reactions all give anthrones in essentially quantitative yield (by NMR), and subsequent reduction/dehydration therefore results in an expeditious route to various polycyclic aromatic hydrocarbons.

Experimental Section

All of the aryl halides were obtained from the Aldrich Chemical Co., except 1-bromopyrene, which was purchased from Cambridge Chemical, Inc., and 2,3-dibromonaphthalene, which was prepared following the literature procedure.[26] The commercial materials were used as received. Other reagents, instruments for analyses, and the general procedure for converting acetal **1** to 1,3-bis(trimethylsilyl)isobenzofuran have been described previously.[2] Combustion analyses were performed by Galbraith Laboratories, Knoxville, TN. All ^1H NMR spectra were recorded at 300 MHz in $CDCl_3$, unless otherwise stated. Reactions were carried out under N_2, with transfers by syringe.

9,10-Bis(trimethylsilyl)-9,10-dihydro-9,10-epoxy-1-methylanthracene (3). A solution of **2** was prepared in an ice bath from 6.0 mmol of **1** in 10 mL of ether by addition of catalytic tetramethylpiperidine (5 mol %) and 19.5 mmol of *n*-butyllithium (in 12.2 mL of hexane), followed after 3 h by 13.4 mmol of Me_3SiCl. To this mixture were added *o*-chlorotoluene (9.0 mmol) and 12 mmol of freshly prepared (at 0 °C) LTMP (in 15 mL of ca. 1:1 ether/hexane), with stirring continued at ambient temperature for 15 h. The mixture was taken up in additional ether, washed with 5% HCl and brine, dried over K_2CO_3, and rotary evaporated to give 2.5 g of crude orange solid. Chromatography (silica gel, 10% CH_2Cl_2 in Skelly-solv) gave 1.89 g (90%) of essentially pure colorless **3**, which upon recrystallization from aqueous methanol afforded 1.60 g (77%) of **3**: mp 93–94 °C; ^1H NMR δ 0.382 (s, 9 H), 0.387 (s, 9 H), 2.40 (s, 3 H), 6.72 (d, 1 H, J = 8 Hz), 6.84 (dd, apparent t, 1 H, J = 8 Hz), 6.92 (m, 2 H), 7.09 (d, 1 H, J = 8 Hz), 7.26 (m, 2 H); MS calcd for $C_{21}H_{28}OSi_2$ 352.1678, found 352.1685. Anal. Calcd: C, 71.53; H, 8.00. Found: C, 71.39; H, 8.09.

9,10-Dihydro-9,10-epoxy-1-methylanthracene (4). To a solution of **3** (0.50 g, 1.4 mmol) in 5 mL of Me_2SO was added 3.5 mmol of powdered KOH. A deep red color developed and TLC indicated that all of the **3** had been consumed within 5 min. The mixture was taken up in a large volume of brine and extracted (3×) with CH_2Cl_2. The organic phase was washed with brine, dried over K_2CO_3, and rotary evaporated to give an off-white solid contaminated with Me_2SO. Chromatography as above gave 0.29 g (100%) of colorless solid (pure by NMR), which was recrystallized from aqueous methanol to give 0.21 g (71%) of pure **4**: mp 115–116 °C; ^1H NMR δ 2.40 (s, 3 H), 6.08 (s, 1 H), 6.16 (s, 1 H), 6.84 (d, 1 H, J = 8 Hz), 6.95 (dd, apparent t, 1 H), 7.05 (m, 2 H), 7.19 (d, 1 H, J = 7 Hz), 7.35 (m, 2 H); MS calcd for $C_{15}H_{12}O$ 208.0888, found 208.0875.

1-(Bromomethyl)-9,10-dihydro-9,10-epoxyanthracene (5a). *N*-bromosuccinimide (97 mg, 0.49 mmol) and a catalytic amount of benzoyl peroxide were added to 0.49 mmol of **4** in 4 mL of CCl_4, and the mixture was refluxed for 1 h. After cooling, the solution was washed with water and 5% NaOH, dried over K_2CO_3, and rotary evaporated to give colorless solid, mp 129–130 °C (with decomposition), in essentially quantitative yield. The diastereotopic methylene protons of **5a** result in an AB q when viewed at 60 MHz and two distinct doublets at 300 MHz: ^1H NMR δ 4.38 (d, 1 H, J = 10.5 Hz), 4.65 (d, 1 H, J = 10.5 Hz), 6.06 (s, 1 H), 6.30 (s, 1 H), 6.96 (m, 4 H), 7.24 (d, 1 H, J = 7 Hz), 7.30 (m, 1 H); MS calcd for $C_{15}H_{11}BrO$ 287.9973, found 287.9982.

1-(Acetoxymethyl)-9,10-dihydro-9,10-epoxyanthracene (5b). A solution of 120 mg (0.42 mmol) of **5a** and NaOAc (103 mg, 1.25 mmol) in 5 mL of DMF was stirred at ambient temperature for 29 h, then taken up in a large volume of water, and extracted with Skelly-solv. After the usual washing and drying, rotary evaporation afforded a pale yellow oil (63 mg, 56%), contaminated by DMF. Chromatography gave crystalline **5b** (35%): mp 111–113.5 °C; ^1H NMR δ 2.10 (s, 3 H), 5.18 (AB q, 2 H, diastereotopic CH_2OAc), 6.06 (s, 1 H), 6.26 (s, 1 H), 6.98 (m, 4 H), 7.30 (m, 3 H); MS calcd for $C_{17}H_{14}O_3$ 266.0943, found 266.0942.

9,10-Bis(trimethylsilyl)-9,10-dihydro-9,10-epoxy-2-methylanthracene (6). The same procedure and scale used to prepare **3** were employed, with 9 mmol of *p*-bromotoluene. Workup after 18 h followed by chromatography gave 1.61 g (77%) of product; recrystallization from aqueous methanol returned 1.50 g (71%) of pure **6**: mp 113–115 °C; ^1H NMR δ 0.39 (s, 9 H), 0.40 (s, 9 H), 2.29 (s, 3 H), 6.73 (d, 1 H, J = 8 Hz), 6.92 (m, 2 H), 7.08 (s, 1 H), 7.14 (d, 1 H, J = 8 Hz), 7.26 (m, 2 H); MS calcd for $C_{21}H_{28}OSi_2$ 352.1679, found 352.1698. Anal. Calcd: C, 71.53; H, 8.00. Found: C, 71.24; H, 8.16.

