# Chapter 10

Organoboran Chemistry

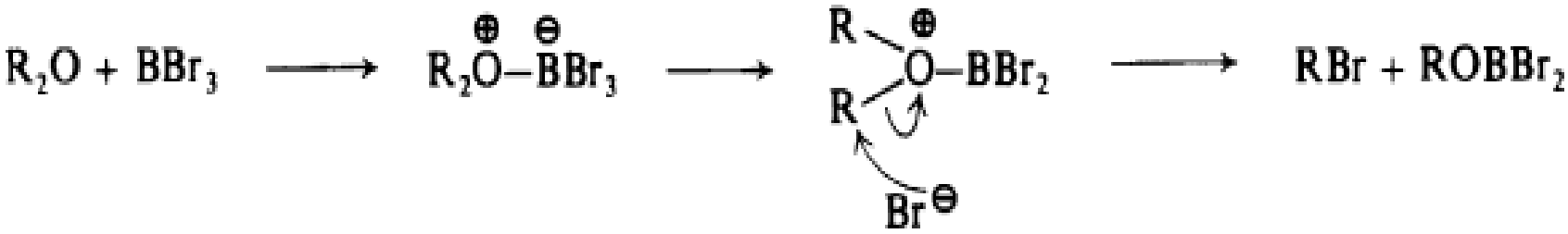
# STABILITY OF ORGANOBORANES EXCHANGE REACTIONS

**According to Ahrland *et al.*, boron is of borderline softness. Borane derivatives are mildly soft if all the ligands are from Groups V and VI. However, boron trifluoride is a hard acid.**

## Boron Trihalides

**Boron trifluoride complexes easily with ethers. The complexes are stabilized by symbiosis of F and O ligands around the boron.**

**Dialkyl ethers are ruptured by $BBr_3$ to furnish alkyl bromides. This is a consequence of the mutual weakening of B-Br and O-R bonds (both are hard-soft pairs) on coordination. The splitting of the bromide ion from the complexes and its return attack on the alkyl group of the oxonium intermediates are favored on HSAB grounds.**



