

SYNTHESIS OF BORON STABILISED CARBANIONS

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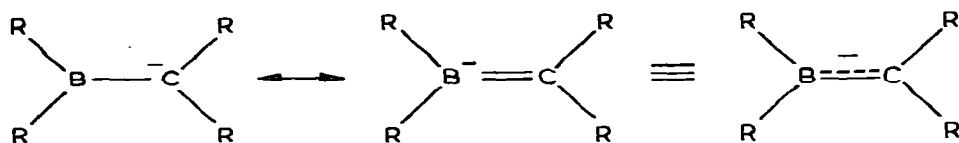
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Summary

Carbanions stabilised by an adjacent boron atom have been made in good yields by proton abstraction from the air stable boranes $R_2B-CHR'R''$ ($R = \text{mesityl}, R', R'' = \text{H, methyl or phenyl}$).

Introduction

Few boron stabilised carbanions of the type I have been reported. The problems associated with their production and characterisation have been described by Matteson and others [1].

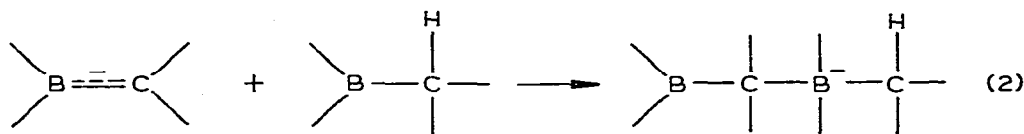
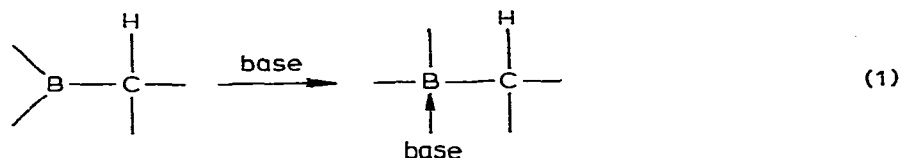


(I)

Species such as I are interesting for several reasons. They are isoelectronic with the corresponding olefins and hence their structural, physical and chemical properties are of fundamental importance. There is also interest in their use as ligands in main group and transition metal organometallic chemistry, arising from the fact that, whereas the chemistry of such ligands as borabenzenes [2], boron containing heterocycles [3] and carborane anions [4] has been investigated quite extensively [5] the chemistry of simple aliphatic ligands containing a boron Lewis acid site has not been explored to any great extent. Finally, the

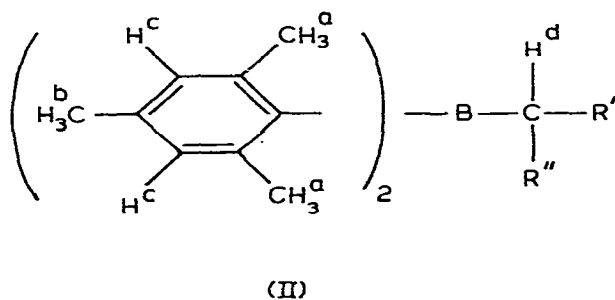
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potential use of such carbanions as synthetic reagents in organic chemistry has been demonstrated [1]. Rathke and Kow have shown that highly hindered bases such as lithio 2,2,6,6-tetramethylpiperidine are capable of abstracting α protons from certain boranes. Furthermore they have pointed out that either reaction 1 or 2 represents a major obstacle to the production of boron stabilised carbanions [1b].



Gridale et al. have shown that the presence of two mesityl groups in a series of dimesitylarylboranes renders the compounds kinetically stable to oxidation [6]. Mislow et al. have prepared dimesitylethylborane and dimesitylisopropylborane [7]. Although not specifically stated, it appears from the work-up procedure used that these compounds also had appreciable air stability. Undoubtedly the steric effects of the orthomethyl groups inhibit the oxidation reaction.

From these observations it seemed feasible that the orthomethyl groups might also block reactions (1) and (2), and hence make possible the synthesis of boron stabilised carbanions from simple, easily prepared dimesitylboranes (II).

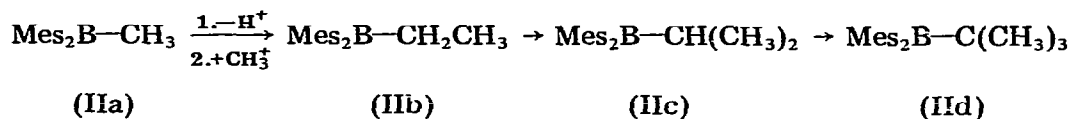


Results and discussion

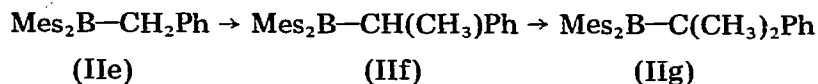
Dimesitylmethylborane (IIa) and dimesitylbenzylborane (IIe) were chosen as trial compounds since methylation of any derived carbanions was expected to give derivatives with relatively simple ^1H NMR spectra.

