# A New Synthesis of 2-Alkylbuta-1,3-dienes from Internal Alkenes and 1,4-Dichlorobut-2-yne *via* Dialkyl(1,4-dichlorobut-2-en-2-yl)boranes

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The successive treatment of borane in tetrahydrofuran with sterically-hindered internal alkenes, 1,4-dichlorobut-2-yne, and alkyl-lithium has provided good yields of 2-alkylbuta-1,3-dienes whose alkyl groups are derived from the alkene.

While exploring the chemistry of functionally-substituted alkenylboranes,[1] we became interested in the dialkyl(1,4-dichlorobut-2-en-2-yl)boranes (**2**), prepared by hydroboration of 1,4-dichlorobut-2-yne (**1**) using dialkylboranes, owing to the polyfunctional character of (**2**) around the alkenyl moiety. We now report a new synthesis of 2-alkylbuta-1,3-dienes (**3**) *via* the reaction of (**2**) with alkyl-lithium.

A stoicheiometric study of the *in situ* hydroboration of (**1**) using dicyclohexylborane, prepared by the addition of cyclohexene to borane in tetrahydrofuran (THF), revealed that the reaction proceeded readily in a 1 : 1 ratio at 0 °C to give (**2a**) quantitatively. The *Z* configuration was assigned to this organoborane by comparing the i.r. and $^1$H n.m.r. spectra of 1,4-dichlorobut-2-ene, obtained by protonolysis of (**2a**) with acetic acid, with those of an authentic sample.

The addition of butyl-lithium in hexane to (**2a**) in THF at 0 °C resulted in the formation of (**3a**)† by concomitant regioselective migration of the cyclohexyl group to the adjacent C-atom with loss of two chlorine atoms and an organoborane. The i.r., $^1$H, and $^{13}$C n.m.r. spectra of (**3a**) were identical with those of the same compound obtained by other methods.[2]

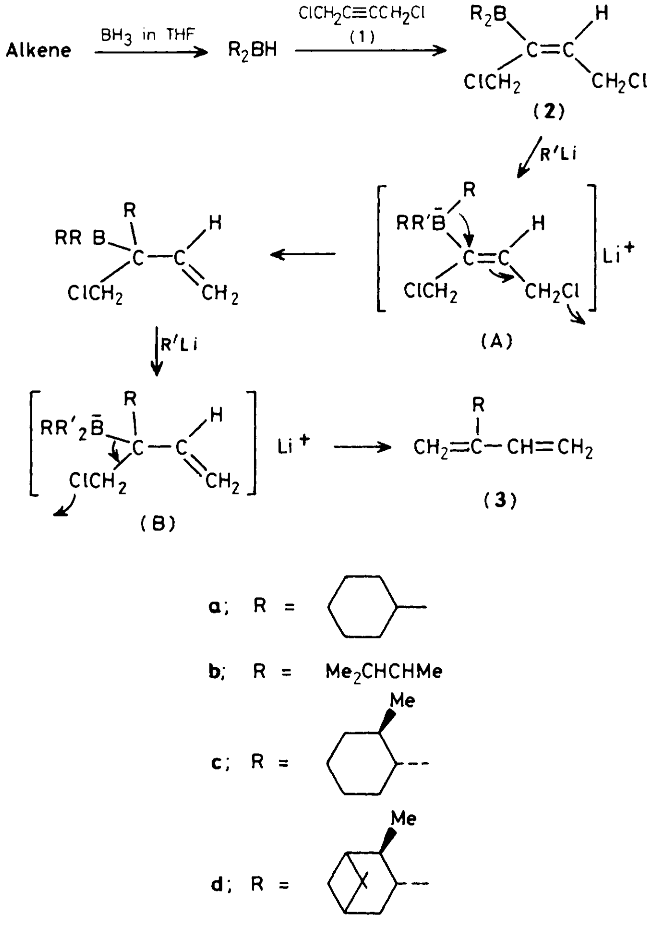
A stoicheiometric study of the reaction of (**2a**) with butyl-lithium revealed that approximately two equiv. of BuLi were required to react with one equiv. of (**2a**); furthermore, alkaline hydrogen peroxide oxidation of the reaction mixture afforded nearly two equiv. of butanol and one equiv. of cyclohexanol. On this basis, we propose a reaction mechanism involving two borate complexes, (A) and (B), as shown in Scheme 1. Reactions similar to the concomitant alkyl group migration and elimination of the allylic chlorine atom from the borate complex (A)[3] and to the β-elimination of the trialkylborane and the chlorine atom from the borate complex (B)[4] have appeared in the literature.

**Table 1.** Yields of 2-alkylbuta-1,3-dienes (**3**).[a]

| Alkene | R'Li | Product | % Yield[b] |
|---|---|---|---|
| Cyclohexene | BuLi | (**3a**) | 83 |
| Cyclohexene | MeLi | (**3a**) | 85 |
| 2-Methylbut-2-ene | MeLi | (**3b**) | 73 |
| 2-Methylcyclohexene | MeLi | (**3c**) | 70 |
| α-Pinene | MeLi | (**3d**) | 68 |

[a] The reaction of 20 mmol of (**1**) with dialkylborane, prepared from 20 mmol of borane and 40 mmol of alkene under appropriate conditions, was carried out *in situ* at 0 °C for 2 h, [except in the case of (**2c**) in which the reaction was carried out at room temperature for 4 h], followed by the addition of 40 mmol of butyl-lithium in hexane or methyl-lithium in diethyl ether at −15 °C and then the reaction mixture was stirred for 1 h at 0 °C. [b] Isolated yield, based on (**1**).

The present reaction provides a new route to (**3**) from a relatively hindered internal alkene whose hydroboration can be stopped at the dialkylborane stage. Thus 2-methylbut-2-ene, 2-methylcyclohexene, and α-pinene were hydroborated with borane in a 2 : 1 ratio and treated successively with (**1**) and methyl-lithium in diethyl ether‡ in a similar manner to cyclohexene. Regioselective formation of the corresponding 2-alkylbuta-1,3-dienes, (**3b**), (**3c**), and (**3d**), resulted. These products were isolated from the reaction mixtures by column chromatography.† Their $^1$H and $^{13}$C n.m.r. spectra show that they are isomerically almost pure and support the expected



**Scheme 1**

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† The product was isolated from the worked-up reaction mixture by column chromatography at low temperature using basic alumina and pentane.

‡ Methyl-lithium in diethyl ether gave better yields than butyl-lithium in hexane when sterically more hindered alkenes than cyclohexene were employed.

structures of the products. The yields of the dienes are shown in Table 1. The configurations of (**3c**) and (**3d**) as shown in Scheme 1 are assigned by analogy with a similar reaction involving transfer of the alkyl group with retention of configuration.[5]

2-Substituted 1,3-butadienes (**3**) are potentially useful in organic synthesis, especially in Diels–Alder reactions, and syntheses of (**3**) involving reactions of 2-(buta-1,3-dienyl)magnesium chloride with primary alkyl,[6] aryl,[6] and trimethylsilylmethyl[7] halides have previously been reported. However it should be noted that in the present reaction the dienes, substituted by a secondary alkyl group, are synthesized from sterically-hindered alkenes using commercially available reagents.

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