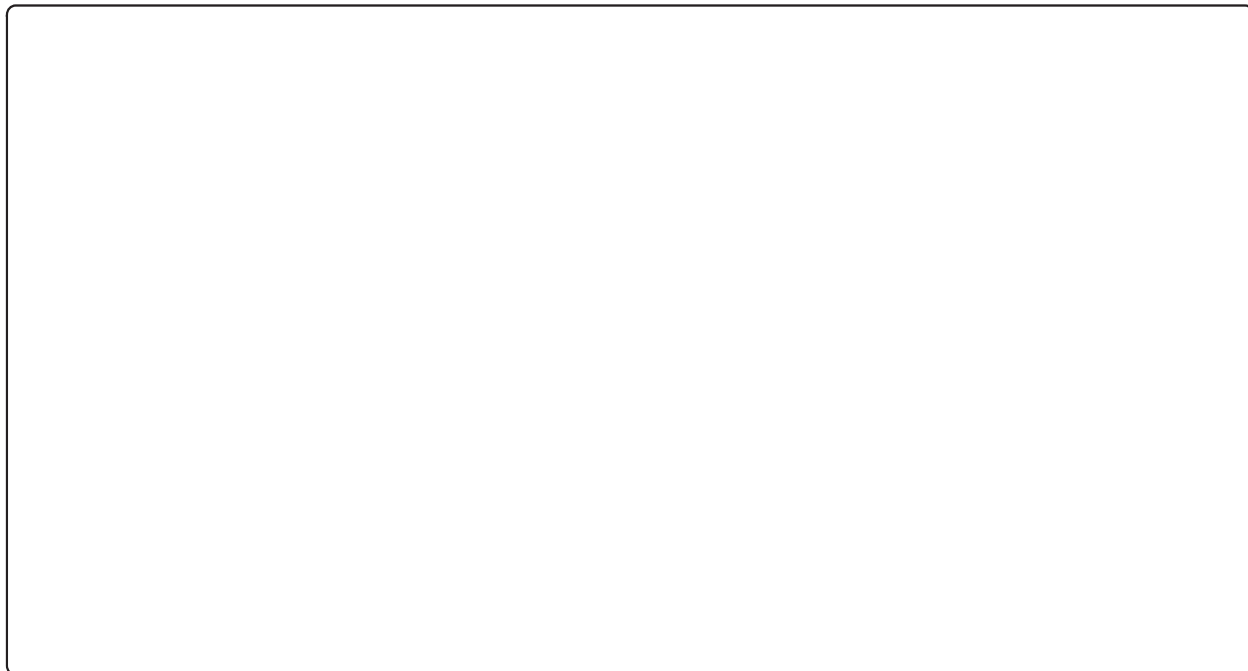


D.2 Hydroboration

The Reaction:

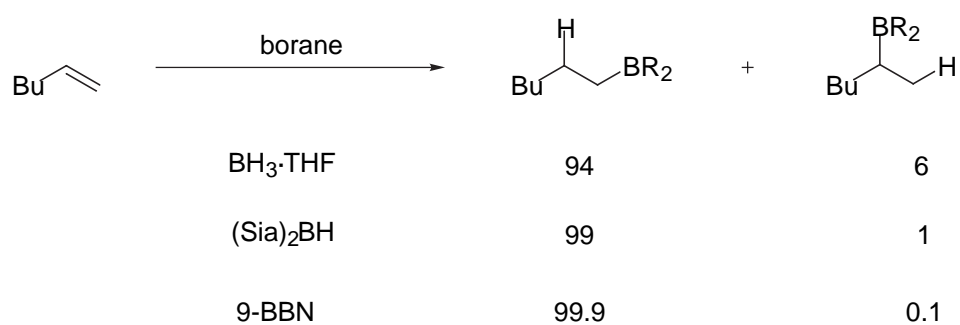


Notes:

1. In the case of borane BH_3 , all three hydrogen substituents can be transferred *i.e.* one molecule of BH_3 can react with three molecules of olefin.
2. The rate of reaction is dependent on a number of factors although steric effects are particularly important.
 - Less hindered olefins react most readily.
 - Substituents on the borane decrease the rate of hydroboration hence the relative rate of transfer of the three hydrogen substituents in BH_3 . With particularly hindered olefins it is therefore possible to stop the reaction after transferring two Hydrogens:

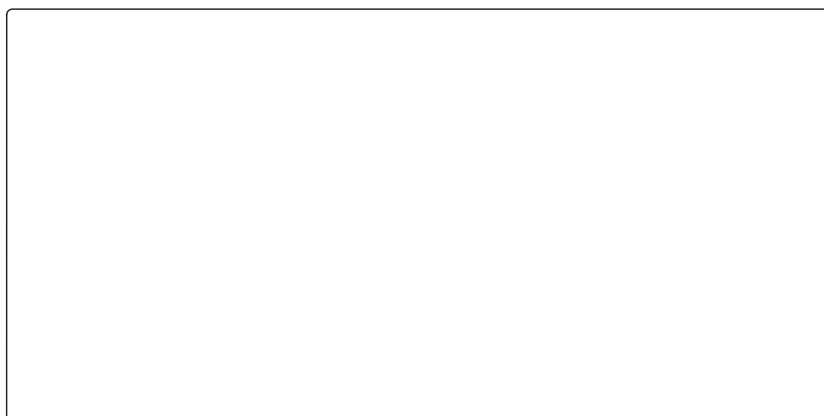
3. *Regioselectivity*

- The borane reacts on the sterically less hindered face of the olefin when the two faces are sterically differentiated.
- The boron substituent usually ends up on the less substituted end of the olefin; dialkylboranes generally give higher regiocontrol than BH_3 :



Origins of Regioselectivity

- simple steric arguments provide the major reason why the B ends up on the less substituted end of the olefin.
- owing to the polarisation of the B–H bond, electrostatic effects also favour B on the less substituted end of the olefin:



- The *syn* selectivity of the reaction implies a concerted process although the two new bonds are formed asynchronously such that there is build-up of charge on the two ends of the olefin. Positive charge is better stabilised on the more substituted end of the olefin; thus on electrostatic grounds the hydridic hydrogen in the borane would be predicted to transfer to the more substituted end of the olefin.

4. *Stereoselectivity:*

The two new bonds are formed on the same face of the olefin; **hydroboration is a *syn* stereospecific process.**



5. *Mechanism of hydroboration*

Borane BH_3 in a coordinating solvent such as THF exists as a complex equilibrium between the free monomer BH_3 , the dimer B_2H_6 and the complexed monomer $\text{BH}_3 \rightarrow \text{THF}$. Furthermore the reaction mechanism is further complicated by the fact that all borane intermediates will also exist in similar forms (dimers and Lewis acid-Lewis base complexes).

We shall consider the hydroboration using a dialkylborane R_2BH which can only react once. This borane will also exist primarily as the dimer or as a Lewis acid-Lewis base complex with a coordinating solvent. However only the non-complexed monomer R_2BH is capable of reacting with an olefin as only this species has a vacant coordination site.

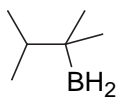


The reagents associate by forming a weak Lewis acid-Lewis base complex before transferring a ' R_2B ' and ' H ' group to the double bond in a *syn* specific fashion.

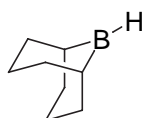
There are many types of boranes used for hydroboration (including chiral boranes); some of the most commonly used are shown below:

$\text{BH}_3 \cdot \text{THF}$

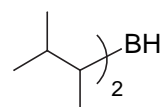
$\text{BH}_3 \cdot \text{DMS}$



thexylborane



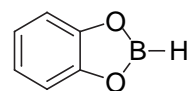
9-borabicyclo[3.3.1]nonane
9-BBN



disiamylborane
(Sia)₂BH

Et_2BH

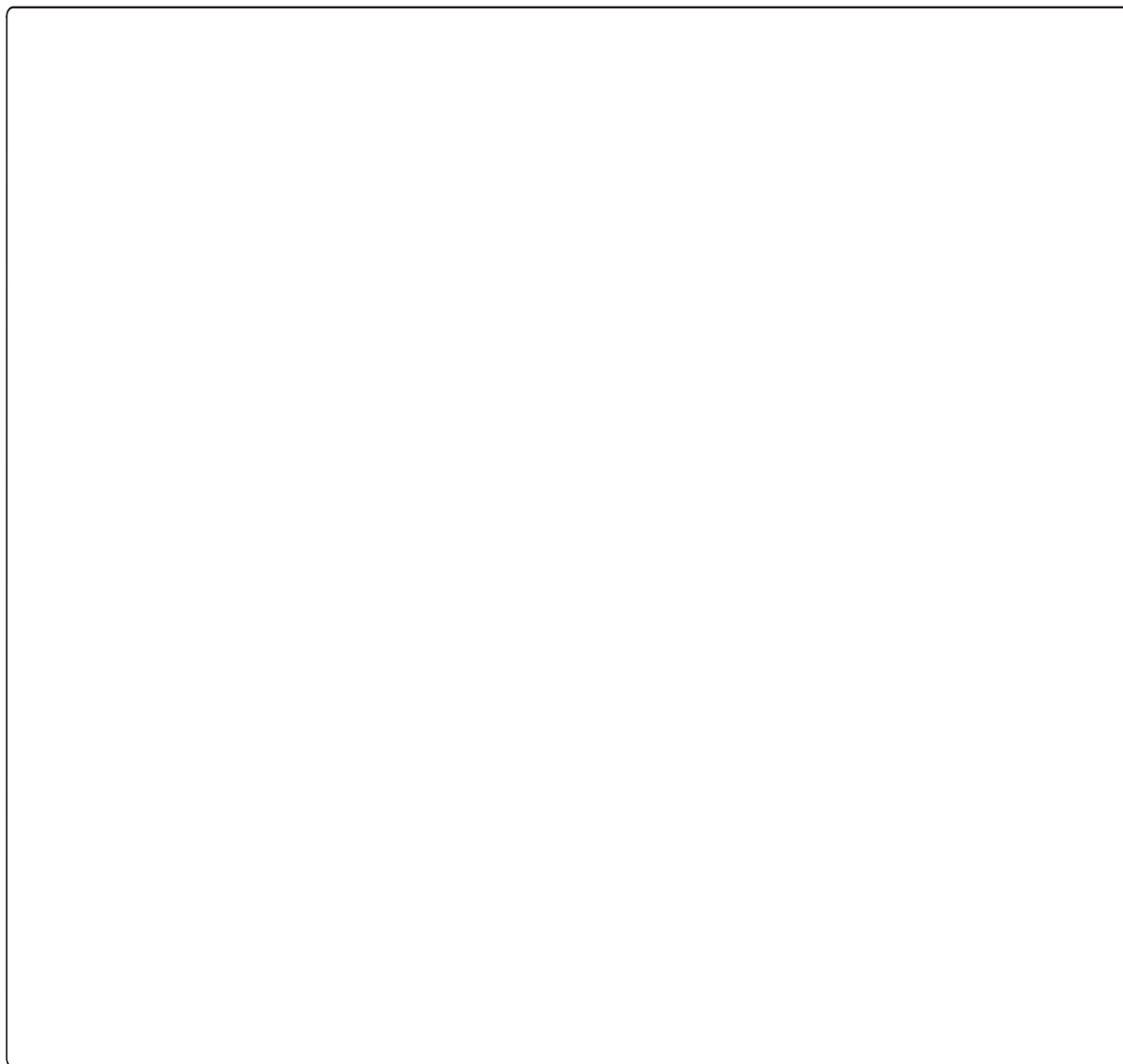
diethylborane



catecholborane

D.2.i Reactions of Organoboranes

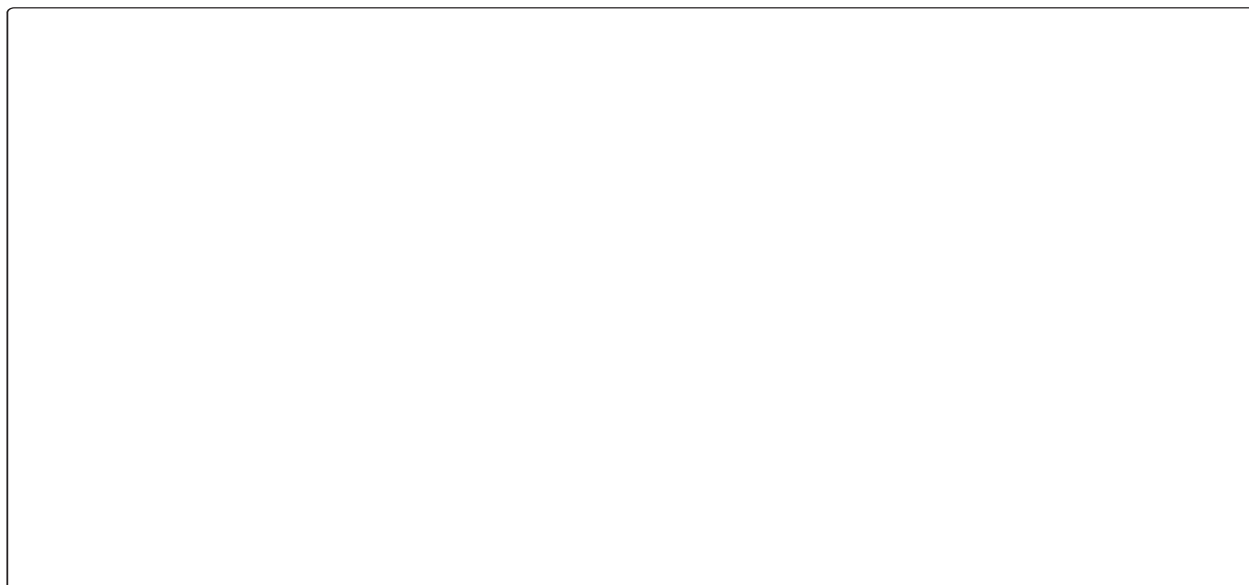
Oxidation



The mechanism of oxidation of a C–B bond is very similar to the Tamao-Fleming oxidation discussed earlier, and again proceeds with complete *retention of configuration*.