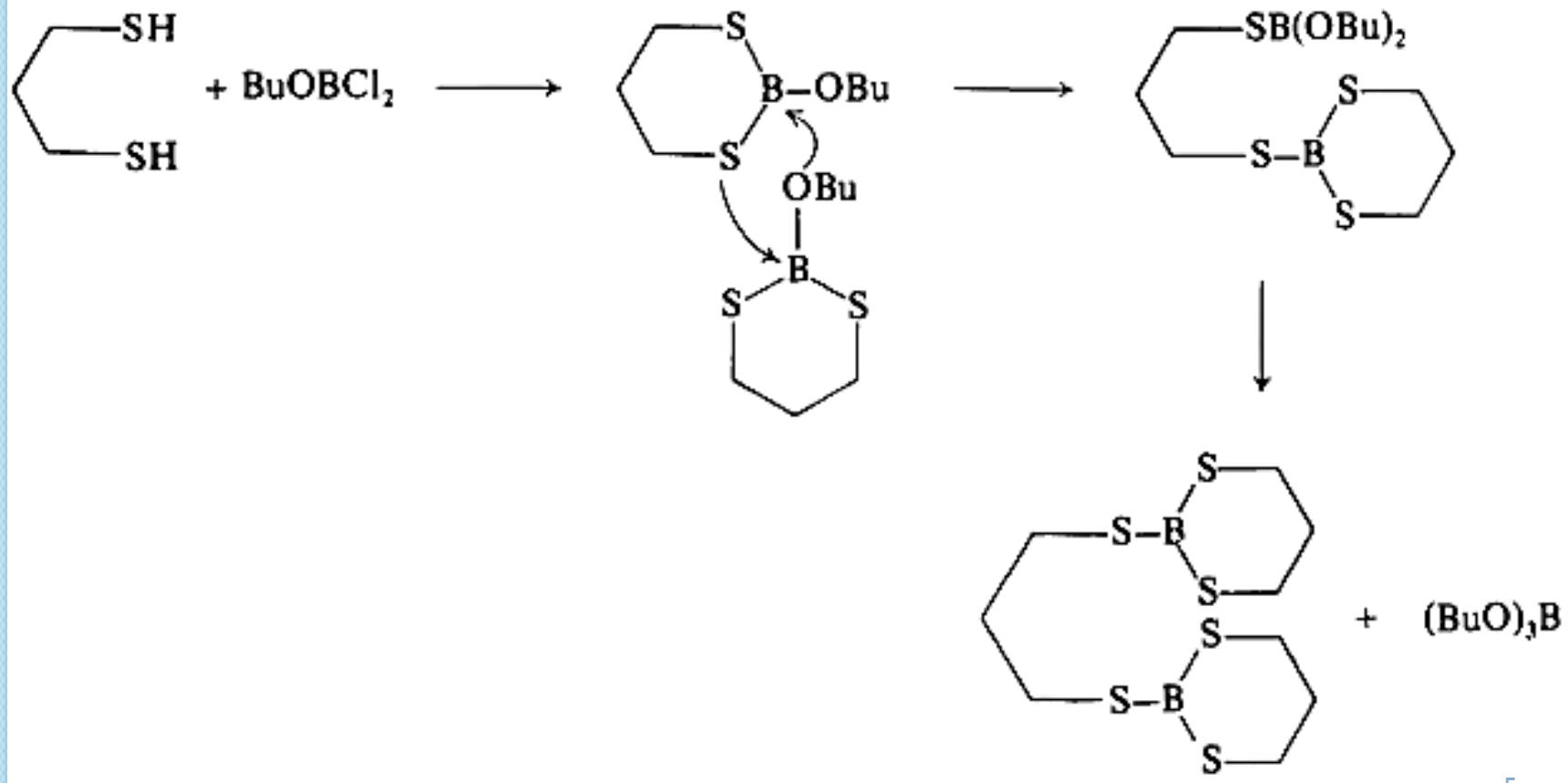
# Thioboranes

**Owing to its borderline softness, boron atom may interact equally well with both hard and soft bases. Thus, the solvolysis of thioboranes is easily ac-complished. A simple admixture of thioboranes with carbonyl compounds affords Dithioacetals.**

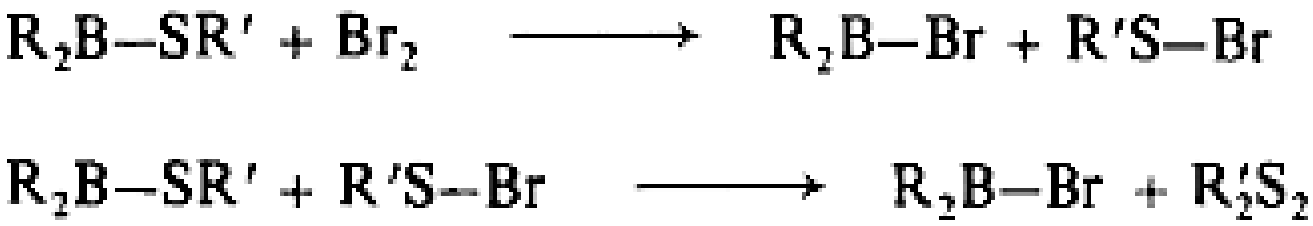
**Mixed disulfides are obtained when sulfenate esters are treated with trialkylthioboranes. This reaction is very efficient because the sulfenates contain an unstable soft-hard bond.**


**It is of interest to note that ethers are also cleaved on exposure to monoalkylthioboranes.**

**An attempt to prepare mixed borates results in disproportionation product. Symbiosis appears to be the driving force for the secondary transformation.**

