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# SILICON-MODIFIED BIRCH REDUCTION AND REDUCTIVE ALKYLATION OF POLYNUCLEAR AROMATICS

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**Abstract:** A trimethylsilyl substituent is used to control regiochemistry, overreduction, and prevent bond cleavage during the metal/ammonia reduction of aromatic and polynuclear aromatic compounds. The trimethylsilyl group is then removed by tetrabutylammonium fluoride and replaced by either hydrogen or primary alkyl, the latter case representing overall reductive alkylation. Results are presented for naphthalene together with its 1-methyl, 2-methyl and 2-methoxy derivatives, phenanthrene and its 9-methyl and 9-ethyl derivatives, biphenyl and triptycene.

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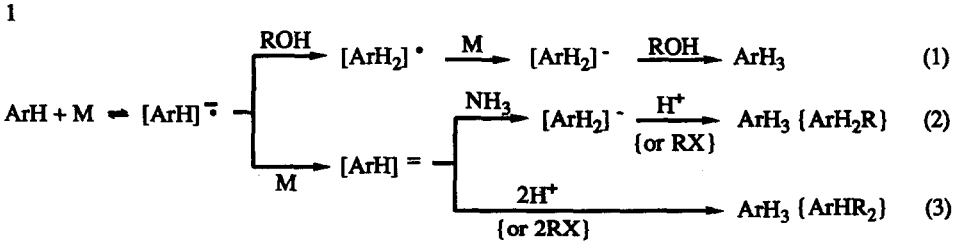
The reaction of aromatic compounds with alkali metals in liquid ammonia represents an important method for the synthesis of dihydroaromatics (Scheme 1).[1,2] In the presence of alcohols as cosolvents (path 1), this reaction

Scheme 1

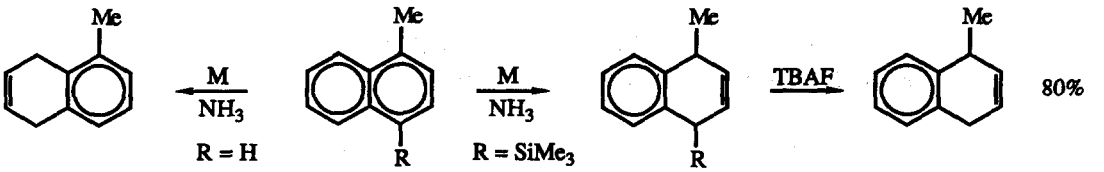



is known as the Birch reduction.[3] Polynuclear aromatics, however, give best results in the absence of protic cosolvents (paths 2 or 3) since initially formed products may be further reduced; with these compounds, overall reductive alkylation is also possible by adding alkyl halides as the final step.

Although this is a very useful reaction, it is nonetheless subject to several limitations; some of these are as follows. (a) *Regiochemistry* is dictated by the electron density distributions in the anionic intermediates. (b) *Overreduction* may occur in cases where the final monoanion is itself protonated by ammonia (a path not shown in Scheme 1) and the neutral compound so produced undergoes a second reduction. (c) *Reductive Alkylation* is not always possible due to the prior protonation of alkylation sites by ammonia. (d) *Bond Cleavage* may occur with certain carbon-carbon and carbon-heteroatom bonds rather than reduction of a multiple bond.

Herein we describe our results whereby we use $SiMe_3$ (TMS) as a stabilizing group to control regiochemistry and prevent overreduction and/or bond cleavage. The $SiMe_3$ group may then be removed by tetrabutylammonium fluoride (TBAF) and replaced by either hydrogen or alkyl,[4] producing overall Birch reduction products not possible by traditional procedures.

**Naphthalenes.** As described in a preliminary communication,[4a] our initial success in using TMS to modify reduction was demonstrated for 1-methylnaphthalene (1; R = H). The normal reduction of **1** provides only reduction in the unsubstituted ring[5] as would be expected on the basis of methyl as an electron donor (EDG). However, the addition of a 4-trimethylsilyl substituent results in a complete reversal and reduction takes place




exclusively in the silyated ring affording **3** in about 80% yield after desilylation (the remaining 20% consists of ~ 5% 3,4-dihydro isomer, ~ 10% tetrahydro and ~ 5% starting material; the TBAF reaction appears to be quantitative). Thus the *Silicon-Modified Reduction* affords the "misoriented" reduction product **3**.