9,10-Dihydro-9,10-epoxy-2-methylanthracene (7). The procedure and scale used to prepare **4** were duplicated here; although the reaction was complete within 15 min, stirring was continued for 1 h without further change. Pure **7**, mp 111–112 °C, was obtained in quantitative yield by chromatography: ^1H NMR δ 2.31 (s, 3 H), 6.04 (s, 1 H), 6.06 (s, 1 H), 6.84 (d, 1 H, J = 7 Hz), 7.03 (m, 2 H), 7.19 (s, 1 H), 7.23 (d, 1 H, J = 7 Hz), 7.33 (m, 2 H); MS calcd for $C_{15}H_{12}O$ 208.0888, found 208.0894.

2-(Bromomethyl)-9,10-dihydro-9,10-epoxyanthracene (8a). This reaction was carried out as described for **5a**, with 140 mg (0.67 mmol) of **7** and 120 mg (0.67 mmol) of NBS. The product was obtained as a viscous oil, which was used in the next step without further purification: ^1H NMR (80 MHz) δ 4.36 (s, 2 H), 6.01 (s, 2 H), 7.15 (m, 5 H), 8.0 (m, 1 H).

2-(Acetoxymethyl)-9,10-dihydro-9,10-epoxyanthracene (8b). The conditions used to prepare **5b** were repeated but with a reaction time of 1 h. Chromatography (CH_2Cl_2) gave 39% of a viscous oil: ^1H NMR δ 2.05 (s, 3 H), 5.01 (s, 2 H), 6.04 (s, 2 H), 7.0 (m, 3 H), 7.30 (s, 1 H, overlapping m, 3 H); MS calcd for $C_{17}H_{14}O_3$ 266.0943, found 266.0939.

7,12-Bis(trimethylsilyl)-7,12-dihydro-7,12-epoxy-5-methylbenz[*a*]anthracene (9). This reaction was carried out by the general method described for the preparation of **3**, with 3 mmol of **1**, 4.5 mmol of 1-bromo-4-methylnaphthalene, and 6.0 mmol of LTMP. After 15 h, the usual workup gave the crude product, which was chromatographed to give **9** contaminated by some of the starting aryl halide. Recrystallization from ethanol

(24) Gribble, G. W.; Perni, R. B.; Onan, K. D. *J. Org. Chem.* **1985**, *50*, 2934.

(25) Clar, E. "Polycyclic Hydrocarbons"; Academic Press: New York 1964; p 423.

(26) Danish, A. A.; Silverman, M.; Tajima, Y. A. *J. Am. Chem. Soc.* **1954**, *76*, 6144. This preparation was skillfully carried out by Russell White.

gave 800 mg (67%) of pure **9**: mp 186–187 °C; ^{1}H NMR δ 0.43 (s, 9 H), 0.48 (s, 9 H), 2.65 (s, 3 H), 6.84 (m, 2 H), 7.38 (s, 1 H, overlapping m, 4 H), 7.93 (d, 1 H, J = 8 Hz), 8.02 (d, 1 H, J = 9 Hz); MS calcd for $C_{25}H_{30}OSi_2$ 402.1836, found, 402.1821. Anal. Calcd: C, 74.57; H, 7.51. Found: C, 74.27; H, 7.64.

7,12-Dihydro-7,12-epoxy-5-methylbenz[*a*]anthracene. A portion of **9** (430 mg, 1.07 mmol) in 8 mL of Me_2SO was treated with 300 mg of powdered KOH, giving a deep red solution. After 1 h, workup as before gave 249 mg (90%) of yellow crystalline solid; recrystallization from ethanol returned 206 mg (83%) of slightly discolored product: mp 186–187.5 °C; ^{1}H NMR δ 2.68 (s, 3 H), 6.24 (s, 1 H), 6.59 (s, 1 H), 6.97 (m, 2 H), 7.48 (s, 1 H, overlapping m, 3 H), 7.97 (dd, apparent t, 2 H); MS calcd for $C_{19}H_{14}O$ 258.1045, found 258.1040.

9,14-Bis(trimethylsilyl)-9,14-dihydro-9,14-epoxydibenz[*a*,*c*]anthracene (10). A water-washed and K_2CO_3-dried solution of **2** (prepared from 6.1 mmol of **1**) was treated with 1.57 g (6.7 mmol) of 9-bromophenanthrene followed by 12.2 mmol of LTMP. After 67 h TLC and NMR examination indicated that a significant amount of the aryl halide remained, and so an additional 12.2 mmol of LTMP was added, with stirring continued for 20 h. The usual workup gave 2.0 g of crude orange-brown solid; the NMR spectrum of this material indicated a major amount of product but contaminated by significant aromatic impurities. Attempts to purify the product at this stage by either chromatography or charcoal decolorization were largely unsuccessful. The best approach involved trituration of the solid with small amounts of methanol, which removed most of the color along with some product, leaving 834 mg of solid in this particular reaction. Recrystallization from methanol gave 690 mg (27%) of pure **10** as off-white crystals: mp 224.5–226 °C; ^{1}H NMR δ 0.59 (s, 18 H), 6.89 (AA′BB′ apparent dd, 2 H, J = 6, 3 Hz), 7.39 (identical with preceding), 7.63 (m, 4 H), 8.19 (d, 2 H, J = 8 Hz), 8.72 (d, 2 H, J = 8 Hz); MS calcd for $C_{28}H_{30}OSi_2$ 438.1835, found 438.1807. Anal. Calcd: C, 76.66; H, 6.89. Found: C, 76.29; H, 6.82.

