300 NMR spectrometer, and to Professor Peter Rinaldi, University of Akron, for performing the NOESY experiments.

Supplementary Material Available: Tables of crystal data, data collection, data reduction, refinement details, positional and thermal parameters, bond distances and angles, and thermal ellipsoid plots for the crystal structures of $C_{15}H_{17}MoO_2$ (**6a**) and $C_{15}H_{18}MoO_3$ (**7**), ^1H NMR spectra for compounds **10**, **12**, **13a**, **13b**, **15**, **17**, **20**, **21**, **22**, and **27**, and a NOESY spectrum for complex **21** (36 pages). Ordering information is given on any current masthead page.

A Convenient Synthesis of 9,9-Dialkyl-9,10-dihydroanthracenes and 10,10-Dialkylanthrones: Silicon-Mediated Regioselective Dialkylation of 9,10-Dihydroanthracene

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Described is a short and convenient approach to the synthesis of 9,9-dialkyl-9,10-dihydroanthracenes, 9,9,10-trialkyl-9,10-dihydroanthracenes, and 10,10-dialkylanthrones, some of which are otherwise unknown or inaccessible by conventional methods. Deprotonation of 9-(trimethylsilyl)-9,10-dihydroanthracene (**2**; 9-(trimethylsilyl)-9,10-DHA) followed by reaction with alkyl halides (RX) produces 9-alkyl-9-(trimethylsilyl)-9,10-DHAs **3-7** in 80-90% yields. Treatment of **3-7** with *n*-BuLi produces the 10-lithio derivatives that rearrange to 9-alkyl-9-lithio-10-(trimethylsilyl) intermediates; subsequent alkylation with RX generates 9,9-dialkyl-10-(trimethylsilyl)-9,10-DHAs **8-19**. Formation of single stereoisomers **13-19** was suggested by NMR and confirmed in two cases, **15** and **16**, by X-ray structure determination. The trimethylsilyl group is removed by tetrabutylammonium fluoride (TBAF) to provide 9,9-dialkyl-9,10-DHAs **20-29** with impressive yields. Oxidation of either the 9,9-dialkyl-9,10-DHAs or 9,9-dialkyl-10-(trimethylsilyl)-9,10-DHAs with Cr(VI) oxidant furnished 10,10-dialkylanthrones **36-41** in 80-90% yields.

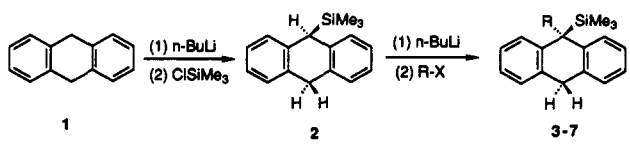
Introduction

9,10-Dihydroanthracenes (9,10-DHAs) substituted in the central ring have received considerable attention due to questions about the possible stereochemical consequences.[1] These compounds have been studied experimentally by X-ray crystallography[2] and dynamic NMR spectroscopy,[3] as well as by theoretical methods[4] in an attempt to understand their structure and dynamic processes such as ring inversion. Our own investigations required several 9,9-dialkyl-9,10-DHAs that are either only available in low yields by long routes[5] or are unknown and inaccessible by conventional methods. Several applications of silicon-modified, regioselective reduction and reductive alkylation have been recently demonstrated for polynuclear aromatics,[6] and, having reported a preliminary account,[7] we now describe in detail the synthesis, scope, and mechanism of silicon-mediated, dialkylation of 9,10-dihydroanthracene.

Results and Discussion

Preparation of 9-(Trimethylsilyl)-9,10-DHA. 9-(Trimethylsilyl)-9,10-DHA (**2**) was prepared in >95% yield by deprotonation and silylation[8] of 9,10-dihydroanthracene (**1**). An alternative route, metal-ammonia reduction[9] of 9-(trimethylsilyl)anthracene, produced lower yields (70%), and so the former method is recommended.

Preparation of 9-Alkyl-9-(trimethylsilyl)-9,10-DHAs. A variety of 9-(trimethylsilyl)-9-alkyl-9,10-DHAs, **3-7**, have been prepared by some modification of the method of Daney and co-workers.[10] Although deprotonation of **2** by *n*-BuLi in THF at -78 or at -35 °C was not successful (Table I), the reaction did proceed at 0 °C and alkylation with 1.5-2.0 equiv of alkyl halide produced



1 2 3-7

Table I. Alkylation of 9-TMS-9,10-DHA with Various Alkyl Halides

entry	*n*-BuLi (equiv)	deprotntn (°C)	time[a] (h)	alkyl iodide (equiv)	product	yield[b] (%)
1	1.0	-78[c]	3.0	MeI (1.1)	**3**	traces
2	1.0	-35[c]	3.0	MeI (1.1)	**3**	traces
3	1.0	0	1.0	MeI (1.1)	**3**	>55
4	1.25	0	1.0	MeI (1.1)	**3**	70
5	1.25	0	1.3	MeI (1.1)	**3**	82
6	1.25	0	1.3	MeI (2.0)	**3**	96
7	1.25	0	1.3	MeI (1.5)	**3**	90
8	1.25	0	1.3	EtI (2.0)	**4**	84
9	1.25	0	2.0	*i*-PrI (2.0)	**5**	70-80
10	1.25	0	1.3	allylI (1.5)	**6**	82
11	1.10	0	1.3	BnI (2.0)	**7**	75

[a] Deprotonation time. [b] Based on GC analysis for runs 1-6, isolated yield for runs 7-11. [c] Warmed to 0 °C after addition of MeI.

