

Synthesis and some properties of alkenyl carbanions stabilised by an α -boron atom

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Abstract. Methods for making boron-stabilised alkenyl carbanions and some of their reactions are presented. The calculated geometry and stabilisation energy of $H_2B\bar{C}=CH_2$ are given.

We have previously investigated the production and properties of carbanions, $R_2^1B\bar{C}HR^2$, derived from hindered organoboranes.¹ Such carbanions were predicted to have a considerable stabilisation energy,^{2,3} a prediction which has been verified.¹ We wondered whether carbanions, $R_2^1B\bar{C}=CHR^2$ would also be stabilised by an overlap that would lead to an allene like species (Fig. 1), in contrast with $R_2^1BCHR^2$ which has a planar alkene like structure.⁴

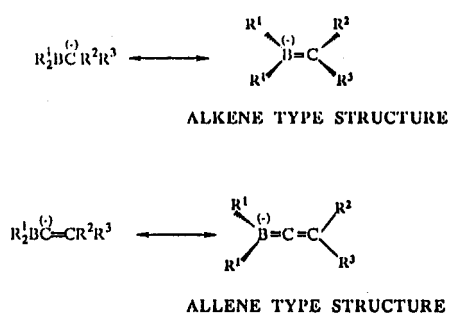
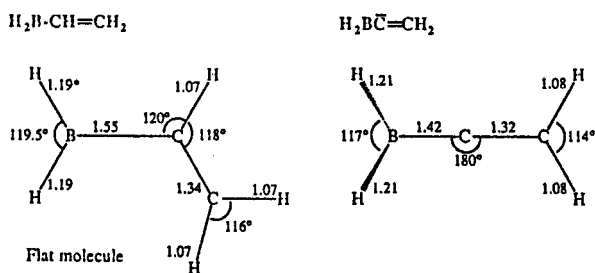


Figure 1.

Preliminary HF/4-31+G Calculations (Dr D. Parry)



Dihedral angle between terminal hydrogens on boron and carbon is almost exactly 90° .

*All bond lengths in Å Figure 2.

Figure 2 shows the most favoured conformations of $H_2B\bar{C}=CH_2$ and its parent compound $H_2B\bar{C}=CH_2$. The carbanion does indeed have an allene like structure, with a B-C bond length of 1.42\AA . This is in line with a C-B bond length of 1.44\AA for Mes_2B-CH_2 , said to show complete C=B character.⁴

Figure 3 presents the stabilisation energies of $X-\bar{C}=CH_2$ ($X=BH_2, CH_3$) relative to $H-\bar{C}=CH_2$. It can be seen that boron has a significant stabilising effect, whilst CH_3 is very slightly destabilising. These results are in line with those for $\bar{C}H_2-X$ ($X=BH_2, CH_3$)² as shown in Figure 3.

HF/4-31 + G CALCULATIONS ON ALKENYL ANIONS (D. Parry)

Anion	Proton Affinities		Stabilisation energies SE/Kcal mol ⁻¹
	PA/a.u.	PA/Kcal mol ⁻¹	
$CH_2=\bar{C}-H$	-0.6788	-427	0
$CH_2=\bar{C}-BH_2$	-0.6121	-385	-42
$CH_2=\bar{C}-CH_3$	-0.6808	-428	+1

Compare² with stabilisation energies for $\bar{C}H_2-BH_2$ and $\bar{C}H_2-CH_3$ of -54.7 and $+5.7$ Kcal mol⁻¹ respectively

Figure 3

We decided to see whether we could produce such anions and characterise them physically and chemically. For their generation we used a displacement approach, either of tin or of silicon. The first approach is illustrated in Figure 4 in which tin is displaced to give a lithio-species (the required "anion"), in which the lithium, if bonded, might retain some of the stereochemistry of the original geminal dimetallo-species. Attack by an electrophile followed by oxidation would yield a ketone, with no stereochemical ambiguities, and we decided to use this to monitor the sequence. At a later stage, hydrolysis of the trapped intermediate would give insight into its stereochemistry.

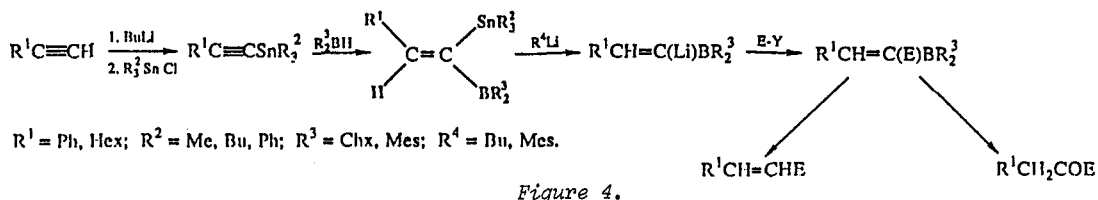


Figure 4.