9,14-Dihydro-9,14-epoxydibenz[*a*,*c*]anthracene. Protiodesilyation of **10** was accomplished by treatment of 0.20 g (0.45 mmol) in 5 mL of THF with 2.3 mmol of tetra-*n*-butylammonium fluoride (TBAF);[2] the reaction was complete within 10 min. The mixture was rotary evaporated to remove most of the THF, taken up in ether, and washed with brine. After the usual drying, evaporation gave crude product in quantitative yield. Recrystallization from ethanol afforded pure product as off-white crystals: mp 247–249 °C; ^{1}H NMR δ 6.74 (s, 2 H), 6.98 (AA′BB′ apparent dd, 2 H, J = 5,3 Hz), 7.65 (identical with preceding), 7.68 (m, 4 H), 8.08 (m, 2 H), 8.71 (m, 2 H); MS calcd for $C_{22}H_{14}O$ 294.1042, found 294.1026. Anal. Calcd: C, 89.77; H, 4.79. Found: C, 89.50; H, 4.65.

Dibenz[*a*,*c*]anthracene. A mixture of 9,14-dihydro-9,14-epoxydibenz[*a*,*c*]anthracene (50 mg, 0.17 mmol) and 82 mg (0.23 mmol) of $Fe_2(CO)_9$ (*Hood*!) in 5 mL of distilled benzene was refluxed for 24 h. The residue after evaporation was taken up in CH_2Cl_2 and filtered through Celite to give, after removal of the solvent, 29 mg (62%) of crude product as a brown solid. Chromatography gave 12.1 mg (25%) of pure dibenz[*a*,*c*]anthracene, mp 206–207.5 °C (mp and NMR identical with those of commercial material).

9,10-Bis(trimethylsilyl)-9,10-dihydro-9,10-epoxy-1-methoxyanthracene (11). This preparation was carried out in the usual one-flask way starting with 3.0 mmol of **1** and employing 4.5 mmol of *o*-bromoanisole. After a 10-h reaction time, workup as before gave crude material in high yield (1.28 g), which by NMR consisted of 11 contaminated mainly by the starting aryl halide. Chromatography (silica gel) caused extensive decomposition of this material, giving only 540 mg of product, still contaminated by a small amount of the aryl halide. Recrystallization of this sample from methanol yielded 335 mg (30%) of pure **11**: mp 150.5–153.5 °C; ^{1}H NMR δ 0.37 (s, 9 H), 0.41 (s, 9 H), 3.83 (s, 3 H), 6.58 (dd, 1 H, J = 5, 3 Hz), 6.95 (m, 4 H), 7.31 (m, 2 H); MS calcd for $C_{21}H_{28}OSi_2$ 368.1627, found 368.1635. Anal. Calcd: C, 68.43; H, 7.66. Found: C, 68.24; H, 7.75.

7,12-Bis(trimethylsilyl)-7,12-epoxy-4,5,7,12-tetrahydrobenz[*k*]acephenanthrylene (12). The usual conditions, with 3.05 mmol of **1** and 0.782 g (3.36 mmol) of 5-bromoacenaphthene and a reaction time of 21 h, were employed. Methylene chloride was used for extraction, yielding 1.08 g of crude red solid, largely the desired product (NMR). Chromatography on silica gel caused extensive decomposition, resulting in the recovery of only 417 mg (33%) of oily and still discolored **12**, which could not be induced to crystallize from hexane or methanol. This material was rechromatographed on Florisil (Skelly-solv) to give 323 mg (26%) of product, which was recrystallized from methanol to give pure **12**: mp 186–188 °C; ^{1}H NMR δ 0.43 (s, 9 H), 0.49 (s, 9 H), 3.24–3.42 (m, 4 H), 6.85 (m, 2 H), 7.11 (d, 1 H, J = 7 Hz), 7.33 (m, 5 H), 7.65 (d, 1 H, J = 8 Hz); MS calcd for $C_{26}H_{30}OSi_2$ 414.1835, found 414.1831. Anal. Calcd: C, 75.30; H, 7.29. Found: C, 75.67; H, 7.34.

7,12-Bis(trimethylsilyl)-7,12-dihydro-7,12-epoxynaphtho[2,1,8a,8-*qra*]naphthacene (13). This reaction was carried out on the same scale as the preceding example, using 0.942 g (3.35 mmol) of 1-bromopyrene and a reaction time of 23 h. The dark crude solid product was charcoal decolorized and then recrystallized (3×) from methanol to give 376 mg (27%) of analytically pure **13**: mp 177–178 °C; ^{1}H NMR δ 0.53 (s, 9 H), 0.57 (s, 9 H), 6.90 (m, 2 H), 7.35 (m, 1 H), 7.43 (m, 1 H), 8.08 (s, overlapping m at 8.03, 7 H total), 8.23 (d, 1 H, J = 9 Hz); MS calcd for $C_{30}H_{30}OSi_2$ 462.1836, found 462.1811. Anal. Calcd: C, 77.87; H, 6.53. Found: C, 77.27; H, 6.63.

9,10-Bis(trimethylsilyl)-9,10-dihydro-9,10-epoxy-2,3-dimethylanthracene (14). In the normal manner, 6.0 mmol of **1**, 9.0 mmol of 4-chloro-1,2-dimethylbenzene, 12.0 mmol of LTMP, and a reaction time of 20 h were used. Chromatography of the crude solid gave pure **14** as colorless crystals: mp 156–158 °C; ^{1}H NMR δ 0.39 (s, 18 H), 2.18 (s, 6 H), 6.91 (AA′BB′ apparent dd, 2 H, J = 5, 2 Hz), 7.04 (s, 2 H), 7.23 (identical with absorption at δ 6.91). Anal. Calcd for $C_{22}H_{30}OSi_2$: C, 72.07; H, 8.25. Found: C, 71.86; H, 8.21.

9,10-Dihydro-2,3-dimethyl-9,10-epoxyanthracene. A deep pink color developed upon addition of KOH (excess) to a solution of **14** (800 mg) in 10 mL of Me_2SO. The usual workup followed by chromatography gave 450 mg (100%) of off-white solid: mp 192–194 °C; ^{1}H NMR δ 2.21 (s, 6 H), 6.02 (s, 2 H), 7.01 (AA′BB′ apparent dd, 2 H, J = 5, 2 Hz), 7.15 (s, 2 H), 7.31 (identical with pattern at δ 7.01, 2 H); MS calcd for $C_{16}H_{14}O$ 222.1045, found 222.1048.

