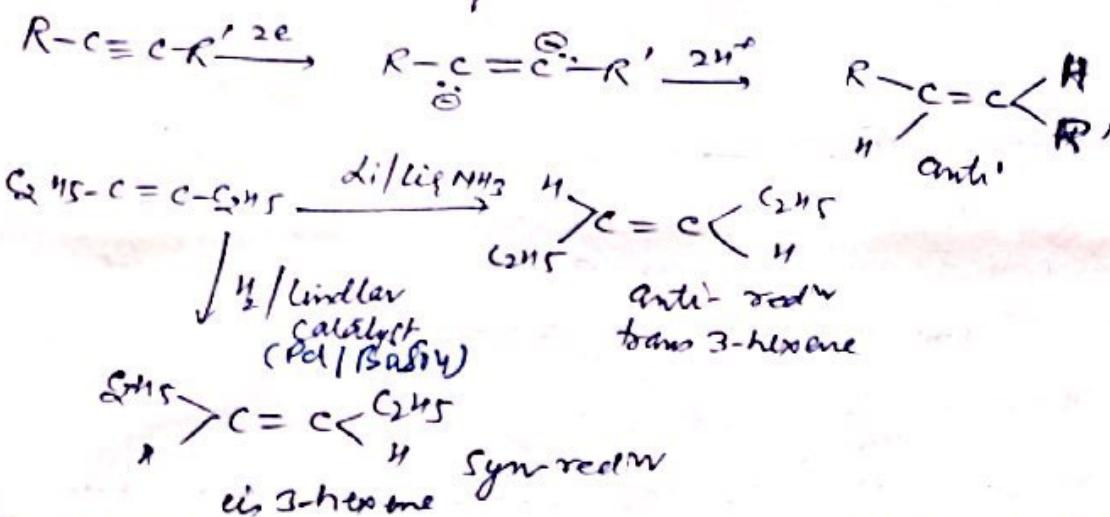


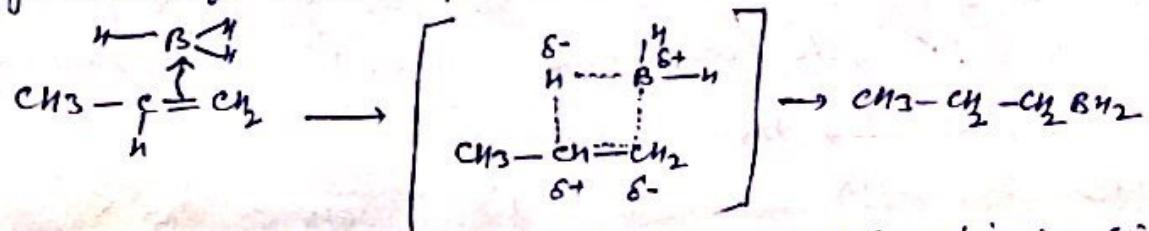
M.Sc. II sem. HR-2008 - 2nd Lect by P.K. Sharma 01-5-20 (5)
Hydrogenation of alkynes (Addition reactions)
 Electrons are transferred to acetylenes more readily than to olefines
 this can be attributed to greater reactivity of acetylenes towards nucleophiles. Reagents are metal amines and metal ammonia systems
 The reduction is selectively anti'.



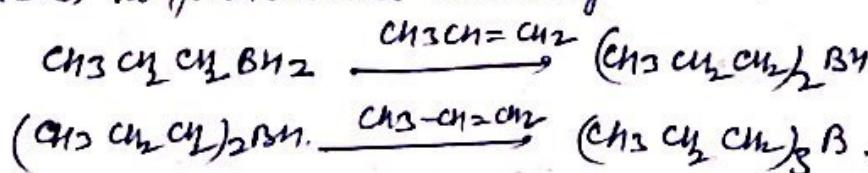
Thus the only product formed from di-substituted alkynes is the corresponding E-alkene. and therefore, the technique complements the formation of Z-alkenes by catalytic hydrogenation of alkynes.

Hydroboration (Dnp)

Borane (BH_3) itself is unknown but its dimer B_2H_6 behaves as if it were BH_3 . As it has a racontabil so borane may be regarded as an electrophile and attacks the π electrons of alkene. Intramolecular hydride shift then completes the reaction



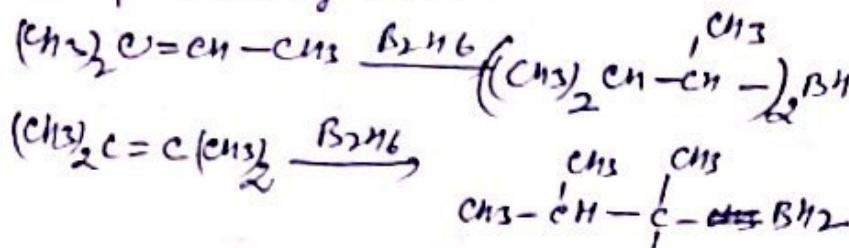
Because of one step - four centre process, hydroboration is a cis-addition. Hydrogen and Boron become attached to the same side of the double bond. Alkyne boranes behave like boranes and react further with excess alkenes to form di and tri alkyl boranes.



