Syntheses of 2-t-Alkylbuta-1,3-dienes and 2-Alkylthiobuta-1,3-dienes from 1,4-Dichlorobut-2-yne *via* Alkenylboranes

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2-t-Alkylbuta-1,3-dienes were synthesized by the successive reaction of dialkylboranes, derived from tetrasubstituted ethenes and borane in tetrahydrofuran, with 1,4-dichlorobut-2-yne and methyl-lithium; 2-alkylthiobuta-1,3-dienes were synthesized by a similar reaction using alkylthiomagnesium bromides instead of methyl-lithium.

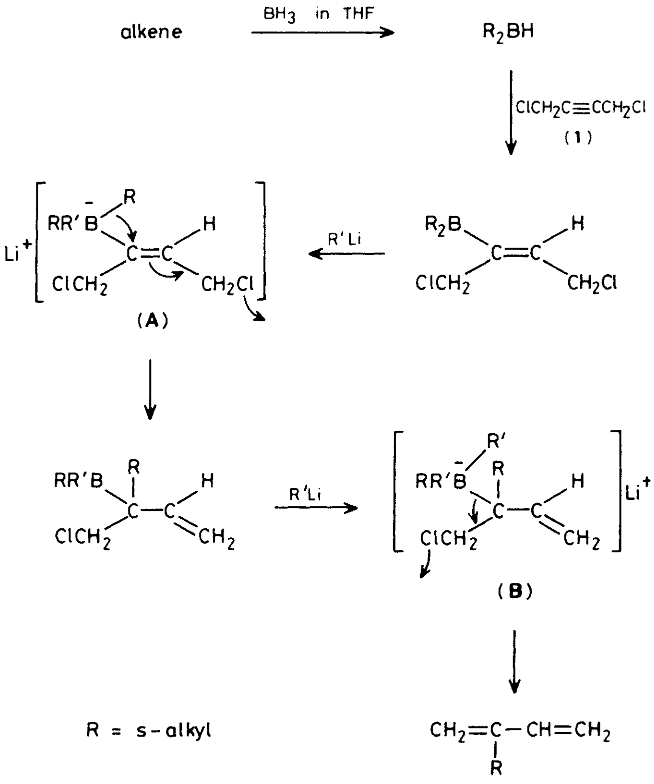
Recently we reported that the successive treatment of dialkylboranes [prepared by the reaction of borane (BH_3) in tetrahydrofuran (THF) with sterically hindered internal alkenes] with 1,4-dichlorobut-2-yne (**1**) and alkyl-lithium afforded good yields of 2-s-alkylbuta-1,3-dienes.[1] A reaction mechanism involving two borate complexes, (**A**) and (**B**), was proposed (Scheme 1).

Based on (**1**) or dialkylborane the yields were good. Although the reaction provides a convenient method for the preparation of 2-substituted buta-1,3-dienes, the waste of at least half the alkene used in the hydroboration is unavoidable.

To solve this problem, 1,1,2-trimethylpropyl-s-alkylboranes (thexyl-s-alkylboranes)[2] were examined as hydroborating agents for (**1**) instead of di-s-alkylborane. In most reactions involving the migration of one alkyl group of a dialkylalkenylborane to the α-alkenyl carbon atom, the thexyl group shows less migratory aptitude than another alkyl group on the same boron atom.[2,3]

However, surprisingly, the thexyl group was found to be more reactive than the s-alkyl group. For example, thexylcyclohexylborane,[2] prepared by the reaction of BH_3 (10 mmol) in THF with 2,3-dimethylbut-2-ene (10 mmol) and cyclohexene (10 mmol), gave two compounds, 2-cyclohexylbuta-1,3-diene (**2a**) and 2-(1,1,2-trimethylpropyl)buta-1,3-diene (**2b**), in yields of 30 and 48%, respectively, on successive treatment with (**1**) (10 mmol) and methyl-lithium (20 mmol) at −15 °C [reaction (i)].†