5,12-Bis(trimethylsilyl)-5,12-dihydro-5,12-epoxynaphthacene (15). A solution of **2** was prepared in the usual way from 6.1 mmol of **1**. To this mixture, 2,3-dibromonaphthalene (1.9 g, 6.7 mmol) was added; the solution was cooled to −65 °C, and then 6.7 mmol of *n*-butyllithium was introduced rapidly. The mixture was allowed to warm slowly overnight. The usual workup and chromatography (neutral III alumina, Skelly-solv/2% ether) gave 1.9 g (78%) of yellow solid. Recrystallization from high boiling petroleum ether returned 52% (1.25 g) of pure **15** as colorless prisms: mp 136–137 °C; ^{1}H NMR δ 0.48 (s, 18 H), 6.98 (dd, 2 H, J = 5, 3 Hz), 7.33 (dd, 2 H, J = 6, 2 Hz), 7.42 (dd, 2 H, J = 6, 3 Hz), 7.61 (s, 2 H), 7.72 (dd, 2 H, J = 6, 3 Hz); MS calcd for $C_{24}H_{28}OSi_2$ 388.1679, found 388.1690. Anal. Calcd: C, 74.17; H, 7.26. Found: C, 74.26; H, 7.42.

5,12-Dihydro-5,12-epoxynaphthacene. A solution of **1** (6.7 mmol) in 10 mL of ether was converted to isobenzofuran by treatment with a catalytic amount of diisopropylamine and 6.7 mmol of *n*-butyllithium. After 2 h, 2,3-dibromonaphthalene (dissolved in THF) was added, the mixture was brought to reflux, and 6.7 mmol of *n*-butyllithium was added via syringe pump over a period of 35 min. The usual workup followed by chromatography gave 50% of impure dark product. This was subjected to charcoal filtration and then recrystallized by taking up in a small volume of CH_2Cl_2 and adding hexane to the cloud point, to afford 20% of the desired product: mp 189.5–190.5 °C; ^{1}H NMR δ 6.18 (s, 2 H), 7.04 (dd, 2 H, J = 5, 3 Hz), 7.36 (dd, 2 H, J = 5, 3 Hz), 7.41 (dd, 2 H, J = 5, 3 Hz), 7.68 (s, 2 H), 7.71 (dd, 2 H, J = 5, 3 Hz); MS calcd for $C_{18}H_{12}O$ 244.0887, found 244.0891.

9,10-Bis(trimethylsilyl)-1-bromo-9,10-dihydro-9,10-epoxyanthracene (16). In a larger scale reaction, 4.85 g (29.6 mmol) of **1** was converted to **2** in the usual way. To this was added 44.4 mmol of *o*-dibromobenzene, followed by 44.6 mmol of LTMP, with stirring continued for 46 h. The mixture was taken up in ether and extracted repeatedly with water, 5% HCl, 5% $NaHCO_3$, and brine. Drying and evaporation gave 16 g of a red pasty residue, which was taken up in 20 mL of refluxing CH_2Cl_2, with subsequent addition of 25 mL of methanol. Pale yellow crystals weighing 7.49

g (61%) were collected; the mother liquor was evaporated to ca. 15 mL and deposited a second crop, 1.26 g (10%). Several attempts to isolate **16** from crude material by chromatography on either silica gel or alumina resulted in complete loss of this product. Pure **16** has mp 146–147 °C: ^{1}H NMR δ 0.38 (s, 9 H), 0.47 (s, 9 H), 6.78 (dd, apparent t, 1 H, J = 8 Hz), 6.97 (m, 2 H), 7.06 (d, 1 H, J = 8 Hz), 7.15 (d, 1 H, J = 7 Hz), 7.26 (m, 1 H), 7.39 (m, 1 H); MS m/z (relative intensity) 418 (parent, 2.1), 416 (parent, 2.1), 347 (3.1), 346 (13.1), 345 (8.7), 344 (13.0), 343 (6.1), 337 (6.0), 322 (4.5), 302 (5.9), 300 (6.0), 147 (10), 73 (100); calcd for $C_{20}H_{25}{}^{79}BrOSi_2$ 416.0626, found 416.0628. Anal. Calcd: C, 57.54; H, 6.04. Found: C, 57.30; H, 5.86.

1-Bromo-9,10-dihydro-9,10-epoxyanthracene. The TBAF procedure was used, followed by recrystallization from methanol, to obtain 67% of this protiodesilylated product: mp 106–106.5 °C; ^{1}H NMR δ 6.15 (s, 1 H), 6.17 (s, 1 H), 6.91 (dd, apparent t, 1 H, J = 8 Hz), 7.07–7.15 (m, 4 H), 7.26 (d, 1 H, J = 7 Hz), 7.37 (m, 1 H), 7.46 (m, 1 H).

9,10-Bis(trimethylsilyl)-2-bromo-9,10-dihydro-9,10-epoxyanthracene (17). This preparation was carried out with 7.3 mmol of **1**, 7.7 mmol of *p*-dibromobenzene, 7.3 mmol of LTMP, and a reaction time of 24 h. Workup and crystallization as above gave 0.69 g (23%) of **17**: mp 109–110 °C; ^{1}H NMR δ 0.39 (s, 9 H), 0.40 (s, 9 H), 6.91 (m, 2 H), 7.00–7.08 (m, 2 H), 7.22 (m, 2 H), 7.30 (s, 1 H). Anal. Calcd for $C_{20}H_{25}BrOSi_2$: C, 57.54; H, 6.04. Found: C, 57.44; H, 5.89.

7,12-Bis(trimethylsilyl)-6-bromo-7,12-dihydro-7,12-epoxybenz[*a*]anthracene (18). The dehydrohalogenation of 2,3-dibromonaphthalene (6.1 mmol) in the presence of **2** (from 6.0 mmol of **1**) was carried out in the usual manner, with 14.4 mmol of LTMP and a reaction time of 55 h (**18** appears to be very resistant to further reaction with LTMP). Chromatography of the crude product (silica gel, 10% CH_2Cl_2/Skelly-solv) gave 64% of essentially pure **18**, which was recrystallized from methanol to provide analytically pure **18**: mp 185–186 °C; ^{1}H NMR δ 0.502 (s, 9 H), 0.506 (s, 9 H), 6.90 (m, 2 H), 7.41 (m, 4 H), 7.71 (s, 1 H, overlapping downfield portion of d, 1 H), 7.99 (d, 1 H, J = 8 Hz); MS calcd for $C_{24}H_{27}BrOSi_2$ 468.0764, found 468.0789. Anal. Calcd: C, 61.65; H, 5.82. Found: C, 61.49; H, 5.62.

