Reactivity of Benzylic Carbanions. 10. [1,4] Rearrangement of the Me_3Si Group in 9,9-Bis(trimethylsilyl)- and 9-Alkyl-9-(trimethylsilyl)-10-lithio-9,10-dihydroanthracenes

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A [1,4] Me_3Si migration has been shown to occur in 9,9-bis(trimethylsilyl)-10-lithio-9,10-dihydroanthracene (C_1); the resulting carbanion (C_2), protonated by H_2O, gives rise exclusively to the *cis*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene ($(Me_3Si)_2DHA$) in high yield. The same migration was also observed in a series of 9-(trimethylsilyl)-9-alkyl-10-lithio-9,10-dihydroanthracenes (alkyl = Me, Et, *i*-Pr), which were transformed into a mixture of cis and trans 9,10-disubstituted DHAs (VII, VIII, IX). Experimental evidence was obtained for an intramolecular shift, and the mechanism of the reaction was considered, particularly the possibility of a reversible Me_3Si migration ($C_2 \rightarrow C_1$). The driving force of the Me_3Si shift is believed to involve easy formation of pentacoordinated silicon derivatives combined with relief of strain in, and formation of, more stable ion pairs. In light of these results, the rearrangements observed in 9-(trimethylsilyl)-9-deuterio-10-lithio-9,10-dihydroanthracenes were reexamined. A comparison with other well-known R_3Si migrations in carbanions, mainly in systems containing heteroatoms, was made, and the structural requirements to observe such reactions in genuine carbanions were delineated; the DHA substrate appears to be well suited for this rearrangement.

Introduction

Rearrangements of atoms or groups of atoms are frequently encountered in organic chemistry.[1] However, the majority are not found in anions. In these species,[2] saturated alkyl groups show a poor migratory aptitude, contrary to unsaturated groups (vinyl, phenyl, etc ⋯); also, groups having central atoms with unfilled d orbitals, such as silicon, are known to undergo facile anionic rearrangements especially when the heteroatoms bear the negative charge. But no silyl group migration in genuine carbanionic species (i.e., in compounds containing only C and H atoms) was known until 1973 when [1,2], [1,4], and [1,3] $SiMe_3$ rearrangements were reported in a short communication by Eisch and Tsai.[3]

In the course of a study of the reactivity of 9,10-dihydroanthracenyl anions (DHA^-), we have uncovered the [1,4] migration of the Me_3Si group in 9,9-bis(trimethylsilyl)-10-lithio-9,10-dihydroanthracenes. Having reported a preliminary account,[4] we describe now, in full, the scope and mechanism of the reaction, which has been extended to some 9-alkyl-9-trimethylsilyl-9,10-dihydroanthryl anions (9-R-9-$(Me_3Si)DHA^-$). In light of the preceding results, it was considered worthwhile to reexamine our previous report about hydrogen migration in 9-(trimethylsilyl)-9,10-dihydroanthracenyl anion.

Results and Discussion

I. Study of the Rearrangement. 1. Experimental Results. Compounds I–IV (concentration $\simeq 5 \times 10^{-2}$ M) were mixed with 1 molar equiv of BuLi in THF at room temperature and were hydrolyzed after a few hours (Scheme I). The products were identified by comparison with authentic samples, and the stereochemistry of the reaction was deduced. Results are collected in Table I.

Before considering the mechanism of the reaction, it should be noted that the method can be used to prepare *cis*-$(Me_3Si)_2DHA$ from I, provided the latter is available. Thus, it seems appropriate to comment upon the preparative aspects of the three *meso*-$(Me_3Si)_2DHAs$ (I, *cis*-VI, and *trans*-VI). The methods collected in Scheme II are from various sources, including our own unpublished results.

The common starting material, anthracene (A), is smoothly reduced only to 9,10-dihydroanthracene (DHA)[5,6] due to the large gap in the reduction potential between anthracene and the benzenic side rings. The monosilyl compound V can be readily prepared pure from DHA.[7,8] 9,9-Bis(trimethylsilyl)-9,10-dihydroanthracene (I) is obtained as the major product in the silylation of V;[8] no 9,10-bis(trimethylsilyl)-9,10-dihydroanthracene was detected in the course of these reactions. The anionic [1,4] trimethylsilyl migration generates stereochemically *pure cis*-VI in high yield. The trans isomer (*trans*-VI) can be obtained as a mixture with *cis*-VI and other products by two different routes: (1) treatment of DHA with BuLi (2 equiv) in TMEDA–cyclohexane, followed by addition of Me_3SiCl,[7] yields *trans*-VI (20%) accompanied by *cis*-VI (12%); (2) reduction of anthracene by lithium in a mixture of ether and benzene and in the presence of an excess of Me_3SiCl[9-11] (reductive silylation) leads to *cis*-VI (20%) and *trans*-VI (11%).[11] The first recipe may appear more attractive, but the second, based on anthracene, is more straightforward. In both cases, however, separation and purification of the isomers proved tedious.

Of note also is the fact that *trans*-VI is quantitatively transformed into *cis*-VI by BuLi in TMEDA–cyclohexane[7]

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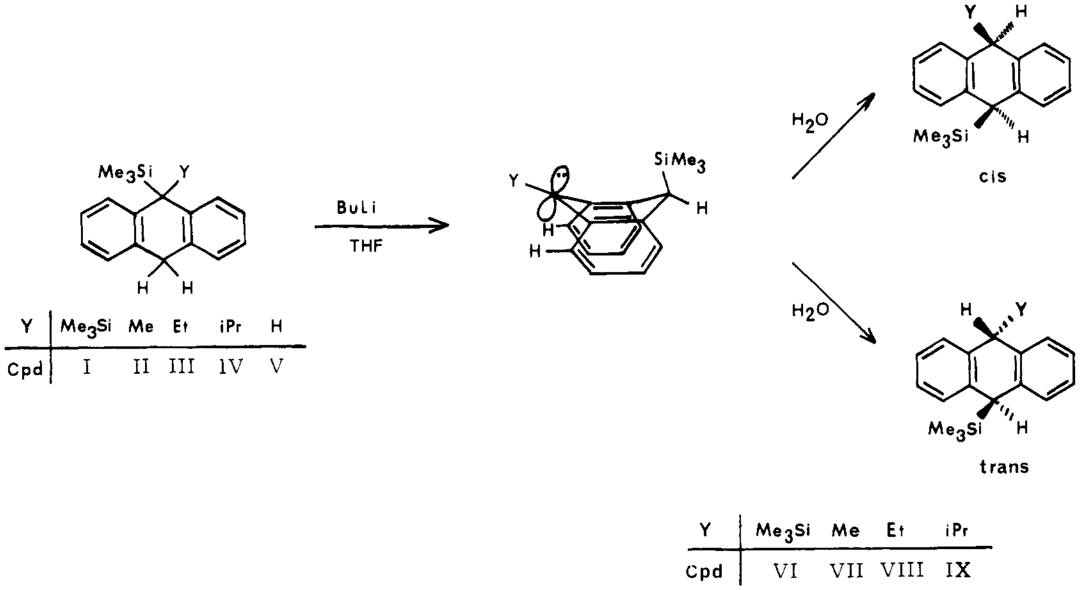
Table I. Rearrangement of 9,9-$(Me_3Si)_2$DHA and 9-Y-Me_3SiDHA with BuLi in THF or Cyclohexane-TMEDA[b] at Room Temperature[d]