A similar sequence involves the displacement of silicon, using F (Fig. 5). The difference lies in that in this case the anion is created as a 'free' anion, with a $\text{Bu}_4\text{N}^+\text{F}^-$ counter ion. We felt it worthwhile to examine both possibilities.

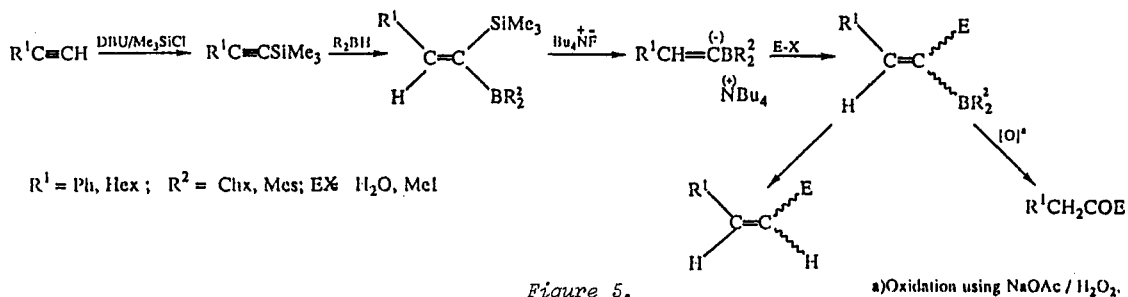
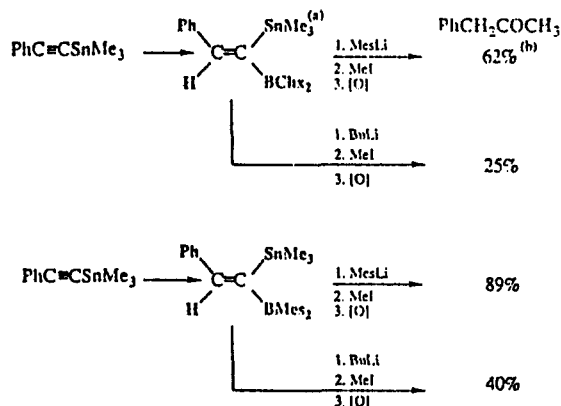


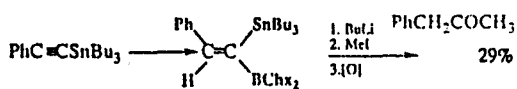
Figure 5.

We used phenylethyne and oct-1-yne as prototypes of aromatic and aliphatic substituted ethynes. Figure 6 illustrates some results starting with phenylethyne. Both dicyclohexylborane and dimesitylborane were used and the substituents on tin were varied from Me to Bu to Ph. With the trimethyltin substituent, the use of mesityllithium as hindered base was clearly superior to the use of butyllithium, presumably due to inhibition of ate complex formation on boron. This reached its climax when dimesitylborane was the hydroborating agent and mesityllithium was used as base. Excellent yields of ketone were produced on methylation and oxidation, this presumably paralleling the production of the desired carbanion. When triphenyltin derivatives were used, very little carbanion was produced (Fig. 7).

$\text{PhC}\equiv\text{CSnMe}_3$; MeI as trapping agent



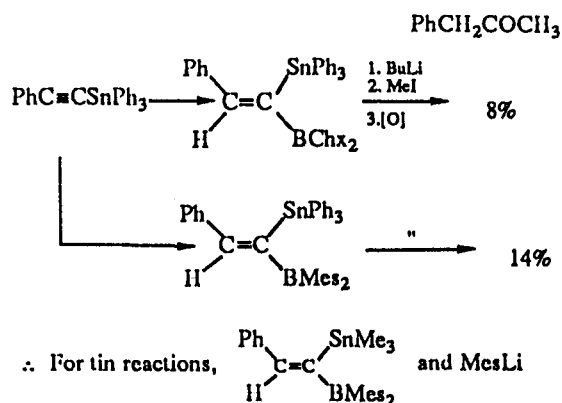
$\text{PhC}\equiv\text{CSnBu}_3$; MeI as trapping agent



a) All hydroborations checked by oxidation to acid
b) G.c. yields based on acetylene starting material.

Figure 6.

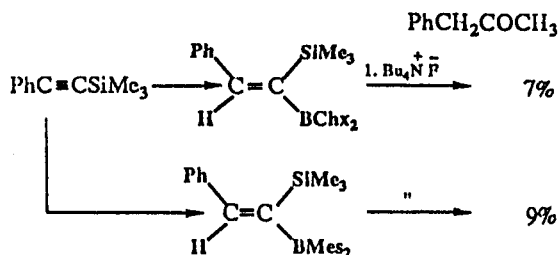
$\text{PhC}\equiv\text{CSnPh}_3$; MeI as trapping agent



best combination by far.

Figure 7.

