Tetrahedron Letters,Vol.24,No.6,pp 623-626,1983 0040-4039/83/060623-04$03.00/0
Printed in Great Britain

THE DIMESITYLBORON GROUP IN ORGANIC SYNTHESIS 1. INTRODUCTION.

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The bulky dimesitylboron group encourages the formation of an α-carbanion from dimesitylalkylboranes by proton abstraction by a relatively hindered base, as compared with ate complex formation. It also stabilises the carbanion so formed. However the dimesitylboron group allows ate complex formation with unhindered bases, so allowing oxidative release of organic moieties from alkyldimesitylboranes. This desirable combination of properties has great potential for organic synthetic methodology.

Organic chemists have long felt that the diorganylboron group of a triorganylborane should behave in a fashion similar to that of organic electron deficient groups. Thus, very recently, it has been suggested that the dimesitylboron group could replace nitro groups in various dyestuffs.[1] In addition it would be expected that an electron deficient, trivalent boron atom should stabilise an adjacent carbanion. Calculations have recently been carried out[2] on a series of anions XCH_2^- for X = Li, BeH, BH_2, CH_3, NH_2, OH, F, CN, NO_2, CHO and other organic functional groups. Not surprisingly a strong stabilising effect is calculated for Π-accepting systems, which, for the inorganic groups, reaches a peak of 61.4 to 71.8 kcal. mol^{-1} for planar $H_2B.CH_2^-$. This is of exactly the same order (60.5 to 71.5 kcal.mol^{-1}) as the stabilisation calculated for the CHO group.

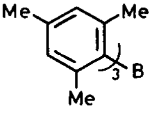
This raises an important question. Why is it that carbanions α to a carbonyl group are of paramount importance in synthetic organic chemistry whereas carbanions α to a boron atom have been made only recently and have found little application as yet? The answer lies in the problem of the formation of carbanions adjacent to boron rather than their stabilisation or reactivity. The usual method for the production of carbanions α to carbonyl groups is proton abstraction by a suitable base. With organoboranes however this process must compete with essentially irreversible attack by the base on the boron atom itself to form a coordinatively saturated ate complex, and this is generally the preferred pathway. Indeed a large number of important reactions of organoboranes rely on initial ate complex formation.[3] Thus the problem of producing carbanions α- to boron by abstraction reduces to the problem of preferential discouraging ate complex formation.[+]

[+] A separate and general method for the production of carbanions α to boron consists of the cleavage of geminal dibora-compounds.[4] However this wastes one of the two boron groupings, requires two mol. equivalents of base and the preparation of costly and not readily accessible starting materials.

The first method tried was to use a highly hindered base (lithium 2,2,6,6-tetramethylpiperidide) at low temperatures with a moderately hindered organoborane.[5] This produced *ca* 75% of the anion which was quenched with cyclohexanone, in the boron analogue of the Wittig reaction.[5] This approach was not pursued to any great extent and has not been reported in full. It suffers from the disadvantages of requiring an expensive base, and low temperatures and proceeding in moderate yields.

A very different method[6] is the attachment to boron of heteroatoms capable of Π-back donation, which discourage ate complex formation. However stabilisation of an adjacent carbanion is also decreased and there is little discrimination between the two effects. In practise stabilisation can be achieved by the use of two dialkyoxyborane units per methylene unit. Once more the process requires low temperatures, hindered non-nucleophilic bases and additionally one of the boron atoms is not utilised. Moreover much of the wealth of reactions developed in organoborane chemistry cannot be applied. Despite this, useful and unusual reactions have resulted from this approach which has been the first to indicate the potential inherent in carbanions stabilised by boron.

Our own approach has been to use triorganylboranes, thus leaving open the utilisation of standard organoborane chemistry, but to sterically modify the environment around the boron. It was early shown[7a] that whilst triphenylborane is readily oxidised and hydrolysed and forms complexes with most bases, trimesitylborane **1** undergoes *none* of these reactions. This result was ascribed to steric shielding of the boron by a cage of six *ortho*-methyl groups.[7] Very recently studies on the reaction of aryldimesitylboranes with methoxide indicate that with four *ortho*-methyl groups, ate complex proceeds but not when five or six are present.[8] *Thus steric shielding can inhibit ate complex formation*, a point also made by the stability of aminodimesitylboranes[9] and alkoxydiarylboranes **2**[10]. The latter resist attack by NaH, $LiAlH_4$, Bu^nLi and $NaOH/H_2O_2$ as well as tertiary amines. They have a $\Delta G^{\#}$ rotation of 11.5 to 12.5 kcal. mol^{-1} uninfluenced by the nature of Y, and therefore the lack of reactivity is steric in origin.