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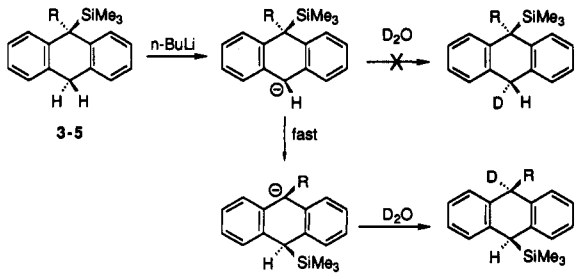
9-R,9-(trimethylsilyl)-9,10-DHAs (3–7; R = Me, Et, *i*-Pr, allyl, Bn) in yields of 80–90%. This represents a modest improvement over the 66–72% previously reported for 3–5.[10] All of these compounds were isolated in solid form either by direct crystallization from a MeOH/hexane mixture or by flash chromatography.

Preparation and Stereochemistry of 9,9-Dialkyl-10-(trimethylsilyl)-9,10-DHA (8–19). Daney, Lapouyade, and Bouas-Laurent discovered[10] the novel 1,4 migration of a trimethylsilyl group in 10-lithio-9,9-bis(trimethylsilyl)-9,10-DHA to produce 9-lithio-9,10-bis(trimethylsilyl)-9,10 DHA. This work served as the stimulus for us to apply this unusual migration to the regioselective dialkylation of 9,10-dihydroanthracene. Thus reaction of 9-R-9-(trimethylsilyl)-9,10-DHA, 3–7, with 1.25 equiv of *n*-BuLi for 1–2 h at 0 °C results in initial deprotonation at the C-10 position followed by rearrangement to afford 9-lithio-9-R-10-(trimethylsilyl)-9,10-DHAs. This anion may then be alkylated with various electrophiles—alkyl halides in the present study.

In attempting to better understand the migration of silicon in the 10-anion, we considered the steric effect caused by two groups at C-9 with the nearby peri hydrogens. If this were to be important, the rates of migration



would be expected to increase in the order 3 < 4 < 5 with increasing size of R (Me < Et < *i*-Pr). On the other hand, the proximity of the silyl group to its migration terminus, C-10, could also be important; in this case the order would be reversed, 5 < 4 < 3, since the puckering of the central six-membered ring increases in that order.[11] To our surprise, migration was rapid in all cases studied, and, in fact, the rate-determining step is not migration of the silicon. Reaction of 3–5 with *n*-BuLi followed by D_2O[12] failed to trap any 10-anion. All of the products contained deuterium at C-9 only, indicating the rate-determining step to be initial deprotonation. Once the 10-anion is formed, the rearrangement is fast and so comparative studies of migration rates could not be examined.

The deprotonation of 3–7 followed by alkylation with R'I (R' = methyl, ethyl, isopropyl, allyl, or benzyl) produced a variety of 9R,9R'-10-(trimethylsilyl)-9,10-DHAs (8–19) in good to excellent yields (Table II). Moreover, in the case of 13–19, only one of the two possible diastereoisomers was detected. The yield of the diisopropyl derivative 10 was lower under the conditions used to produce the other DHAs, but it improved significantly with an increase in R'I concentration, suggesting that alkylation of the more hindered anionic center (i.e., where R = isopropyl) is likely to be the limiting step. The isolated 9,9-dialkyl-10-(trimethylsilyl)-DHA's 8–19 were subsequently desilylated in 90–95% yields with tetrabutylammonium fluoride (TBAF) in THF to complete the synthesis of a variety of 9,9-dialkyl-9,10-dihydroanthracenes (20–29; Table III).

Table II. Alkylation of 10-TMS-9-alkyl-9-anion with Various Alkyl Iodides

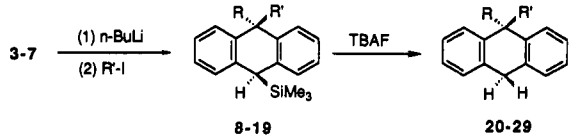
entry	R	R'I[a]	product	stereochem[b]	yield[c] (%)
1	Me	MeI	8		90
2	Et	EtI	9		81
3[d]	*i*-Pr	*i*-PrI	10		30 (70)[e]
4	allyl	allylI	11		75
5	Bn	BnI	12		70
6	Me	EtI	13	A	90
7	Et	MeI	14	B	86
8	Me	*i*-PrI	15	A	85
9	*i*-Pr	MeI	16	B	76
10	Et	*i*-PrI	17	C	70
11	Me	allylI	18	A	80
12	Me	BnI	19	A	76

[a] Alkyl iodide used = 1.5–2 equiv. [b] Formation of exclusively one stereoisomer: A = Me and TMS are cis; B = Me and TMS are trans; C = Et and TMS are cis. [c] Isolated yields. [d] By GC analysis (not isolated). [e] 4 Equiv of alkyl iodide used.

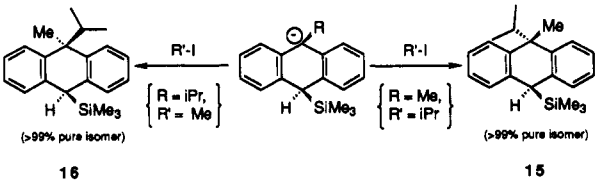
Table III. Desilylation of 9-R-9-R'-10-TMS-9,10-DHA with TBAF[a]

entry	R	R'	product	yield[b] (%)
1	Me	Me	20	92
2	Et	Et	21	94
3	*i*-Pr	*i*-Pr	22	95
4	allyl	allyl	23	90
5	Bn	Bn	24	90
6	Me	Et	25	91
7	Me	*i*-Pr	26	93
8	Et	*i*-Pr	27	93
9	Me	allyl	28	93
10	Me	Bn	29	90

[a] TBAF = tetrabutylammonium fluoride. [b] Isolated yields.