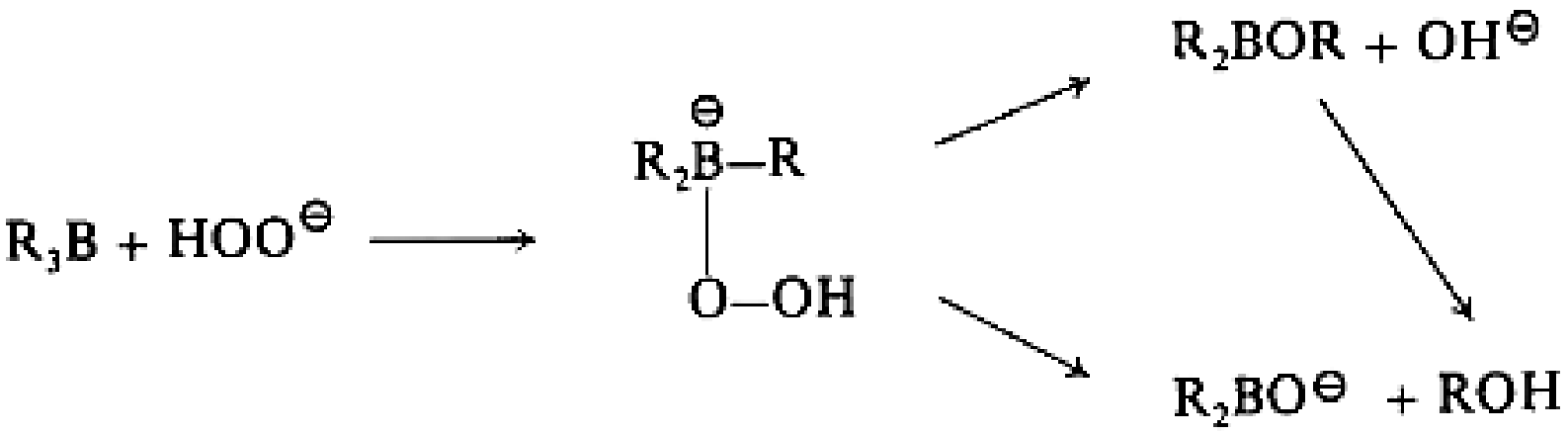


**Thioboranes also undergo bromolysis as shown below:**

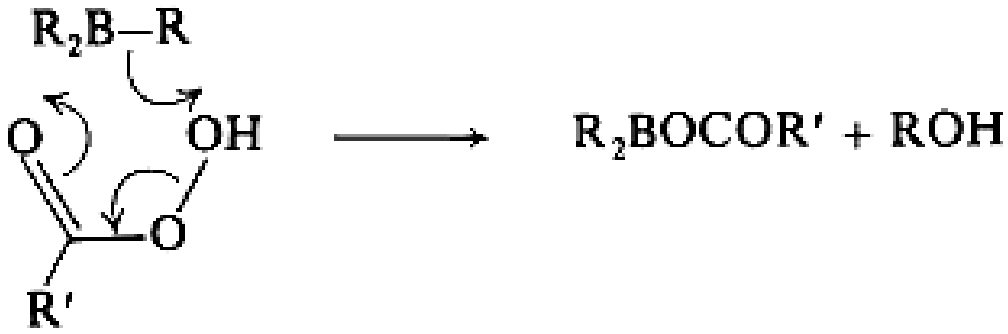


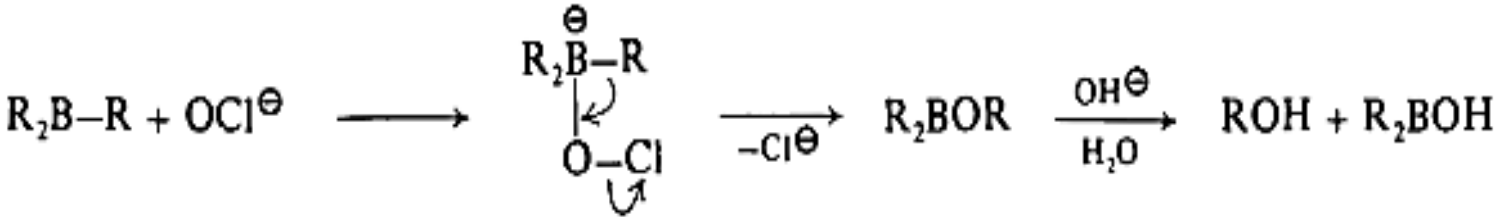
# Oxygenative Degradation of Organoboranes

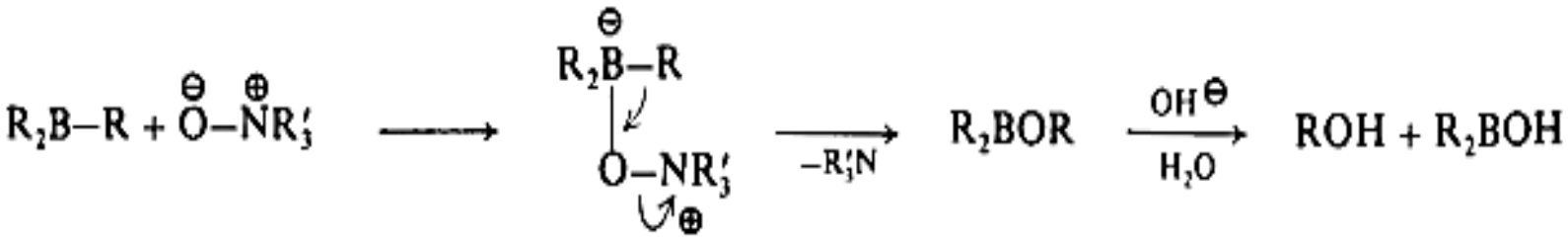
**The treatment of organoboranes with alkaline hydrogen peroxide leads to alcohols, this involves addition of $HO_2^-$ to boron followed by migration of a soft alkyl group to the soft oxy center of the hydroperoxyboranide intermediates.**