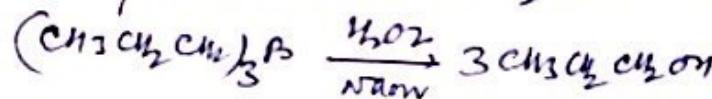
The rate of addition of borane to alkenes decreases with increase in the number of alkyl substituents on the double bond.

(5)

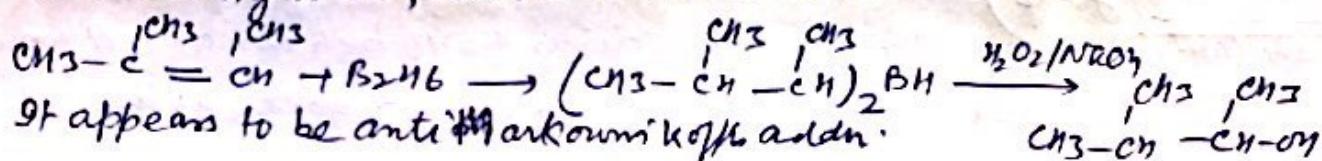
Tri-sub. alkene normally give di-alkyl boranes and tetra-sub-butenes.
form only mono-alkyl boranes.



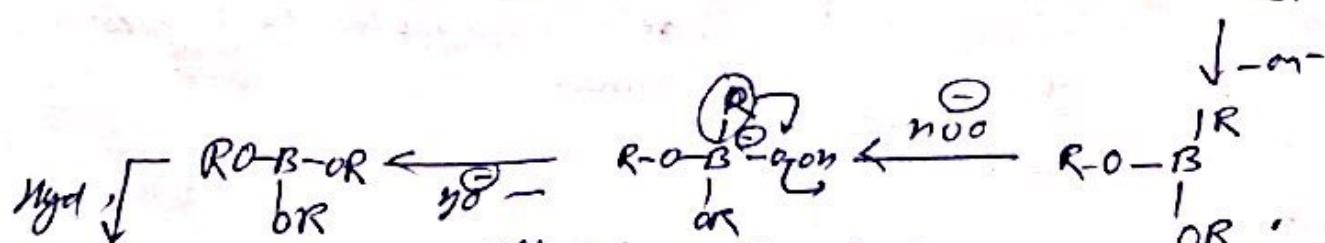
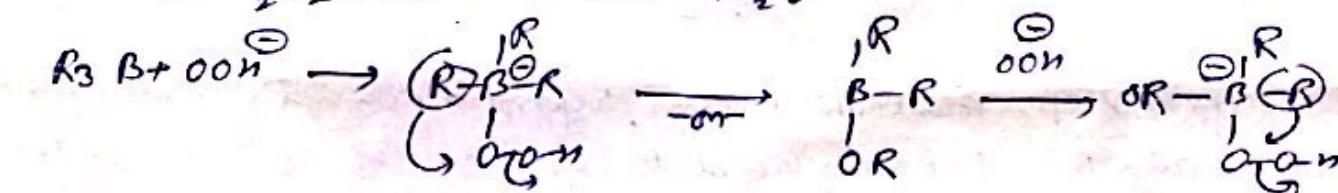
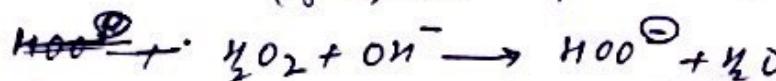
This is due to steric factor. ~~This~~^{CH₃} hydroboration has been a reaction of tremendous synthetic utility because alkylboranes undergo a variety of useful transformations. e.g. alkyl boranes can be oxidised by treatment with $\frac{1}{2}O_2$ to alcohols.



The overall result of these two steps - reaction with diborane followed by oxidation of alkyl boranes appears like anti-Markovnikoff addition, although hydroboration does not violate Markovnikoff's rule. Another important feature is stereo-specificity which results in *cis*-addition of water, across a double bond.



Mech- of involves initial attack of HOO^\bullet on 3-oxo-2-butane hydroperoxide (in to Boron), followed by migration of alkyl groups from boron to oxygen, resulting Borate ester liberates alcohol on hydrolysis.



$$3\text{Rn} + \text{B(OH)}_3$$

OR
alkyl boranes can also be oxidized to carbonyl compounds on treatment with Chromic acid