				product yield, %			
					9-Y-10-Me_3Si-DHA		
run	starting compound	solvent	BuLi, equiv (time, h)	recovered 9-Y-9-Me_3SiDHA	cis	trans	cis:trans
1	I	THF	1 (2 h)	5	95	[a]	
2	I	THF	0.1 (3.5)	95	5	[a]	
3	I	THF	1 (3.5)	17	83	[a]	
4	I	CH/TMEDA[b]	1.5 (2)	6	94	[a]	
5	II	THF	1 (4)	8	68	24	74:26
6	III	THF	1 (4)	25	60	15	80:20
7	III	THF	1.1 (2)	42	47[c]	11	81:19
8	III	CH/TMEDA	1.1 (2)	1	98	1	99:1
9	IV	THF	1 (2)	4	91	5	95:5

[a] No trace of trans isomer was detected (GLC); the trans:cis ratio was estimated less than 1%. [b] CH, cyclohexane; TMEDA; tetramethylethylenediamine. [c] Another run provided *cis*-VIII with D 87% on the 9-position, 13% on the 10-position. [d] Concentration of starting materials, $\simeq 5 \times 10^{-2}$ M.

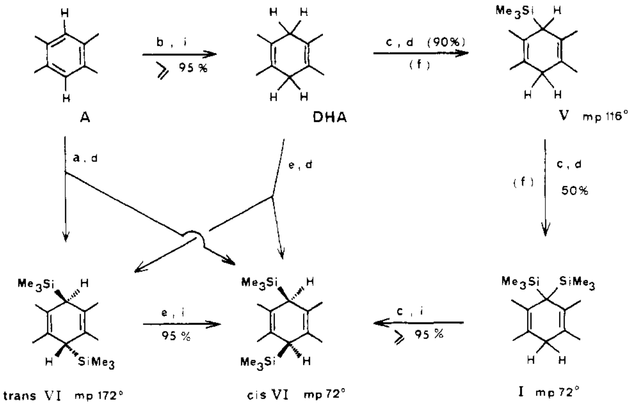
Scheme I



Y	Me_3Si	Me	Et	iPr	H
Cpd	I	II	III	IV	V

Y	Me_3Si	Me	Et	iPr
Cpd	VI	VII	VIII	IX

Scheme II[a]



[a] (Top) Preparation of DHA, 9-Me_3SiDHA, 9,9-$(Me_3Si)_2$DHA, and 9,10-$(Me_3Si)_2$DHA. Yields are in isolated pure compounds. (Bottom) (a) 1, Li(Na) in ether/benzene,[9] 2, Li in ether/benzene[10,11] (see Experimental Section). The reduction of anthracene by lithium or sodium also leads to V in variable yields. (b) 1, Na in THF-HMPA;[6] 2, Na-EtOH,[5a] Na-NH_3-$FeCl_3$.[5b] (c) BuLi in THF. (d) Me_3SiCl. (e) BuLi, TMEDA, cyclohexane.[7] (f) See ref 8. (i) H_2O.

followed by hydrolysis. By contrast, whatever the experimental conditions used, *cis*-VI was not transformed into the trans isomer.

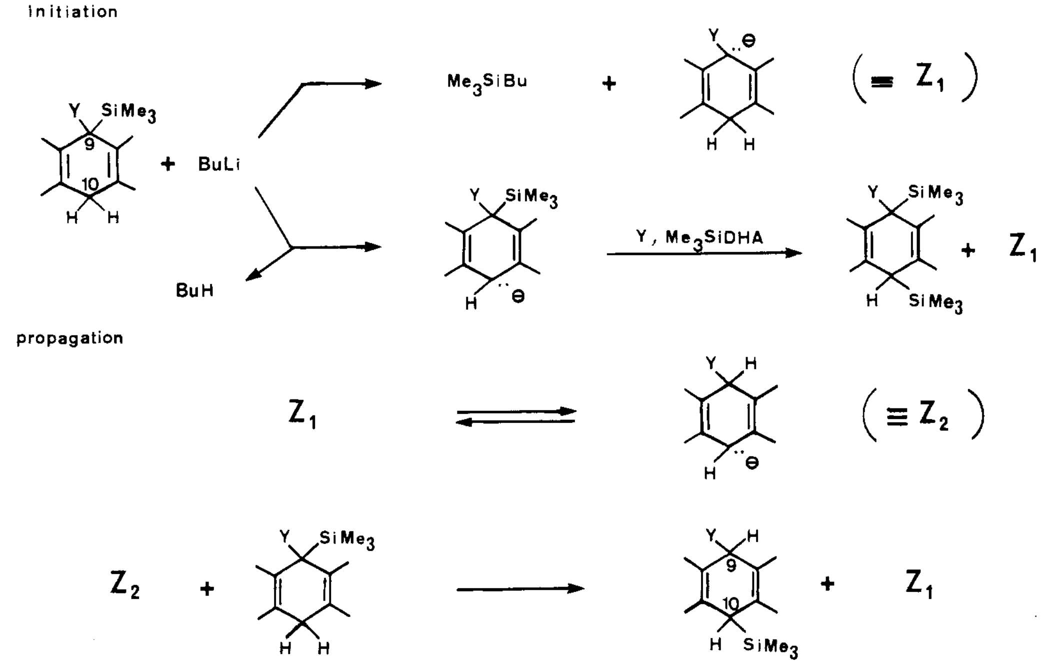
2. Mechanism of the Me_3Si Migration in DHA Anions. a. Intra- vs. Intermolecular Rearrangement. Firstly, the possibility of a bimolecular Me_3Si transfer was examined by using an equimolar mixture of 9-isopropyl-9-(trimethylsilyl)-9,10-dihydroanthracene (IV) and 9-lithio-9,10-dihydroanthracene (DHA^-, Li^+) in THF. The reaction did not lead to a mixture of V and 9-*i*-PrDHA after hydrolysis but to IV and DHA; thus, no intermolecular transfer could be detected.