Standard conditions for oxidation involve alkaline peroxide H_2O_2 / NaOH . A phosphate buffer is also frequently used to maintain the reaction at pH 8.

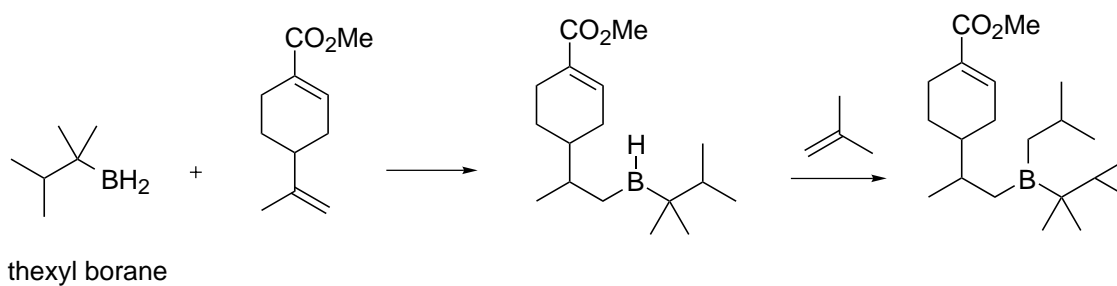
Amination



Amines possessing good leaving groups such as chloride (chloramine) react in a similar mechanism to peroxides. Only two groups can be transferred thus the yield is restricted to a maximum of 67%.

Q? Why does the reaction stop after two groups have been transferred?