$\text{PhC}\equiv\text{CSiMe}_3$; MeI as trapping agent



In this case attack on boron rather than silicon, to give *silicon* stabilised carbanion.

Figure 8.

The silicon species were of great interest as the fluoride efficiently attacked at *boron* rather than silicon (Fig. 8), to give an important route to *silicon-stabilised* carbanions! Thus for the aromatic species only one combination of organometallics and base efficiently yields the required carbanion. This involves hydroboration of the trimethyltin alkyne with Mes_2BH followed by reaction with MesLi .

Starting with oct-1-yne, either trimethyltin or trimethylsilicon were effective adjuncts, and either BuLi or Bu_4NF could be used to produce the carbanion (Fig. 9). The simple and readily available combination of trimethylsilicon and dicyclohexylboron is standardly used.

Other alkylating agents such as benzyl bromide, allyl bromide and even *n*-heptyl iodide (slow reaction) can be used to trap the carbanions, the overall synthetic process being an effective conversion of alkynes to a variety of ketones.

Protonation as a trap for the 'carbanions' produced from the tin reactions could be deceptive. Aldehydes were produced, presumably by hydrolysis (which might or might not involve a carbanion) followed by oxidation. The contrast with methylation is shown in Figure 10.

$\text{HexC}\equiv\text{CH}$; SnR_3 or SiMe_3 ; MeI as trapping agent

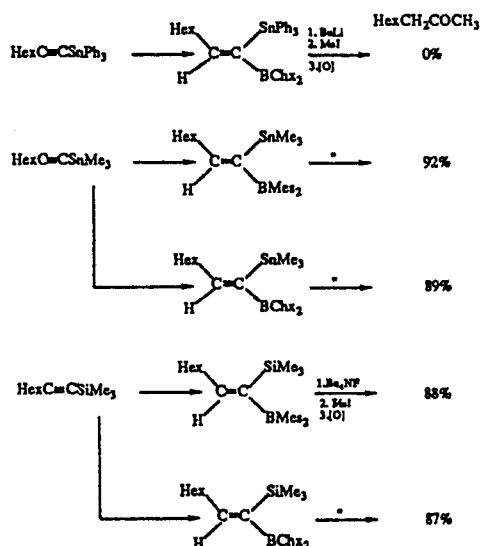
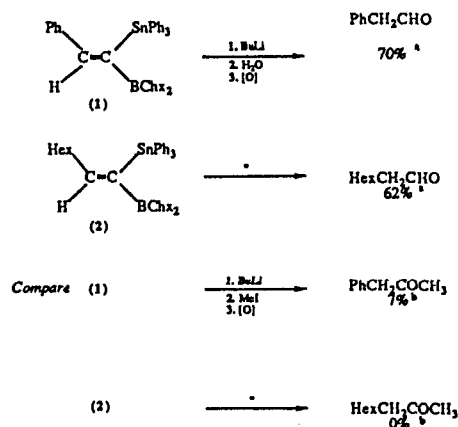


Figure 9.



These compounds do not form anions with BuLi , and therefore the aldehydes arise from hydrolysis / oxidation.

a) Isolated as DNP b) G.c. yield.

Figure 10.

The silicon species does not suffer from this defect (Fig. 11) but the nature of the displacing agent is important. In addition to Bu_4NF , we used a combination of $\text{BF}_3 \cdot \text{OEt}_2$ and water (1:1) to generate anhydrous HF and other uncharacterised species.

This reagent gives reasonable yields of aldehydes, probably not *via* the alkenyl anions.

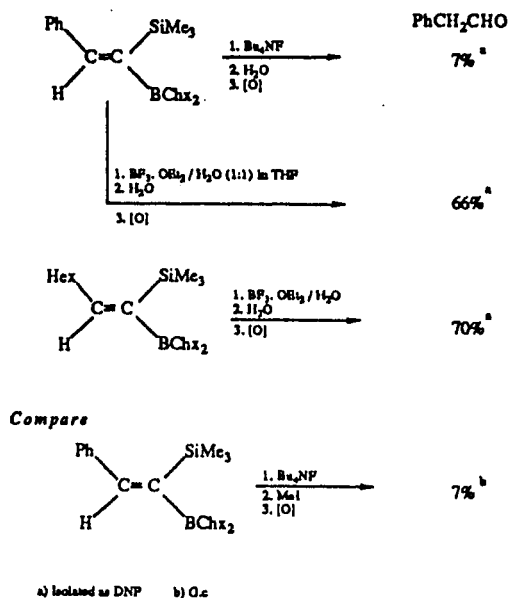


Figure 11.

We now have defined conditions for producing a variety of alkenyl anions stabilised by an α -boron atom. Their further characterisation and reactions with other electrophiles, particularly carbonyl compounds will be reported later. The stereochemistry of the carbanions is not known, but protonation of $\text{PhCH}=\text{CBMe}_2$, yields the *E*-alkene only.

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