Similarly, reduction of 7-methyl-1-trimethylsilylnaphthalene followed by silyl removal afforded 7-methyl-1,4-dihydronaphthalene (**4**) in 85% yield. Once again, this is significant since **4** is the minor product in the normal


reduction of 2-methylnaphthalene.[5] The prevention of bond cleavage by TMS was also demonstrated with the production of **5** from 1-trimethylsilyl-6-methylnaphthalene after reduction and desilylation. Normal reduction of 2-methoxynaphthalene results in extensive cleavage of the ether function,[6] and **5** is not formed at all.

**Reductive Alkylation.** We have since learned that the silyl group in reduced silylated naphthalenes can be replaced by primary alkyl groups under the proper conditions. As shown in Table 1, yields are improved by lower temperatures and by drying the TBAF, presumably due to competition between residual water and alkyl halide for the anion generated by the TBAF. Moreover, since it appears difficult to exclude all traces of water, it is important that RI be present at the time of TBAF addition. It is noteworthy that **6**, which is primarily trans,

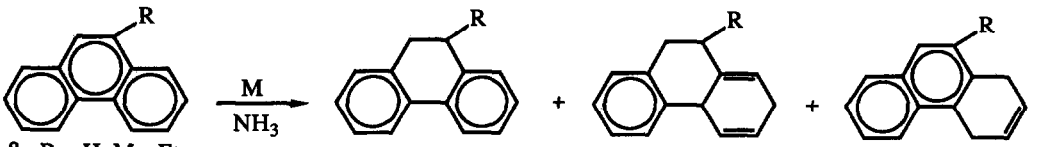
provides the cis-dimethyl derivative **7**. This indicates that there is no stereochemical control in the replacement of silyl since the methylation of 1-methyl-4-sodio-1,4-dihydronaphthalene also produces the cis product.[7] Hence we assume the intermediate to be the monoanion.

Table 1. Desilylation/Alkylation of 1-Trimethylsilyl-1,4-dihydronaphthalene and 1-Methyl-4-trimethylsilyl-1,4-dihydronaphthalene.

| substrate[a] | TBAF[b] | temp (°C) | RX[c] | product ratio[d] R | product ratio[d] H |
|---|---|---|---|---|---|
| 1-TMS-DHN | commercial[e] | 0 | MeI | 48 | 52 |
| 1-TMS-DHN | commercial[e] | -30 | MeI | 68 | 32 |
| 1-TMS-DHN | commercial[e] | -78 | MeI | 70 | 30 |
| 1-TMS-DHN | dried[f] | 0 | MeI | 70 | 30 |
| 1-TMS-DHN | dried[f] | -30 | MeI | 94 | 6 |
| 1-TMS-DHN | dried[f] | -78 | MeI | 96 | 4 |
| 1-Me-4-TMS-DHN[h] | dried[f] | -30 | MeI | 92[i] | 8 |
| 1-Me-4-TMS-DHN[h] | dried[f] | -30 | EtI | 80[j] | 20 |

[a]TMS = trimethylsilyl, DHN = 1,4-dihydronaphthalene. [b]Tetrabutylammonium fluoride. [c]Present with the substrate in THF before TBAF addition. [d]Uncorrected GLPC. [e]1.0 M solution in THF containing ~ 5% water. [f]Dried under vacuum (see Experimental). [h]A mixture of stereoisomers (cis/trans ≈ 20/80). [i]Mainly the cis isomer. [j]A ca. 60/40 mixture of cis/trans isomers.

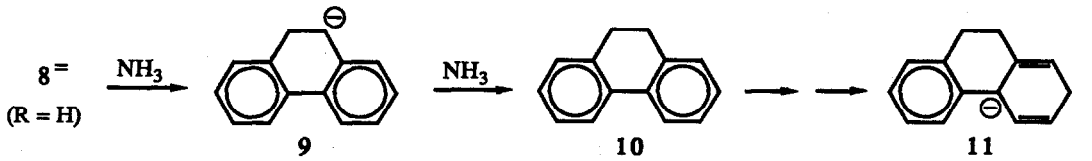
**Phenanthrene.** Early efforts to reduce phenanthrene by metal/ammonia solutions were unsuccessful affording either overreduction or little product.[8] The use of methods by the Harvey group that had produced good results with many other polynuclear aromatics were less successful with phenanthrene although notable improvement in yields (50-70%) were achieved.[9] The use of catalytic amounts of iron salts with reaction times of 1-3 hours provided even greater improvement (70-80%) although conditions under which all of the starting material