The alkylation of the rearranged anions to form 13–19 proceeded with a high degree of stereoselectivity as evidenced by the isolation of only one isomer in each case. The alkylation of 9-lithio-9-R-10-(trimethylsilyl)-DHA with R'X was investigated for (1) R = Me, R' = *i*-Pr and (2) R = *i*-Pr, R' = Me to illustrate this point. In the first case,



9-methyl-9-(trimethylsilyl)-DHA was deprotonated in the usual manner and then reacted with isopropyl iodide to afford a crystalline product, mp 82 °C (15). In the second case, 9-isopropyl-9-(trimethylsilyl)-DHA was deprotonated and reacted with methyl iodide, resulting in a different diastereomer with mp 109 °C (16).

Deprotonation of either 15 or 16 with *n*-butyllithium produced the 10-anion in each case, but subsequent re-

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(11) Greater ring puckering, i.e., closer proximity of the silyl group to C-10, in the order 5 > 6 > 7 was confirmed by molecular mechanics calculations and X-ray structural analysis.

(12) *n*-BuLi (2.1 equiv) was added by syringe to well-stirred, dilute solutions of 5–7 (2 mmol) in THF at 0 °C. Aliquots were taken after 30 s and immediately quenched with D_2O. Analysis of the products by GC/MS and NMR indicated only 9-alkyl-10-(trimethylsilyl)-9,10-DHA-d_1 and no deuterated 9-alkyl-9-(trimethylsilyl)-9,10-DHA. Attempts to intercept any 10-anion by deprotonation at lower temperatures were unsuccessful.

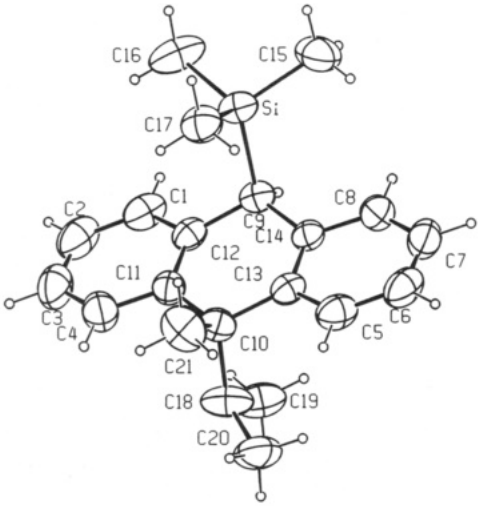


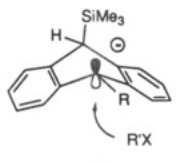
Figure 1. ORTEP drawing of compound **15**.

action with water afforded only **16** regradless of which isomer served as the starting structure (eq 1).

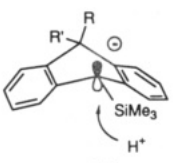
$$\textbf{15 or 16} \xrightarrow{\text{n-BuLi}} \textbf{10-anion} \xrightarrow{H_2O} \textbf{16 (only)} \qquad (1)$$

The methyl group at C-9 in each structure was irradiated in an attempt to distinguish between the two possible structure by proton NMR. With the isomer of mp 82 °C, this resulted in an enhancement of the integrated intensity of the aromatic protons by only 5% while under the same conditions the isomer with mp 109 °C showed an enhancement in the aromatics of >20%. Hence these nuclear Overhauser experiments indicate that compound **15** has the methyl group pseudoaxial—and consequently the *i*-Pr group pseudoequatorial—whereas compound **16** has the opposite stereochemistry. The NOE isomer assignments were also confirmed by X-ray structural determination.[13,14] Moreover, the X-ray results revealed that the central ring in **15** is a flattened chair conformation, close to planarity, with a dihedral angle between the phenyl planes of 3.9 (8)° (maximum deviation of any of the six atoms of the central ring from their best plane is 0.088 (3) Å for C-9) (Figure 1); **16** is puckered into a slightly twisted boat conformation with the dihedral angle between the phenyl planes as 37.4 (1)° (Figure 2).

The intermediates in both the alkylation and protonation reactions are expected to be somewhat folded about the central ring with the largest groups in the pseudoaxial positions; this corresponds to **30** in the case of alkylation and **31** for protonation. Thus both alkylation and protonation occur on the bottom-side relative to the largest pseudoaxial substituent, and the stereochemistry observed in these reactions would appear to be due simply to a steric effect retarding electrophilic attack from the top-side.[15]



30



(R > R')

31

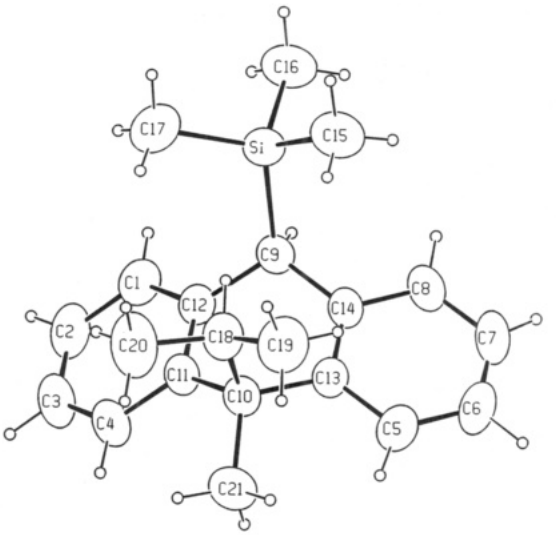
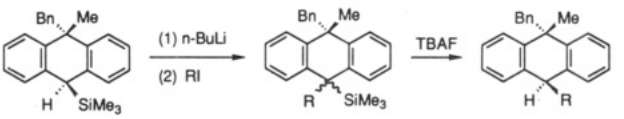


Figure 2. ORTEP drawing of compound **16**.

