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Silicon Mediated Alkylations in the 9,10-Dihydroanthracene System: a Convenient Synthesis of 9,9-Dialkyl-9,10-Dihydroanthracenes.

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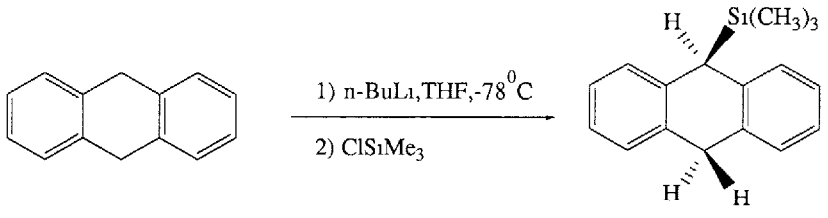
Abstract: A trimethylsilyl (TMS) substituent is used to control the regiochemistry of alkylation in 9,10-dihydroanthracene (9,10-DHA) furnishing 9,9-dialkyl-10-TMS-9,10-DHAs The TMS group is subsequently removed resulting in the first convenient synthesis of a variety of 9,9-dialkyl-9,10-DHAs in good to excellent yields

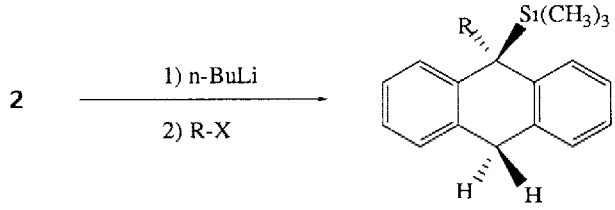
The structure of 9,10-dihydroanthracenes (9,10-DHA) substituted in the central ring has received considerable attention by such methods as X-ray crystallography,[1] dynamic NMR spectroscopy [2] and theoretical calculations.[3] Our own investigations required several 9,9-dialkyl-9,10-DHAs that are either only available in low yields by lengthy routes,[4] or are unknown and inaccessible by conventional methods. We now report the first convenient and versatile synthesis of 9-R,9-R'-9,10-dihydroanthracenes.

Numerous applications of silicon-modified reductions to the chemistry of polynuclear aromatics have recently been demonstrated.[5] Herein, the silicon-mediated, regioselective alkylation of 9-trimethylsilyl-9,10-dihydroanthracene (**2**) serves as the starting point for the synthesis of 9,9-dialkyl-9,10-DHAs The preparation of **2** was accomplished by deprotonation/trimethylsilylation[6] of 9,10-DHA (**1**) in yields greater than 95%. Alternatively, **2** was prepared via halogen/metal exchange between n-butyllithium and 9-bromoanthracene followed by trimethylsilylation to produce 9-trimethylsilylanthracene which was subsequently converted to **2** by metal/ammonia reduction.[7] However, the yields were lower (70%) and so the former method is preferred.



1 **2**

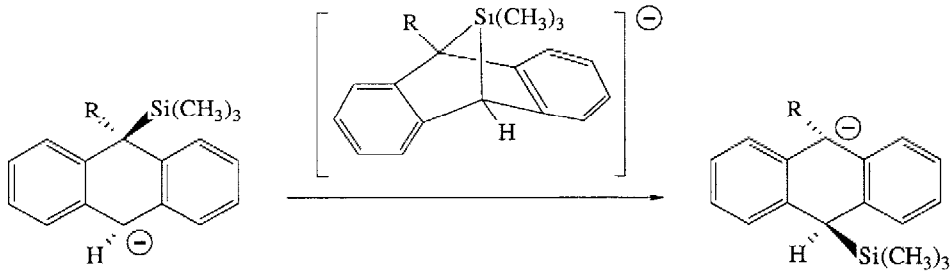
The deprotonation and subsequent alkylation of **2** was carried out by a modification of the procedure by Daney, Lapouyade and Bouas Laurent [8a] Accordingly, 2 in dry THF was reacted with 1.2 equiv. n-BuLi for



3 R=CH_3 (90%)
4 R= CH_2CH_3 (84%)
5 R=$CH(CH_3)_2$ (80%)

1.5h at 0 ^{0}C, followed by the addition of 1.5 equiv alkyl halide. The yields of 9-R-9-TMS derivatives **3-5** produced in this way ranged from 80 to 90%, representing some improvement over the 66-72% previously reported.[8a]