Secondly, an intermolecular process, should it occur, should proceed via a chain mechanism such as the one depicted in Scheme III. Thus, a small amount of BuLi should suffice to initiate the reaction. The result of two experiments, run in parallel with compound I (Table I, runs 2 and 3) shows that the rearranged product (*cis*-VI) yield is a function of the initial concentration of base; therefore, a chain mechanism can be discarded.

The above experiments leave an intramolecular rearrangement as the most likely mechanism.

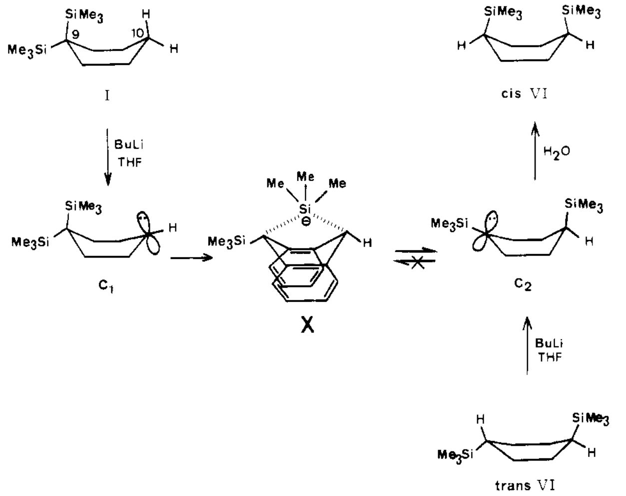
b. Alkyl vs. Trimethylsilyl Shift in 9-Alkyl-9-(trimethylsilyl)-9,10-dihydroanthracene Anions. The

Scheme III[a]



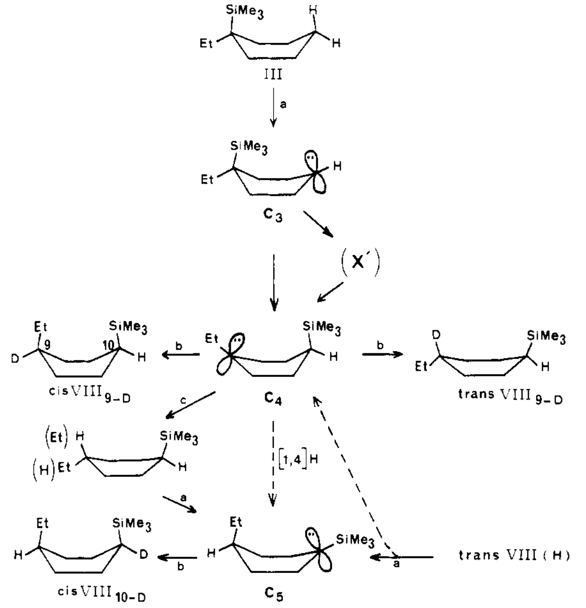
[a] Hypothetical chain reaction mechanism for an intermolecular trimethylsilyl migration.

Scheme IV[a]



[a] Overall reaction scheme of intramolecular [1,4]trimethylsilyl shift in 9,9-$(Me_3Si)_2$DHA anion. The countercation and its solvation shell are omitted for clarity.

Scheme V[a]



[a] (Top) Overall reaction scheme of intramolecular [1,4]trimethylsilyl shift in 9-alkyl-9-(trimethylsilyl)-9,10-dihydroanthracene anions illustrated with compound III. The countercation and its solvation shell are omitted for clarity. X′ is an activated complex or intermediate. (Bottom) (a) BuLi, THF. (b) D_2O. (c) Protonating species.

rearrangement undergone by 9-R-9-(Me_3Si)DHAs in the presence of BuLi in THF (Scheme I) may be interpreted by a trimethylsilyl *or* an alkyl migration. In the same way as for 9,9-$(Me_3Si)_2$DHA, the possibility of a rearrangement in some 9,9-R_2DHA anions was explored. 9,9-Dimethyl-9,10-dihydroanthracene (XIa) and 9,9-diethyl-9,10-dihydroanthracene (XIb) in the presence of an equivalent amount of BuLi in THF developed a red color characteristic of DHA anions (which disappeared on quenching with water). No rearrangement could be detected under these conditions, and when D_2O was used instead of H_2O, the isolated product was deuterated (85%) in position 10.

Indeed, [1,*n*] migrations of simple alkyl groups in genuine carbanions are known to occur only with difficulty and in special cases.[2a] Thus, the above results indicate a preferred Me_3Si migration in the rearrangement of carbanions derived from compounds II–IV. An alternative hypothesis of an alkyl and hydrogen [1,4] successive rearrangement cannot be completely discarded. But it will be seen later that hydrolysis of an anion with deuterium oxide substantiates the Me_3Si shift.

c. Overall Reaction Scheme. From previously reported results,[4] it is possible to propose a preliminary mechanism, depicted in Schemes IV and V. For the sake of clarity, the countercation and solvent molecules surrounding the ions are not represented. The common features of Schemes IV and V are the formation of a 10-carbanion (C_1 or C_3), which rearranges irreversibly to another carbanion (C_2 or C_4) through a species X or X′.

Table II. Protonation Stereochemistry after Me_3Si Rearrangement of Carbanions Generated by Reaction of VI or VIII with BuLi in THF, TMEDA, or Et_2O-HMPA

run	starting compound	solvent	BuLi, equiv	*T*, °C	product yield, % cis	product yield, % trans	cis:trans
					VI		
1	*cis*-VI	THF	1	reflux	100	[a]	
2	*cis*-VI	THF	4	20	100	[a]	
3	*cis*-VI	TMEDA	4 (4 days)	20	68[b]	[a]	
4	*trans*-VI	Et_2O + HMPA (5.5 equiv)	1.1	−40	100	[a]	
					VIII		
5	*cis*-VIII	THF	2	0[c]	100	[a]	
6	*trans*-VIII	THF	2	20	93	7	93:7

[a] No trace of trans isomer was detected; limits of detection are ≤1%. [b] Other compounds: 9-(trimethylsilyl)anthracene (20%); 9,10-bis(trimethylsilyl)anthracene (10%); unidentified (≃2%). [c] At room temperature partial desilylation was observed without formation of the trans isomer.

