1,4,4-Trimethyl-8-(hydroxymethylene)-*exo*-11-oxatricyclo[5.3.1.0^{2,6}]undecan-9-one (21). To 0.047 g (0.23 mmol) of **13** in 2 mL of benzene was added 0.037 g (0.68 mmol) of sodium methoxide and 0.18 mL (0.17 g, 2.3 mmol) of ethyl formate. The mixture was stirred at room temperature for 18 h. Ice and water (5 mL) were then added along with 0.5 mL of 5% aqueous NaOH. After separation of the layers, the organic phase was washed with 3 × 1 mL of aqueous NaOH. The combined aqueous portions were washed once with 2 mL of ether and then brought to pH 3 with concentrated HCl after cooling in ice. This acidic aqueous mixture was then extracted with 4 × 2 mL ether. The combined ether extracts were washed with water and saturated aqueous NaCl, and dried (Na_2SO_4). Concentration afforded 0.022 g (0.09 mmol) of **21** as a yellow oil (42% yield). The original organic mixture (after NaOH wash above) was washed with water and saturated aqueous NaCl and dried (Na_2SO_4). Concentration afforded 0.018 g (0.09 mmol) of **13**. The yield based on recovered **13** is 67%. Crude **21**, a mixture of β-hydroxyenone stereoisomers and ketoaldehyde, was used without further purification; ^{1}H NMR ($CDCl_3$, 300 MHz, major component) δ 0.88 (s, 3 H), 1.07 (s, 3 H), 1.34 (s, 3 H), 1.19–1.51 (series of m, 4 H), 2.37 (d, J = 19.2 Hz, 1 H), 2.46–2.76 (m, 2 H), 2.61 (d, J = 19.2 Hz, 1 H), 4.37 (s, 1 H), 7.63 (s, 1 H), 13.40 (br s, 1 H); IR (CH_2Cl_2) 3056, 1644, 1619 cm^{-1}; high-resolution MS calcd for $C_{14}H_{20}O_3$ m/e 236.1412, found m/e 236.1420.

Furanether B (1). To a solution of 0.02 g (0.14 mmol) of butanethiol in 3.5 mL of benzene was added 0.022 g (0.9 mmol) of **21** and 8 mg *p*-TsOH. The solution was refluxed, with removal of water, for 1 h. Upon cooling the mixture was washed twice with 1 mL of 2.5% aqueous NaOH, 2 × 1 mL of water, and saturated aqueous NaCl and dried (Na_2SO_4). Concentration afforded 0.033 g of yellow oil that was used directly in the next reaction.

The crude thiomethylene ketone was dissolved in 0.6 mL of dichloromethane. To this solution was added 0.035 g (0.19 mmol) of trimethylsulfonium methylsulfate and 0.25 mL of 50% aqueous NaOH. The mixture was stirred at reflux (48 °C oil bath) for 24 h. After this cooled, 0.5 mL dichloromethane was added and the organic layer was separated from the aqueous layer. The aqueous layer was then diluted with 0.25 mL of water and extracted with 3 × 1 mL of ether. The combined organic layers were washed with water, and saturated aqueous NaCl and dried (Na_2SO_4). Concentration afforded a lemon yellow oil that was let stand at room temperature for 24 h. The oil was then dissolved in 0.5 mL of THF, and 0.25 mL of 2 N HCl was added. This mixture was stirred at room temperature for 3 h. After saturation with solid $CaCO_3$, the organic layer was diluted with 1 mL of ether, and the layers were separated. The aqueous layer was extracted with 2 × 1 mL of ether. The combined organic portions were washed with water and saturated aqueous NaCl, and dried (Na_2SO_4). Concentration yielded 0.029 g of yellow oil. Flash chromatography on silica gel (2:98 ethyl acetate:hexane) yielded 0.010 g of unreacted thiomethylene ketone and 0.010 g of furanether B (46% yield based on **21**, 70% based on unrecovered starting material); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.877 (s, 3 H), 1.091 (s, 3 H), 1.271–1.400 (m, 2 H), 1.404 (s, 3 H), 1.474 (m, 2 H), 2.531–2.619 (m, 2 H), 2.695–2.830 (m, 2 H), 4.797 (s, 1 H), 7.131 (s, 1 H), 7.172 (s, 1 H); high-resolution MS calcd for $C_{15}H_{20}O_2$ m/e 232.1463, found m/e 232.1475.

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Registry No. (±)-**1**, 123164-81-8; (±)-**2**, 89920-04-7; (±)-**3**, 99327-50-1; (±)-**4**, 99327-49-8; (±)-**5a**, 123099-16-1; (±)-**5b**, 123099-27-4; (±)-**6a**, 123164-82-9; (±)-**6b**, 123164-90-9; (±)-**7a**, 123099-17-2; (±)-**7b**, 123099-28-5; (±)-**8a**, 123099-18-3; (±)-**8b**, 123099-29-6; (±)-**9a**, 123099-19-4; (±)-**9b**, 123099-30-9; (±)-**10a**, 123099-20-7; (±)-**10b**, 123164-91-0; (±)-**10c**, 123164-97-6; (±)-**11**, 123099-21-8; (±)-**11** (R = H), 123099-31-0; (±)-**12**, 123099-22-9; (±)-**13**, 123099-23-0; (±)-**14a**, 123164-83-0; (±)-**14b**, 123164-93-2; (±)-**15a**, 123164-84-1; (±)-**15b**, 123164-94-3; (±)-**16a**, 123164-85-2; (±)-**16b**, 123164-95-4; (±)-**17a**, 123164-86-3; (±)-**17b**, 123164-96-5; (±)-**17c**, 123099-33-2; (±)-**18a**, 123164-87-4; (±)-**18b**, 123237-24-1; (±)-**18c**, 123099-32-1; (±)-**19**, 123099-24-1; (±)-**20**, 123164-88-5; (±)-(*E*)-**21**, 123164-92-1; (±)-(*Z*)-**21**, 123099-25-2; (±)-(*E*)-**22**, 123164-89-6; (±)-(*Z*)-**22**, 123099-26-3; $CH_3C{\equiv}CH{\cdot}Co_2(CO)_8$, 41026-24-8.

Supplementary Material Available: NMR spectra for **5a/b**, **6a/b**, **12**, **13**, **15a/b**, **17a**, **17b**, **20**, and **1** (9 pages). Ordering information is given on any current masthead page.

Synthesis of 1,4-, 2,4-, and 3,4-Dimethylphenanthrenes: A Novel Deoxygenation of Arene 1,4-Endoxides with Trimethylsilyl Iodide

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Received May 24, 1989

A mild, efficient synthesis of the carcinogen 1,4-dimethylphenanthrene (**2**) and its bay-region methyl-bearing regioisomers 2,4-dimethyl- and 3,4-dimethylphenanthrenes (**3** and **4**) is described. The synthesis involves a generally applicable strategy that features a furan/dimethyl-1-naphthyne cycloaddition reaction followed by a convenient direct deoxygenation of the resulting endoxide with excess trimethylsilyl iodide generated in situ. The Friedel–Crafts cyclization of *p*-xylene with γ-butyrolactone/$AlCl_3$ or γ-(2,5-dimethylphenyl)butyric acid via its trifluoromethanesulfonic anhydride derivative results in the formation of a mixture of 5,8-, 6,8-, and 5,7-dimethyl-1-tetralones (**17**, **20**, and **21**, respectively) through migration of aromatic methyl groups. The precursor to 6,8-dimethyl-1-naphthyne (**10**) was prepared from tetralone **20**, isolable only as a 5:1 inseparable mixture with **17** from the direct Friedel–Crafts cyclization of *p*-xylene with γ-butyrolactone, by α-dibromination with $CuBr_2$, dehydrobromination, and tosylation. The precursors to 5,8-dimethyl-1-naphthyne (**9**) and 7,8-dimethyl-1-naphthyne (**11**) were synthesized from the corresponding 1-naphthols **15** and **31**, respectively. The synthesis of these naphthols involved cycloaddition between the corresponding dimethylated benzyne and furan followed by acid-catalyzed isomerization.

Introduction

Methylated polycyclic aromatic hydrocarbons (PAHs) are of considerable interest since they have frequently been shown to possess biological activity that would not have been predicted based on studies of their parent hydrocarbons.[1] There appears to be a general rule regarding

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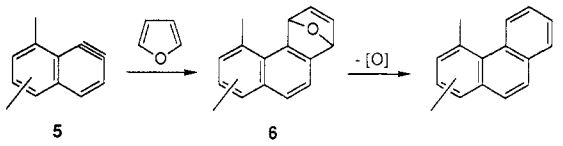
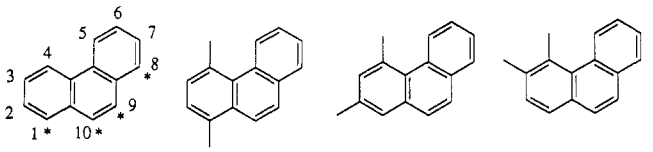
Scheme I

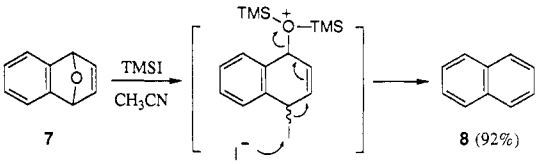


the biological activity of the methyl-substituted alternant PAHs: the structural requirements favoring mutagenic activity upon their metabolic activation are the presence of a bay-region methyl group and a free peri-position, both adjacent to an unsubstituted angular ring.[2,3] However, a dichotomy seems to exist in this area. It has been known for some time that substitution of a hydrogen by a methyl group at peri-positions of the PAH molecule enhances carcinogenic activity. This is well documented in the phenanthrene (1) series, where introduction of a methyl group in a peri-position such as C-1 or C-9 enhances its mutagenic and/or tumorigenic activities.[1] For example, 1-methylphenanthrene, 9-methylphenanthrene, 1,4-dimethylphenanthrene, and 4,10-dimethylphenanthrene are potent mutagens when they are metabolically activated, whereas 4-methylphenanthrene is not.[1,4] However, it is clear from studies such as these that more extensive knowledge of the structure–activity relationships of PAHs is needed for our understanding of carcinogenesis and/or mutagenesis by these agents, and for predicting more accurately the biological activity of PAH molecules.