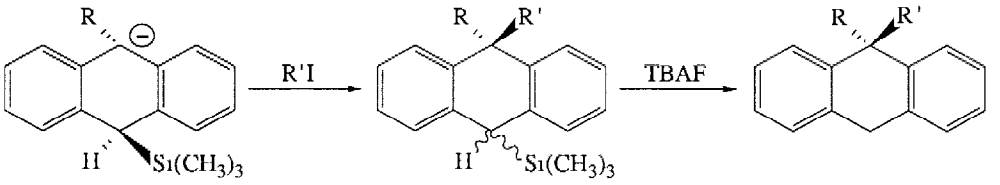
Further reaction of the 9-R-9-TMS-9,10-DHAs **3-5** with 1.25 equiv. n-BuLi for 1-2h at 0 ^{0}C results in rearrangement. Initial deprotonation occurs at the 10-position followed by 1,4 migration of the TMS group to afford the 10-TMS-9-anion. This anion may then be alkylated by RI, where R is methyl, ethyl, isopropyl,



allyl or benzyl, to produce 9-R-9-R'-10-TMS-9,10-DHAs. This rearrangement, originally observed by Daney, Lapouyade and Bouas-Laurent[8a] during the deprotonation of 9,9-bis(TMS)-9,10-DHA (to ultimately produce 9,10-bis-TMS-9,10-DHA) seems to have considerable potential for the synthesis of 9,10-DHAs which has not heretofore been exploited.

The driving force of the rearrangement is presumed to be facile formation of the pentacoordinate, silylated intermediate.[8] It might be expected that such processes would be accelerated by (a) boat-like conformations of the substituted 9,10-DHA systems, and/or (b) relief of strain due to 9,9-geminal disubstitution.[3,9] Further studies are underway to evaluate these effects.

The results summarized in Table 1 indicate good to excellent yields for the synthesis of 9,9-dialkyl-10-TMS-9,10-DHAs **6-13.** The yield of diisopropyl derivative **13** was lower, however, but improved significantly with an increase in R'I concentration. This suggests that alkylation of the more hindered anionic center (i.e , where R = isopropyl) is likely to be the limiting step.



6-13 **14-21**

Table 1. Alkylation of 10-TMS-9-Alkyl-9-Anion

Compound	R	R'I[a]	9-R,9-R'-10-TMS-9,10-DHA, % yield[b]
6	Me	Me-I	90
7	Me	Et-I	90
8	Me	*i*-Pr-I	85
9	Me	Allyl-I	80
10	Me	Bn	76
11	Et	Et-I	81
12	Et	*i*-Pr-I	70
13[c]	*i*-Pr	*i*-Pr-I	30 (66)[d]

(a) 1.5 equiv. alkyl iodide used. (b) Isolated yield. (c) Conversion determined by GC-analysis. (d) 4 equiv. alkyl iodide used.

The isolated 9,9-dialkyl-10-TMS-DHAs were then desilylated to complete the synthesis of 9,9-dialkyl-DHAs.[10,11] This was accomplished with tetrabutylammonium fluoride (TBAF) in THF, and the dialkylated products **14-21** were produced in 90-95% yields as indicated in Table 2.

Table 2. Desilylation of 9-R,9-R'-10-TMS-9,10-DHA with TBAF.

Compd.	% Yield of 9-R,9-R'-DHA[a]	Compd.	% Yield of 9-R,9-R'-DHA[a]
14	92	**18**	90
15	91	**19**	94
16	92	**20**	93
17	93	**21**	95

(a) Isolated yield.

We expect that this new procedure will represent an important route for the synthesis of 9,9-dialkyl-9,10-dihydroanthracenes, some of which are inaccessible by other methods Studies are currently underway to determine the applicability of this new methodology to other suitable polynuclear aromatics.

ACKNOWLEDGEMENT

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9. Molecular mechanics calculations and x-ray structural analysis of compounds **3-5** confirm the favorable geometry of **3** and **4** for migration of silicon (TMS) although **5** contains a less puckered central ring (results to be submitted for publication). (b) Kinetics experiments are underway to compare the rate of silicon migration in **3-5.**
10. A typical procedure for the overall synthesis of 9,9-dialkyl-9,10-dihydroanthracenes is as follows: n-BuLi (60 mmol) was added via syringe to 9-TMS-9,10-DHA (50 mmol) in 250 mL dry THF at 0 °C. After 2 h, the appropriate alkyl iodide (75 mmol) was added via syringe and the solution was allowed to stir for 30 min before warming to room temperature where it was kept for 1 h The 9-alkyl-9-TMS-9,10-DHAs were isolated by ether extraction and recrystallized from methanol. Exactly the same procedure was used for the second deprotonation/alkylation to afford the 9,9-dialkyl-10-TMS-9,10-DHAs which were purified by column chromatography on silica gel, or if possible by recrystallization from methanol. Desilylation was accomplished on the latter compounds (5 mmol in 25 mL THF) by the addition of an excess (1 5-2 equiv.) of TBAF followed by stirring for 30 min. The products (9,9-dialkyl-9,10-DHAs) were washed with water, isolated by ether extraction and purified by flash chromatography on silica gel or if possible by recrystallization from methanol
11. All new compounds gave consistent NMR and MS results as well as correct C, H analyses.

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