Postulation of transient species X and X′ (as intermediates or activated complexes) rests on the well-known ability of silicon atoms to pentacoordinate[12a] by using empty d orbitals to bear the negative charge. The driving force of the rearrangement is presumably an easy formation of pentacoordinate silylated derivatives[12b] (due to favorable conformations of the DHA systems) combined with relief of strain (in 9,9 geminal disubstitution) and formation of more stabilized ion pairs.

It is of note that I yields 95% of the rearranged product (5% of I recovered, see Table I, run 1). Several attempts to improve the yield met with failure, and this raised the question of the reversibility of the rearrangement ($C_2 \rightarrow C_1$). The carbanion C_2 was generated by another route (from *trans*-VI) under the same experimental conditions, i.e., with BuLi in THF; C_2 was transformed into *cis*-VI upon hydrolysis. In THF, *cis*-VI did not undergo any isomerization (Table II, runs 1 and 2). According to Harvey,[7] the conversion of *trans*-VI into *cis*-VI is quantitative in refluxing cyclohexane/TMEDA with excess BuLi. We obtained similar results in Et_2O–HMPA at −40 °C (Table II). In any case, no trace of compound I could be detected as a product of these reactions. We conclude that the rearrangement (at least for I) is irreversible. The fact that the yield in rearranged product was not 100% may be ascribed to the great difficulty of eliminating traces of water when dealing with small amounts of compounds in fairly diluted solutions ($(\simeq 2–5) \times 10^{-2}$ M). A large excess of BuLi could not be employed since it results in the formation of dianions.

Similar comments apply to 9-R-9-Me_3SiDHAs that do not rearrange quantitatively in THF. However, taking III as a reference, the yield of *cis*-VIII was significantly improved (99%) by using BuLi in TMEDA–cyclohexane (Table I). There is little doubt that the rearrangements of II–IV are also irreversible within experimental errors (see below, results of deuteration).

However, the mechanism of the rearrangements of II–IV may be more complex, as illustrated in Scheme V, because of a possible [1,4] H shift ($C_4 \rightarrow C_5$) following the [1,4] Me_3Si migration. Carbanion C_5 could react with D_2O, leading to VIII deuterated α to the silicon atom. A reaction of III with BuLi in THF followed by hydrolysis with D_2O led to a 4:1 cis/trans mixture of VIII with an overall yield of 60% (Table I, run 7). Most of the deuterium atoms were located α to the ethyl groups. From NMR spectroscopy it was difficult to estimate the percentage of deuterium α to silicon, but if the cascade rearrangement $C_3 \rightarrow C_4 \rightarrow C_5$ occurs at all, it cannot represent more than 15% of the reaction (Table I, run 7).

Carbanion C_5 was produced independently: reaction of *trans*-VIII with BuLi in THF gave *cis*-VIII, deuterated mainly (92%) α to silicon, in high yield; the remaining 8% of deuterium, which was α to the ethyl group, may arise from carbanion C_4 (Table II, run 6).

In the above experiments, no 10-deuterated III was detected in the recovered starting material. This is again consistent with the irreversibility of the rearrangement $C_4 \rightarrow C_3$.

It is interesting to note that, under our conditions, carbanion C_4 is essentially generated from 9-ethyl-9-(trimethylsilyl)-9,10-dihydroanthracene (III) and carbanion C_5 from *trans*-9-ethyl-10-(trimethylsilyl)-9,10-dihydroanthracene (*trans*-VIII). Indeed, carbanion C_4 could not be obtained from *cis*-VIII. The latter, in the presence of BuLi (Table II, run 5), does not isomerize to *trans*-VIII; neither incorporates deuterium when the reaction is quenched by MeOD. This points to a striking difference in kinetic acidity between *cis*-VIII and *trans*-VIII. This is also the case between *cis*-VI and *trans*-VI (Table II). Both examples reflect an important conformational difference between the isomers.[13]

3. Reexamination of the Rearrangement observed in 9-(Trimethylsilyl)-9-deuterio-10-lithio-9,10-dihydroanthracene. In a previous paper[8] we reported the results of the deuteration, alkylation, and silylation of 9-(Me_3Si)-9-Li-9,10-DHA, which appeared to yield exclusively 9,9-substituted products (Scheme VI). These products were thought to result either from abstraction of proton 9 followed by substitution or by abstraction of proton 10, fast [1,4] H migration, and substitution. When 9-deuterated V was taken as starting material to study alkylation, we observed some 9-alkylated products deuterated in position 10 (IV_D in Scheme VI). This was interpreted as evidence of partial abstraction of proton 10 by BuLi followed by [1,4] D migration.

In light of the present results, the reaction with isopropyl iodide was reproduced and the deuterium content of the products were determined with better accuracy by NMR and mass spectroscopy. Thus, we also found some 9-deuterio-9-isopropyl-10-(trimethylsilyl)-9,10-dihydroanthracene ($IX_{9\text{-}D}$, Scheme VI) whose presence is ascribable to [1,4] Me_3Si migration. It should be noted that the formation of XIII in low yield, although explicable by [1,4] D migration, might also occur from carbanion C_8 through

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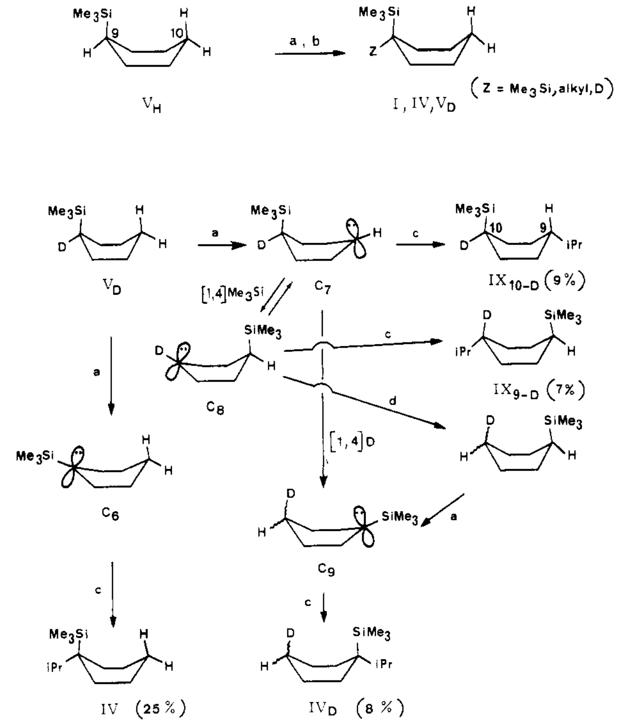
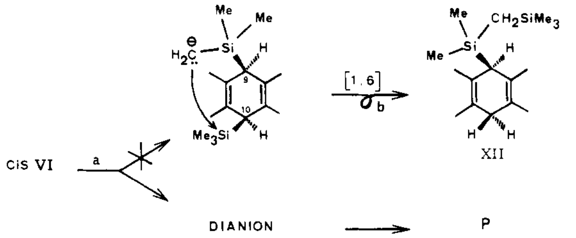
Scheme VI[a]



[a] (Top) Reactions of 9-(trimethylsilyl)-9,10-dihydroanthracene in the presence of BuLi with some electrophiles. Representation of the different pathways and possible rearrangements from 9-deuterio-9-(trimethylsilyl)-9,10 dihydroanthracene (V_D 80% deuterium). (Bottom) (a) BuLi, THF. (b) Z Halide or D_2O. (c) Isopropyl iodide. (d) Protonating species.