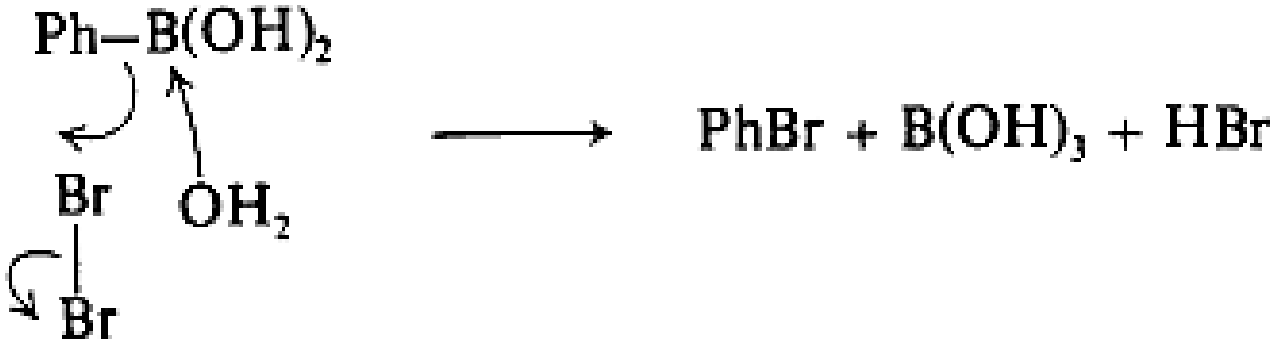
**Peracid, alkaline hypochlorite, and tertiary amine oxides may be employed as alternative reagents as they provide appropriate interacting loci for the organoboranes.**



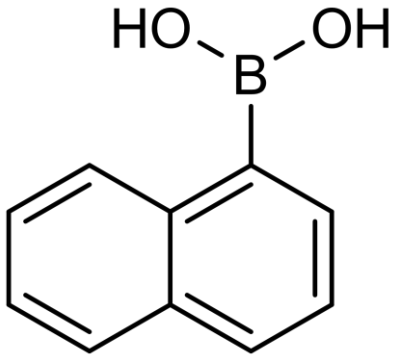



**Degradation of benzeneboronic acid with bromine is greatly facilitated by added hard bases such as water. The findings suggest a *push-pull mechanism* in which the aromatic ring is activated by the hard donor which supplies electrons on bonding with the boron atom.**