Our interest in this area was directed toward the synthesis of biologically significant 1,4-dimethylphenanthrene (1,4-DMPh) (**2**) and its bay-region methyl-bearing regioisomers 2,4-dimethylphenanthrene (2,4-DMPh) (**3**) and 3,4-dimethylphenanthrene (3,4-DMPh) (**4**). Compound **2** is a commonly detected PAH in the environment, and its carcinogenic and tumorigenic activities are well established.[1] In contrast, the environmental occurrence and biological activities of **3** and **4** are not yet known. Although syntheses of these PAHs have already been reported, some of them are lengthy and inefficient.[5-7] Therefore, the development of mild and efficient routes to **2**, **3**, and **4** would facilitate their analytical detection and biological studies and further contribute to the understanding of the significance of the methyl substitution pattern which could be expected to influence their activity.

Scheme II



The synthetic strategy to these PAHs involves the use of a cycloaddition reaction between furan and a dimethyl-1-naphthyne (**5**), to be generated in situ, followed by deoxygenation of the resulting 1,4-epoxy-1,4-dihydrophenanthrene (phenanthrene 1,4-endoxide) derivatives **6** (see Scheme I). A variety of reagents for expeditious single-step deoxygenation have been reported. Zinc in acetic acid,[8,9] lithium naphthalenide,[10] low-valent metals,[11] $TiCl_4$-$LiAlH_4$,[12] $NaBH_4/CF_3COOH$,[14] and enneacarbonyldiiron[12] as well as thermolysis[9] have been used for this deoxygenation method. However, none of these seems generally applicable. With acid-sensitive or highly substituted 1,4-endoxides, other reactions such as rearrangement are often observed. Thus, the main emphasis was placed on developing a milder and more general procedure than the existing deoxygenation methods.

Trimethylsilyl iodide (TMSI),[15] first reported in the late 1940s, has recently gained considerable attention as a versatile reagent in organic synthesis. Among the many applications of TMSI, its reaction with epoxides was of particular interest to us since treatment of an epoxide with 2 equiv of TMSI in carbon tetrachloride is reported to result in deoxygenation of the epoxide to yield stereospecifically an alkene with overall retention of stereochemistry.[16] It was thus envisaged that the use of TMSI might be extended to the deoxygenation of 1,4-endoxides leading to the highly efficient synthesis of various biologically important PAHs.

Results and Discussion

At the outset, it was deemed essential to establish the general applicability of the single-step deoxygenation method of 1,4-endoxides with TMSI. While TMSI can be prepared in situ via several procedures,[15] the most convenient method appeared to be the one developed by Olah, who obtained TMSI by the reaction of TMSCl with NaI in acetonitrile.[17] A study of deoxygenation by TMSI generated in situ from TMSCl and NaI in acetonitrile was first undertaken with commercially available 1,4-epoxy-

(1) (a) LaVoie, E. J.; Tulley-Freiler, L.; Bedenko, V.; Hoffmann, D. *Cancer Res.* **1981**, *41*, 3441. (b) *Ibid.* **1982**, *42*, 4045. (c) *Mut. Res.* **1983**, *116*, 91. (d) Hecht, S. S.; Melikian, A. A.; Amin, S. In *Polycyclic Aromatic Hydrocarbon Carcinogenesis: Structure–Activity Relationship*; Yang, S. K., Silverman, B. D., Eds.; CRC: Boca Raton, FL, 1988; Vol. 1, p 95.

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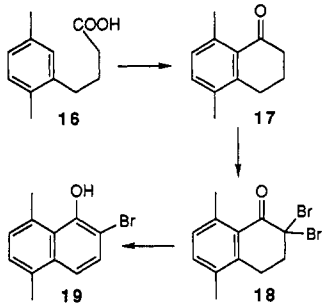
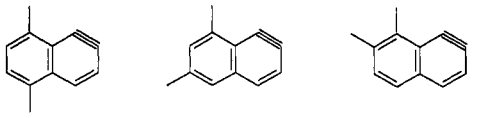
Scheme III

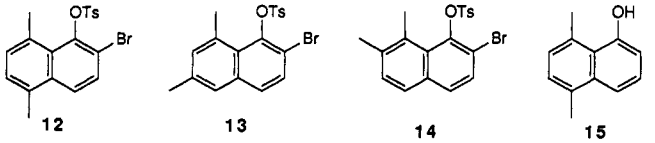


1,4-dihydronaphthalene (**7**). As anticipated, **7** underwent the smooth deoxygenation reaction at room temperature within 3 h upon treatment with 3 equiv each of TMSCl and NaI in acetonitrile, giving rise to naphthalene (**8**) in 92% yield. The mechanism of this reaction presumably involves initial ether bridge opening with TMSI, followed by Lewis acid (TMSI) promoted aromatization expelling hexamethyldisiloxane and iodine (see Scheme II).

Attention was next turned to the synthesis of three dimethylated phenanthrenes **2–4**. For the use of this deoxygenation method in the synthesis of these hydrocarbons, access to 1,4-epoxy-1,4-dihydronaphthalene skeleton (see **6**) is required. To this end, an approach involving the cycloaddition reaction between dimethylnaphthynes such as **9**, **10**, and **11** and furan was undertaken. These naphthynes were expected to be readily generated from their corresponding *o*-bromotosylates through metal–halogen exchange with *n*-butyllithium followed by the elimination of the lithium tosylate unit.[18]

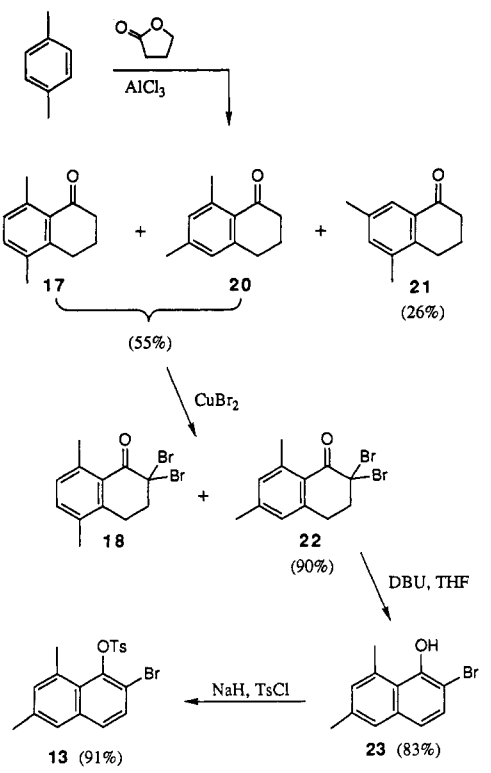


Synthesis of the Dimethylnaphthyne Precursors. The Diels–Alder cycloaddition approach to **2**, **3**, and **4** requires an efficient route for the synthesis of dimethylnaphthyne precursors such as **12**, **13**, and **14**. The required *o*-bromotosylate **12** may be obtained from naphthol **15** in two steps by the use of the procedure developed by Gribble.[19] The synthesis of this seemingly simple naphthol derivative **15** turned out to be more than a trivial synthetic exercise.



It was initially envisioned that mild intramolecular Friedel–Crafts acylation of γ-arylbutyric acid **16**, via its mixed trifluoromethanesulfonic anhydride,[20] followed by α-dibromination of the resulting 1-tetralone derivative **17** with copper(II) bromide[21] (Scheme III), would provide 2,2-dibromo-1-tetralone **18**. Dehydrobromination of **18** with DBU was expected to result in the direct formation of ortho-brominated derivative **19**. This would be an extremely efficient route toward the aryne precursors bypassing the step for the formation of phenol **15**.

Scheme IV



The required γ-(2,5-dimethylphenyl)butyric acid (**16**) was prepared by a Friedel–Crafts reaction of succinic anhydride with *p*-xylene,[22] followed by Clemmensen reduction[23] in 52% overall yield. The intramolecular Friedel–Crafts reaction of **16** was, however, quite puzzling. While many unsubstituted γ-arylbutanoic acids undergo highly efficient intramolecular Friedel–Crafts reactions via the mixed trifluoromethanesulfonic anhydride,[20] application of this procedure to **16** led to the formation of an inseparable mixture of 5,8-dimethyl-1-tetralone (**17**) and 6,8-dimethyl-1-tetralone (**20**) in a 5:1 ratio (53% yield), along with 5,7-dimethyl-1-tetralone (**21**)[24] in 32% yield. Singlet peaks at δ 6.898 and 6.990 ppm in the ^{1}H NMR spectrum of the minor component of this mixture suggest that it is the meta isomer **20**. The ^{1}H NMR spectrum of **21** showed a diagnostic down-field shifted aromatic hydrogen peak at 7.773 ppm as a singlet indicating the presence of the proton at C-8.[24]

As an alternate approach, the direct Friedel–Crafts reaction of *p*-xylene with γ-butyrolactone in the presence of excess aluminum chloride[25] was then explored. Somewhat surprisingly, the reaction resulted in considerably more methyl migration, leading to the a 1:5 inseparable mixture of **17** and **20** in 55% yield, along with **21** in 26% yield (Scheme IV).