**8**; R = H, Me, Et

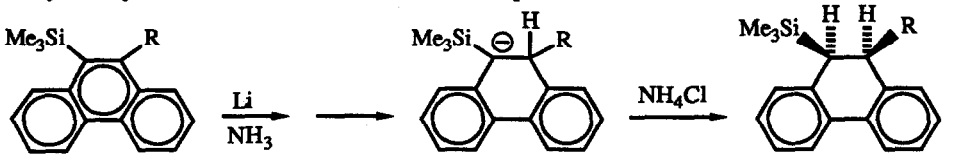
was consumed (i.e., excess metal) produced unacceptable levels of overreduction, and consequently a compromise to accept some level of both unreduced and overreduced material was necessary.[9]

The reduction of phenanthrene is problematic since the monoanion **9** resulting from protonation of the dianion by ammonia is itself protonated by ammonia to afford **10** which is reactive under these conditions.



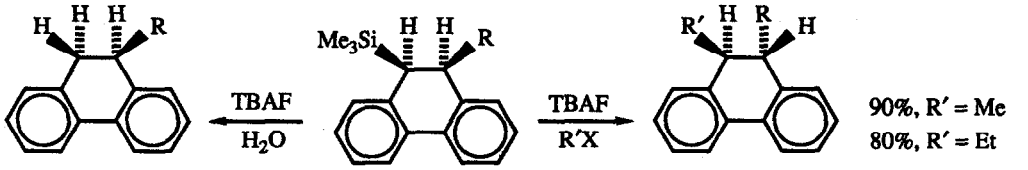

Ultimately anion **11** is produced as demonstrated by its methylation.[9] For this reason, 9-alkylated products cannot be produced by reductive alkylation of phenanthrene.

9,10-Dihydrophenanthrene and its 9-methyl and 10-ethyl derivative can be produced in essentially quantitative yields by a silicon modified reduction.[46] The improvement results from stabilization of the monoanion



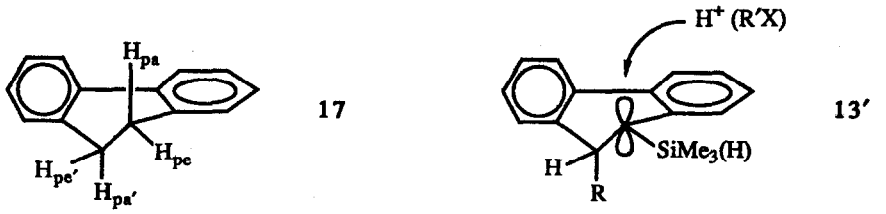

**12**; R = H, Me, Et **13** **14**

**13** by silicon so that reduction beyond the initial stage does not take place. As with naphthalene, the silyl group can be replaced with either H or R′. The stereochemistry of the reduction of **12** as well as the alkylation step can be rationalized from the same model of the dihydrophenanthrene monoanion (**13′**).




**15** (quantitative) **14**; R = H, Me, Et **16**

The reduction products of **12** with R = Me or Et were assigned as cis isomers. This was easily determined from the proton NMR since the various geometric relationships between $H_9$ and $H_{10}$ (**17**) give rise to

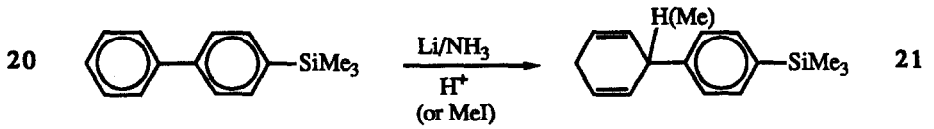



characteristically different vicinal coupling constants.[15] They are $J_{pa,pa} \approx 16$ Hz, $J_{pa,pe} \approx 5.5$-7.5 Hz and $J_{pe,pe} \approx 2$ Hz. With **18**, $J_{9,10} = 5.3$ Hz for R = Me, and 5.0 Hz for R = Et. The stereochemistry of the reduction of **12**, as well as of the desilylation/alkylation of **18**, can be understood from a model of the intermediate anion **13′**. Pseudoaxial (pa) preference for the substituent R results in the opposite side being more accessible for either protonation or alkylation. This is quite important for the production of **16** since this represents the opposite isomer from that obtained by simple reduction of 9,10-dialkylphenanthrenes.