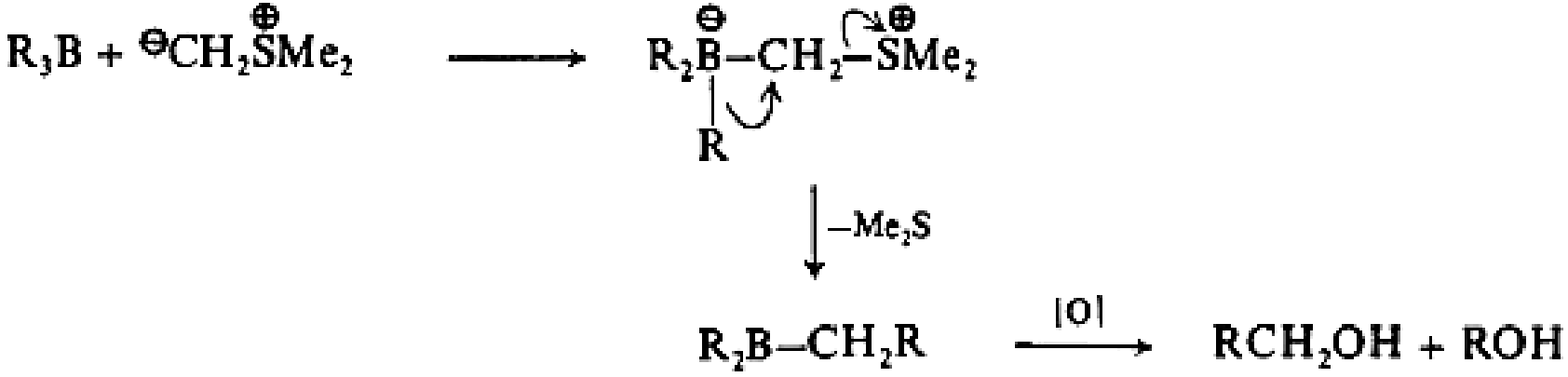



**Iododeboronation of naphthaleneboronic acids has also been studied.**

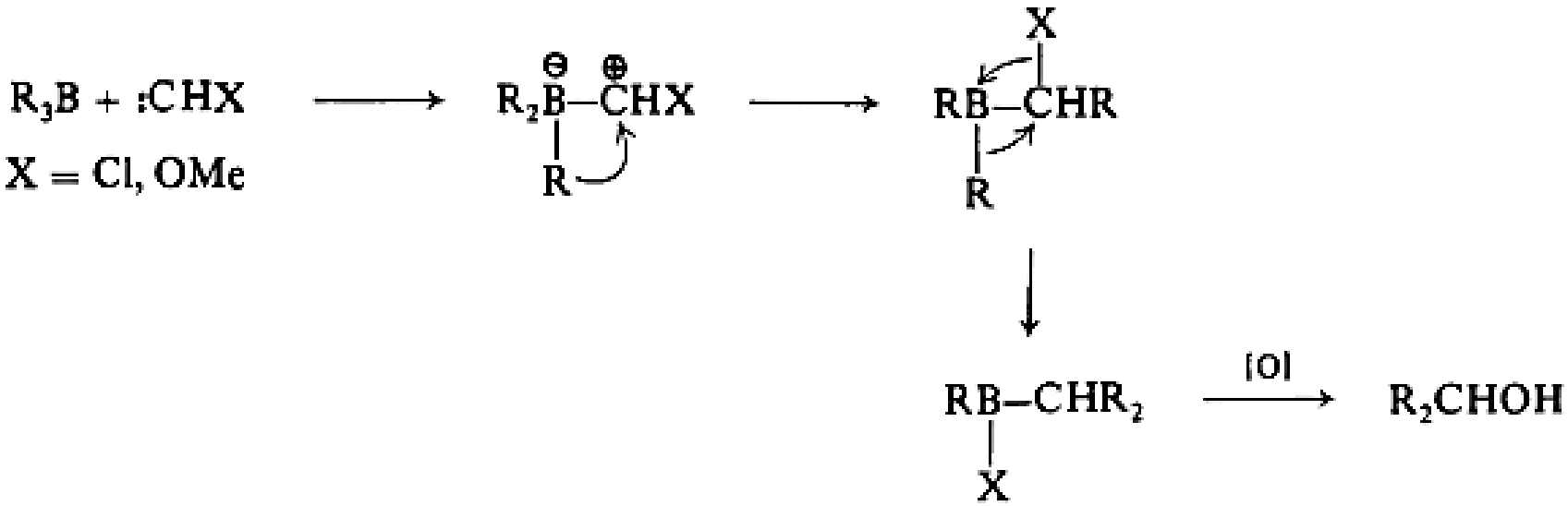


# Cleavage of C-B Bond by Other Nucleophiles

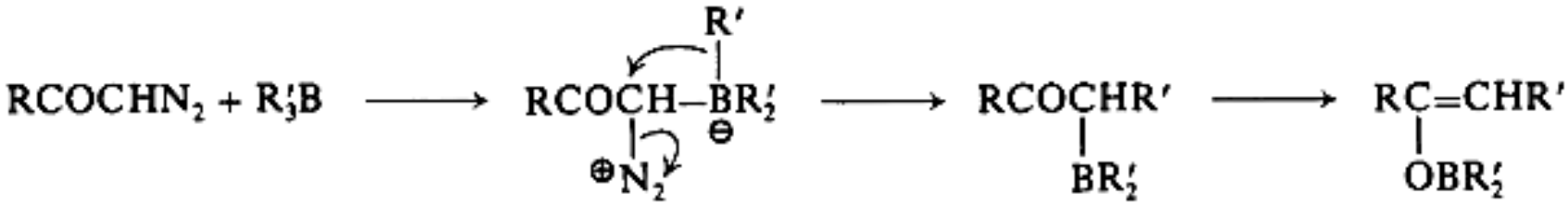
**Homologous alcohols may be synthesized by treating trialkylboranes with dimethylsulfonium methylide or dimethyloxosulfonium methylide , followed by oxidative workup.**

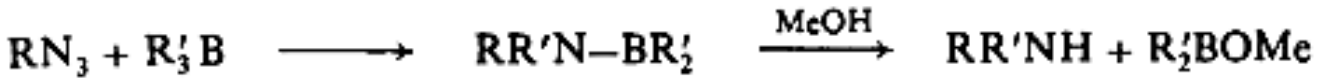


**Although carbenes are electron-deficient species, they react, as donors, with boranes. Secondary alcohols are produced via two successive alkyl migrations from the boron to carbenium centers of the intermediates when chlorocarbene and methoxycarbene are employed.**