The methyl migration observed in this Friedel–Crafts reaction may be explained as follows. The expected ketone

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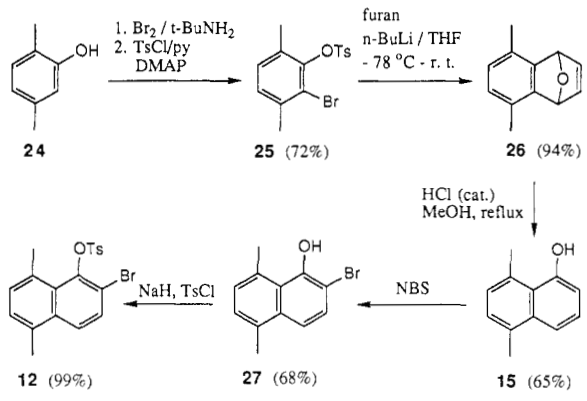
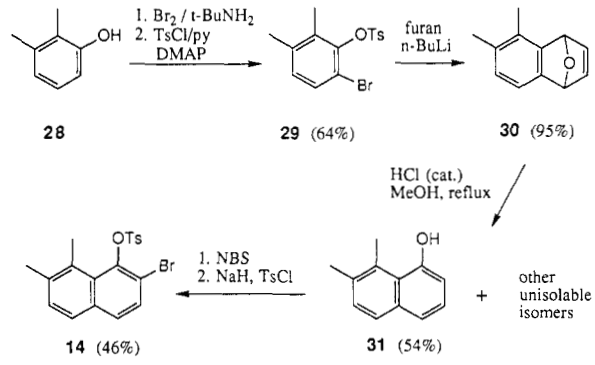
(25) Olson, C. E.; Bader, A. R. *Organic Syntheses*; Rabjohn, N., Ed.; John Wiley: New York, 1963; Collect. Vol. IV, p 898.

Scheme V



Scheme VI



17 is likely to be produced first. Under intensely acidic conditions, however, Lewis acid catalyzed 1,2-migration of a methyl group may take place, resulting in a mixture of **17**, **20**, and **21**. The meta isomers **20** and **21** are expected to be more stable than **17**, which has the peri-interactions involving the methyl groups and the hydrogen at C-4 or the carbonyl oxygen. Apparently, the conditions employed for the intramolecular Friedel–Crafts cyclization of the acid chloride derivative of **16** were not sufficiently acidic to reach to the expected thermodynamic equilibrium between **17** and **20**. This type of alkyl migration is by no means unique as similar 1,2-methyl migrations have been observed in the Friedel–Crafts alkylation of mesitylene[26] and toluene.[27]

The isomeric ketones **17** and **20** obtained as a 1:5 mixture from the direct Friedel–Crafts reaction with γ-butyrolactone were inseparable either by chromatography or distillation. This mixture was thus directly converted to a mixture of dibromides **18** and **22** with $CuBr_2$. Major isomer **22** could now be isolated in pure form by recrystallization from ether. Likewise, the 5:1 mixture of **17** and **20** obtianed from trifluoromethanesulfonic anhydride mediated Friedel–Crafts reaction was converted to a mixture of **18** and **22**. It was not possible, however, to isolate **18**, which was expected to be the major product, from the crude reaction mixture. Moreover, further conversion of the 5:1 mixture of **17** and **20** to a mixture of *o*-bromotosylate **12** and **13** in three steps [(1) $CuBr_2$; (2) DBU/THF; (3) NaH, TsCl] did not result in isolation of the desired **12** in pure form since separation by either chromatography or recrystallization was not effective.

In contrast, the isomeric 6,8-dimethyl-*o*-bromotosylate (**13**) was readily prepared from pure **22** by successive dehydrobromination and tosylation (Scheme IV). The conventional tosylation procedure with pyridine as the base afforded only a trace of **13**, whereas the use of NaH as the base proved to successful. This relatively low reactivity may be attributable to decreased nucleophilicity of the phenolic hydroxyl group of **23** due to the methyl group at C-8.

The successful route to **12** involving a benzyne–furan cycloaddition as the key step is outlined in Scheme V. The commercially available 2,5-dimethylphenol (**24**) was converted to benzyne precursor **25** in two steps. When *N*-bromosuccinimide was used as the brominating agent for **24**, polybrominated products were produced, with only a trace of the desired *o*-monobromide. Treatment of **24** with Br_2 (0.5 equiv)/*tert*-butylamine (1.0 equiv)[28] resulted in the formation of a mixture of ortho-monobrominated and ortho,para-dibrominated products, which proved inseparable by chromatography. This mixture was thus directly converted to the corresponding tosylates. The desired *o*-bromotosylate **25** was then easily separated by flash column chromatography. Upon treatment of **25** with *n*-butyllithium in the presence of furan, cycloaddition reaction of the benzyne produced from **25** with furan took place smoothly to give 1,4-endoxide **26**. The presence of a catalytic amount of HCl in refluxing methanol was highly effective in aromatizing **26**. Regioselective ortho-bromination of phenol **15** with *N*-bromosuccinimide, followed by tosylation with tosyl chloride/NaH, afforded the desired *o*-bromotosylate **12**. This route to *o*-bromotosylate **12** is highly effective (29.5% overall yield from **24**) and should be generally applicable to the synthesis of various aromatic *o*-bromotosylates.

Bromotosylate **14** was prepared by following the same method used for the synthesis of **12**, starting from 2,3-dimethylphenol (**28**) (see Scheme VI). The desired phenol **31** was obtained as the major product in 54% yield by acid-catalyzed ring opening of **30**. The regiochemistry of the phenolic OH group was ascertained by a ^1H NMR study of **31** (0.30M in $CDCl_3$) with a shift reagent, $Eu(fod)_3$, at 0.1 and 0.4 molar ratios (mole of $Eu(fod)_3$/mol of **31**). The methyl group and H-2 signals appear at δ 2.886 and 6.683 ppm, respectively, in the absence of the shift reagent. The magnitude of the lanthanide induced shifts (Δδ ppm) of the methyl and H-2 signals were identical; 0.03 and 0.11 ppm at 0.1 and 0.4 molar ratios, respectively. This suggests that both the methyl and the aromatic proton H-2 are located at the similar proximity to the phenolic OH. It should be noted that the additional methyl peak at 2.446 ppm as well as other aromatic proton peaks showed no significant lanthanide-induced shifts under these conditions.

While the mechanistic details of this regiocontrolled ring opening of **30** remain ambiguous, bromotosylate **14** was conveniently prepared from this readily accessible phenol **31**. For comparison purpose, unsubstituted bromotosylate **32** was prepared by tosylation of commercially available 1-bromo-2-naphthol with *p*-tosyl chloride/pyridine.

Deoxygenation of 1,4-Endoxides. A potential source of concern was the effect of the methyl group present at the peri-position on the cycloaddition reaction involving naphthynes. Interestingly, the naphthyne generated in situ from the corresponding *o*-bromotosylates **32**, **12**, **13**, and **14**, upon treatment with *n*-butyllithium at −78 °C in the presence of furan, underwent smooth cycloaddition reactions with furan, giving rise to adducts **33**–**37** in good yields as summarized in Table I.

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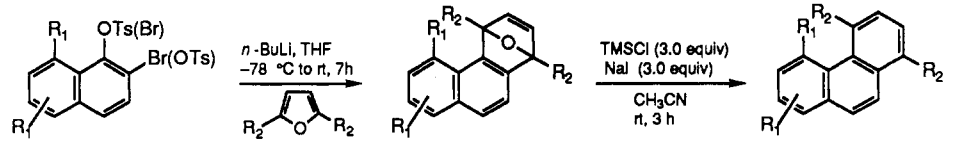
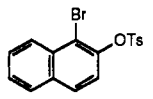
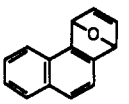
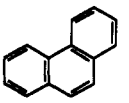
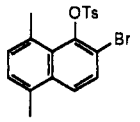
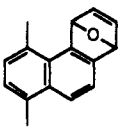
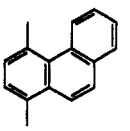
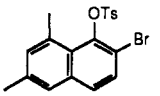
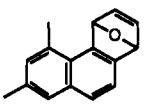
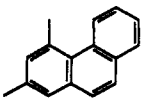
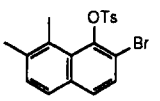
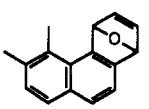
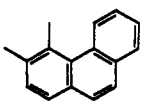
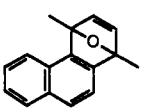
(28) Pearson, D. E.; Wysong, R. D.; Breder, C. V. *J. Org. Chem.* **1967**, *32*, 2358.

Table I. Synthesis of 1,4-Endoxides and Phenanthrenes



naphthyne precursors	furans	1,4-endoxides (% yield)	phenanthrenes (% yield)
 32		 33 (87)	 1 (98)
 12		 34 (89)	 2 (84)
 13		 35 (78)	 3 (81)
 14		 36 (72)	 4 (88)
32	 38	 37 (75)	2 (78)

The crucial deoxygenation of these 1,4-endoxides was successfully achieved by treating with 3 equiv each of TMSI and NaI in acetonitrile at room temperature. Thus, phenanthrene and its dimethyl-substituted derivatives **2**, **3**, and **4** were obtained in excellent yields (see Table I). In connection with this synthetic work, we wished to examine the deoxygenation of sterically hindered 1,4-endoxides such as **37**, prepared from the cycloaddition of 1-naphthyne and 2,5-dimethylfuran (**38**). In spite of potential steric interference due to the presence of the methyl groups at the bridged positions, similar treatment of the endoxide as above resulted in the formation of 1,4-DMPh (**2**) in 78% yield, thus constituting an extremely efficient synthesis of this hydrocarbon.