The synthetic procedure described here is easily extended to the synthesis of 9,9,10-trialyl-9,10-DHAs. For example, 9-benzyl-9-methyl-10-(trimethylsilyl)-9,10-DHA (**19**) was treated with 1.25 equiv of *n*-BuLi followed by addition of methyl or benzyl iodide to produce 9-benzyl-9,10-dimethyl-10-(trimethylsilyl)-9,10-DHA (**32**) and 9-benzyl-9-methyl-10-benzyl-10-(trimethylsilyl)-9,10-DHA (**33**) in 85–90% yields. Desilylation produced the corresponding trialkylated-9,10-DHAs **34** and **35**. A nuclear Overhauser experiment on 9-benzyl-9,10-dimethyl-9,10-DHA (**34**) demonstrated that the methyl groups are cis to one another.



32, R = Me
33, R = Bn

34, R = Me
35, R = Bn

This method can also be extended to the synthesis of anthrones. This is significant since the C-alkylation and C,C-dialkylation of anthrones can sometimes be difficult.[16] For example, an attempt to alkylate anthrone with methyl iodide in the presence of aqueous potassium hydroxide was reported to yield 10-methyl-9-methoxyanthracene as the major product with less than 3% yield of the desired 10,10-dimethylanthrone.[17] Subsequently, the use of the lithium salt of anthrone has led to significant improvements in the yield of 10,10-dimethylanthrone, but this procedure is not generally successful for the synthesis of a variety of anthrones.[17] Recently some progress has been made in obtaining 10,10-dialkylanthrones via the phase-transfer-catalyzed alkylation of anthrone,[16] but success has been limited to alkylations with allylic and other especially reactive alkyl halides and where both R groups in the anthrone are identical.

The method described herein provides easy access to the synthesis of dialylated anthrones, including derivatives where the two alkyl groups are different. This is accom-

(13) Crystal data for isomer **15**: $C_{21}H_{28}Si$, M_r 308.5, monoclinic space group $P2_1/c$, a = 12.634 (2), b = 9.093 (2), and c = 16.374 (3) Å, β = 91.11 (2)°, V = 1880.7 (11) Å^3, Z = 4, D_c = 1.090 g cm^{-3}, R = 0.045 for 1954 observed data.

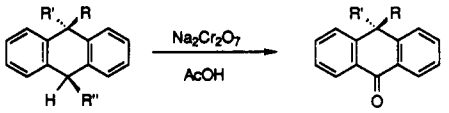
(14) Crystal data for isomer **16**: $C_{21}H_{28}Si$, M_r 308.5, orthorhombic space group $Pna2_1$, a = 19.597 (2), b = 9.8730 (11), and c = 9.8070 (9) Å, V = 1897.5 (6) Å^3, Z = 4, D_c = 1.080 g cm^{-3}, R = 0.029 for 1888 observed data.

(15) (a) For a review, see ref 6a. (b) For a discussion of ion pairing effects in DHA anion protonation, see: Daney, M.; Lapouyade, R.; Bouas-Laurent, H. *Tetrahedron Lett.* **1978**, 783.

(16) Majumdar, K. C.; Chattopadhya, S. K.; Khan, A. T. *Synthesis* **1988**, 552 (see references therein).

(17) Curtin, D. Y.; Tuites, R. C.; Dybvig, D. H. *J. Org. Chem.* **1960**, 25, 155 (see the references therein for the related work prior to 1960).

plished in 80–89% yields by oxidation of the 9,9-diialkyl-9,10-DHAs or by direct oxidation of the 9,9-dialkyl-10-(trimethylsilyl)-9,10-DHAs by sodium dichromate ($Na_2Cr_2O_7$) in acetic acid. Direct oxidation of the sili-



R" = H or $SiMe_3$

36, R = R' = Me
37, R = Me, R' = iPr
38, R = R' = Et
39, R = R' = iPr
40, R = R' = Bn
41, R = Me, R' = Bn

con-containing derivatives seems to produce slightly greater yields as evidenced by three cases where both methods were employed: **39**, **40**, and **41** were produced from the silylated derivatives in 90, 89, and 87% yields, respectively.

Conclusion

In conclusion, this new and simple procedure provides a convenient route for the synthesis of 9,9-dialkyl-9,10-DHAs, 9,9,10-trialkyl-9,10-DHAs, and 10,10-dialkylanthrones, some of which are likewise inaccessible. In addition, the synthesis of tetraalkyl-9,10-DHAs represents a simple extension of the procedure.

