

Hindered Organoboron Groups in Organic Chemistry. Part 22.† Some Interesting Properties of 2,4,6-Triisopropylphenylborane (Tripylborane, TripBH_2), A New Useful Monoarylborane

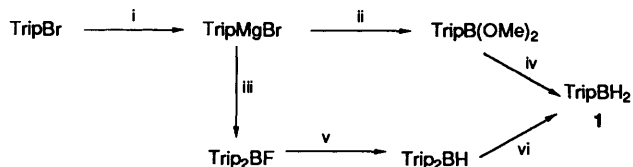
Keith Smith,* Andrew Pelter* and Zhao Jin

Department of Chemistry, University College of Swansea, Swansea SA2 8PP, UK

2,4,6-Triisopropylphenylborane (tripylborane, TripBH_2) is a solid, stable, hydroborating agent that hydroborates monosubstituted alkenes to give either TripBHR^1 or TripBR_2^1 . TripBHR^1 can be converted into mixed boranes $\text{TripBR}^1\text{R}^2$ ($\text{R}^1, \text{R}^2 = \text{primary alkyl, R}^p$) and $\text{TripBR}^p\text{R}^a$ and TripBR_2^1 are also readily available. Oxidation of these products gives the corresponding alcohols in excellent yields, with a high selectivity for alkan-1-ols in the cases of groups derived from alk-1-enes. Cyanidation of TripBR_2^1 proceeds to give ketones without migration of the aryl group. This establishes the low migratory aptitude of the aryl group and also that no scrambling of alkyl groups occurs. The tripyl group of TripBR_2^1 can be selectively removed.

As part of a continuing investigation of the chemistry of highly hindered organoboron compounds¹⁻⁶ we have studied the chemistry of compounds having the 2,4,6-triisopropylphenyl (tripyl) group attached to boron. Ditripylborane⁷ is a stable, monomeric diarylborane which does not readily hydroborate alkenes. Dimesitylborane is a highly selective reagent for the hydroboration of alkynes, but it too does not readily hydroborate alkenes.⁸ We therefore turned our attention to monoarylboranes derived from bulky aryl groups.

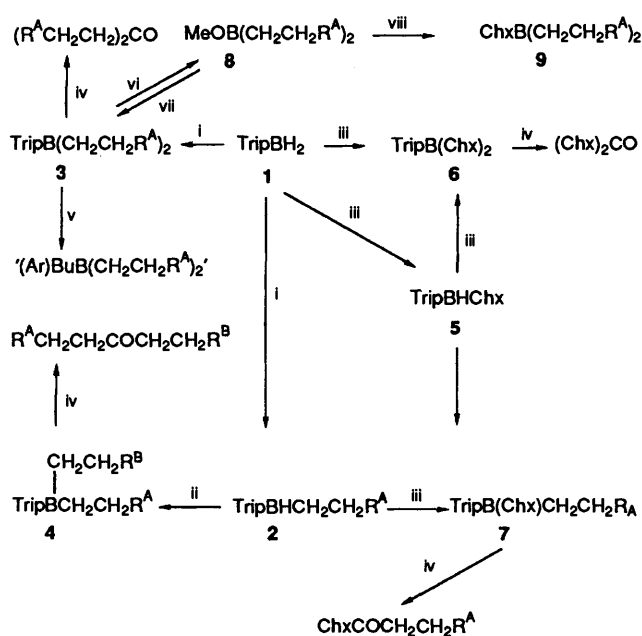
Although monoalkylboranes, and in particular thexylborane⁹ and methylborane,¹⁰ have been well investigated, little is known of the properties of monoarylboranes. We have recently reported the preparation of 2,4,6-triisopropylphenylborane [tripylborane, $(\text{TripBH}_2)_2$] ‡ 1, by either of the two methods outlined in Scheme 1, thus making 1 readily available.¹¹ We now report on some of its properties and potential utility.



Scheme 1 Reagents and yields: i, Mg, 96%; ii, $\text{B}(\text{OMe})_3$, 75%; iii, $\text{BF}_3 \cdot \text{OEt}_2$, 74%; iv, (a) LiAlH_4 , (b) Me_3SiCl , 84%; v (a) LiAlH_4 , (b) Me_3SiCl , 92%; vi, $\text{BH}_3 \cdot \text{THF}$, 100%

Tripylborane 1 is a remarkably stable monoorganylborane. As the solid, m.p. 67–70 °C, it showed no sign of decomposition, redistribution or isomerisation after standing under nitrogen for 21 days at room temp. In THF solution there was a loss of 20% hydride activity in 36 h at room temp. and then no further decomposition in up to 180 h. Nor was there any redistribution or isomerisation. *This is in sharp contrast to the widely used thexylborane¹² which must be freshly prepared at –25 °C and suffers from ready retrohydroboration as well as isomerisation.* It also contrasts with methylborane² which is prepared and used in solution and is described as ‘remarkably stable’ because little redistribution is observed over 2–3 h at room temp.

Some reactions of tripylborane 1 are given in Scheme 2.