6-Bromo-7,12-dihydro-7,12-epoxybenz[*a*]anthracene. The KOH/Me_2SO method was used (30 min) to convert **18** to its protiodesilyated derivative, which was isolated by chromatography as a solid: mp 89–92 °C; ^{1}H NMR δ 6.37 (s, 1 H), 6.67 (s, 1 H), 7.03 (m, 2 H), 7.49 (m, 4 H), 7.73 (s, 1 H, overlapping d, 1 H), 7.89 (d, 1 H, J = 8 Hz); MS calcd for $C_{18}H_{11}BrO$ 323.9973, found 323.9970.

7,12-Bis(trimethylsilyl)-7,12-dihydro-7,12-epoxy-6-methylbenz[*a*]anthracene (19). Three attempts were made to convert **18** to **19**. In a preliminary small-scale reaction, the conversion appeared to be quite clean, but lower yields were encountered in the later trials. All were done in THF at 0 °C, by addition of CH_3Li (1.2 equiv, in ether), followed after 10 min by excess CH_3I (5–15 equiv). The combined crude products of the later reactions appeared to contain some **18**, and these were resubjected to this treatment, with some apparent improvement (suggesting the Li/Br exchange may be somewhat slower than usual for aromatic substrates). The product was isolated by addition of ether, washing with water and brine, drying over K_2CO_3, and evaporation; a material estimated to be ca. 50% **19** was obtained. Chromatography on silica gel with Skelly-solv gave about 90% recovery of a fast moving material, with slight improvement in purity (the aromatic region of the NMR gave too high an integral). Recrystallization from methanol (2×) gave pure **19**, mp 129–131 °C, in about 30% yield: ^{1}H NMR δ 0.46 (s, 9 H), 0.52 (s, 9 H), 2.62 (s, 3 H), 6.88 (m, 2 H), 7.2–7.4 (m, 4 H), 7.33 (s, 1 H), 7.73 (d, 1 H, J = 8 Hz), 8.01 (d, 1 H, J = 8 Hz). Anal. Calcd for $C_{19}H_{30}OSi_2$: C, 74.57; H, 7.51. Found: C, 74.30; H, 7.28.

5,14:7,12-Diepoxy-5,7,12,14-tetrahydro-5,7,12,14-tetrakis(trimethylsilyl)pentacene (20). A solution of **2** was prepared from 3.1 mmol of **1**, and treated with 1.6 mmol of *p*-dibromobenzene followed by 9.3 mmol of LTMP. The initially dark brown solution/slurry gradually lightened in color over the 24-h reaction time. Normal workup and evaporation gave a dark solid weighing 0.75 g. Trituration with methanol and filtration gave 388 mg (39%) of colorless solid, mp 287–329 °C. NMR features indicated that this was a ca. 1:1 mixture of cis and trans isomers of **20**. The MS of the mixture showed peaks at m/z (relative intensity) 601 (1.5), 600 (4.1), 599 (7.5), 598 (parent, 13.8), 526 (17), 525 (13), and 73 (100): MS calcd for $C_{34}H_{46}O_2Si_4$ 598.2575, found 598.2550. One of the isomers (a) was obtained in essentially pure form by removal of the other more soluble component by trituration with $CHCl_3$, allowing the following assignments.

Isomer a: mp 338–341 °C; ^{1}H NMR δ 0.29 (s, 36 H), 6.88–6.92 (m, 4 H), 7.12 (s, 2 H), 7.19–7.24 (m, 4 H).

Isomer b: ^{1}H NMR δ 0.33 (s, 36 H), 6.80–6.85 (m, 4 H), 7.14 (s, 2 H), 7.13–7.17 (m, 4 H).

5,14:7,12-Diepoxy-5,7,12,14-tetrahydropentacene. The TBAF/THF procedure (1 h, CH_2Cl_2 workup) was used to protiodesilylate a sample of **20**, giving a colorless powdery product, mp 238–243 °C, in high yield: MS, m/z (relative intensity) 312 (3.7), 311 (24.2), 310 (parent, 100), 294 (30.7), 252 (86.3), 149 (23.8), 126 (36.4); calcd for $C_{22}H_{14}O_2$ 310.0993, found 310.0976. This material was sparingly soluble in $CDCl_3$, and the spectrum described may indicate that only one isomer had dissolved: ^{1}H NMR δ 5.95 (s, 4 H), 6.93–6.97 (m, 4 H), 7.22–7.26 (m, 4 H).

Two attempts were made to deoxygenate the mixture, with 2 and 11 mol equiv of $Fe_2(CO)_9$ in refluxing benzene.[2] The starting material was consumed, but we were unable to obtain evidence indicating the formation of pentacene under these conditons.

9(10*H*)-Anthracenone (22). Treatment of **21** (available from previous work[2]) in $CDCl_3$ solvent with ca. 4 mol equiv of TFA gave **22**, with the reaction complete within a few minutes; the product was formed in essentially quantitative yield and was identical (mp, NMR) with commercial material.

4-Methyl-9(10*H*)-anthracenone (23). A solution of **3** (300 mg, 0.852 mmol) in 2 mL of CCl_4 was treated with 2.6 mmol of TFA; an exotherm and yellow-orange coloration were observed. The starting material was consumed within 5 min (TLC, NMR). In this experiment, the mixture was taken up in additional CCl_4, washed and dried over K_2CO_3, and vacuum evaporated to give 147 mg (83%) of colorless crystalline **23**: mp 127–128 °C (lit.[27] mp 128–129 °C); ^{1}H NMR δ 2.43 (s, 3 H), 4.12 (s, 2 H), 7.47 (m, 5 H), 8.25 (d, 1 H, J = 8 Hz), 8.34 (d, 1 H, J = 8 Hz); ^{13}C NMR (20 MHz) 19.12, 30.45, 125.51, 126.64, 126.93, 127.40, 128.64, 131.70, 132.61, 134.06, 136.00, 138.71, 140.24, 185.17 ppm (one Ar C not separately detected).