Scheme VII[a]



[a] (Top) Hypothetical [1,6] Me_3Si migration in the anionic rearrangement of *cis*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene. (Bottom) P = anthracenic derivatives (see Table II, run 3). (a) BuLi (4 equiv), TMEDA, 4 days at room temperature. (b) H_2O.

a succession of steps: protonation by the medium, reaction with base, and finally alkylation.

Therefore, we believe that BuLi abstracts proton 9 very easily from V_H to generate carbanion C_6, but, due to an important isotopic effect in V_D, abstraction of proton 10 can compete with abstraction of deuterium 9; it is then possible to observe products from carbanions C_7 and C_8.

II. Protonation Stereochemistry. It is observed that the cis/trans ratios of the products (VI–IX) in THF (Table I) decreases in the order I >>> IV >> III > II, i.e., with the volume of group Y.

We propose the following explanation based on previous studies by us[14] and others[15] on similar compounds.

The stereochemistry of the rearrangement reaction is controlled by the protonation of the carbanion. It has been shown[16] that under our experimental conditions the products are obtained under kinetic control. In this series, it has been established[15,17] that the semiequatorial position is more crowded (due to steric interactions with the so-called peri H atoms, see Scheme I) than the semiaxial position. Therefore, in the intermediate carbanions, the bulky Me_3Si group prefers to be axial; this creates a differentiation between the two faces of the carbanion (Scheme I). Whatever the equilibrium position of the ion pairs (intermediate), the activated complexes (not presented in Scheme I) must accommodate groups Y in the "equatorial" or "axial" positions so that the bulkier the Y group the higher the population in the semiaxial position.

In cyclohexane–TMEDA, the rearranged carbanions are expected to exist as contact ion pairs[14] and adopt a structure where the lithium cation is probably located in a semiequatorial position,[18] leading essentially to the cis product as actually observed (Table I, runs 4 and 8).

III. Discussion on Related Anionic Rearrangements. As mentioned in the introduction, Eisch and Tsai[3] reported the first examples of [1,*n*] Me_3Si migrations with $n = 2–4$ in genuine carbanions. Whereas we report a [1,4] Me_3Si rearrangement in *monocarbanions*, the authors observed the same type of migration in a *dicarbanion* formed from 1,2-bis(trimethylsilyl)-1,2-diphenylethane (E) with excess BuLi (4 equiv) in TMEDA. One of the carbanions is believed to be benzylic, the second being methylenic, both α to the silicon atom.[3]

Under Eisch's experimental conditions, compound *cis*-VI (which has some structural analogy with E) yielded 9-trimethylsilyl and 9,10-bis(trimethylsilyl) anthracenes (94% of the converted starting material) and another unidentified product (6%), which is different from the already known[8] and anticipated product XII, which could result from a [1,6] Me_3Si shift (Table II, run 3 and Scheme VII). Indeed, the reactivities of *cis*-VI and E are quite different. Although *cis*-VI seems unreactive with BuLi in THF, it is transformed into the 9,10-dibenzylic dianion with BuLi in TMEDA.

In a preceding paragraph, we have considered the possibility of a [1,4] H migration following the [1,4] Me_3Si shift in III ($C_4 \rightarrow C_5$) in Scheme V as well as a [1,4] D shift in V ($C_7 \rightarrow C_9$) in Scheme VI. Rearrangements of these types have been observed by Seyferth et al.[19] in an example where the driving force seems to be largely of steric origin (hindrance to solvation of a lithium cation) as well as stabilization of a carbanion α to silicon.[20,21] An example of a [1,5] H migration was provided by Maercker et al.[22] who studied ω-lithio alkyltrimethylsilanes in THF. Stabilization of a carbanion α to a silyl group was again invoked as the main factor controlling the reaction. More recently, Maercker[23] showed that (4-phenylbutyl)lithium in diethyl ether and THF undergoes an intramolecular [1,4] H shift, yielding (1-phenylbutyl)lithium as expected

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by stabilization of a carbanion by conjugation with a benzene ring.

Nevertheless, most of the organosilicon anionic rearrangements are known to occur in species containing one or more heteroatoms, the first to be recognized involving a [1,2] migration from one nitrogen atom to the other in anions of silicon-substituted hydrazines.[24] This reaction was later shown to be of wide scope, very rapid, intramolecular, and quantitative. These rearrangements, mostly [1,2], thoroughly investigated in particular by West[12] and Brook,[25,26] are considered to involve nucleophilic attack on silicon by the lone-pair electrons of a sterically accessible, adjacent atom, which frequently is electronegative. Hypothesized five-coordinate silicon species account for the very high migratory aptitude of a silyl group. The higher affinity of the silicon atom for oxygen and nitrogen than for carbon is presumably the reason why most of the shifts have been observed with these heteroatoms.[27] Nevertheless, in certain cases[12] the driving force seems to be also the formation of a more stable ion pair. Carbanions, isoelectronic with oxygen or nitrogen anions, are also candidates for these rearrangements even if the Si–C bond energy is not as strong as that of the Si–O or Si–N bonds.[1c,28]

Among others, one can find a [1,4] Me_3Si rearrangement in an ylide, where the presence of a positive nitrogen atom[29] drives the migration, which is accompanied by an elimination.

Indeed, a carbon to carbon R_3Si rearrangement in a genuine carbanion requires several structural, conformational, and electronic conditions that are not often encountered. An anionic carbon (generally organometallic) $R_3SiCXY(CH_2)_nCR_2^-M^+$ can abstract SiR_3 only if the activated complex is not too sterically hindered and the newly formed carbanion is stabilized by a group X (aryl, silyl, ...); but, if Y = H, there is a possibility of $[1,n]$ H shift competing with the SiR_3 shift. This may explain why the present report is only the second example of trimethylsilyl shifts found in carbanionic species.