Scheme 2 Reagents: i, $\text{R}^A\text{CH}=\text{CH}_2$; ii, $\text{R}^B\text{CH}=\text{CH}_2$; iii, Cyclohexene; iv, (a) NaCN, (b) TFAA, (c) NaOH, H_2O_2 ; v, (a) Diglyme, $\text{R}(\text{Ar})\text{Li}$, (b) H_2O , heat; vi, Br_2 , MeOH; vii, TripMgBr ; viii, ChxMgBr

The first noteworthy feature of the chemistry of 1 is that addition of equivalent amounts of alkenes such as hex-1-ene or oct-1-ene to 1 leads cleanly to the monohydroboration products 2. Thexylborane in such conditions gives only dialkylboranes.⁹ Moreover, the first hydroboration proceeds with very high regioselectivity to place 99.4% of the boron at C-1, far better than thexylborane (94% at C-1 as an average of two hydroborations, the second of which will be more selective than the first).⁹ Boranes 2 react with methanol to yield $\text{TripB}(\text{OMe})\text{CH}_2\text{CH}_2\text{R}^A$ which can be isolated and fully characterised. Compounds 2 react with an equivalent of another monosubstituted alkene to give the mixed boranes 4 and with cyclohexene to give 7, also available from borane 5. Compound 1 reacts with two equivalents of cyclohexene to give $\text{TripB}(\text{Chx})_2$ 6, a very hindered borane. Thexylborane undergoes retrohydroboration on reaction with somewhat hindered alkenes such as cyclohexene (57% retrohydroboration

† Part 21, A. Pelter, G. F. Vaughan-Williams and R. H. Rosser, *Tetrahedron*, 1993, 49, in the press.

‡ For simplicity TripBH_2 will be used to designate tripylborane.

Table 1 Oxidation of TripBR¹R²

Exp.	R ¹	R ²	Yield ^a (%)		
			TripOH	R ¹ OH	R ² OH
1	octyl	octyl	92	92	92
2	hexyl	octyl ^b	94	91	97
3	octyl	cyclohexyl	96	97	92
4	cyclohexyl	octyl	97	95	92
5	cyclohexyl	cyclohexyl	89	78	78

^a GC yield calculated on the overall processes shown in eqn. (1). ^b The reverse order of addition of the alkenes gives trialkylborane in the same yield.

Table 2 Cyanidation of TripBR¹R²

Exp.	R ¹	R ²	Yield ^a (%)	
			TripOH	R ¹ COR ²
6	octyl	octyl	93	84
7	hexyl	octyl	91	78
8	octyl	cyclohexyl	89	70
9	cyclohexyl	octyl	78	69
10	cyclohexyl	cyclohexyl	96	82

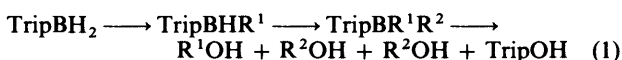
^a GC yield for the overall process of hydroboration and cyanidation based on TripBH₂.

Table 3 Reactions of TripBR¹R² with R³Li according to eqn. (4)

Exp.	R ¹	R ²	R ³	Yield (%)		
				R ¹ OH	R ² OH	R ³ OH
11	octyl	octyl	butyl	76	76	84
12	hexyl	hexyl	phenyl	96	90	96

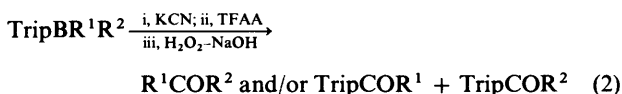
at 90% reaction)^{9,10} and the reaction has not been recorded for methylborane.¹⁰

Triplyldiorganylboranes, TripBR¹R², are very stable. Not only can they be detected and estimated by GC and HPLC, but they can often be isolated and purified by normal column chromatography. Despite this, oxidation with alkaline hydrogen peroxide readily yields the corresponding alcohols [eqn. (1)



and Table 1]. Overall yields in general are very satisfactory. The regioselectivity of the placement of the second primary alkyl group is 100%.

We then examined the cyanidation^{13,14} of our various diorganyltripylboranes (eqn. 2) to establish two points. (i) Does the triptyl group migrate in competition with primary or secondary alkyl groups? (ii) Is there any redistribution of the alkyl groups in TripBR¹R²? Our results are presented in Table 2.



In no case could we identify any TripCOR products, showing that the triptyl group does not migrate in this reaction. Of particular interest is experiment 7, in which only the mixed ketone was obtained and none of either of the symmetric ketones was present, according to GC analysis. The yields compare well with those presented previously for the

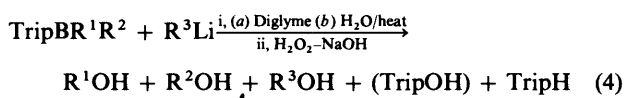
cyanidation of dialkylhexylborane,^{13,14} but with the added advantage that the reaction can be used in cases in which the analogous hexylborane derivatives cannot be made.

An extension of the usage of dialkyltripylboranes, not available to either hexyl- or methyl-dialkylboranes is the selective removal of the triptyl group by bromination to give methoxydialkylboranes **8** [eqn. (3)]. From these, of course, a wide variety of triorganylboranes can be made.¹²



The bromination of either dihexyl- or dioctyl-tripylboranes was very rapid and gave TripBr in up to 91% yield. Reaction of **8** (R¹=R²=octyl) with cyclohexylmagnesium bromide gave cyclohexyldioctylborane **9** in 68% yield based on starting TripBH₂ **1**. Reaction of **8** (R¹=R²=hexyl) with triptylmagnesium bromide gave back dihexyltripylborane in an overall yield of 63%. Clearly this process has excellent potential for the production of an extremely wide variety of boranes.

A further, extremely interesting selective process is shown in eqn. (4).



The results are shown in Table 3. It should be noted that when R³Li alone was oxidised under the normal oxidation conditions, no R³OH was produced.

The mechanism of this reaction is not clear, but taken together with the stepwise hydroboration of **1**, it presents a very direct way to bond three different organyl groups to boron. In this case the triptyl group acts as a novel 'protecting' group at boron, that is readily and directly displaced by another, less bulky, organyl group.

Acknowledgements

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