1,10-Dimethylanthracene (24). To a solution of CH_3MgBr (1.0 mmol) in 5 mL of ether was added 1 mL of THF containing freshly prepared **23** (118 mg, 0.33 mmol). The solution developed a yellow color. After being stirred for 0.5 h, the mixture was taken up in additional ether, washed with 5% HCl, $NaHCO_3$, and brine, dried, and evaporated to give 73 mg of an orange oil. Chromatography (silica gel, Skelly-solv/CH_2Cl_2) afforded 36 mg (52%) of solid **24**, which was recrystallized from aqueous ethanol to return 29 mg of brilliant yellow-green crystals: mp 88.5–89.5 °C (lit.[16] mp 88–89 °C); ^{1}H NMR δ 2.82 (s, 3 H), 3.10 (s, 3 H), 7.42 (m, 4 H), 8.04 (d, 1 H, J = 8 Hz), 8.17 (d, 1 H, J = 9 Hz), 8.23 (d, 1 H, J = 9 Hz), 8.47 (s, 1 H).

2- and 3-Methyl-9(10*H*)-anthracenone (25 + 26). The addition of 4.6 mmol of TFA to 1.53 mmol of **7** in 5 mL of CCl_4 caused a slight exotherm. After 1 h, vacuum evaporation gave crude product as an orange viscous oil. The ^{1}H NMR of this material indicated that it was a mixture of isomers **25** and **26** in a ratio of ca. 70/30, but peak separation was insufficient for complete characterization: δ 2.38 (minor) and 2.40 (major methyl), 4.18 (minor, shoulder) and 4.19 (major methylene), 7.16–7.6 (m, 5 H), 8.14 (s, H-1 of **25**), 8.21 (d, one H peri to carbonyl of minor isomer), and 8.34 (d, H-8 of **25** overlapping other peri H of **26**). The ^{13}C NMR of this material also supported this conclusion, in particular by showing two peaks for both the methyl and methylene carbons in an approximate 70/30 ratio.

Reduction of 325 mg of this crude mixture with excess (300 mg) of LAD in 5 mL of ether, followed by 5% HCl treatment and normal workup gave 250 mg of crude product, mainly alcohol; this was subjected to a catalytic amount of TFA in $CDCl_3$, causing rapid dehydration to a mixture of **27** and **28**, analyzed as described in the text.

4-Methoxy-9(10*H*)-anthracenone (29). TFA (0.14 mL, 1.8 mmol) was added to 227 mg (0.617 mmol) of **11** in 5 mL of CCl_4;

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after 1 h, rotary evaporation gave product as an off-white solid. A portion was recrystallized from THF (2×) to provide colorless **29**: mp 134–136 °C, with darkening on melting (lit.[19] mp 134–135 °C); ^{1}H NMR δ 3.90 (s, 3 H), 4.07 (s, 2 H), 7.04 (d, 1 H, J = 8 Hz), 7.41 (m, 2 H), 7.59 (m, 1 H), 7.92 (d, 1 H, J = 8 Hz), 8.38 (d, 1 H, J = 8 Hz).

2,3-Dimethyl-9(10*H*)-anthracenone (30). A similar but more dilute reaction of **14** (84 mg, 0.23 mmol) in 5 mL of CCl_4 with 0.053 mL of TFA required 3.5 h for completion (TLC). Evaporation gave **30** as pale yellow crystals: mp 157–163 °C to a dark melt (lit.[21] mp 160.5–162 °C); ^{1}H NMR[21] δ 2.39 (s, 6 H), 4.30 (s, 2 h), 7.25 (s, 1 H), 7.47 (m, 2 H), 7.60 (m, 1 H), 8.14 (s, 1 H), 8.38 (d, 1 H, J = 8 Hz).

4-Bromo-9(10*H*)-anthracenone (31). Treatment of 50 mg (1.2 mmol) of **16** in 5 mL of benzene with TFA (4.8 mmol) for 2 h, followed by evaporation, gave essentially pure **31** as a yellow solid (100%). Recrystallization from methanol returned 75% of crystalline **31**: mp 137.5–138.5 °C; ^{1}H NMR δ 4.19 (s, 2 H), 7.3–7.6 (m, 4 H), 7.80 (d, 1 H, J = 8 Hz), 8.29 (dd, apparent t, 2 H, J = 8 Hz); MS, m/z (relative intensity) 275 (7.2), 274 (parent, 46), 273 (47), 272 (parent, 47), 194 (16.9), 193 (100), 165 (42), 164 (17), 163 (27.8); calcd for $C_{14}H_9{}^{79}BrO$ 271.9837, found 271.9844.

Repetition of this experiment gave crude product which was reduced with excess LAD in THF. After the usual workup, TFA was added to the ethereal solution to effect dehydration. Evaporation gave 45 mg (96%) of deuterated 1-bromoanthracene (**32**). The ^{1}H NMR of this material was identical with that described below for the undeuterated compound, except for diminished singlets at δ 8.3 (representing ca. 6% of product containing H-10) and 8.78 (ca. 94% of H-9). The MS indicated that **32** contained one D/mol: MS, m/z (relative intensity) 260 (15.2), 259 (99.5), 258 (16.9), 257 (100), 179 (10.8), 178 (34.9), 177 (41.9), 176 (11), 175 (5.6); calcd for $C_{14}H_8{}^{79}BrD$ 256.9950, found 256.9950.