Experimental Section

All glassware used for the experiments was thoroughly dried in an oven and cooled and assembled under a stream of nitrogen. THF was freshly distilled from sodium benzophenone ketyl prior to use. Melting points were taken on a micro melting point apparatus. Flash column chromatography was carried out on Aldrich silica gel, 70–230 mesh, 60 Å. 9,10-Dihydroanthracene (97%) and the alkyl halides were obtained from Aldrich Chemical Co. and used without further purification. ^1H NMR spectra were taken at 90, 100, 200, or 400 MHz. ^1H NMR spectra of silylated compounds are reported with reference to the trimethylsilyl group present in the compound which was found to be within 0.02–0.2 ppm of internal tetramethylsilane. For nonsilylated compounds, tetramethylsilane was used as internal reference. ^{13}C NMR spectra were recorded at 50 MHz using $CDCl_3$ as the reference. GC analysis was performed on a Varian 3400 capillary gas chromatograph.

Preparation of 9-(Trimethylsilyl)-9,10-dihydroanthracene (2). *n*-BuLi (1.25 equiv; 20.83 mL of a 3 M solution) was added to a cold (−78 °C) solution of 9,10-DHA (1; 9 g, 50 mmol) in anhydrous THF (200 mL) under an inert atmosphere. The solution turned to orange and finally to dark red within 20–30 min of the reaction. After 2 h, 1.25 equiv (62.5 mmol, 20.83 mL) of trimethylsilyl chloride was added slowly by syringe. The solution was stirred for another 30 min before being allowed to warm to rt where it was kept for an additional 1 h. The red color of the solution changed to pale yellow after completion of the reaction. The solution was concentrated, washed with water, and extracted with ether. Slow crystallization from MeOH–ether solution gave >99.5% GC-pure **2** in 90–95% isolated yield. The product was identified by NMR and GC-MS and comparison with authentic spectral data.[10a] The above procedure was found to be successful for scaling up the reaction to a 500-mmol scale without any difficulty.

General Procedure for the Preparation of 9-(Trimethylsilyl)-9-alkyl-9,10-dihydroanthracenes 3–7. *n*-BuLi (12 mmol; 4.8 mL of a 2.5 M solution) was added via syringe to a cooled solution of 9-(trimethylsilyl)-9,10-DHA (**2**; 2.52 g, 10 mmol) in 30 mL of dry THF at 0 °C. After 2 h, the appropriate alkyl iodide (1.5–2 equiv) was added and the solution was allowed to stir for 30 min before being warmed to rt, where it was kept for an additional 60–90 min. The 9-alkyl-9-(trimethylsilyl)-9,10-DHAs **3–7** were concentrated, washed with water, and isolated by ether extraction. Recrystallization from a methanol–ether solvent mixture furnished **3–7**. The following compounds were produced in this way.

9-(Trimethylsilyl)-9-methyl-9,10-dihydroanthracene (3): yield 2.39 g (90%); white crystals, mp 109–110 °C (lit.[10a] mp 110–111 °C).

9-(Trimethylsilyl)-9-ethyl-9,10-dihydroanthracene (4): yield 2.35 g (84%); white crystals, mp 114–114.5 °C (lit.[10a] mp 114 °C).

9-(Trimethylsilyl)-9-isopropyl-9,10-dihydroanthracene (5): yield 2.36 g (80%); white crystals, mp 117–118 °C (lit.[10a] mp 120–121 °C).

9-(Trimethylsilyl)-9-allyl-9,10-dihydroanthracene (6): yield 2.4 g (82%); pale yellow needles, mp 60–61 °C; ^1H NMR ($CDCl_3$) δ 3.36 (d, 2 H, J = 5.1 Hz), 4.16 (s, 1 H), 4.2 (s, 1 H), 4.95–5.32 (m, 3 H), 7.28–7.38 (m, 8 H); MS (EI) m/z 292 (M^+), 218 (base peak). Anal. Calcd for $C_{24}H_{26}Si$: C, 82.12; H, 8.27. Found: C, 82.19; H, 8.44.

9-(Trimethylsilyl)-9-benzyl-9,10-dihydroanthracene (7): yield 2.56 g (75%); pale yellow crystals, mp 115–116 °C; ^1H NMR ($CDCl_3$) δ 3.99 (s, 2 H), 4.19 (s, 1 H), 4.22 (s, 1 H), 6.86–7.35 (m, 8 H); MS m/z 342.2 (M^+), 268 (base peak). Anal. Calcd for $C_{24}H_{26}Si$: C, 84.15; H, 7.65. Found: C, 83.84; H, 7.66.

General Procedure for the Preparation of 9,9-Dialkyl-10-(trimethylsilyl)-9,10-dihydroanthracenes 8–19. *n*-BuLi (3.1 mmol) was added to a solution of the 9-(trimethylsilyl)-9-alkyl-9,10-DHA (2.5 mmol) in 10 mL of dry THF at 0 °C, and the contents were stirred for 2 h. This was followed by addition of the appropriate alkyl iodide (1.5–2.0 equiv) and continued stirring for 30 min at 0 °C before allowing the solution to warm to rt, where the mixture was stirred for an additional 1.3 to 2 h. This was followed by the same isolation procedure used for **3–7**. In this way, the following 9,9-dialkyl-10-(trimethylsilyl)-9,10-dihydroanthracenes were produced.

9,9-Dimethyl-10-(trimethylsilyl)-9,10-dihydroanthracene (8): yield 630 mg (90%); colorless oil; ^1H NMR ($CDCl_3$) δ 1.65 (s, 3 H), 1.83 (s, 3 H), 3.94 (s, 1 H), 7.25–7.75 (m, 8 H); MS m/z 280 (M^+). Anal. Calcd for $C_{19}H_{24}Si$: C, 81.36; H, 8.62. Found: C, 81.30; H, 8.62.