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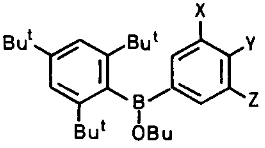

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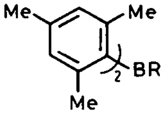
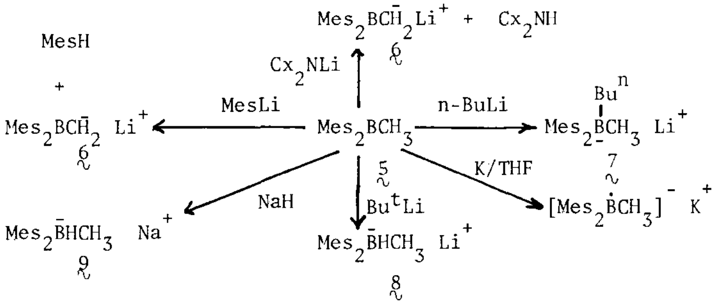


3

We did not require such efficient shielding of boron as is evidenced by **1** and **2**. For synthetic purposes it is not enough to produce and manipulate a carbanion. At some stage the boron must be removed to leave a modified organic moiety and this frequently involves prior ate complex formation.[3] Hence we needed compounds in which the boron was sufficiently shielded to inhibit complex formation with moderately hindered bases but would form complexes with bases of small steric requirements. For this purpose we settled on alkyldimesitylboranes, **3**, readily produced by the interaction of fluorodimesitylborane **4** with Grignard reagents.[11] Fluorodimesitylborane itself could not be prepared on any scale by the original method[7] but after extensive experimentation and modification of the preparation and use of mesitylmagnesium bromide[12] the material can be reproducibly made in ca 75% isolated yield from bromomesitylene.[+]

Compounds 3 were generally solids, crystallisable from methanol but decomposing on long exposure to air. We were gratified to find that, despite their stability they are readily oxidised by alkaline hydrogen peroxide and undergo the cyanoborate process.[3] Thus small anions form ate complexes with Mes_2BR and the organic moieties can be released or used to form carbon-carbon bonds.

We therefore undertook a study of the reactions of bases with 5, the simplest example of 3. (Scheme), in order to establish in detail the synthetic potential of these systems. It had already been shown[13] that lithium dicyclohexylamide, a cheap moderately hindered base reacts with 5 to give the anion and the present study confirms this. In addition we found that mesityl lithium, (readily prepared from bromomesitylene and tert-butyl lithium or more cheaply, lithium dispersion),acts as an excellent carbon base with no β-hydrogen atoms and quantitatively yields the desired carbanion 6. The reactions can be carried out at room temperature in THF, in which conditions 6 appears to be completely stable. These results are a great contrast to the inability of $CH_3B(OR)_2$ to form an anion[14] and illustrates the power of the steric shielding approach. Reaction of 5 with n-butyl lithium gives only the ate complete 7 with no trace of anion 6, a nice example of steric potentiation between carbanion and ate complex formation. The bulky base, tert-butyl lithium behaves in yet another fashion and transfers a β-hydrogen atom by a known process[15] to give lithium dimesitylmethylhydroborate 8 , the first of a new series of hindered organylhydroborates, whose chemistry is under active investigation. The same class of compounds can be made from 5 with sodium hydride and we have shown that the sodium salts 9 so produced reduce alkyl iodides to the corresponding alkanes, with regeneration of 5 which should therefore be catalytic for the process. The reaction of potassium in THF with 5 gives the corresponding radical anion. The reactions with bases so outlined are not confined to compound 5, but proceed generically with all compounds 3 when R = primary alkyl. Dynamic n.m.r. studies on the anion $Mes_2B\bar{C}HPh$ show that it thermally decomposes in diglyme at 140°C before rotation effects about the B-$\bar{C}$HPh bond are observed. This gives a $\Delta G^{\#}$ rot. >22 kcal.mol^{-1} very similar to the isoelectronic Mes_2BNHR,[16] and confirms that there



Cx = cyclohexyl; Mes = 2,4,6-trimethylphenyl

Scheme

[+] Prior to the publication of full papers, details of this preparation are available on request.

is appreciable overlap, as predicted, between the carbanionic centre and the neighbouring boron atom.

Thus it is proven that the dimesitylboron group can stabilise and promote the formation of α-carbanions using cheap, moderately hindered bases. However the use of less hindered bases gives ate complex formation which allows the release and utilisation of any products formed from the anions. Some of the results beginning to flow from these observations are given in the following papers.

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(Received in UK 29 November 1982)