1-Bromoanthracene. To a solution of **31** (331 mg, 1.2 mmol) in 30 mL of THF was added 300 mg of LAH; a bright yellow color developed. After 15 min, the mixture was quenched, dehydrated, washed, dried, evaporated, and chromatographed to give 283 mg (92%) of the desired product. Recrystallization from methanol returned 247 mg (80%) of pure 1-bromoanthracene: mp 97.5–99.5 °C (lit.[22] mp 97–100 °C); ^{1}H NMR δ 7.18 (dd, apparent t, 1 H, J = 7 Hz), 7.44 (m, 2 H), 7.71 (d, 1 H, J = 7 Hz), 7.85 (d, 1 H, J = 8 Hz), 7.89–8.02 (m, 2 H), 8.29 (s, 1 H), 8.74 (s, 1 H).

2-Bromoanthracene. A sample of **17** (100 mg, 0.24 mmol) in 1 mL of CCl_4 was treated with 0.72 mmol of TFA, with stirring for 20 h (some precipitate observed). Vacuum evaporation gave 65 mg (100%) of the bromoanthrones as a nearly colorless powder: ^{1}H NMR δ 4.21 [with shoulder (ca. 15%) at δ 4.24] (s, 2 H), 7.25–7.7 (m, 5 H), 8.15 (d, ca. 7% of 1 H, attributed to a peri proton of the minor isomer, J = 8 Hz), 8.28 (d, 1 H, J = 8 Hz; H-8 of major isomer overlapping other peri H of minor isomer), 8.40 (s, ca. 1 H, H-1 of major isomer). The latter absorption indicates that the major anthrone (ca. 85%) is 2-bromo-9(10*H*)-anthracenone; i.e., the regioselectivity of this reaction parallels that of the 2-methyl analogue.

Unlike the 1-bromo analogue, reaction of the 2-bromoanthrone with excess LAH (5 mol equiv) in either THF or ether (ice bath, 15–30 min) caused extensive debromination, with eventual formation of anthracene. Use of ca. 0.1 mmol of LAH (ether, 0 °C) largely suppressed this overreduction, affording from 0.24 mmol of starting material **17**, 33 mg (53%) of the desired product. Recrystallized twice from methanol, pure 2-bromoanthracene has mp 223–224 °C (lit.[28] mp 211–212 °C): ^{1}H NMR δ 7.49 (m, 3 H), 7.88 (d, 1 H, J = 9 Hz), 7.99 (m, 2 H), 8.17 (s, 1 H), 8.32 (s, 1 H), 8.40 (s, 1 H).

7(12*H*)-Benz[*a*]anthracenone (34). Treatment of **33**[2] (273 mg, 0.704 mmol) with TFA (2.1 mmol) in 2 mL of CCl_4 for 1 h gave crude **34** as a yellow-orange solid; mp 160–169 °C (lit.[29] mp 181 °C). Compound **34**: ^{1}H NMR δ 4.69 (s, 2 H), 7.54 (m, 6 H), 7.84 (m, 2 H), 8.18 (m, 1 H), 8.36 (d, 1 H, J = 9 Hz).

Reduction of crude **34** with LAD, followed by TFA-catalyzed dehydration and column chromatography gave colorless 7-deuteriobenz[*a*]anthracene (**35**), mp 159–161 °C. The ^{1}H NMR spectrum of this product was identical with that of commerical benz[*a*]anthracene, except that no signal could be detected at δ 8.2 (position of H-7), allowing the conclusion that the sample contained >97% D at C-7.

5-Methyl-7(12*H*)-benz[*a*]anthracenone (36). A yellow precipitate appeared within 0.5 h when **9** (111 mg, 0.276 mmol) in 1 mL of $CDCl_3$ was treated with 3 equiv of TFA. An additional milliliter of solvent failed to redissolve the product completely. After the mixture was stirred for 1 day, the solvent was evaporated to give a yellow solid, mp >165 °C dec. A dilute (homogeneous) solution was prepared for NMR examination, which indicated that some oxidation (probably to bianthronyl diastereomers) had occurred at some stage of this treatment: ^{1}H NMR [of **36**] δ 2.80 (s, 3 H), 4.70 (s, 2 H), 7.54 (d, 1 H, J = 8 Hz), 7.63–7.75 (m, 5 H), 8.28 (s, 1 H), 8.34 (d, 1 H, J = 8 Hz), 8.43 (d, 1 H, J = 8 Hz). The absence of absorptions downfield of δ 8.5 rules out the presence of the alternative bay region anthrone or bianthronyls derived from this alternative structure.

4,5-Dihydro-7(12*H*)-benz[*k*]acephenanthrylenone (37). A solution of **12** (63 mg, 0.15 mmol) in 2 mL of CCl_4 was treated with 0.035 mL of TFA; a precipitate appeared after 2 h at ambient temperature. The volatiles were vacuum evaporated to give **37** as a yellow solid: mp 180–184 °C dec; ^{1}H NMR δ 3.46 (s, 4 H), 4.65 (s, 2 H), 7.51 (m, 2 H), 7.62 (m, 3 H), 7.95 (d, 1 H, J = 8 Hz), 8.30 (s, 1 H), 8.43 (d, 1 H, J = 8 Hz); MS calcd for $C_{20}H_{14}O$ 270.1044, found 270.1026.

7(12*H*)-Naphtho[2,1,8a,8-*qra*]naphthacenone (38). A solution of **13** (92 mg, 0.20 mmol) in 2 mL of $CDCl_3$ was treated with 0.046 mL of TFA. After 10 min, a yellow-orange precipitate was observed; 10 min later the volatiles were vacuum evaporated to give **38**, yellow-orange solid, mp >150 °C (darkens and gives a black melt below 240 °C). This product was too insoluble in common solvents to obtain an NMR: MS calcd for $C_{24}H_{14}O$ 318.1045, found 318.1032.

9(14*H*)-Dibenz[*a*,*c*]anthracenone (39). A mixture of **10** (400 mg, 0.91 mmol) and TFA (2.74 mmol) in 5 mL of $CDCl_3$ was examined by TLC periodically until starting material was consumed (36 h). Evaporation gave yellow solid **39**: mp 255–260 °C dec; ^{1}H NMR (CD_2Cl_2) δ 4.79 (s, 2 H), 7.67 (m, 7 H), 8.29 (d, 1 H, J = 8 Hz), 8.40 (d, 1 H, J = 8 Hz), 8.76 (m, 2 H), 9.63 (m, 1 H); MS/Cl (methane flow gas) calcd for $C_{22}H_{15}O$(P+H) 295.1122, found 295.1111.