9,9-Diethyl-10-(trimethylsilyl)-9,10-dihydroanthracene (9): yield 620 mg (81%); colorless oil; ^1H NMR ($CDCl_3$) δ 0.54 (t, 3 H, J = 6.2 Hz), 0.76 (t, 3 H, J = 6.2 Hz), 1.75 (q, 2 H, J = 6.5 Hz), 2.18 (q, 2 H, J = 6.5 Hz), 4.04 (s, 1 H), 7.1–7.6 (m, 8 H); MS m/z 308 (M^+). Anal. Calcd for $C_{21}H_{28}Si$: C, 81.75; H, 9.15. Found: C, 81.57; H, 8.98.

9,9-Diisopropyl-10-(trimethylsilyl)-9,10-dihydroanthracene (10): yield 70% (based on GC analysis). This product was difficult to purify and desilylation (see below) was carried out without purification.

9,9-Diallyl-10-(trimethylsilyl)-9,10-dihydroanthracene (11): yield 620 mg (75%); low melting solid; ^1H NMR ($CDCl_3$) δ 2.46 (d, 2 H, J = 7.4 Hz), δ 3.14 (d, 2 H, J = 5.4 Hz), 4.01 (s, 1 H), 4.6–5.8 (6 H, m), 7.0–7.5 (8 H, m); MS m/z 291.2 (base peak). Anal. Calcd for $C_{23}H_{28}Si$: C, 83.07; H, 8.48. Found: C, 83.11; H, 8.46.

9,9-Dibenzyl-10-(trimethylsilyl)-9,10-dihydroanthracene (12): yield 755 mg (70%); mp 134–135 °C; ^1H NMR ($CDCl_3$) δ 3.64 (s, 2 H), 3.73 (s, 2 H), 6.8–7.5 (m, 18 H); ^{13}C NMR ($CDCl_3$) δ −0.44, 38.45, 48.33, 50.47, 124.32, 125.04, 125.47, 126.17, 126.89, 127.64, 128.20, 129.84, 131.47, 136.19, 137.84, 137.99. Anal. Calcd for $C_{31}H_{32}Si$: C, 86.05; H, 7.45. Found: C, 86.14; H, 7.50.

9-Ethyl-9-methyl-10-(trimethylsilyl)-9,10-dihydroanthracene (13, 14). Diastereomer **13**: yield 660 mg (90%); mp 44 °C; ^1H NMR ($CDCl_3$) δ 0.34 (t, 3 H, J = 7.2 Hz), 1.74 (s, 3 H), 2.25 (q, 2 H, J = 7.2 Hz), 3.94 (s, 1 H), 7.2–7.7 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ −1.19, 9.16, 34.23, 38.30, 39.29, 42.52, 125.04, 125.10, 126.24, 127.21, 136.94, 139.23. Anal. Calcd for $C_{20}H_{26}Si$: C, 81.56; H, 8.89. Found: C, 81.30; H, 8.89. Diastereomer **14**: yield 630 mg (86%); colorless oil; ^1H NMR ($CDCl_3$) δ 0.78 (t, 3 H, J = 7.4 Hz), 1.58 (q, 2 H, J = 7.6 Hz), 1.78 (s, 3 H), 4.01 (s, 1 H), 7.1–7.6 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ −0.10, 9.55, 24.40, 38.03, 40.36, 42.11, 124.60, 125.44, 126.24, 127.31, 133.44, 138.08, 141.36. Anal. Calcd for $C_{20}H_{26}Si$: C, 81.56; H, 8.89. Found: C, 81.33; H, 8.85.

9-Isopropyl-9-methyl-10-(trimethylsilyl)-9,10-dihydroanthracene (15, 16). Diastereomer **15**: white crystals, 650 mg (85%); mp 82 °C; ^1H NMR ($CDCl_3$) δ 0.75 (d, 6 H, J = 6.88 Hz), 2.07 (s, 3 H), 2.16–2.23 (m, 1 H), 4.06 (s, 1 H), 7.1–7.6 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ −1.83, 18.64, 27.47, 39.29, 44.93, 45.10, 124.19, 124.85, 126.95, 135.5, 139; MS m/z 308.2 (M^+). Anal. Calcd for

$C_{21}H_{28}Si$: C, 81.75; H, 9.14. Found: C, 81.47; H, 9.31. Diastereomer **16**: white crystals, 585 mg (76%); mp 108.5–109 °C; ^1H NMR ($CDCl_3$) δ 0.69 (d, 6 H, J = 6.8 Hz), 1.48 (m, 1 H), 1.68 (s, 3 H), 4.0 (s, 1 H), 7.1–7.4 (m, 8 H); ^{13}C NMR ($CDCl_3$) 0.193, 15.10, 17.75, 35.61, 41.34, 45.18, 124.06, 125.42, 126.67, 127.48, 139.09, 140.63; MS m/z 308.2 (M^+). For crystal data of isomer **15** and **16** see refs 13 and 14.

9-Ethyl-9-isopropyl-10-(trimethylsilyl)-9,10-dihydroanthracene (17): yield 560 mg (70%); oil; ^1H NMR ($CDCl_3$) δ 0.429 (d, 6 H, J = 6.8 Hz), 0.72 (t, 3 H, J = 7.2 Hz), 1.6–1.95 (m, 1 H), 2.35 (q, 2 H, J = 7.1 Hz), 3.98 (s, 1 H), 6.9–7.6 (m, 8 H). Anal. Calcd for $C_{22}H_{30}Si$: C, 81.92; H, 9.37. Found: C, 81.93; H, 9.44.