**Anthracenes.** As expected, 9-trimethylsilylanthracene and its 10-methyl derivative were easily reduced by metal/ammonia solution to afford the 9,10-dihydro products **18**. Subsequent desilylation with TBAF in the

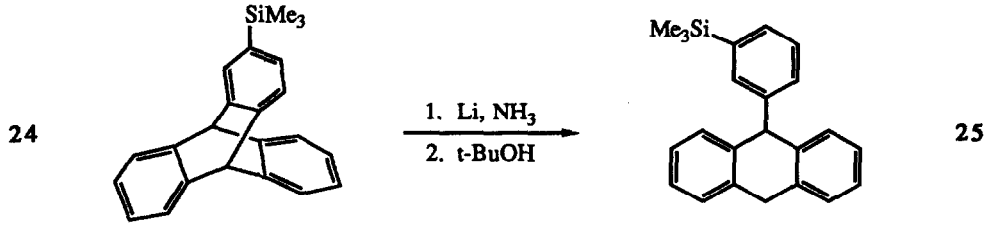

presence of methyl or ethyl iodide produced the alkylated product **19** in yields ranging from 78% (R = H, R′ = Et) to 94% (R = Me, R′ = Me). The cis/trans ratios observed for R = Me were similar to the deprotonation/alkylation of 9-methyl-9,10-dihydroanthracene,[10] and so again, the intermediate appears to be the anion.

**Biphenyl and Triptycene.** Thus far, our results have been confined to polynuclear aromatics containing fused rings. Biphenyl and triptycene represent cases with multiple aromatic rings that are independent of one another save for conjugative effects in biphenyl. Both reduction and reductive methylation of 4-trimethylsilylbiphenyl (**20**) took place in the unsubstituted ring. This may appear puzzling at first since if trimethylsilyl is indeed activating in this reaction, one might expect reduction to occur in the silylated ring.




However, if monoanion stability plays a role in regiochemical outcome, then this result can be rationalized by the (expected) greater stability of **22** over **23**. Alternatively, **22** may simply result from faster protonation at an unencumbered site of high electron density (i.e., C-4′ vs. C-4).


With 2-trimethylsilyltriptycene (**24**), reaction with lithium/ammonia produced bond cleavage rather than ring reduction. This is somewhat surprising since while triptycene itself does undergo cleavage with potassium/THF, it does not under these conditions.[11] A possible explanation is that the 2-trimethylsilyl group causes greater charge




localization on the C-4a carbon which plays an important role in the cleavage process. This might also explain the regiospecificity of the reaction since only the silylated ring cleaves and only at the C-4a position.

**Conclusions.** We feel that silicon-modification will provide some exciting new avenues for the Birch Reduction and related metal/ammonia reduction and reductive alkylation processes. We have demonstrated that regiochemistry can be controlled in a number of cases. Moreover, synthetic opportunities provided by the removal of silicon from these compounds with electrophiles[4b] has yet to be explored. This will provide conjugated dienes and allow the incorporation of proton, acyl, t-alkyl and other electrophilic groups.

## Experimental Section

Proton NMR spectra were obtained on a 90-MHz Varian EM-390 spectrometer. Mass spectra were determined on a HP 5988A GC/MS spectrometer at an ionization potential of 30 eV. Gas chromatographic analyses were performed on a Tracor 500 (fid) instrument using either 10% OV-101 or 10% DEGS on Chromasorb W. Microanalyses were obtained for all new compounds by Galbraith Laboratories, Inc. THF was distilled from benzophenone ketyl immediately before use. n-Butyllithium (2.5 M in hexane), TBAF x $3H_2O$, 1-bromonaphthalene, 1 bromo-4-methylnaphthalene, 9-bromophenanthrene, 9-bromoanthracene, and 4-bromobiphenyl were purchased from Aldrich Chemical Co. 1-Bromo-4-methylanthracene was synthesized according to the previously described procedure.[12] 2-Bromotriptycene was prepared by reacting anthracene with bromodehydrobenzene generated from the diazotized 2-amino-5-bromobenzoic acid.[13] Anhydrous TBAF was prepared[14] by heating the trihydrate under high vacuum at 45°C for 2 days and then used as a ~ 0.1 M solution in THF.