Experimental Section

I. General Methods. 1. Physical Methods. Except where stated otherwise, ^1H NMR spectra were recorded on either a Perkin-Elmer R 24 A (60 MHz) or a Bruker WH 90 (90 MHz) spectrometer. Chemical shifts are given in δ (ppm) relative to tetramethylsilane (Me_4Si) as the internal reference. The solvents were carbon tetrachloride (Merck) and deuterated chloroform (Commissariat à l'Energie Atomique, Saclay).

Gas–liquid chromatography (GLC) was performed with an Intersmat IGC 15 chromatograph equipped with flame ionization detection; 3-m ($^1/_8$ in. diameter) columns were used, filled with silicon QFl on Varaport 100-120, temperature 180 °C. Authentic samples were used for calibration of the chromatograms and identification of the peaks. Quantitative analyses were performed by calculation of the area under the peaks.

2. Solvents and Starting Materials. a. Solvents. THF (Aldrich) was distilled from KOH and cuprous chloride after heating under reflux for half a day and then distilled again from benzophenone and sodium. It was kept in the presence of sodium under argon. Immediately before use THF was redistilled under argon from benzophenone and sodium.

HMPA (Prolabo) was dried and distilled under vacuum in the presence of calcium hydride directly before use.

Diethyl ether (Prolabo), kept dry and oxygen-free on sodium wires, cyclohexane (Prolabo), and tetramethylethylenediamine (TMEDA) (Merck) were distilled from $LiAlH_4$, under argon, just before use. Chlorotrimethylsilane (Rhône-Poulenc) was employed freshly distilled.

b. Starting Materials. The *n*-BuLi concentration in hexane (Merck) was determined by the classical double-titration method of Gilman,[30] or, more recently, by using the handy method based on the reaction of organolithium compounds with 1-(hydroxymethyl)-2,5-dimethoxybenzene.[31]

9,9-Bis(trimethylsilyl)-9,10-dihydroanthracene (I) and the 9-(trimethylsilyl)-9-alkyl-9,10-dihydroanthracenes (II–IV) were prepared from 9-(trimethylsilyl)-9,10-dihydroanthracene (V). These preparations were described in an earlier paper.[8]

Preparation of 9,10-Bis(trimethylsilyl)-9,10-dihydroanthracenes (*cis*-VI and *trans*-VI). Small pieces of lithium (4 g, 0.57 mol), beaten flat under liquid paraffin and rinsed with benzene, were added to a solution of anthracene (20 g, 0.112 mol) in Et_2O (80 mL) and benzene (80 mL). The dark purple mixture was stirred under nitrogen for 90 h at room temperature, and then freshly distilled Me_3SiCl (34 g, 0.296 mol) was added dropwise. Stirring was maintained for an hour after the end of the addition; this was followed by filtration of the contents of the flask. The yellow filtrate was hydrolyzed by an acidic (HCl) aqueous solution, extracted with ether, neutralized, washed, and dried over anhydrous Na_2SO_4. Removal of the solvent left a yellow oil (30.5 g) containing fine particles in suspension. NMR analysis allowed an estimation of *cis*-VI (58%), *trans*-VI (17%), 9-(trimethylsilyl)-9,10-dihydroanthracene (V, 10%), and 9,10-dihydroanthracene (15%). The yellow oil was rapidly filtered under vacuum, which allowed the separation of white crystals (mp 168 °C, essentially *trans*-VI) and an oily filtrate, which crystallized on cooling.

The white crystals were recrystallized from cyclohexane to yield *trans*-VI (3.2g): mp 172 °C; NMR (CCl_4) δ −0.15 (s, 18 H, CH_3), 3.62 (s, 2 H, H benzyl), 6.87 (s, 8 H, H Ar).[16] Chromatography of the yellow filtrate (alumina activity of II–III, eluent petroleum ether) gave *trans*-VI (0.8 g, yield 11%) and *cis*-VI (7.1 g, yield 20%): mp 72 °C; NMR (CCl_4) δ 0 (s, 18 H, CH_3), 3.76 (s, 2 H, H benzyl), 6.90 (appt s, 8 H, H Ar).[16] This last product must be handled with care due to its relative instability toward oxygen.

II. Transposition of the $SiMe_3$ Group under Different Conditions. 1. In THF at Room Temperature. a. 9,9-Bis(trimethylsilyl)-9,10-dihydroanthracene (I). To a solution of I (0.20 g, 0.62 mmol) in THF (10 mL) was added *n*-butyllithium in hexane (0.35 mL, 0.66 mmol) dropwise. The solution turned orange and then red. After 30 min of stirring, excess H_2O (2 mL) was added dropwise until the red solution was decolorized. Acidified (HCl) ice water was then added, and the reaction mixture was worked up by a conventional extraction procedure with ether.

Analysis of the crude product by NMR and GLC showed that *cis*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene (yield 95%) had been formed. It was identified by comparison of its chromatographic and spectroscopic properties with those of a previously obtained authentic sample.[16]

b. 9-Alkyl-9-(trimethylsilyl)-9,10-dihydroanthracenes (II–IV). The same experimental method was employed for the three compounds (R = Me, Et, *i*-Pr), the only difference being the length of stirring of the anionic solution before deuteration (see Table I).

i. General Procedure. 9-Alkyl-9-(trimethylsilyl)-9,10-dihydroanthracene (recrystallized) in THF (5×10^{-2} M) was added to a round-bottomed flask equipped with a magnetic stirrer. An equimolar quantity of *n*-butyllithium dissolved in hexane was added dropwise. The course of the reaction was followed by GLC; aliquots of the anionic solution were taken at regular intervals and hydrolyzed. When the reaction was finished, D_2O was added dropwise until the dark red solution was decolorized. The solution was then hydrolyzed with acidified (HCl) ice water, and the

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products were extracted with ether and worked up by a conventional procedure.

The *cis*- and *trans*-9-alkyl-10-(trimethylsilyl)-9,10-dihydroanthracenes formed here were identified by comparison of their spectroscopic and chromatographic properties with those of previously prepared authentic samples.[16] The relative percentages of the products were evaluated by NMR and GLC. Determination of the amount of deuterium in some of these compounds was carried out on the pure products, which were obtained after separation of the isomers from the crude products by chromatography through a silica column containing 10% (w/w) picric acid, eluting with petroleum ether.

ii. Estimation of the Amount of Deuterium. 9-Ethyl-9-(trimethylsilyl)-9,10-dihydroanthracene (III). A colorless oil was obtained, which was found to be a mixture of III (22%), *cis*-VIII (66%), and *trans*-VIII (12%). *cis*-VIII was obtained pure after chromatography. NMR (270 MHz) revealed a very small percentage (less than 3%) of the triplet characteristic of H_9, δ 3.65, which showed that the product was deuterated at the 9 position. The *trans*-VIII isomer isolated by chromatography was lightly contaminated with III; this prevented determination of the precise amount of deuterium present.