In conclusion, since a wide range of arene 1,4-endoxides is readily accessible by the cycloaddition between arynes and furans,[18] this deoxygenation approach with TMSI should have great potential for the synthesis of specifically substituted derivatives of PAH systems. In addition, because of the ease of generating TMSI in situ and the mild conditions employed, it is believed that this may be one of the most convenient, reliable methods for the deoxygenation of various arene 1,4-endoxides. Current efforts from these laboratories include examination of various types of biological activities of these dimethylated phenanthrenes.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$. The multiplicity indicated for each ^{13}C NMR chemical shift represents the observed splitting pattern of the corresponding ^{13}C peak when run in an off-resonance decoupling mode. Those multiplicities which are not given were undeterminable due to extensive overlapping. Infrared spectra were recorded with sodium chloride plates or potassium bromide pellets.

Melting points were taken on a hot stage apparatus and are uncorrected. All boiling points are uncorrected. Kugelrohr distillations were carried out on a Büchi apparatus, and temperatures reported are those of the oven.

Flash column chromatographic separation was carried out with Merck 230–400 mesh silica gel. Reactions were monitored by thin-layer chromatography (TLC) with Analtech 250 plates with fluorescent indicator. Spots were detected by ultraviolet light (254 nm), iodine vapor, and ceric ammonium sulfate–sulfuric acid.

Air- and/or moisture-sensitive reactions were performed under a static pressure of dry nitrogen after flushing the reaction vessel with a stream of dry nitrogen. All glassware was oven-dried. Reagents and solvents were transferred by standard syringe techniques through rubber septa. The following solvents were dried and purified under dry nitrogen atmosphere just prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Methylene chloride, acetonitrile, and pyridine were distilled from calcium hydride.

5,8-Dimethyl- and 6,8-Dimethyl-3,4-dihydro-1(2*H*)-naphthalenone (17 and 20). A 500-mL, three-necked, round-bottomed flask was fitted with a magnetic stirrer, a reflux condenser capped by a drying tube filled with calcium chloride, and a wide-bore rubber tube leading to a 250-mL Erlenmeyer flask. Dry *p*-xylene (245 mL, 2.0 mol) and γ-butyrolactone (15.6 mL, 0.2 mol) were placed in the reaction flask. Reagent grade anhydrous aluminum chloride (105 g, 0.8 mol) was placed in the Erlenmeyer flask, and added to the stirred reaction mixture during a period of 2 h. The mixture became dark brown and evolved HCl gas. After addition of all aluminum chloride, the rubber tube was replaced with a glass stopper, and the mixture was heated at 75 °C with continued stirring for 20 h. It was then cooled down to room temperature, poured onto 500 g of crushed ice drenched with 85 mL of concentrated hydrochloric acid. The aqueous layer was separated and extracted with about 150 mL of benzene. The

original brown organic layer and the benzene extract were combined, washed successively with water and 20% aqueous potassium hydroxide, and distilled under reduced pressure to remove *p*-xylene, benzene, and trace amounts of water. Purification of the resulting brown residue by flash column chromatography on silica gel with ethyl acetate/hexanes (1:9) as the eluent afforded an early eluting mixture of tetralones **17** and **20** (19.2 g, 55%) and late eluting **21** (9.1 g, 26%), both as a pinkish oil. NMR analysis of the early eluting fraction revealed that it was a 1:5 mixture of **17** and **20**. Separation of this mixture was achieved after the next step. For a 1:5 mixture of **17**[29] and **20**:[30] R_f 0.42 (1:9 ethyl acetate/hexanes); bp 74 °C (5 mmHg) (Kugelrohr); ^{1}H NMR (300 MHz) δ 2.01–2.14 (m, 2 H, 3-Hs, **17**, and m, 2H, 3-Hs, **20**), 2.26 (s, 3 H, 5-CH_3, **17**), 2.31 (s, 3 H, 6-CH_3, **20**), 2.59–2.64 (m, 2 H, 4-Hs, and s, 3 H, 8-CH_3, **17**, and m, 2 H, 4-Hs and s, 3 H, 8-CH_3, **20**), 2.83 (t, 2 H, J = 6.2 Hz, 2-Hs, **17**), 2.90 (t, 2 H, J = 6.1 Hz, 2-Hs, **20**), 6.90 (s, 1 H, 7-H, **20**), 6.90 (s, 1 H, 5-H, **20**), 7.00 (d, 1 H, J = 7.7 Hz, 6-H, **17**), 7.19 (d, 1 H, J = 7.7 Hz, 7-H, **17**); ^{13}C NMR (75.3 MHz) for **17** δ 19.50 (q), 22.51 (t), 22.93 (q), 27.50 (t), 40.67 (t), 129.84 (d), 131.70 (s), 133.62 (d), 135.62 (s), 138.73 (s), 143.45 (s), 200.32 (s); ^{13}C NMR (75.3 MHz) for **20** δ 21.27 (q), 22.90 (q), 23.12 (t), 31.06 (t), 41.00 (t), 127.21 (d), 129.07 (s), 131.38 (d), 141.57 (s), 142.62 (s), 145.71 (s), 199.40 (s). For **21**:[24] R_f 0.38 (1:9 ethyl acetate/hexanes); bp 106 °C (0.5 mmHg) (Kugelrohr) [lit.[24] bp 98–100 °C (0.2 mmHg)]; ^{1}H NMR (300 MHz) δ 2.13 (tt, 2 H, J = 6.1, 6.5 Hz), 2.28 (s, 3 H), 2.32 (s, 3 H), 2.61 (t, 2 H, J = 6.5 Hz), 2.82 (t, 2 H, J = 6.1 Hz), 7.18 (s, 1 H), 7.73 (s, 1 H); ^{13}C NMR (75.3 MHz) δ 18.96 (q), 19.71 (q), 23.32 (t), 28.98 (t), 38.89 (t), 124.81 (s), 127.51 (d), 129.51 (s), 130.31 (s), 135.52 (s), 141.85 (s), 198.63 (s).

2,2-Dibromo-6,8-dimethyl-3,4-dihydro-1(2*H*)-naphthalenone (22). A solution of a 1:5 mixture of **17** and **20** (1.437 g, 10 mmol) in 25 mL of dry acetonitrile was stirred vigorously and heated at reflux as $CuBr_2$ (12.46 g, 55 mmol) was added in small portions cautiously over a period of 1 h. Immediately after addition of the $CuBr_2$ vigorous liberation of hydrogen bromide commenced. Dibromination was completed within 5 h. Toward the end of the reaction, indicated by the cessation of the liberation of hydrogen bromide, the reaction mixture was cooled down to room temperature and most of the acetonitrile was removed under reduced pressure. The resulting dark-colored residue was taken up in chloroform (200 mL) and washed with water (3 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered. To remove the purple color of the filtrate, Norit-A (1 g) was added and filtered through a Celite pad. The filtrate was concentrated to dryness under reduced pressure. The resulting residue was purified by flash column chromatography with methylene chloride/hexanes (1:3) as the eluent to give **22** as greenish crystals (2.99 g, 90%). The product was recrystallized twice from diethyl ether to give an analytical sample as colorless crystals: mp 113–114 °C; R_f 0.39 (2:3 methylene chloride/hexanes); ^{1}H NMR (300 MHz) δ 2.34 (s, 3 H, 6-CH_3), 2.66 (s, 3 H, 8-CH_3), 3.02–3.10 (m, 4 H, 3- and 4-Hs), 6.92 (s, 1 H, 5-H), 7.00 (s, 1 H, 7-H); ^{13}C NMR (75.3 MHz) δ 21.41 (t), 23.48 (q), 30.09 (q), 45.91 (t), 69.69 (s), 127.19 (d), 132.27 (d), 143.26 (s, 2×C?), 144.32 (s), 144.52 (s), 184.89 (s); IR (KBr) 1690 (s), 1608, 1568, 1435, 1421, 1220, 1164, 873, 842 cm^{-1}. Anal. Calcd for $C_{12}H_{12}OBr_2$: C, 43.40; H, 3.65; Br, 48.13. Found: C, 43.31; H, 3.54; Br, 48.14.

2-Bromo-6,8-dimethyl-1-naphthol (23). To a stirred solution of 2,2-dibromo-6,8-dimethyl-3,4-dihydro-1(2*H*)-naphthalenone (**22**) (3.64 g, 10 mmol) in 210 mL of dry THF was added DBU (4.9 mL, 30 mmol) or DBN (3.7 mL, 30 mmol) at room temperature under nitrogen. Stirring was continued for 4 h at that temperature under nitrogen. THF was then evaporated under reduced pressure, and the resulting residue was taken up in diethyl ether (2 × 200 mL) and washed with 2% aqueous HCl solution (200 mL) and water (200 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The dark purple residue thus obtained was purified by flash column chromatography on silica gel with methylene chloride/hexanes (1:4) as the eluent to afford **23** as a white solid (2.09 g, 83%). Recrystallization from benzene/hexanes gave an analytical sample as colorless needles: mp 91–92 °C; R_f 0.52 (1:3 methylene chloride/hexanes); ^{1}H NMR (300 MHz) δ 2.40 (s, 3 H, 6-CH_3), 2.88 (s, 3 H, 8-CH_3), 6.03 (s, 1 H, OH), 7.06 (s, 1 H, 5-H), 7.15 (d, 1 H, J = 8.8 Hz, 3-H), 7.32 (s, 1 H, 7-H), 7.38 (d, 1 H, J = 8.8 Hz, 4-H); ^{13}C NMR (75.3 MHz) δ 21.20 (q), 24.40 (q), 105.03 (s), 121.38 (d), 122.43 (s), 125.25 (d), 128.15 (s and d), 131.15 (d), 135.14 (s), 136.10 (s), 150.05 (s); IR (KBr) 1595, 1442 (s), 1364, 1207, 1128, 1048, 1034, 979, 856, 820, 813, 763 cm^{-1}. Anal. Calcd for $C_{12}H_{11}OBr$: C, 57.39; H, 4.42; Br, 31.82. Found: C, 57.30; H, 4.40; Br, 31.96.

