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THE DIMESITYLBORON GROUP IN ORGANIC SYNTHESIS. 3. REACTIONS OF ALLYLDIMESITYLBORANE

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Allyldimesitylborane readily yields an anion that is attacked by electrophiles in a regio- and stereospecific fashion. Alkylation is at the γ-position to give trans-vinylboranes that can be oxidised to aldehydes. Reaction with trimethylsilyl chloride gives the new, highly differentiated three carbon synthon, $\mathrm{Mes_2BCH\overset{t}{:}CHCH_2SiMe_3}$ also by γ-attack and reaction with benzaldehyde proceeds similarly to give rise to a novel γ-lactol synthesis.

Allylic moieties play an important role in the construction of complex organic molecules in both a chemical and biochemical context.[1,2,3] For this reason there has been a sustained effort to control the regio- and stereochemistry of substitution both of neutral allylic compounds[2,4,5] and of unsymmetrical charged species.[1,6]

We have previously shown[7] that suitable bases can abstract a proton from a methylene group adjacent to a dimesitylboron group and that the resultant stabilised carbanions can be alkylated. We therefore decided to examine the anion **1** derived from allyldimesitylborane **2** to see whether or not the large substituent group would sterically favour γ-attack by electrophiles. In the only other reported reaction of a boron stabilised allylic anion (derived from disiamyloct-1-enylborane) the position of attack was electrophile dependent and not always regiospecific.[8]

Unlike 9-allyl-9-BBN,[9] **2** is readily made in excellent yields with no complications, simply by the interaction of allylmagnesium bromide and fluorodimesitylborane in ether.[10] It is a crystalline compound, m.p. 68°C, stable enough to be recrystallised from ethanol and is an excellent source of a functionalised allyl group.

We are pleased to report that **2** readily yields **1** with either mesityl lithium or lithium dicyclohexamide, but for ease of work up we use the former base with which all the following experiments were carried out.

Quenching **1** with water gave a quantitative yield of trans-propenyldimesitylborane (**3**, R = H) demonstrating that reaction proceeds at the γ-position of **1** in a stereospecific fashion (eq. 1). Quenching with alkylating agents went in an exactly similar fashion as shown in Table 1.

$$\underset{\mathbf{2}}{\mathrm{Mes_2BCH_2CH{:}CH_2}} \longrightarrow \underset{\mathbf{1}}{\mathrm{Mes_2B\overset{-}{\dot{C}}H\dot{:}\dot{C}H\dot{:}CH_2\ \ Li^+}} \xrightarrow{\mathrm{RX}} \underset{\mathbf{3}}{\mathrm{Mes_2BCH\overset{t}{:}CHCH_2R}} \qquad (1)$$

Table 1

Reactions of Anion 1 with Electrophiles

Experiment	Electrophile	R of product 3	Yield %[a]
1	H_2O	H	95
2	Me_2SO_4	Me	96
3	EtI	Et	95
4	PrI	Pr	90

a) All yields are of isolated, characterised alkenylboranes 3.

In the first instance we isolated the alkenylboranes 3 so that we could check the stereochemistry of the reaction, and also because vinylboranes are themselves compounds of great interest as synthetic intermediates.[11] However in order to check that the vinylboranes 3 can be converted to useful organic products and to further generalise the reactions we carried out a different set of alkylations which were followed by oxidation to the corresponding aldehyde (Table 2).

Table 2

Alkylation/oxidation of 1

Experiment	Electrophile	Aldehyde	Yield %[a]
5	$C_6H_{13}I$	$C_8H_{17}CHO$	95
6	$C_7H_{15}I$	$C_9H_{19}CHO$	90
7	$C_8H_{17}I$	$C_{10}H_{21}CHO$	90
8	$PhCH_2I$	$PhCH_2CH_2CHO$	95

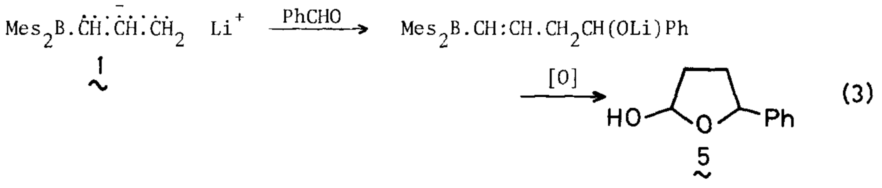
a) Yields are g.c. estimated on isolated crude product.

