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REACTIVITY OF BENZYLIC CARBANIONS IX.
[1,4] REARRANGEMENT OF THE Me_3Si GROUP IN 9,9-bis(TRIMETHYLSILYL) 10-LITHIO 9,10-DIHYDROANTHRACENE

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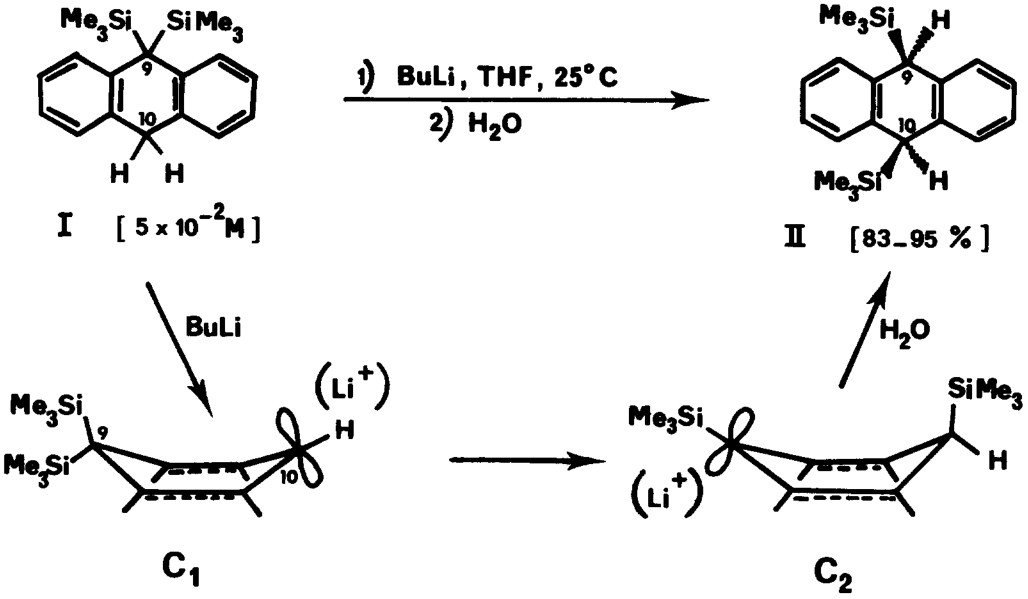
Summary : 9,9-bis (trimethylsilyl) 10-lithio 9,10-dihydroanthracene undergoes an intramolecular [1,4] rearrangement to lead, after protonation, to cis 9,10-bis (trimethylsilyl) 9,10-dihydroanthracene (II) with a high yield. This shift, rarely encountered in anionic carbon skeletons, is believed to be favoured by structural factors and stabilisation of a carbanion α to silicon.

Compared with other short-lived intermediates, rearrangements in carbanions not including heteroatoms are rather scarce[1-3]. Although rearrangements of silylated groups in compounds containing one or several heteroatoms are well documented[4], we are aware of only one report of a Me_3Si group migration in an anionic carbon skeleton[5]. We report a second example of such a migration in a monocarbanion and show that it is a [1,4] rearrangement.

In the presence of BuLi in THF, 9,9-bis (trimethylsilyl)-9,10-dihydroanthracene[6] (I) is smoothly converted to cis 9,10-bis (trimethylsilyl) 9,10 dihydroanthracene[7] (9,10-bis(Me_3Si) DHA) (II) after hydrolysis (scheme). The reaction is achieved in less than a few minutes. Probably owing to difficulties to scavenge all traces of humidity in the absence of an excess of base, the yield was not quantitative but high enough to exclude the intermediacy of a dianion, because only one equivalent of BuLi was added to (I). An intermolecular mechanism would imply a chain reaction and a catalytic amount of base would be sufficient to induce the rearrangement. An experiment run with 0.1 equivalent of BuLi gave (II) with 5% yield, the rest of (I) being recovered. We thus believe the transfer is intramolecular. The boat shape geometry of the central ring of DHA[8] and the ability of the silicon atom to pentacoordination[9] strongly favour a concerted reaction; it may be viewed as a 6 electron-supra-supra thermally allowed process[10]. The driving force is likely to be due to the relief of the steric strain in 9 position and the formation of the more stable α silylated carbanion[11] (C_2) from (C_1). Of note is the exclusive formation of a product of cis configuration (II) : probably the bulky Me_3Si group would undergo steric hindrance in quasi equatorial position in the hydrolysis transition state; a catalysis by the lithium cation should also be considered[12,13]. Let us recall that HARVEY could completely isomerize trans 9,10-bis(Me_3Si)DHA to (II) in presence of n-BuLi-TMEDA-cyclohexane[14]. EISCH[5] observed a consecutive [1,2] and [1,4] Me_3Si shifts in the anionic rearrangement of 1,1-bis (Me_3Si) 1,2-diphenylethane; the author used an excess of BuLi in TMEDA-hexane; the [1,2] rearrangement occurs presumably in a monocarbanion whereas the [1,4] shift seems to take place in a dianion.

Thinking that 9,10-DHA anions are well fitted to study carbanion reactivity, we are currently investigating the scope and mechanism of this rearrangement.



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