General Procedure for the Tosylation of Dimethyl-Substituted 2-Bromo-1-naphthols. Dry THF (20 mL) was added to NaH (60% oil dispersion) (234 mg, 1.2 equiv), which had been washed twice with 3 mL of hexanes to remove the oil, and the resulting suspension was cooled to 0 °C at which point a solution of 2-bromodimethyl-1-naphthol **27** or **23** (1.226 g, 4.89 mmol) in 20 mL of dry THF was added cautiously. Vigorous evolution of hydrogen gas commenced immediately upon addition of the solution. After 30 min hydrogen gas evolution subsided, and the mixture was treated with *p*-toluenesulfonyl chloride (1.025 g, 1.1 equiv) and stirred for 3 h at 0 °C. The reaction was quenched with water (20 mL), and the resulting mixture was extracted with diethyl ether (100 mL), and the organic layer washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to give a yellow solid. The solid residue was purified by flash column chromatography on silica gel with methylene chloride/hexanes (2:3) as the eluent.

2-Bromo-5,8-dimethyl-1-naphthyl *p*-Toluenesulfonate (12). Chromatographic purification of the crude product gave 1.961 g of **12** (99%) as a white solid. Recrystallization from diethyl ether gave an analytical sample as colorless prisms: mp 126–126.5 °C; R_f 0.35 (2:3 methylene chloride/hexanes); ^{1}H NMR (300 MHz) δ 2.44 (s, 3 H, CH_3), 2.62 (s, 3 H, CH_3), 2.79 (s, 3 H, CH_3), 7.17–7.29 (m, 4 H including 2 tosyl aromatic Hs), 7.49 (d, 1 H, J = 9.0 Hz, 3-H), 7.69 (d, 2 H, J = 8.3 Hz, tosyl aromatic Hs), 7.76 (d, 1 H, J = 9.0 Hz, 4-H); ^{13}C NMR (75.3 MHz) δ 19.62 (q), 21.69 (q), 23.51 (q), 116.06 (s), 125.07 (d), 127.67 (d), 129.07 (d, 2 tosyl aromatic Cs), 129.21 (d), 129.68 (d, 2 tosyl aromatic Cs), 130.06 (s), 130.70 (d), 131.89 (s), 131.97 (s), 133.94 (s), 134.28 (s), 143.40 (s), 145.55 (s); IR (KBr) 1365 (s), 1194, 1177 (s), 1090 cm^{-1}. Anal. Calcd for $C_{19}H_{17}O_3SBr$: C, 56.30; H, 4.24; S, 7.91; Br, 19.71. Found: C, 55.92; H, 4.17; S, 7.02; Br, 19.47.

2-Bromo-6,8-dimethyl-1-naphthyl *p*-Toluenesulfonate (13). Chromatographic purification of the crude product gave 1.803 g of **13** (91%) as a white solid. Recrystallization from diethyl ether gave an analytical sample as colorless prisms: mp 124–125 °C; R_f 0.29 (2:3 methylene chloride/hexanes); ^{1}H NMR (360 MHz) δ 2.44 (s, 3 H, 6-CH_3 or tosyl CH_3), 2.47 (s, 3 H, tosyl CH_3 or 6-CH_3), 2.84 (s, 3 H, 8-CH_3), 7.18 (s, 1 H, 7-H), 7.31 (d, 2 H, J = 8.3 Hz, tosyl aromatic Hs), 7.42 (s, 1 H, 5-H), 7.43 (d, 1 H, J = 8.7 Hz, 3-H), 7.52 (d, 1 H, J = 8.7 Hz, 4-H), 7.72 (d, 2 H, J = 8.3 Hz, tosyl aromatic Hs); ^{13}C NMR (90.56 MHz) δ 21.17 (q), 21.71 (q), 23.30 (q), 114.88 (s), 125.16 (d), 127.92 (s), 128.38 (d), 129.07 (d, 2 tosyl aromatic Cs), 129.45 (d), 129.67 (d, 2 tosyl aromatic Cs), 133.29 (d), 133.48 (s), 133.81 (s), 135.47 (s) 136.43 (s), 143.07 (s), 145.55 (s); IR (KBr) 1595, 1435, 1382 (s), 1370 (s), 1192 (s), 1169 (s), 1032, 833, 776, 720 (s), 662 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{17}O_3SBr$: C, 56.30; H, 4.24; S, 7.91; Br, 19.71. Found: C, 56.39; H, 4.25; S, 7.94; Br, 19.80.

General Procedure for the Preparation of Dimethyl-Substituted 1-Bromo-2-(tosyloxy)benzenes. A mixture of 50 mL of dry toluene and 4.2 mL of *tert*-butylamine (40 mmol) was cooled to −30 °C, and bromine (1.0 mL, 20 mmol) was added dropwise over a period of 10 min. The solution was then cooled to −78 °C, at which time dimethylphenol **24** or **28** (4.88 g, 40 mmol) dissolved in 20 mL of dry methylene chloride was added over a period of 5 min. The reaction mixture was allowed to warm to room temperature over a period of 5 h and washed thoroughly with water (4 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure, and the resulting solid residue was purified by flash column chromatography on silica gel with hexanes to yield a mixture of *o*-bromodimethylphenol and *o,p*-dibromodimethylphenol. Separation of these products was achieved after the next step.

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The mixture of products thus obtained was dissolved in 50 mL of dry pyridine and treated with *p*-toluenesulfonyl chloride (3.8 g), and 4-(dimethylamino)pyridine (400 mg). The resulting solution was stirred for 24 h at room temperature, at which time the reaction mixture was poured into cold water (40 mL) and extracted with diethyl ether (5 × 50 mL). The combined ethereal extracts were washed thoroughly with water (4 × 200 mL) and dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure to afford a solid residue. The crude product thus obtained was purified by flash column chromatography on silica gel with ethyl acetate/hexanes (1:9) as the eluent.

1-Bromo-2-(tosyloxy)-3,6-dimethylbenzene (25). Chromatographic purification of the crude product gave 5.115 g of **25** (72%). Recrystallization from petroleum ether gave an analytical sample as colorless prisms: mp 102–103 °C; R_f 0.39 (1:9 ethyl acetate/hexanes); ^{1}H NMR (300 MHz) δ 2.27 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 6.99 and 7.05 (AB q, 2 H, J_{AB} = 7.7 Hz, 4- and 5-Hs), 7.33 (d, 2 H, J = 8.4 Hz, tosyl aromatic Hs), 7.88 (d, 2 H, J = 8.4 Hz, tosyl aromatic Hs); ^{13}C NMR (75.3 MHz) δ 17.88 (q), 21.72 (q), 23.19 (q), 119.88 (s), 128.48 (d, 2 tosyl aromatic Cs), 128.52 (d), 129.61 (d, 2 tosyl aromatic Cs), 129.84 (d), 131.70 (s), 134.71 (s), 137.74 (s), 145.18 (s), 146.44 (s); IR (KBr) 1595, 1479, 1455, 1374 (s), 1192, 1177 (s), 1089, 1030, 941, 837 (s), 821 (s), 769 (s), 712 (s), 666 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{15}O_3SBr$: C, 50.72; H, 4.26; S, 9.02; Br, 22.49. Found: C, 50.60; H, 4.37; S, 9.13; Br, 22.51.

1-Bromo-2-(tosyloxy)-3,4-dimethylbenzene (29). Chromatographic purification of the crude product gave 4.547 g of **29** (64%). Recrystallization from diethyl ether gave an analytical sample as colorless needles: mp 77–78.5 °C; R_f 0.45 (1:4 ethyl acetate/hexanes); ^{1}H NMR (360 MHz) δ 2.24 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 6.93 (d, 1 H, J = 8.1 Hz, 6-H), 7.27 (d, 1 H, J = 8.1 Hz, 5-H), 7.36 (d, 2 H, J = 8.4 Hz, tosyl aromatic Hs), 7.89 (d, 2 H, J = 8.4 Hz, tosyl aromatic Hs); ^{13}C NMR (90.56 MHz) δ 16.21 (q), 21.65 (q), 23.22 (q), 114.42 (s), 128.43, 128.56, 129.63, 131.29, 133.04 (s), 134.00 (s), 138.42 (s), 145.96 (s), 147.11 (s); IR (KBr) 1463, 1451, 1400, 1371 (s), 1191, 1174, 1063, 917, 805, 754 (s), 739 cm^{-1}. Anal. Calcd for $C_{15}H_{15}O_3SBr$: C, 50.72; H, 4.26; S, 9.02; Br, 22.49. Found: C, 50.60; H, 4.13; S, 9.14; Br, 22.56.