**Preparation of aryltrimethylsilanes** was accomplished by halogen/metal exchange of the corresponding aryl bromides with n-butyllithium according to the following procedure. A flame dried, three-neck, round bottom flask equipped with stirring bar, nitrogen inlet and a rubber septum, was charged with dry THF (100 mL) and the appropriate aryl bromide (10 mmol). The solution was cooled to -78°C, and n-butyllithium in hexane (2.5 M, 4.4 ml, 11 mmol) was added via syringe. After stirring for 1 h, chlorotrimethylsilane (1.6 mL, 12.7 mmol) in 20 mL THF was slowly injected from a syringe. The solution was stirred for an additional 20 min before it was allowed to warm to room temperature for 1 h. Products were isolated immediately by ether extraction and identified by NMR and GC/MS. In most cases the aryltrimethylsilanes (> 96% yield) so obtained were used without further purification. In such a way 1-trimethylsilylnaphthalene, 1-methyl-4-trimethylsilylnaphthane, 9R-10-trimethylsilylphenanthrene (12; R = H, Me, Et), 9R-10-trimethylsilylanthracene, (R = H, Me) 4-trimethylsilylbiphenyl (20) and 2-trimethylsilyltriptycene (24) were synthesized.

**General procedure for metal-ammonia reduction.** Excess (1.25 equiv) lithium was added to the aryltrimethylsilane dissolved in ammonia/tetrahydrofuran solution (2:1) at -78°C under positive argon pressure. The reaction mixture was stirred for 20-30 min and then pumped (argon pressure) through a glass tube into a large volume of saturated ammonium chloride solution (inverse quench).[15] Products were isolated by ether extraction, and purified (if necessary) by column chromatography on silica gel (Merck).

**Naphthalenes.** 1-Trimethylsilylnaphthalene and 1-methyl-4-trimethylsilylnaphthalene were reduced with lithium according to the general procedure to produce 1-trimethyl-1,4-dihydronaphthalene or 1-methyl-4-trimethyl-1,4-dihydronaphthalene as a mixture of cis/trans isomers (~ 20/80). Both compounds are known and identification was made by comparison with authentic spectral data.[4a]

**Phenanthrenes.** Lithium/ammonia reduction of 9-trimethylsilylphenanthrene, 9-methyl-10-trimethylsilylphenanthrene and 9-ethyl-10-trimethylsilylphenanthrene (i.e., 12; R = H, Me, Et) afforded the corresponding 9,10-dihydro derivatives in nearly quantitative yields.

**9-Trimethylsilyl-9,10-dihydrophenanthrene** (14, R = H) is a known compound and was compared with authentic spectral data.[17]

**Cis-9-methyl-10-trimethylsilyl-9,10-dihydrophenanthrene** (14, R = Me) was isolated as a colorless oil: NMR ($CCl_4$) δ -0.30 (s, 9H, Me), 1.50 (d, 3H), 2.32 (d, 1H; $J_{9,10}$ = 5.3 Hz), 3.30 (m, 1H, $H_9$), 6.90 - 7.30 (m, 6H), 7.50 - 7.80 (m, 2H); MS, 266 ($M^+$). Anal. Calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. Found: C, 81.56; H, 8.24.

**Cis-9-Ethyl-10-trimethylsilylphenanthrene** (**14**, R = Et) was isolated as a colorless oil: NMR ($CCl_4$) δ -0.30 (s, 9, $CH_3$), 1.17 (t, 3H), 1.90 (m, 2H), 2.40 (d, 1H; $J_{9,10}$ = 5.0 Hz), 2.97 (m, 1H), 6.87 - 7.20 (m, 6H), 7.40 - 7.67 (m, 2H); MS 280 ($M^+$). Anal. Calcd for $C_{19}H_{24}Si$: C, 81.36; H, 8.63. Found: C, 81.08; H, 8.73.