Clearly allyldimesitylborane is an excellent reagent for three carbon homologation of primary halides (iodides, bromides)[7] to the corresponding aldehydes, by γ-attack on anion 1. In only one case, that of methyl iodide, was there any α-attack on 1. Synthetically this is of little significance as the required product (3, R = Me) is available in high yield simply by the use of dimethyl sulphate (Table 1, exp. 2).

To check whether other electrophiles behaved with 1 in the same way as water and alkylating agents, the anion was reacted with trimethylsilyl chloride (eq. 2). The reaction was sluggish at room temperature and an excess of the chloride was required. However, the new synthon 4 resulted in 90% isolated yield, (based on 2) showing that again reaction was stereospecific and directed to the γ-position. We are further investigating the reactions of the new synthon 4, which has something in common with $MeSi_3CH{:}CHCH_2SiMe_3$[12] but with the potential advantage that the two ends of the three carbon systems are well differentiated from each other.

$$\underset{\mathbf{1}}{\mathrm{Li^{+}\ Mes_2B\overset{-}{\dot{C}}H{:}\dot{C}H{:}\dot{C}H_2}} + \mathrm{Me_3SiCl} \longrightarrow \underset{\mathbf{4}}{\mathrm{Mes_2BCH\overset{t}{:}CH.CH_2SiMe_3}} \qquad (2)$$

As an example of reaction with yet another class of electrophile, anion 1 was condensed with benzaldehyde. Condensation at the α- position would give a 1-phenylbutadiene by a 'boron Wittig reaction'[13] but in fact this product was not seen. Instead γ-attack occurred as usual and oxidation gave the γ-lactol 5 in 70% yield after column chromatography (eq. 3). We are exploring the scope of this reaction.



Thus allyldimesitylborane is a stable heterosubstituted allyl compound which gives a stabilised anion that reacts with almost all electrophiles stereospecifically and exclusively at the γ-position. The trans-vinylboranes which result may be manipulated to yield useful organic products.

General procedure for the alkylation of allyldimesitylborane.

Mesityl lithium is prepared as before from mesityl bromide (9.6 mmole using 0.5M solution in THF) and tertiary butyl lithium (19.2 mmole, 12.4 ml. of 1.55M solution in hexane) and cooled to -78°C. Allyldimesitylborane (8.0 mmole 8 ml. of 1M solution in THF) is added to the base using a syrings, the reaction mixture allowed to warm to 25°C, and then stirred for 2h. at this temperature.

Aliquots (8.0ml. = 1.6 mmole) are withdrawn, equivalent amounts of the anhydrous alkylating agents at 20°C are added and the mixtures left for 2h. at this temperature. Ether (30ml.) is added and the mixture washed quickly with water (10 ml.) dried ($MgSO_4$) filtered and the solvent evaporated under reduced pressure to give the corresponding vinylboranes (see Table).

The vinylboranes (1.6 mmole) are oxidised to the corresponding aldehydes by dissolution in THF (0.5M solution) and addition to a cold solution of 6M NaOH (0.4 ml.), 5M NaH_2PO_4 (0.5 ml.) and 30% hydrogen peroxide (1 ml.) and stirred for 2h. at 0°C and 4h. at 20°C. Solid potassium carbonate is added to separate the organic layer and the aqueous layer washed with ether (10 ml.). The combined organic extracts are dried ($MgSO_4$) filtered and the solvent removed at ca 65°C. The residue is dissolved in 95% ethanol (5 ml.) and added slowly to a solution of 2,4-dinitrophenylhydrazine (0.347g ≡ 1.8 mmole) in 95% ethanol (7.5 ml.) and concentrated hydrochloric acid (2 ml.). The mixture is warmed on a water bath until a clear solution is obtained, then cooled to room temperature. The orange crystals are filtered, washed with 95% ethanol, and recrystallised from 95% ethanol. Yields of ca 75-82% of the pure hydrazone are thus obtained and compared with authentic samples.

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