This result led us to compare the migratory aptitude of the



Scheme 1

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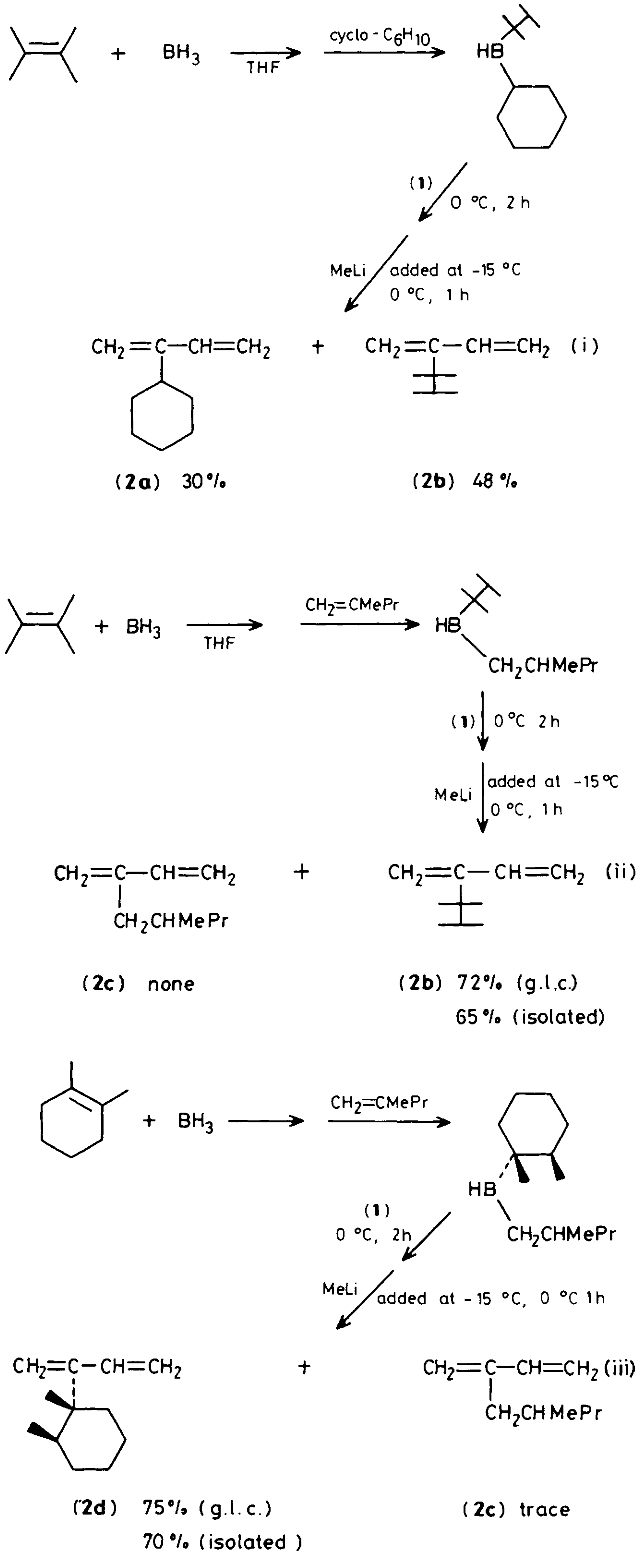
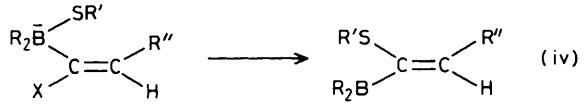
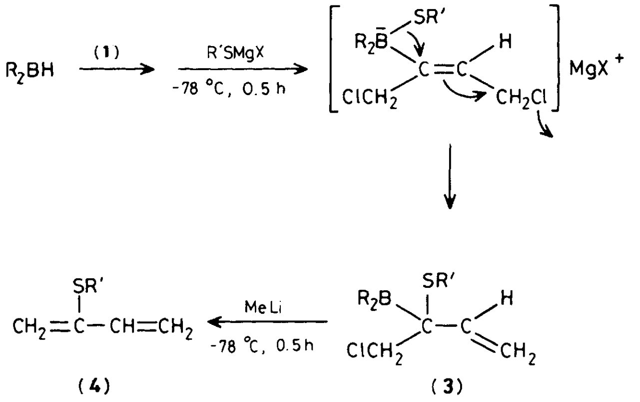
† The reaction mixture was hydrolysed with ice-cooled water and the organic layer was analysed by g.l.c.