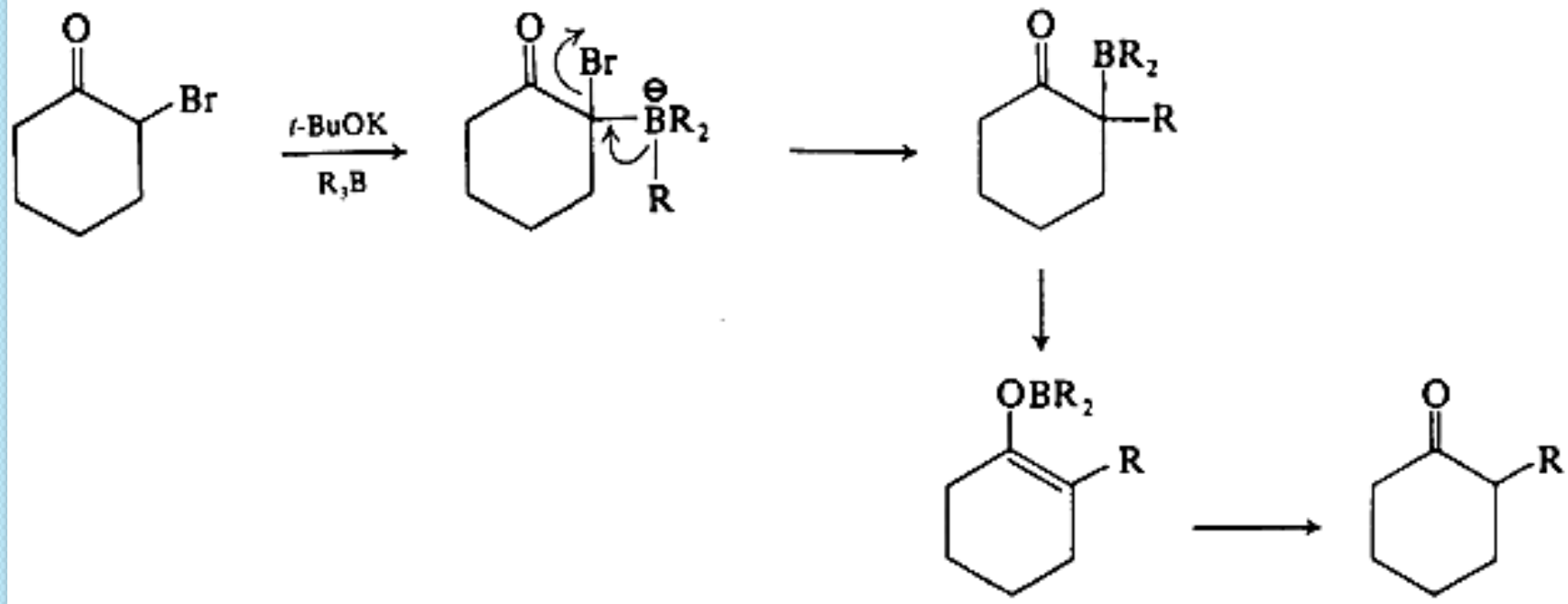


**By having a carbanionoid center, diazo compounds react with boranes easily. For example, diazoketones yield ß-oxoboranes which rearrange *in situ* to generate enol borates. The use of organoazides instead of diazo compounds leads to secondary amines.**