General Procedure for the Diels–Alder Cycloaddition between Dimethylbenzyne and Furan. A stirred solution of **25** or **29** (5.11 g, 14.4 mmol) and freshly distilled furan (4.32 mL, 4.0 equiv) in 36 mL of THF was cooled under nitrogen to −78 °C, and 11.7 mL of 1.35 M *n*-butyllithium (15.8 mmol, 1.1 equiv) was added dropwise. Stirring was continued for 10 h, during which time the solution was allowed to warm to room temperature. The reaction was quenched by the addition of a few drops of saturated aqueous ammonium chloride solution. The solvent was evaporated, and the resulting brownish residue was taken up in 50 mL of diethyl ether. The ethereal solution was washed with brine (50 mL) and water (50 mL), and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure followed by purification by flash column chromatography on silica gel with ethyl acetate/hexanes (1:9) as the eluent gave the desired product.

5,8-Dimethyl-1,4-epoxy-1,4-dihydronaphthalene (26). Chromatographic purification of the crude product gave 2.32 g of **26** (94%) as a colorless solid. Recrystallization from petroleum ether gave an analytical sample as colorless needles: mp 70–71.5 °C; R_f 0.30 (1:9 ethyl acetate/hexanes; ^{1}H NMR (300 MHz) δ 2.27 (s, 6 H, 5- and 8-CH_3's), 5.78 (dd, 2 H, J = 1.0, 1.0 Hz, 1- and 4-Hs), 6.68 (s, 2 H, 6- and 7-Hs), 7.03 (dd, 2 H, J = 1.0, 1.0 Hz, 2- and 3-Hs); ^{13}C NMR (75.3 MHz) δ 17.63 (q), 81.13 (d), 126.67 (d), 127.30 (s), 142.77 (d), 146.94 (s); IR (KBr) 1487, 1280, 1031, 986, 870 (s), 831 (s), 718 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.45; H, 7.00.

5,6-Dimethyl-1,4-epoxy-1,4-dihydronaphthalene (30). Chromatographic purification of the crude product gave 2.35 g of **30** (95%) as an oil. Kugelrohr distillation gave an analytical sample: bp 83–84.5 °C (5 mmHg); R_f 0.37 (1:4 ethyl acetate/hexanes); ^{1}H NMR (300 MHz) δ 2.20 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 5.67 (dd, 1 H, J = 0.7, 1.0 Hz, 4-H), 5.80 (dd, 1 H, J = 0.7, 1.0 Hz, 1-H), 6.75 (d, 1 H, J = 7.0 Hz, 7-H), 6.99 (d, 1 H, J = 7.0 Hz, 8-H), 7.02 (m, 2 H, 2- and 3-Hs); ^{13}C NMR (90.56 MHz) δ 15.32 (q), 19.19 (q), 81.03 (d), 82.56 (d), 117.51 (d), 125.52 (d), 129.11 (s), 133.71 (s), 142.33 (d), 143.15 (d), 145.98 (s), 147.65 (s); IR (neat) 1467, 1456, 1448, 1280, 863 (s), 814 (s), 715 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.61; H, 7.08.

General Procedure for the Aromatization of Dimethyl-Substituted 1,4-Epoxy-1,4-dihydronaphthalene. A stirred solution of dimethyl-substituted 1,4-epoxy-1,4-dihydronaphthalene (2.06 g, 12 mmol) in 40 mL of methanol was treated with concentrated HCl (400 μL), and the mixture was refluxed for 3 h. The solution was cooled down to room temperature and concentrated to about 10 mL under reduced pressure. The resulting concentrated solution was poured into 50 mL of water and extracted with diethyl ether (3 × 30 mL). The combined ethereal extracts were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product thus obtained was purified by flash column chromatography on silica gel with methylene chloride/hexanes (2:3) as the eluent to give the dimethylnaphthol.

5,8-Dimethyl-1-naphthol (15). Chromatographic purification of the crude product gave 1.34 g of **15** (65%) as pale yellow prisms. Recrystallization from hexanes afforded an analytical sample as colorless needles: mp 74–74.5 °C (lit.[31] mp 76 °C); R_f 0.33 (2:3 methylene chloride/hexanes); ^{1}H NMR (300 MHz) δ 2.60 (s, 3 H, 5- or 8-CH_3), 2.91 (s, 3 H, 8- or 5-CH_3), 5.41 (s, 1 H, OH), 6.73 (dd, 1 H, J = 1.1, 7.4 Hz, 2-H), 7.07 (d, 1 H, J = 7.2 Hz, 6- or 7-H), 7.16 (d, 1 H, J = 7.2 Hz, 7- or 6-H), 7.27 (dd, 1 H, J = 7.4, 8.5 Hz, 3-H), 7.53 (dd, 1 H, J = 1.1, 8.5 Hz, 4-H); ^{13}C NMR (75.3 MHz) δ 20.12 (q), 24.73 (q), 110.21 (d), 117.54 (d), 123.89 (s), 125.29 (d), 126.91 (d), 127.70 (d), 131.76 (s), 132.79 (s), 135.49 (s), 154.22 (s); IR (KBr) 3500–3100 (br), 1589, 1414, 1270, 1239, 1137 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.59; H, 6.97.

7,8-Dimethyl-1-naphthol (31). Chromatographic purification of the crude product gave 1.11 g of **31** (54%) as pale yellow prisms. Recrystallization from benzene/hexanes gave an analytical sample as colorless minute prisms: mp 58.5–60 °C; R_f 0.40 (2:3 methylene chloride/hexanes); ^{1}H NMR (300 MHz) δ 2.45 (s, 3 H, 7-CH_3), 2.87 (s, 3 H, 8-CH_3), 5.21 (s, 1 H, OH), 6.68 (dd, 1 H, J = 1.2, 7.4 Hz, 2-H), 7.16 (dd, 1 H, J = 7.4, 8.1 Hz, 3-H), 7.26 (d, 1 H, J = 8.3 Hz, 6-H), 7.35 (dd, 1 H, J = 1.2, 8.1 Hz, 4-H), 7.52 (d, 1 H, J = 8.3 Hz, 6-H); ^{13}C NMR (75.3 MHz) δ 18.32 (q), 20.98 (q), 110.80 (d), 121.58 (d), 124.38 (d), 125.54 (d), 128.22 (s), 129.39 (d), 131.79 (s), 133.68 (s), 135.43 (s), 153.43 (s); IR (KBr) 3500–3100 (br), 1569, 1421, 1280, 1232, 1130 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.65; H, 7.08.

2-Bromo-5,8-dimethyl-1-naphthol (27). A stirred suspension of *N*-bromosuccinimide (2.85 g, 16.0 mmol) in 150 mL of dry toluene was cooled to −78 °C under nitrogen, and 5,8-dimethyl-1-naphthol (**15**) (2.70 g, 15.7 mmol) in 50 mL of dry methylene chloride (50 mL) was added slowly over a period of 5 min at that temperature. The reaction mixture was allowed to warm to room temperature over a period of 10 h. The resulting solution was poured into 150 mL of water and extracted with diethyl ether (2 × 100 mL). The combined ethereal extracts were washed with water (100 mL) and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was then purified by flash column chromatography on silica gel with hexanes as the eluent to give **27** as a white solid (2.68 g, 68%). Recrystallization from hexanes gave an analytical sample as colorless needles: mp 40–41 °C; R_f 0.43 (hexanes); ^{1}H NMR (300 MHz) δ 2.54 (s, 3 H, 5-CH_3), 2.87 (s, 3 H, 8-CH_3), 6.07 (s, 1 H, OH), 7.10 (d, 1 H, J = 7.2 Hz, 6- or 7-H), 7.16 (d, 1 H, J = 7.2 Hz, 7- or 6-H), 7.37 (d, 1 H, J = 9.1 Hz, 3-H), 7.46 (d, 1 H, J = 9.1 Hz, 4-H); ^{13}C NMR (90.56 MHz) δ 19.83 (q), 24.85 (q), 105.97 (s), 117.89 (d), 124.13 (s), 127.33 (d), 127.71 (d), 128.49 (d), 131.68 (s), 133.33 (s), 134.42 (s), 150.18 (s); IR (KBr) 3469 (s), 1581, 1441, 1409, 1265, 1239, 1201, 1126, 818, 811 cm^{-1}. Anal. Calcd for $C_{12}H_{11}OBr$: C, 57.39; H, 4.42; Br, 31.82. Found: C, 57.31; H, 4.45; Br, 31.80.

2-Bromo-7,8-dimethyl-1-naphthyl *p*-Toluenesulfonate (14). A stirred suspension of *N*-bromosuccinimide (3.56 g, 20.0 mmol) in 185 mL of dry toluene was cooled to −78 °C under nitrogen, and **31** (3.38 g, 19.6 mmol) in 60 mL of dry methylene chloride

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was added slowly over a period of 5 min at that temperature. The reaction mixture was allowed to warm to room temperature over a period of 10 h. The resulting solution was poured into 200 mL of water and extracted with diethyl ether (2 × 150 mL). The combined ethereal extracts were washed with water (150 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure followed by purification of the resulting residue by flash column chromatography on silica gel with hexanes as the eluent gave 2.95 g of solid product: R_f 0.64 (hexanes). NMR analysis of the product revealed that it was a 5:1 mixture of 2-bromo-1-naphthol and 2,4-dibromo-7,8-dimethyl-1-naphthol. Separation of these products was achieved after the next step.