9-Allyl-9-methyl-10-(trimethylsilyl)-9,10-dihydroanthracene (18): yield 610 mg (80%); pale yellow crystals mp 44 °C; ^1H NMR ($CDCl_3$) δ 3.04 (d, 2 H, J = 6.6 Hz), 3.93 (s, 3 H), 4.66–5.16 (m, 3 H), 7.10–7.58 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ −1.17, 33.94, 39.28, 42.20, 49.54, 116.39, 125.02, 125.22, 126.71, 127.27, 135.20, 136.57, 138.95. Anal. Calcd for $C_{21}H_{28}Si$: C, 82.28; H, 8.54. Found: C, 82.44; H, 8.70.

9-Benzyl-9-methyl-10-(trimethylsilyl)-9,10-dihydroanthracene (19): yield 675 mg (76%); white crystals, mp 113–114 °C; ^1H NMR ($CDCl_3$) δ 2.11 (s, 3 H), 3.5 (s, 2 H), 3.68 (s, 1 H), 6.2–7.8 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ −1.61, 32.82, 38.58, 43.54, 53.43, 124.70, 125.14, 126.73, 127.25, 129.58, 135.88, 138.48, 138.66. Anal. Calcd for $C_{25}H_{28}Si$: C, 84.20; H, 7.91. Found: C, 84.28; H, 7.99.

Preparation of Trialkyl-9,10-dihydroanthracenes. The same procedure used for the preparation of the dialkyl-DHAs above was employed for the synthesis of 9,9,10-trialkyl-10-(trimethylsilyl)-9,10-dihydroanthracenes **32–33**.

9-Benzyl-9,10-dimethyl-10-(trimethylsilyl)-9,10-dihydroanthracene (32) was prepared from 9-benzyl-9-methyl-10-(trimethylsilyl)-9,10-dihydroanthracene: yield 166 mg (90%); oil; ^1H NMR ($CDCl_3$) δ 1.86 (s, 3 H), 2.04 (s, 3 H), 3.41 (s, 2 H), 7.0–7.6 (m, 13 H); MS m/z 370.2 (M^+).

9,10-Dibenzyl-9-methyl-10-(trimethylsilyl)-9,10-dihydroanthrancene (33) was prepared from 9-benzyl-9-methyl-10-(trimethylsilyl)-9,10-dihydroanthracene: yield 189 mg (85%); pale yellow solid, mp 121–123 °C; ^1H NMR ($CDCl_3$) δ 1.29 (s, 3 H), 3.59 (s, 2 H), 3.83 (s, 2 H), 6.5–7.9 (m, 18 H); MS m/z 446.4 (M^+).

General Procedure for the Desilyation of 9,9-Dialkyl-10-(trimethylsilyl)-9,10-dihydroanthracenes. Tetrabutylammonium fluoride (TBAF), 1.5–2.0 equiv, was added to 2 mmol of the silylated DHA in 8 mL of THF, and the contents were stirred for 60 min at rt. The products were washed with water, isolated by ether extraction, and purified by flash chromatography on silica gel or if possible by recrystallization from methanol. The following products were produced in this way.

9,9-Dimethyl-9,10-dihydroanthracene (20): yield 383 mg (92%); oil; ^1H NMR ($CDCl_3$) δ 1.59 (s, 6 H), 4.05 (s, 2 H), 7.1–7.6 (m, 8 H); MS m/z 208.2 (M^+). Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.73. Found: C, 92.24; H, 7.75.

9,9-Diethyl-9,10-dihydroanthracene (21): yield 443 mg (94%); oil; ^1H NMR ($CDCl_3$) δ 0.458 (t, 6 H, J = 7.5 Hz), 2.04 (q, 4 H, J = 7.3 Hz), 4.06 (s, 2 H) 7.1–7.5 (m, 8 H); MS m/z 236.2 (M^+). Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.52. Found: C, 91.42; H, 8.57.

9,9-Diisopropyl-9,10-dihydroanthracene (22): yield 501 mg (95%); mp 87–88 °C; ^1H NMR ($CDCl_3$) δ 0.83 (d, 6 H, J = 6.7 Hz), 2.5–2.8 (m, 2 H), 4.19 (s, 2H), 7.1–7.7 (m, 8 H); MS m/z 264.2 (M^+). Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.14, Found: C, 90.96; H, 9.03.

9,9-Diallyl-9,10-dihydroanthracene (23): yield 486 mg (90%); low melting solid; ^1H NMR ($CDCl_3$) δ 2.79 (d, 4 H, J = 5.9 Hz), 4.03 (s, 2 H), 4.55–5.6 (m, 6 H), 7.1–7.6 (m, 8 H); MS m/z 219 (base peak).

9,9-Dibenzyl-9,10-dihydroanthracene (24): yield 648 mg (90%); mp 177–178 °C; ^1H NMR ($CDCl_3$) δ 3.33 (s, 2 H), 3.51 (s, 4 H), 6.35–7.65 (m, 18 H). Anal. Calcd for $C_{28}H_{24}$: C, 93.29; H, 6.70. Found: C, 93.24; H, 6.75.

9-Ethyl-9-methyl-9,10-dihydroanthracene (25): yield 404 mg (91%); oil (lit.[4d] mp 51.5–52.5 °C).

9-Isopropyl-9-methyl-9,10-dihydroanthracene (26): yield 439 mg (93%); mp 57–58 °C (lit.[4d] mp 58.5–59.5 °C).