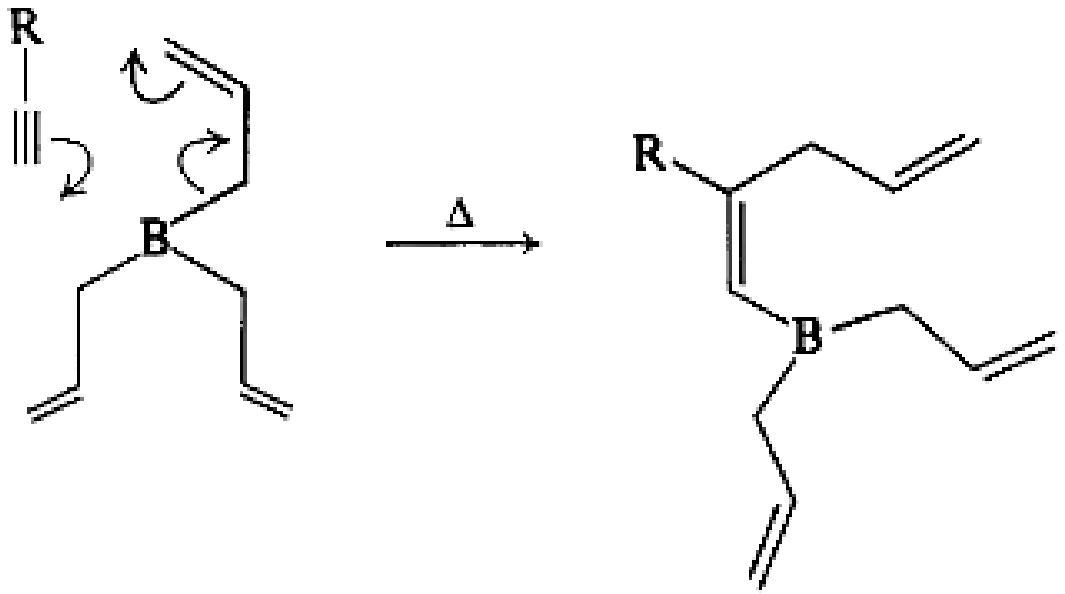


**Indirect alkylation of ketones and esters via their α-bromo derivatives can be achieved by base-catalyzed reactions with trialkylboranes.**

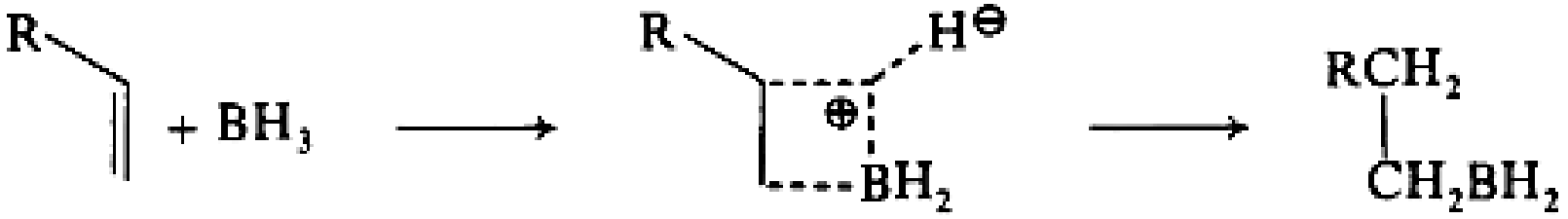


**Triallylborane reacts with monosubstituted acetylenes by an ene-type process. This could be a reflection of the fact that boron prefers bonding to a slightly harder $sp^2$ carbon.**



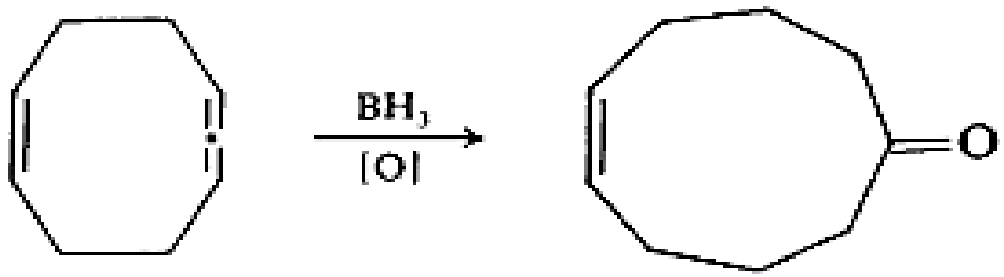
# HYDROBORATION

**Borane is a soft Lewis acid, therefore its complexation with soft olefin linkages is very favorable. Apparently the initial borane-alkene complexes collapse rapidly to a four-centered transition state leading to the organoboranes without the participation of external nucleophiles. This process is called hydroboration.**