Dry THF (40 mL) was added under nitrogen to NaH (60% oil dispersion) (472 mg), which had been washed twice with 3 mL each of hexanes to remove the oil, and the resulting suspension was cooled to 0 °C. To this stirred suspension was added cautiously a solution of the above mixture of bromonaphthols (2.95 g) in 40 mL of dry THF. Vigorous evolution of hydrogen gas occurred immediately. After 30 min, at which time hydrogen gas evolution subsided, the mixture was treated with *p*-toluenesulfonyl chloride (2.5 g) and stirred for 3 h at 0 °C. The reaction was quenched by the addition of 40 mL of water, and the resulting solution was extracted with diethyl ether (200 mL). The organic layer was separated and washed with brine (100 mL) and water (100 mL). The organic extract was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to give a yellowish solid. The solid residue was then purified by flash column chromatography on silica gel with methylene chloride/hexanes (2:3) as the eluent to afford 3.654 g of **14** (46%) as a white solid. Recrystallization from diethyl ether gave an analytical sample as colorless needles: mp 170.5–171.5 °C; R_f 0.26 (1:9 methylene chloride/hexanes); ^{1}H NMR (360 MHz) δ 2.38 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 7.25 (d, 2 H, J = 8.0 Hz, tosyl aromatic Hs), 7.31 (d, 1 H, J = 8.3 Hz, 6-H), 7.42 (d, 1 H, J = 8.3 Hz, 5-H), 7.54 (d, 2 H, J = 8.0 Hz, tosyl aromatic Hs), 7.62 and 7.64 (AB q, 2 H, J_{AB} = 6.0 Hz, 3- and 4-Hs); ^{13}C NMR (90.56 MHz) δ 18.70 (q), 21.01 (q), 21.66 (q), 116.60 (s), 125.31 (d), 128.51, 128.69, 128.98, 129.51, 129.69 (s), 130.05, 131.12 (s), 133.61 (s), 133.73 (s), 137.12 (s), 142.59 (s), 145.47 (s); IR (KBr) 1350 (s), 1195 (s), 1180 (s), 1092 cm^{-1}. Anal. Calcd for $C_{19}H_{17}O_3SBr$: C, 56.30; H, 4.24; S, 7.90; Br, 19.71. Found: C, 56.35; H, 4.22; S, 7.95; Br, 19.79.

Diels–Alder Reactions between 1-Naphthyne Derivatives and Furan: General Procedure. A stirred solution of 1-bromo-2-naphthyl *p*-toluenesulfonate (**32**) (377 mg, 1.00 mmol) or its dimethylated analogue **12**, **13**, or **14** (405 mg, 1.00 mmol) and freshly distilled furan (0.44 mL, 6.0 equiv) in 35 mL of dry THF was cooled to −78 °C under nitrogen, and 0.71 mL of 1.55 M *n*-butyllithium in hexanes (1.1 equiv) was added dropwise. The solution was allowed to warm to room temperature over a period of 7 h. A few drops of saturated aqueous ammonium chloride solution were added to quench the reaction. The solvent was evaporated under reduced pressure and the resulting brownish residue taken up in 100 mL of diethyl ether. The ethereal solution was then washed with water (100 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under the reduced pressure, and the resulting crude product was purified by flash column chromatography with diethyl ether/hexanes (1:4) as the eluent. A solid, analytical sample was obtained by recrystallization from the indicated solvent(s).

5,8-Epoxy-5,8-dihydrophenanthrene (33). Ether **33** (169 mg) was prepared from 1-bromo-2-naphthyl *p*-toluenesulfonate (**32**) and furan in 87% yield. Recrystallization from petroleum ether gave colorless prisms: mp 86–86.5 °C (lit.[14] mp 86 °C); R_f 0.45 (1:4 diethyl ether/hexanes); ^{1}H NMR (300 MHz) δ 5.93 (dd, 1 H, J = 1.1, 2.0 Hz, 1-H), 6.26 (dd, 1 H, J = 0.9, 1.7 Hz, 4-H), 7.18–7.20 (m, 2 H, 2- and 3-Hs), 7.37 (ddd, 1 H, J = 1.3, 7.4, 8.5 Hz, 7-H), 7.47 (ddd, 1 H, J = 1.2, 8.0, 8.5 Hz, 6-H), 7.53 and 7.60 (AB q, 2 H, J_{AB} = 7.9 Hz, 9- and 10-Hs), 7.81 (dd, 1 H, J = 1.2, 7.4 Hz, 8-H), 7.83 (dd, 1 H, J = 1.3, 8.0 Hz, 5-H); ^{13}C NMR (75.3 MHz) δ 81.10 (d), 83.24 (d), 119.21 (d), 122.49 (d), 124.92 (d), 125.31 (d), 126.12 (d), 127.49 (s), 128.66 (d), 131.69 (s), 143.27 (d), 144.78 (d), 147.82 (s), 148.79 (s).

5,8-Epoxy-1,4-dimethyl-5,8-dihydrophenanthrene (34). Ether **34** (198 mg) was prepared from 2-bromo-5,8-dimethyl-1-naphthyl *p*-toluenesulfonate (**12**) and furan in 89% yield. Recrystallization of the product from petroleum ether gave colorless needles: mp 111–112 °C; R_f 0.49 (1:4 diether ether/hexanes); ^{1}H NMR (300 MHz) δ 2.60 (s, 3 H, 1-CH_3), 2.77 (s, 3 H, 4-CH_3), 5.85 (d, 1 H, J = 1.2 Hz, 8-H), 6.60 (d, 1 H, J = 1.3 Hz, 5-H), 7.06 and 7.08 (AB q, 2 H, J_{AB} = 6.9 Hz, 2- and 3-Hs), 7.16 (dd, 1 H, J = 1.2, 7.1 Hz, 7-H), 7.19 (dd, 1 H, J = 1.2, 7.1 Hz, 6-H), 7.52 (d, 1 H, J = 8.1 Hz, 9-H), 7.71 (d, 1 H, J = 8.1 Hz, 10-H); ^{13}C NMR (75.3 MHz) δ 20.20 (q), 23.29 (q), 82.52 (d, 5- or 8-C), 84.53 (d, 8- or 5-C), 118.72 (d), 122.49 (d), 125.45 (d), 127.52 (d), 128.74 (s), 130.67 (s), 131.91 (s), 133.09 (s), 144.25 (d), 144.72 (d), 148.00 (s), 148.54 (s); IR (KBr) 1612, 1448, 1281 (s), 1029 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{14}O$: C, 86.44; H, 6.36. Found: C, 86.50; H, 6.29.

5,6-Epoxy-2,4-dimethyl-5,8-dihydrophenanthrene (35). Ether **35** (173 mg) was prepared from 2-bromo-6,8-dimethyl-1-naphthyl *p*-toluenesulfonate (**13**) and furan in 78% yield. Recrystallization of the product from petroleum ether gave colorless prisms: mp 115–116 °C; R_f 0.36 (1:4 diethyl ether/hexanes); ^{1}H NMR (300 MHz) δ 2.40 (s, 3 H, 2-CH_3), 2.78 (s, 3 H, 4-CH_3), 5.83 (dd, 1 H, J = 0.8, 1.7 Hz, 8-H), 6.55 (dd, 1 H, J = 1.1, 1.8 Hz, 5-H), 7.06 (s, 1 H, 3-H), 7.15 (ddd, 1 H, J = 1.1, 1.7, 5.5 Hz, 7-H), 7.19 (ddd, 1 H, J = 0.8, 1.8, 5.5 Hz, 6-H), 7.42 (s, 1 H, 1-H), 7.45 (s, 2 H, 9- and 10-Hs); ^{13}C NMR (75.3 MHz) δ 21.34 (q), 23.04 (q), 82.63 (d, 5- or 8-C), 84.33 (d, 8- or 5-C), 119.08 (d), 125.69 (d), 126.08 (d), 126.97 (s), 130.34 (d), 132.22 (s), 133.15 (s), 133.97 (s), 144.36 (d), 144.58 (d), 147.28 (s), 147.99 (s); IR (KBr) 1623, 1476, 1448, 1286 (s), 1026 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{14}O$: C, 86.44; H, 6.36. Found: C, 86.39; H, 6.30.

5,8-Epoxy-3,4-dimethyl-5,8-dihydrophenanthrene (36). Ether **36** (160 mg) was prepared from 2-bromo-7,8-dimethyl-1-naphthyl *p*-toluenesulfonate (**14**) and furan in 72% yield as a colorless resinous oil: R_f 0.48 (1:4 diethyl ether/hexanes). Attemped Kugelrohr distillation resulted in decomposition of the compound: ^{1}H NMR (300 MHz) δ 2.43 (s, 3 H, 3-CH_3), 2.68 (s, 3 H, 4-CH_3), 5.82 (dd, 1 H, J = 1.6, 1.7 Hz, 8-H), 6.61 (dd, 1 H, J = 1.5, 1.7 Hz, 5-H), 7.12 (d, 1 H, J = 8.5 Hz, 2-H), 7.17 (ddd, 1 H, J = 1.5, 1.7, 5.5 Hz, 7-H), 7.23 (ddd, 1 H, J = 1.6, 1.7, 5.5 Hz, 6-H), 7.42 and 7.49 (AB q, 2 H, J_{AB} = 7.8 Hz, 9- and 10-Hs), 7.55 (d, 1 H, J = 8.5 Hz, 1-H); ^{13}C NMR (75.3 MHz) δ 18.11 (q), 20.73 (q), 82.66 (d), 84.98 (d), 118.22 (d), 126.45 (d), 126.85 (d), 127.35 (s), 128.39 (d), 131.75 (s), 132.46 (s), 134.23 (s), 144.35 (d), 144.59 (d), 147.46 (s), 149.30 (s); IR (neat) 1618, 1452, 1449, 1279 (s), 1025 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{14}O$: C, 86.44; H, 6.36. Found: C, 86.35; H, 6.39.