6-Methyl-7(12*H*)-benz[*a*]anthracenone (40). Treatment of **19** under the usual conditions with TFA did not cause reaction. However, when 80 mg (0.20 mmol) of **19** in 1 mL of $CDCl_3$ was stirred with 0.6 mmol of methanesulfonic acid, the solution darkened and loss of starting material was judged complete after 43 h (TLC). The mixture was taken up in CH_2Cl_2 and washed with water, which caused the dark color to disappear. After drying over $MgSO_4$ the solvent was vacuum evaporated, to give 45 mg (88%) of a yellow solid: mp >135 °C (broad range with darkening); ^{1}H NMR δ 2.96 (s, 3 H), 4.66 (s, 2 H), 7.45–7.65 (m, 6 H), 7.78 (d, 1 H, J = 7 Hz), 8.20 (d, 1 H, J = 8 Hz), 8.31 (d, 1 H, J = 7 Hz); MS, m/z (relative intensity) 272 (1.7, possible quinone impurity), 260 (2.4), 259 (20.8), 258 (parent, 100), 257 (17.5), 244 (13.9), 243 (29.6), 229 (15.4), 228 (15.2), 226 (13.3), 215 (30.9); calcd for $C_{19}H_{14}O$ 258.1044, found 258.1030.

5(12*H*)-Naphthacenone (41). Benzene (1 mL) was used as the solvent for the reaction of **15** (50 mg, 0.129 mmol) with TFA (0.03 mL, 0.39 mmol). Vacuum evaporation after 3 h gave 31 mg (100%) of yellow solid **41** (pure by NMR). Recrystallization from benzene afforded 27 mg (90%) of **41** as yellow flocculent crystals: mp 184–185 °C (lit.[30] mp 184 °C); ^{1}H NMR δ 4.37 (s, 2 H), 7.34–7.58 (m, 5 H), 7.78 (m, 2 H), 7.97 (d, 1 H, J = 8 Hz), 8.35 (d, 1 H, J = 8 Hz), 8.85 (s, 1 H); MS, m/z (relative intensity) 246 (1.9), 245 (19.2), 244 (parent, 100), 243 (14.9), 215 (55.3), 213 (13.3), 108 (18.0).

Naphthacene. A solution of LAH (300 mg) in 10 mL of THF was prepared, **41** (0.50 g, 2.0 mmol) was added, and the mixture was stirred at room temperature for 3 h. After quenching by addition of a few milliliters of moist ethyl acetate, the solvents were vacuum evaporated to give a green-brown solid residue. This was treated with 5% HCl and extracted several times with CH_2Cl_2.

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The combined organic phase was dried over K_2CO_3 and evaporated to afford 389 mg (83%) of brilliant orange solid naphthacene. A portion was recrystallized from xylenes to give material with mp ca. 345 °C dec: ^1H NMR δ 7.39 (m, 4 H), 8.00 (m, 4 H), 8.67 (s, 4 H); MS, m/z (relative intensity) 229 (19.7), 228 (parent, 100), 227 (4.6), 226 (16.5), 114 (20.4), 113 (10.0).

Pentacene. A mixture of isomers of **20** (200 mg, 0.33 mmol) in 20 mL of benzene (heterogeneous) was treated with TFA (0.26 mL, 3.3 mmol), resulting in the development of a deep red color and after 3 h the formation of a pink precipitate. The volatiles were vacuum evaporated to afford 115 mg of pink solid, presumably diketone(s), virtually insoluble in common solvents: mp ca. 300 °C dec; MS, m/z (relative intensity) 311 (24.4), 310 (parent, 100), 309 (15.3), 281 (11.6), 278 (23.8), 252 (29.5); IR (KBr) 3060, 2880, 1660, 1601, 1286, 950, 718 cm^{-1}.

A slurry of this material (250 mg) in 40 mL of THF was treated with 400 mg of LAH; the initially pink suspension developed a green color which darkened with continued stirring for 2 h at ambient temperature. The excess hydride was quenched with moist ethyl acetate; rotary evaporation at this stage gave a black solid mass. This was washed extensively with 5% HCl, with warming on a steam bath, and suction filtered to give 256 mg (119% of theory) of crude blue-black solid. Recrystallization of a portion from benzene gave pentacene as a dark purple-blue powder. The UV spectrum (*o*-dichlorobenzene solvent) was in accord with that shown by Clar:[25] MS, m/z (relative intensity) 280 (5.2), 279 (25.8), 278 (parent, 100), 276 (14.1) 139 (20.2).

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α,β-Unsaturated Acyl Cyanides. 6.[1] Self-Condensation and Conjugate Addition of Allyl-, Allenyl-, Propargyl-, and Alkynyltrimethylsilanes

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The base-induced reaction of α,β-unsaturated acyl cyanides leads to lactones resulting from a self-condensation reaction. Neutral nucleophiles such as trimethylsilyl derivatives react with α,β-unsaturated acyl cyanides in the presence of titanium tetrachloride. δ-Ethylenic acyl cyanides, δ-acetylenic acyl cyanides, γ-allenic acyl cyanides, and γ-acetylenic acyl cyanides (or the corresponding acids or methyl esters) are obtained from α,β-unsaturated acyl cyanides by condensation respectively with allyl-, allenyl-, propargyl- and alkynyltrimethylsilanes.

Although the chemistry of aromatic and saturated aliphatic acyl cyanides has been developed in some detail,[2] relatively few studies on the reactivity of α,β-unsaturated acyl cyanides have appeared.[2c,3] These latter conjugated systems are expected to be good acceptors for 1,2 and/or 1,4-nucleophilic additions, since the cyano group is inductively a strong electron-withdrawing substituent which does not show a compensating electron-donating resonance effect.[4] From a synthetic point of view, acyl cyanides are the equivalent of the corresponding acids and esters into which they can be readily converted. We described here a part of our program concerned with developing applications of α,β-unsaturated acyl cyanides in organic synthesis.

Results and Discussion

Reaction of the corresponding α,β-unsaturated acid chlorides with CuCN in acetonitrile leads to the desired

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