Using lithium dicyclohexylamide [8] as the abstracting base and dimethylsulphate as the methylating agent it proved possible to make each member of the following series, in good yields, by sequential replacement of all the α hydrogen atoms.

SERIES 1.



SERIES 2.



All were colourless crystalline compounds with the distinct advantage of being fairly stable to atmospheric conditions. Only IIa and IIb showed signs of deterioration when stored for one month in plastic capped containers in air. Their relevant properties are given in Table 1. Solutions of what must assumed to be the derived carbanions I in tetrahydrofuran (THF) were strongly coloured (see experimental section). The chemistry of such carbanions is under investigation and results will be reported subsequently.

Experimental

All reactions using Grignard reagents and alkyl lithium solutions were carried out under purified nitrogen using dry oxygen-free solvents. Dicyclohexylamine (Merck) was stored over calcium hydride. A freshly opened bottle of dimethylsulphate (Merck) was transferred to a flask and stored under dry nitrogen. Otherwise commercially available reagents and solvents were used as received. ¹H NMR spectra were recorded on a Bruker WP80CW instrument.

Compounds IIa and IIe were prepared in 90% and 70% yields, respectively, from dimesitylfluoroborane and the appropriate Grignard reagent, according to the general method of Mislow et al. [7].

The generation of the carbanions and their subsequent methylation was identical in each case and involved the following procedure. The solid borane (II) (2 mmol) was added to a stirred solution of the stoichiometric amount plus 10% of lithium dicyclohexylamide in THF (25 cm³) under nitrogen at room temperature. The times for complete reaction and the colours of the final solutions were as follows: IIa (3h, orange); IIb (3h, red); IIc (12h, brown); IIe (3h, gold); IIf (20h, crimson) *. On addition of the stoichiometric amount of dimethylsulphate the colours changed to pink (IIa, b) or yellow-orange (IIc, e, f). The nature of these species is as yet unknown. The THF was removed by vacuum distillation to give a viscous oil. Addition of wet ether gave a clear, colourless two phase system. The dicyclohexylamine by-product was removed by extraction with dilute citric acid solution. The ether layer was washed with distilled water (25 cm³) and dried over MgSO₄. Removal of the ether by vacuum distillation produced a solid or viscous oil whose ¹H NMR spectrum was that of the expected product with traces of impurities. Recrystallation

* These reaction times have not been optimised.

TABLE 1
ANALYTICAL AND ¹H NMR DATA FOR BORANES IIa-IIg

	m.p. ^a	Analysis		¹ H NMR ^b					
		Found (Calc.)(%)		a	b	c	d	CH ₃	Ph
		C	H						
IIa	78	86.20 (86.37)	9.77 (9.54)	2.21(s)	2.27(s)	6.80(s)	1.50(s)	—	—
IIb	77	86.19 (86.33)	9.90 (9.78)	2.20(s)	2.25(s)	6.78(s)	1.87(q)	1.03(t)	—
IIc	89	86.52 (86.30)	10.06 (10.00)	2.20(s)	2.24(s)	6.75(s)	^c	1.08(d)	—
IId	106	86.46 (86.27)	10.29 (10.20)	2.34(s)	2.24(s)	6.78(s)	—	1.18(s)	—
IIe	87	88.09 (88.23)	8.62 (8.59)	2.23(s)	2.28(s)	6.78(s)	3.50(s)	—	7.09(m)
IIf	106	88.20 (88.13)	9.02 (8.82)	2.12(s)	2.22(s)	6.69(s)	3.81(q)	1.45(d)	7.05(m)
IIg	110	88.29 (88.03)	9.12 (9.03)	2.13(s)	2.24(s)	6.73(s)	—	1.52(s)	7.10(m)

^a In unsealed tubes and uncorrected. ^b δ (ppm) in CDCl₃, external TMS. ^c Could not be detected. Ref. [7] indicates that the multiplet lies underneath the mesityl methyl signals.

from methanol gave the products in yields between 70 and 80%. As a check procedure, compounds (IIb-d) were prepared directly from dimesitylfluoroborane and the appropriate Grignard or lithium (t-butyl) reagent [7]. The products from both methods were identical in all respects.

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