1,4-Epoxy-1,4-dimethylphenanthrene (37). A stirred solution of 1-bromo-2-naphthyl *p*-toluenesulfonate (32) (292 mg, 0.77 mmol) and freshly distilled 2,5-dimethylfuran (38) (0.50 mL, 6.0 equiv) in 25 mL of dry THF was cooled to −78 °C under nitrogen, and 0.55 mL of 1.55 M *n*-butyllithium in hexanes (0.85 mmol, 1.1 equiv) was added dropwise. The solution was allowed to warm to room temperature over a period of 6 h. A few drops of saturated aqueous ammonium chloride solution were added to quench the reaction. The solvent was evaporated under reduced pressure, and the resulting brownish residue was taken up in 50 mL of diethyl ether. The ethereal solution was washed with brine (50 mL) and water (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the resulting crude product was purified by flash column chromatography on silica gel with ethyl acetate/hexanes (1:9) as the eluent to give **37** (128 mg, 75%) as a colorless resinous oil: R_f 0.35 (1:4 ethyl acetate/hexanes). Attempted Kugelrohr distillation resulted in decomposition: ^{1}H NMR (360 MHz) δ 2.00 (s, 3 H, 1-CH_3), 2.29 (s, 3 H, 4-CH_3), 6.91 (d, 1 H, J = 5.3 Hz, 2-H), 7.01 (d, 1 H, J = 5.3 Hz, 3-H), 7.34 (ddd, 1 H, J = 1.9, 6.8, 8.3 Hz, 7-H), 7.40–7.46 (m, 2 H, 6- and 10-Hs), 7.59 (d, 1 H, J = 7.9 Hz, 9-H), 7.84 (dd, 1 H, J = 0.6, 8.3 Hz, 8-H), 8.03 (dd, 1 H, J = 1.9, 9.6 Hz, 5-H); ^{13}C NMR (90.56 MHz) δ 15.39 (q), 18.73 (q), 88.87 (s, 1-C), 90.69 (s, 4-C), 117.39 (d), 122.38 (d), 124.42 (d), 125.80 (d), 126.02 (d), 127.77 (s), 129.15 (d), 132.12 (s), 148.15 (d), 148.31 (d), 149.38 (s), 152.39 (s); IR (neat) 1628, 1455, 1443, 1282 (s), 1034 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{14}O$: C, 86.44; H, 6.36. Found: C, 86.49; H, 6.31.

Deoxygenation of 1,4-Epoxy-1,4-dihydroarenes (Arene 1,4-Endoxides) with Trimethylsilyl Iodide: General Procedure. A solution of an arene 1,4-endoxide (1.0 mmol) and anhydrous sodium iodide (3.0 mmol) in 10 mL of dry acetonitrile was treated with trimethylsilyl chloride (3.0 mmol) at room temperature under nitrogen and stirred for 3 h. The reaction was

quenched with the addition of 5 mL of 5% aqueous $Na_2S_2O_3$. The resulting mixture was then extracted with diethyl ether (50 mL). The organic layer was washed with 5% aqueous $Na_2S_2O_3$ (20 mL) and brine (50 mL) and dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue thus obtained was purified by flash column chromatography on silica gel with hexanes as the eluent. Recrystallization from petroleum ether afforded an analytical sample.

1,4-Dimethylphenanthrene (2). 1,4-Dimethylphenanthrene (2) was prepared as a white solid from either **34** or **37**. Yields: 173 mg (84%) from **34** and 161 mg (78%) from **37**. Recrystallization from petroleum ether gave colorless needles: mp 50–51 °C (lit.[5b] mp 49.5–50.5 °C); R_f 0.70 (hexanes); ^{1}H NMR (300 MHz) δ 2.74 (s, 3 H, 1-CH_3), 3.12 (s, 3 H, 4-CH_3), 7.35 and 7.39 (AB q, 2 H, J_{AB} = 7.3 Hz, 9- and 10-Hs), 7.58-7.62 (m, 2 H, 6- and 7-Hs), 7.76 (d, 1 H, J = 9.1 Hz, 2-H), 7.92 (dd, 1 H, J = 2.7, 9.4 Hz, 8-H), 7.96 (d, 1 H, J = 9.1 Hz, 3-H), 8.89 (dd, 1 H, J = 2.3, 9.4 Hz, 5-H); ^{13}C NMR (75.3 MHz) δ 20.25 (q), 27.30 (q), 123.38 (d), 125.24 (d), 125.62 (d), 126.79 (d), 127.27 (d), 127.67 (d), 128.43 (d), 130.32 (s), 130.62 (d), 131.89 (s), 132.17 (s), 132.69 (s), 133.10 (s), 133.27 (s); IR (KBr) 1452, 1431, 819 (s), 747 (s), 711 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.85. Found: C, 93.02; H, 6.80.

2,4-Dimethylphenanthrene (3). Purification by column chromatography gave **3** (167 mg, 81%) as a white solid. Recrystallization from petroleum ether gave white flakes: mp 108–109.5 °C (lit.[5d] mp 111 °C); R_f 0.76 (hexanes); ^{1}H NMR (300 MHz) δ 2.52 (s, 3 H, 2-CH_3), 3.12 (s, 3 H, 4-CH_3), 7.34 (s, 1 H, 3-H), 7.53–7.70 (m, 5 H, 1-, 6-, 7-, 9-, and 10-Hs), 7.89 (dd, 1 H, J = 1.8, 7.7 Hz, 8-H), 8.87 (dd, 1 H, J = 1.5, 8.0 Hz, 5-H); ^{13}C NMR (75.3 MHz) δ 20.99 (q), 27.16 (q), 125.30 (d), 125.48 (d), 127.07 (d), 127.11 (d), 127.16 (d), 127.31 (s), 127.74 (d), 128.65 (d), 131.75 (s), 132.97 (d), 133.21 (s), 134.00 (s), 135.30 (s), 135.38 (s); IR (KBr) 1452, 1432, 865, 856, 813 (s), 748 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.85. Found: C, 93.07; H, 6.72.

3,4-Dimethylphenanthrene (4). Purification by column chromatography provided **4** (182 mg, 88%) as a glassy resin, which gradually solidified upon standing in the refrigerator. Recrystallization from petroleum ether gave white flakes: mp 38–39 °C (lit.[7b] mp 53–54 °C); R_f 0.75 (hexanes); ^{1}H NMR (300 MHz) δ 2.56 (s, 3 H, 3-CH_3), 2.95 (s, 3 H, 4-CH_3), 7.45 (d, 1 H, J = 7.0 Hz, 2-H), 7.52–7.59 (m, 2 H, 6- and 7-Hs), 7.62 (s, 2 H, 9- and 10-Hs), 7.64 (d, 1 H, J = 7.0 Hz, 1-H), 7.87 (dd, 1 H, J = 1.8, 9.1 Hz, 8-H), 8.71 (dd, 1 H, J = 1.6, 9.4 Hz, 5-H); ^{13}C NMR (75.3 MHz) δ 21.58 (q), 21.65 (q), 124.73 (d), 125.65 (d), 126.06 (d), 126.14 (d), 127.53 (d), 128.24 (d), 128.32 (d), 128.66 (s), 128.76 (d), 131.15 (s), 132.04 (s), 133.26 (s), 133.90 (s), 136.41 (s); IR (KBr) 1449, 1441, 839 (s), 797, 745 (s), 716 cm^{-1}. Anal. Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.85. Found: C, 93.20; H, 6.79.

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Synthesis of New Chiral Auxiliaries Derived from L-Threitol

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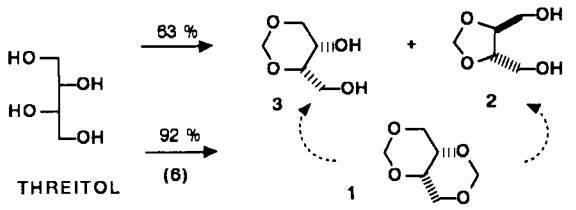
Several new chiral auxiliaries are derived from L-threitol by cleavage reactions of the methylene acetal of threitol diformal **1**. Total acetolysis (Ac_2O/H_2SO_4) leads to an acyclic tetraacetate that is converted to 1,4-diol **2** by treatment with $ZnBr_2$. A limited acetolysis procedure ($AcOH/(CF_3CO)_2O$) leads either to 1,3-diol **3** or, upon chemical manipulations, to each of its corresponding monoprotected monohydroxy derivatives.

Tartaric acid is a widely used source of reagents and chelating ligands to induce chirality in stereoselective chemical reactions.[1] We have studied the preparation of new chiral auxiliaries from L-threitol, a little examined commercially available reduced form of tartaric acid[2] that would bear a stable methylene acetal ring and the chemically active hydroxy group. A search of the literature revealed that little attention has been paid to these substrates,[3] most of the studies on butanetetrol being related to the stereoisomeric erythritol.[4] Due to its optical activity, threitol would have greater utility in synthesis, provided that protection of the hydroxy groups could be introduced both selectively and practically.

Scheme I



Direct methylenation of threitol using aqueous formaldehyde and hydrochloric acid led to a mixture of various products and optimization of this reaction seems of little hope. A much simpler result was achieved when (±)-threitol was submitted to acid-catalyzed transacetalization with dimethoxymethane.[5]

According to experimental conditions either a mixture of two diols in a moderate yield or the pure 1,3:2,4-di-*O*-methylene-L-threitol (**1**) in preparative yield can be obtained[6] (Scheme I).

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