**Anthracenes.** 9-Trimethylsilylanthracene and 9-methyl-10-trimethylsilylanthracene were reacted with lithium in ammonia according to the general procedure to give 9-trimethysilyl-9,10-dihydroanthracene[18] or 9-methyl-10-trimethylsilyl-9,10-dihydroanthracene (a mixture or cis/trans isomers 79/21) in essentially quantitative yields. In the latter case, silica gel chromatography followed by recrystallization from methanol gave pure cis-9-methyl-10-trimethylsilyl-9,10-dihydroanthrancene (**18**, R = Me) as white needles: mp. 82-83°C.[18]

**Biphenyl.** Lithium/ammonia reduction of 4-trimethylsilylbiphenyl (**20**) took place exclusively in the non-methylated ring with 92% conversion to produce 4′-trimethylsilyl-1,4-dihydrobiphenyl (**21**) (R = H) as an unstable oil (gradually rearomatizes; microanalysis was not possible); NMR ($CCl_4$) δ 0.20 (s, 9, $CH_3$), 2.60 (m, 2H), 3.72 (m, 1H), 5.60 (br s, 4H), 7.10 (ABq, 4H); MS 228 ($M^+$). Analogous reductive methylation of **26** afforded 1-methyl-4′-trimethylsilyl-1,4-dihydrobiphenyl (R = Me) as a colorless oil: NMR ($CCl_4$) δ 0.23 (s, 9, $CH_3$), 1.42 (s, 3H), 2.67 (br s, 2H), 5.60 (br s, 4H), 7.25 (ABq, 4H); mass spectrum, m/e 242 ($M^+$). Anal. Calcd for $C_{16}H_{22}Si$: C, 79.27; H, 9.15. Found: C, 78.81; H, 9.10.

**Triptycene.** 2-Trimethylsilyltriptycene (**24**) was reduced according to the general procedure to produce exclusively the ring opening product, 9-(3-trimethylsilylphenyl)-9,10-dihydroanthracene (**25**) as a colorless oil: NMR ($CCl_4$) δ 0.18 (s, 9, $CH_3$), 3.52 (d, 2H), 5.08 (s, 1H), 7.13 (m, 12H); MS 328 ($M^+$). Anal. Calcd for $C_{23}H_{24}Si$: C, 84.09; H, 7.36. Found: C, 83.83; H, 7.44.

**Desilylation/Alkylation Reactions - General Procedure.** To a stirred solution of the corresponding dihydrosilane (2 mmol) and alkyl iodide (excess) in 10 mL dry THF at - 30°C under nitrogen was added by syringe a solution of anhydrous TBAF in THF (ca. 1M, 3 mmol). The reaction was stirred for 2 h; products were separated by ether extraction and analyzed by NMR, GC and MS.

**Naphthalenes.** Replacement of the TMS group by alkyl in dihydronaphthalenes gives the corresponding 1-alkyl or 1,4-dialkyl-1,4-dihydronaphthalenes (see Table 1). Both 1-methyl-1,4-dihydronaphthalene and cis-1,4-dimethyl-1,4-dihydronaphthalene are known compounds.[7] Desilylation/ethylation of 1-methyl-4-trimethylsilyl-1,4-dihydronaphthalene produces a 60/40 mixture of cis/trans isomers: NMR ($CCl_4$) δ 0.73 (t, 1.2H) 0.82 (t, 1.8H), 1.2 (d, 1.2H), 1.27 (d, 1.8H), 1.60 (m, 2H), 3.20 (m, 2H), 5.68 (m, 2H), 7.0 (m, 4H); MS 172 ($M^+$).

**Phenanthrenes.** Replacement of the TMS group by alkyl in cis-9-R-10-TMS-9,10-dihydrophenanthrenes produces the corresponding trans-9-R-10-R′-dihydrophenanthrenes. 9-Methyl- and 9-ethyl-9,10-dihydrophenanthrene as well as trans-9,10-dimethyl-9,10-dihydrophenanthrene are known compounds and identification was made by comparison with authentic spectral data.[9,19] Desilylation/ethylation of 9-methyl-10-trimethylsilyl-9,10-dihydrophenanthrene gives trans-9-methyl-10-ethyl-9,10-dihydrophenanthrene (**16**) as an oil: NMR ($CCl_4$) δ 0.82 (t, 3H), 1.03 (d, 2H), 1.27 (m, 2H), 2.3 (m, $1H_{10}$, $J_{9,10}$ = 1.8), 2.83 (m, $1H_9$), 7.10, 7.63 (m, 8H); MS 222 ($M^+$). Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.38; H, 8.30.

**Anthracenes.** The products from desilylation/alkylation of **18**, R = H or Me [9-methyl-9,10-dihydroanthracene, 9-ethyl-9,10-dihydroanthracene, cis- and trans-9,10-dimethyl-9,10-dihydroanthracene and cis and trans-9-methyl-10-ethyl-9,10-dihydroanthracene] are known compounds.[20]

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