9-Isopropyl-9-(trimethylsilyl)-9,10-dihydroanthracene (IV). The crude product analyzed by GLC and NMR contained IV (4%), *cis*-IX (91%), and *trans*-IX (5%). The *cis*-IX isomer was obtained pure after chromatography. *cis*-IX incorporated 71% D exclusively at the 9 position.

2. In Cyclohexane–TMEDA at Room Temperature. a. 9,9-Bis(trimethylsilyl)-9,10-dihydroanthracene (I). *n*-Butyllithium (1 mL, 1.5 equiv) in hexane was added to a solution of I (0.326 g, 1 mmol) in cyclohexane (40 mL) and TMEDA (0.23 mL); after 2 h of stirring, H_2O was added and the products were extracted following the normal procedure. Analysis of the crude product by GLC revealed that it was a mixture of I (6%) and *cis*-VI (94%).

b. 9-Ethyl-9-(trimethylsilyl)-9,10-dihydroanthracene (III). The experimental method is identical with that followed in THF. *n*-Butyllithium in hexane (2.35 mL, 3.3 mmol) was added dropwise to a solution of III (0.840 g, 3 mmol) in cyclohexane (120 mL) and TMEDA (0.69 mL, 1.5 equiv) at room temperature. The dark red solution was stirred for 2 h, followed by addition of excess D_2O (2 mL) dropwise. The reaction medium slowly went colorless and was then hydrolyzed by acidified (HCl) ice water and extracted with ether. The crude product was found to be a mixture of *cis*-VIII (98%), *trans*-VIII (1%), and III (1%). Product *cis*-VIII was isolated pure by column chromatography using silica doped with picric acid and eluting with petroleum ether. The amount of deuterium incorporation, evaluated by NMR, was 100%.

The NMR spectrum (270 MHz) of *cis*-VIII revealed the quasi-absence of the triplet due to H_9 (the integration corresponds to less than 3% H_9).

III. Attempts To Obtain Intermolecular Transposition of $SiMe_3$ in a Dihydroanthracene Carbanion. 1. With 9-Lithio-9,10-dihydroanthracene and IV. In a flask kept rigorously dry, under an atmosphere of argon, at room temperature, a solution of *n*-butyllithium in hexane (0.14 mmol) was added dropwise to a solution of dihydroanthracene (0.025 g, 0.14 mmol) in THF (10 mL). The dark red solution was then stirred for 30 min, and a solution of IV (0.042 g, 0.14 mmol) in THF (10 mL) was added. Analysis by GLC of an aliquot taken after 60 min and then hydrolyzed revealed that no trace of either V or 9-isopropyldihydroanthracene was present. Only 9,10-dihydroanthracene and IV were observed. An excess of *n*-butyllithium (0.14 mmol) in hexane was then added; another aliquot taken and hydrolyzed after 90 min showed, on GLC analysis, the presence of *cis*-IX and IV but not V or 9-isopropyldihydroanthracene.

2. With 0.1 Equiv of *n*-Butyllithium. In a flask kept rigorously dry and under an atmosphere of argon, at room temperature, *n*-butyllithium (0.02 mL, 0.025 mmol) in hexane was added to a solution of I (0.080 g, 0.25 mmol) in THF (10 mL). The orange-red solution was stirred for $3^{1}/_{2}$ h; then D_2O was added and the solution was extracted in the normal way. Analysis of the crude product by GLC and NMR revealed the presence of VI (5%) and I (95%).

In parallel to the above experiment, a solution of I (0.080 g, 0.25mmol) in THF (10 mL) was added to 1 molar equiv of *n*-butyllithium (0.2 mL, 0.25 mmol) in hexane at room temperature. After $3^{1}/_{2}$ h of agitation, the crude product, extracted in the usual procedure, was found by GLC and NMR to be a mixture of VI (83%) and I (17%).

IV. Attempts To Obtain Transposition of Alkyl Groups in Dihydroanthracene Anions. 1. Preparation of Compounds XIa,b from the Corresponding Anthrones. a. 9,9-Dimethylanthrone was prepared following the procedure of Curtin and Coll:[32] mp 103 °C (lit.[33] mp 102–103 °C); NMR ($CDCl_3$) δ 1,75 (6 H, s, CH_3), 7.1–7.7 (6 H, m, H Ar), 8.1–8.4 (2 H, m, H Ar).

b. The above technique was modified in order to obtain **9,9-diethylanthrone**. The mixture of anthrone (4 g, 20 mmol), lithium (0.6 g, 0.085 mol), ethyl iodide (5 mL), ethanol (100 mL), and 2-methyl-2-propanol (10 mL) was heated for 14 h. After hydrolysis by acidified (HCl) ice water, the reaction mixture was extracted with ether. The mixture was fractionated by chromatography on a silica column (eluent petroleum ether, then petroleum ether/diethyl ether mixtures). The first fractions contained a mixture of products (2.2 g) including 9-ethoxyanthracene; from later fractions 9,9-diethylanthrone was isolated pure (white crystals): mp 140 °C (lit.[34] mp 136 °C) (2.1 g, yield 40%).

c. 9,9-Dimethyl-9,10-dihydroanthracene (XIa). A solution of 9,9-dimethylanthrone (1.1 g, 5 mmol) in diethylene glycol (50 mL) was heated under reflux for 60 min in the presence of potassium (6.75 g, 0.17 mol) and hydrazine (25 g, 5 mmol, 85% aqueous solution). The water was then removed by distillation and the solution was heated under reflux for three more hours. After cooling, the mixture was acidified by HCl and extracted with benzene. XIa (oil) was isolated pure following chromatography of the crude product on a silica column (eluent petroleum ether): (lit. mp 49.5–50.5 °C[33] 51–52 °C;[35] an oil[36]); NMR (CCl_4) δ 1.6 (6 H, s, CH_3), 4.01 (2 H, s, H benzyl), 6.9–7.6 (8 H, m, H Ar).

d. 9,9-Diethyl-9,10-dihydroanthracene (XIb). A mixture of 9,9-diethylanthrone (1.9 g, 7.6 mmol), zinc (10 g, 0.15 mol), mercuric chloride (1 g, 4 mmol), concentrated hydrochloric acid (17.5 mL), water (7.5 mL), and toluene (15 mL) was heated under reflux for 48 h. After the usual extraction procedure and chromatography of the crude product on a silica column (eluent petroleum ether), XIb was isolated pure (colorless oil, 0.802g, yield 44%): (lit.[37] mp 48–50 °C); NMR (CCl_4) δ 0.43 (6 H, t, CH_3), 2 (4 H, q, CH_2), 3.96 (2 H, s, H_{10}), 6.9–7.5 (8 H, Ar).