Carbonylation: a convergent route to ketones

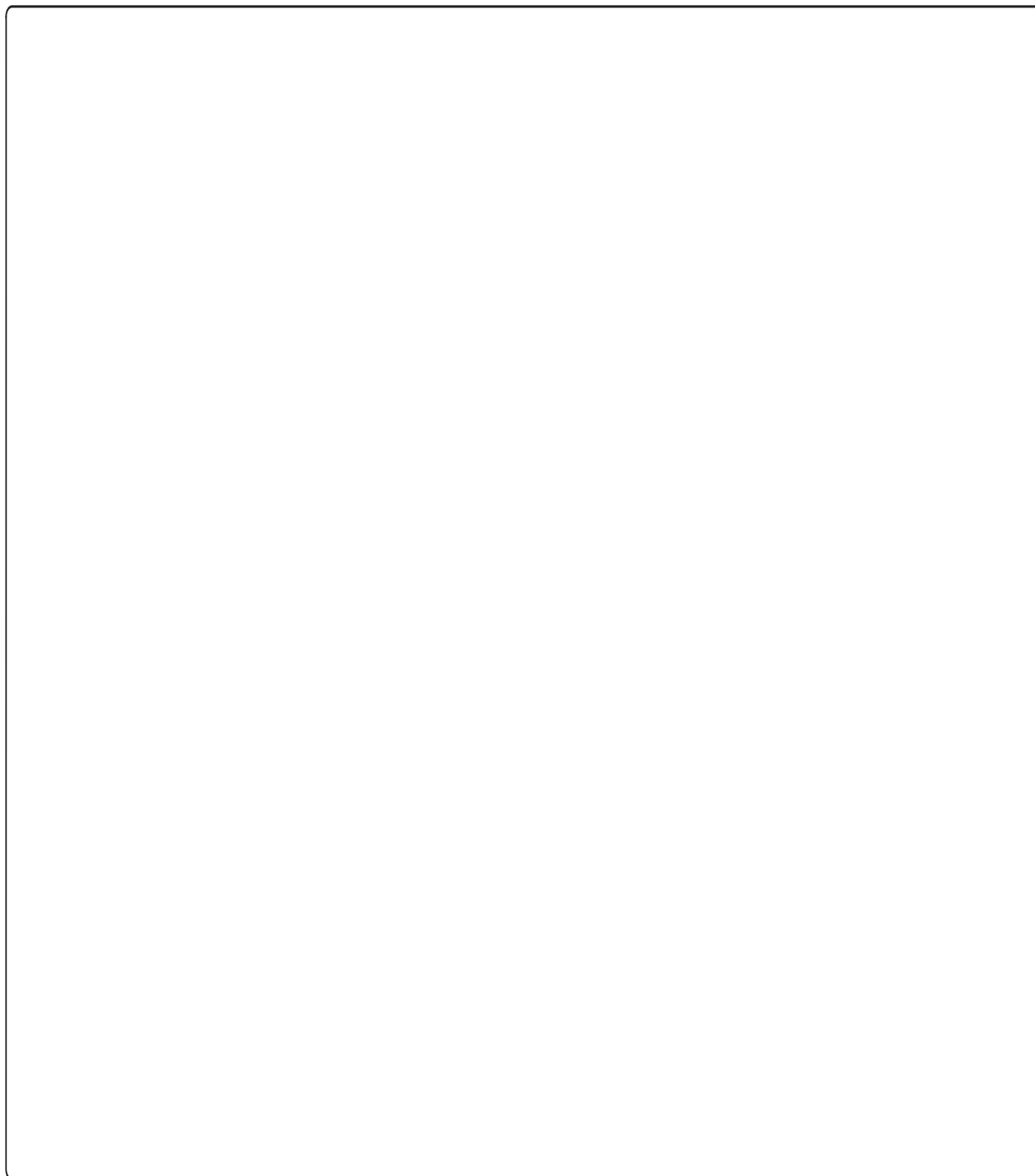


Thexylborane is the borane of choice in this transformation:

- it has two hydrogen substituents and so can react with two olefins.
- The sterically very bulky nature of the thexyl group ensures that the second hydroboration reaction is much slower than the first allowing the sequential use of different alkenes and the preparation of an unsymmetrical trialkylborane.
- The thexyl group shows a very low tendency to migrate.

- Thus treatment of the unsymmetrical trialkylborane with CO and water followed by peroxide work-up provides a ketone product.

Cyanide is isoelectronic with CO and also reacts with trialkylboranes. The borate adducts are stable and require an electrophile such as trifluoroacetic anhydride to induce alkyl group migration.



Summary

1. Hydroboration is a highly regioselective and *syn*-stereospecific process.
2. A concerted [2+2]-type cycloaddition mechanism accounts for the product outcome.
3. A wide variety of boranes are available. The number of hydrogen substituents on the borane determines the number of olefins with which it can react.
4. The rate of hydroboration is strongly affected by the substituents on the B atom - sterically bulky substituents can appreciably reduce the rate of successive hydroboration reactions.
5. $\text{sp}^3\text{-C-B}$ bonds can be manipulated in a number of ways including oxidation, amination and carbonylation.