Scheme 2





(4) a; R' = Bu, 78% (g.l.c.), 68% (isolated)
b; R' = cyclo-C$_6$H$_{11}$, 58% (g.l.c.), 51% (isolated)
c; R' = PhCH$_2$, 75% (g.l.c.), 68% (isolated)

tertiary alkyl group with that of the primary one. Complete preferential migration of the thexyl group was demonstrated in a similar reaction where thexyl-2-methylpentylborane,[2] prepared from BH$_3$ in THF, 2,3-dimethylbut-2-ene, and 2-methylpent-1-ene, was employed as the hydroborating agent [reaction (ii)]. In this case (**2b**) was obtained in 72% yield unaccompanied by 2-(2-methylpentyl)buta-1,3-diene (**2c**). A similar result was also obtained in reaction (iii), where 2-(*cis*-1,2-dimethylcyclohexyl)buta-1,3-diene (**2d**) was produced by using 1,2-dimethylcyclohexene instead of 2,3-dimethylbut-2-ene.

The participation of the tertiary alkyl group in preference to the other alkyl group is one of very few examples in organoborane chemistry.[4]

Compounds (**2b** and **d**) were isolated on a silica gel column cooled at −20 °C.‡ Their ^{1}H and ^{13}C n.m.r. spectra showed that they were isomerically pure, and supported the structures depicted. No isomerization of the tertiary alkyl groups was observed. Accordingly, the present reaction is a convenient method for the preparation of 2-substituted buta-1,3-dienes having a very bulky tertiary alkyl group derived from a sterically hindered alkene which can form monoalkylborane on hydroboration with BH$_3$ in THF, though it sacrifices the relatively hindered alk-1-ene.

On the other hand, in our previous work it was noticed that an alkylthio or an alkylseleno group migrated to the adjacent alkenyl carbon atom in preference to a secondary alkyl group when they were attached to the same boron atom in the borate complex [reaction (iv)].[5] If the present reaction involves the borate complex (**A**) in Scheme 1, use of an alkylthio- or alkylseleno-magnesium bromide instead of an alkyl-lithium would be expected to provide the corresponding 2-alkylthio- or 2-alkylseleno-buta-1,3-dienes.

Thus bis-(1,2-dimethylpropyl)borane, prepared from BH$_3$ (10 mmol) in THF and 2-methylbut-2-ene (20 mmol), was treated successively with (**1**) (10 mmol) and butylthiomagnesium bromide (20 mmol)§ at 0 °C, then the reaction mixture

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‡ By a jacket through which cold ethanol was circulated.

§ Butylthiomagnesium bromide was prepared by the reaction of equimolar amounts of butanethiol and ethylmagnesium bromide.

was washed with ice-cooled water. As expected, 2-butylthiobuta-1,3-diene (**4a**) was obtained, in 86% yield based on BH_3 (estimated by g.l.c.), and no 2-(1,2-dimethylpropyl)buta-1,3-diene was observed. In this case, however, an appreciable amount of butanethiol was present in the worked-up solution and this made the isolation of (**4a**) by column chromatography or by distillation difficult.

In a modified procedure, bis-(1,2-dimethylpropyl)borane was treated successively with (**1**), butylthiomagnesium bromide, and methyl-lithium in the molar ratio 1 : 1 : 1 : 1 (Scheme 2) to give (**4a**) almost uncontaminated by butanethiol, though the yield was only 78%. From this result, the reaction seems to involve the intermediate (**3**), which then gives 2-alkylthiobuta-1,3-diene as depicted in Scheme 2. Though neat (**4a**) is unstable at room temperature, it was isolated from the worked-up solution as in the case of 2-t-alkylbuta-1,3-dienes.

The reaction seems to be general; yields obtained in similar reaction procedures using cyclohexyl- and benzyl-thiomagnesium bromides are also shown in Scheme 2.

The synthesis of 2-alkylselenobuta-1,3-dienes by a similar reaction procedure was also examined. However these compounds seem to be unstable and they have not been isolated so far.

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