2. Attempts at Transposition. a. 9,9-Dimethyl-9,10-dihydroanthracene (XIa). To a solution of XIa (0.146 g, 0.67 mmol) in THF (10 mL) and HMPT (1 mL) was added *n*-butyllithium (1 mL, 0.8 mmol) in hexane dropwise at room temperature. The red solution was stirred for 3 h; then, after hydrolysis with acidified (HCl) ice water, the products were extracted following the usual procedure. Analysis of the crude product by GLC and NMR revealed that it consisted exclusively of XIa.

b. 9,9-Diethyl-9,10-dihydroanthracene (XIb). *n*-Butyllithium in hexane (1.4 mL, 2.2 mmol) was added over a period of 15 min to a solution of XIb (0.472 g, 2 mmol) in THF at room temperature. After the dark red solution was stirred for 3 h, D_2O was added; the reaction mixture was immediately decolorized. After the usual workup procedure, deuterated 9,9-diethyl-9,10-dihydroanthracene (XIb) was obtained as the only product. The amount of deuterium incorporation, evaluated by NMR, was 85% (monodeuterated XIb).

V. Evidence of the Irreversibility of the Transposition of $SiMe_3$. 1. In Et_2O + HMPT at -40 °C. A solution of *n*-butyllithium in hexane (0.65 mL, 0.91 mmol) was added to a solution of *trans*-VI (0.272 g, 0.83 mmol) in diethyl ether (30 mL) and HMPT (0.62 mL, 4.15 mmol). The orange solution was stirred for 2 h at constant temperature. After decolorization of the

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solution by addition of H_2O, the products were extracted following the usual procedure. Analysis of the crude product (mp 72 °C) by GLC and NMR showed that only *cis*-VI was present. No trace of I was detected.

2. In THF at 20 °C. *n*-Butyllithium in hexane (1 mL, 1.2 mmol) was added dropwise to a solution of *trans*-VIII (0.171 g, 0.6 mmol) in THF (10 mL). The dark red solution was stirred for 1 h and then D_2O was added. After extraction with ether following the usual procedure, an oily product was obtained. Analysis by GLC and NMR showed that the crude product consisted of *trans*-VIII (7%) and *cis*-VIII (93%). *cis*-VIII was isolated pure following chromatography on a silica column doped with picric acid (eluent petroleum ether). The amount of deuterium incorporation, determined by NMR, was 100% (8% on the 9 and 92% on the 10 positions).

Another experiment was carried out under the same conditions except that 1.1 equiv of n-butyllithium was used. In this run analysis of the crude reaction mixture by GLC and NMR showed that it was composed of *cis*-VIII and *trans*-VIII in a ratio of 65:35.

VI. Isopropylation of 9-(Trimethylsilyl)-9-deuterio-9,10-dihydroanthracene (V_D). To a stirred solution of V_D (0.806 g, 3.2 mmol, 80% deuterated) in THF (80 mL), under argon, at room temperature, was added a solution of *n*-butyllithium in hexane (2.62 mL, 3.2 mmol). Stirring was maintained for 1 h. Upon addition of isopropyl iodide (2 mL, excess) the solution turn pale yellow. Addition of acidified (HCl) ice water and ether, followed by conventional workup, afforded a pale yellow oil (0.846 g). GLC and NMR analysis showed IV, *trans*-IX, and V in a molar ratio of 33:16:51. Chromatography of the product mixture through a column of silica doped with picric acid (10% w/w), eluted with petroleum ether, gave successively IV (0.116 g), a mixture of IV and *trans*-IX (0.312 g), and V_D (0.350 g). Recristallization of the mixture from ethanol gave pure *trans*-IX (0.102 g). Mass spectrometry (MICROMASS VG 70-70) indicates that the compound is 97% monodeuterated. NMR analysis points to 42% D on the 9-position and 55% on the 10-position.

From NMR and mass spectrometry it is possible to evaluate the deuterium content for IV (25%) and recovered V_D (79%).

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Registry No. I, 68573-98-8; II, 68573-95-5; III, 68573-96-6; IV, 68573-97-7; V, 18002-83-0; V_D, 68574-01-6; *cis*-VI, 56272-38-9; *trans*-VI, 56272-37-8; *cis*-VII, 62257-79-8; *trans*-VII, 62257-80-1; *cis*-VIII, 62257-81-2; *trans*-VIII, 62257-82-3; *cis*-IX, 62257-83-4; *trans*-IX, 62257-84-5; XIa, 42332-94-5; XIb, 22702-34-7; Me_3SiCl, 75-77-4; anthracene, 120-12-7; 9,10-dihydroanthracene, 613-31-0; 9-lithio-9,10-dihydroanthracene, 17228-13-6; 9,9-dimethylanthrone, 5447-86-9; 9,9-diethylanthrone, 32363-34-1; isopropyl iodide, 75-30-9.

Stereochemistry of Intramolecular Amidoalkylation Reactions in the Synthesis of Polycyclic Isoquinoline Derivatives[1]

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N-Acyliminium cyclizations onto benzenoid rings to give tetrahydroisoquinoline ring systems were studied. Particular attention was paid to the stereochemical effect of substituents present on the isoquinoline ring. High stereoselectivity (≥90%) was observed with aryl substituents at (local) 4 and 3 positions of the isoquinoline ring (e.g., **2** → **3** and **30** → **31**). In addition to cyclizations onto benzenoid rings, some cyclizations onto heterocycles (pyrrole, thiophene, indole) were examined. Base-induced equilibration of isomer pairs was performed to obtain relative stabilities. The cyclizations were determined to be kinetic in nature. A discussion of our iminium cyclizations and relevant examples from the literature is presented.

Cationic π cyclization reactions have been used to fashion rings of complex multicyclic compounds with excellent stereochemical control.[3-6] A classical example is that of biomimetic polyene cyclizations, which have produced steroid-like polycycles with impressive stereoselectivity at ring junctions and substituent stereocenters on the carbocyclic framework.[4] For successful polyene cyclizations, a suitable cationic initiator functionality, such as an epoxide, acetal, or allyl alcohol, is important. Recent attention has been directed to *N*-acyliminium ions, which

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