9-Isopropyl-9-ethyl-9,10-dihydroanthracene (27): yield 465 mg (93%); mp 75–76 °C; ^1H NMR ($CDCl_3$) δ 0.52 (t, 3 H, J = 7.2 Hz), 0.62 (d, 6 H, J = 5.9 Hz), 1.85–2.15 (m, 1 H), 2.36 (q, 2 H, J = 7.3 Hz), 4.05 (AB q, 2 H), 7.15–7.75 (m, 8 H); MS m/z 250.1 (M^+). Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.64; H, 8.35.

9-Allyl-9-methyl-9,10-dihydroanthracene (28): yield 435 mg (93%); low melting solid; ^1H NMR ($CDCl_3$) δ 1.68 (s, 3 H), 2.46 (d, 2 H, J = 6.5 Hz), 4.03 (AB q, 2 H), 4.65–5.55 (m, 3 H), 7.15–7.65 (m, 8 H); MS m/z 234 (M^+), 193 (base peak). Anal. Calcd for $C_{18}H_{18}$: C, 92.25; H, 7.74. Found: C, 92.31; H, 7.68.

9-Benzyl-9-methyl-9,10-dihydroanthracene (29): yield 511 mg (90%); mp 84–85 °C; ^1H NMR ($CDCl_3$) δ 1.75 (s, 3 H), 2.83 (s, 2 H), 3.65 (AB q, 2 H), 6.25–7.25 (m, 8 H). Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.08. Found: C, 92.97; H, 7.02.

9-Benzyl-9,10-dimethyl-9,10-dihydroanthracene (34): yield 122 mg, oil (82%); ^1H NMR ($CDCl_3$) δ 1.53 (d, 3 H, J = 7.2 Hz), 1.83 (s, 3 H), 3.27 (s, 2 H), 3.83 (q, 1 H, J = 6.8 Hz), 6.2–7.6 (m, 13 H); MS m/z 298 (M^+).

9-Methyl-9,10-dibenzyl-9,10-dihydroanthracene (35): yield 151 mg (81%); pale yellow solid, mp 156–159 °C (GC purity 93%); ^1H NMR ($CDCl_3$) δ 1.13 (s, 3 H), 3.03 (d, 2 H, J = 4.9 Hz), 3.25 (s, 2 H), 4.14 (t, 1 H, J = 5.0 Hz), 6.1–7.6 (m, 18 H); MS m/z 283 (base peak).

General Procedure for the Oxidation of 9,9-Dialkyl-10-(trimethylsilyl)-9,10-dihydroanthracenes and 9,9-Dialkyl-9,10-dihydroanthracenes. Oxidation of either 9,9-dialkyl-10-(trimethylsilyl)-9,10-dihydroanthracene or 9,9-dialkyl-9,10-dihydroanthracene (2 mmol) was accomplished with $Na_2Cr_2O_7$ (2 mmol) in acetic acid (20 mL) at room temperature for 12 h. However, the time of the reaction can be reduced by using reflux temperatures. After completion of the oxidation, products were washed with water and extracted with ether. Final washing of the ether extract by $NaHCO_3$ removed traces of acetic acid. Products were either extracted by flash chromatography on silica gel or recrystallized from methanol–ether solution. The following compounds were produced in this way.

10,10-Dimethylanthrone (36): prepared in >90% (GC yield) upon oxidation of **8**. Compound is known and the identification was made by comparison with reported data.[16]

10-Isopropyl-10-methylanthrone (37): prepared in >92% (GC yield) upon oxidation of **15**; mp 93–94 °C; ^1H NMR (CCl_4) δ 0.50 (d, 6 H, J = 6.8 Hz), 1.74 (s, 3 H), 1.6–2.0 (m, 1 H), 7.0–7.5 (m, 6 H), 8.25 (d, J = 7.5 Hz); MS 250 (M^+). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.11; H, 6.95.

10,10-Diethylanthrone (38): yield 413 mg (82%); white crystals, mp 139–140 °C (lit.[10c] mp 140 °C); ^1H NMR ($CDCl_3$) δ 0.7 (t, 6 H, J = 6.5 Hz), 2.6 (q, 4 H, J = 6.2 Hz), 7.6–8.2 (m, 6 H), 8.85 (d, J = 7.5 Hz); MS m/z 250.2 (M^+).

10,10-Diisopropylanthrone (39): yield 505 mg (91%); white crystals, mp 150 °C; ^1H NMR ($CDCl_3$) δ 0.79 (d, 12 H, J = 6.8 Hz), 2.6–2.9 (m, 2 H), 7.2 (m, 6 H), 8.45 (dd, ^3J = 7.5 Hz, ^4J = 1.9 Hz); MS m/z 278 (M^+). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 86.06; H, 8.10.

10,10-Dibenzylanthrone (40): yield 665 mg (89%); white crystals, mp 226–227 °C (lit.[16] mp 226–227 °C); ^1H NMR ($CDCl_3$) δ 3.73 (s, 4 H), 6.2–8.2 (m, 18 H); MS m/z 374 (M^+).

10-Benzyl-10-methylanthrone (41): yield 518 mg (87%); white crystals, mp 100–101 °C; ^1H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 3.32 (s, 2 H), 6.0–8.2 (m, 13 H); MS m/z 298 (M^+).

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Supplementary Material Available: X-ray experimental procedure, coordinates for non-hydrogen and hydrogen atoms, anisotropic thermal parameters, bond distances, bond angles, torsion angles, and least-square planes calculations for isomer **15** and **16** (15 pages). Ordering information is given on any current masthead page.