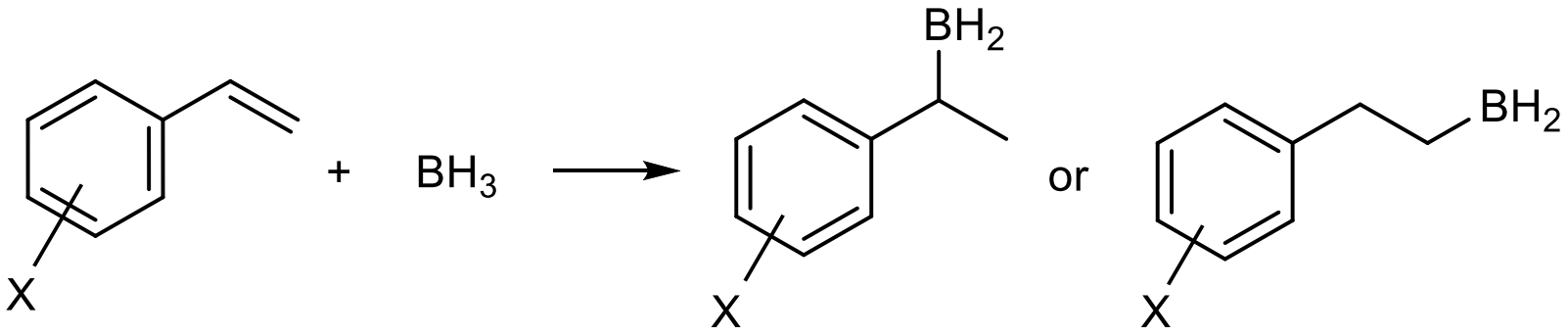



**The unusual orientation of addition of the B-H elements across double bonds may be due to the thermodynamic stability of the transition state which has a certain degree of polar character.**

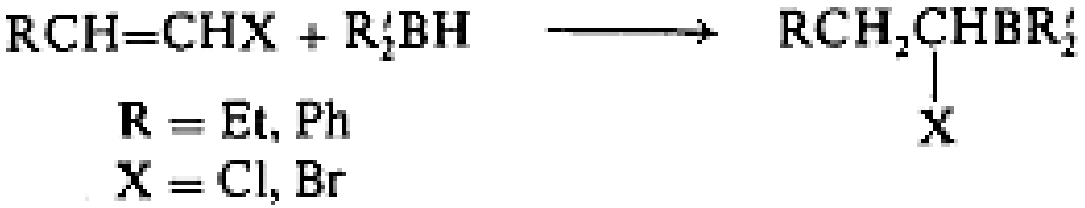
**It has been found that the central atom of the allenic bond is the preferred boron-bonding site during hydroboration. This center is harder than the terminal $sp^2$ carbons.**

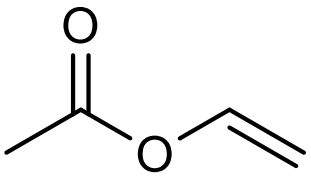


**In the hydroboration of styrene derivatives, the orientation is influenced to some extent by the substituent on the benzene ring. The presence of an electron-withdrawing group stabilizes the transition state leading to boron attachment to the benzylic position. This carbon is harder than that of styrene. On the other hand, an electron-donating function tends to direct the C-B bonding toward the terminal carbon.**

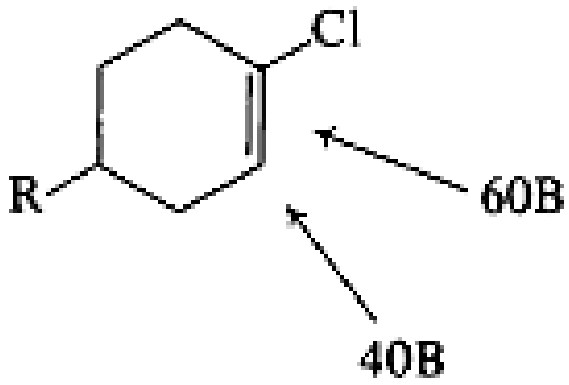


**Hydroboration of 1-haloalkenes and enol acetates places the boron atom predominantly at the α-carbon.**



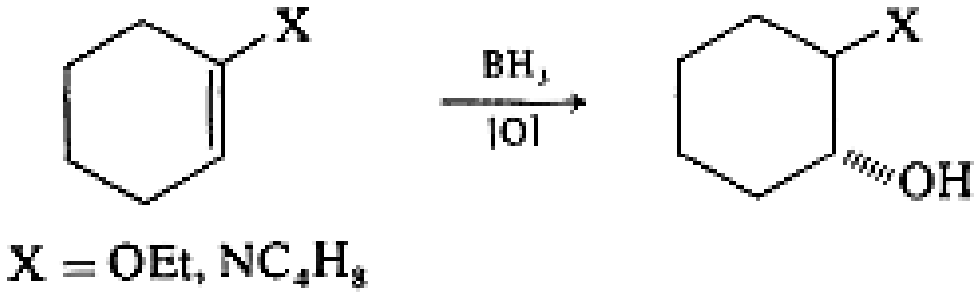




enol acetate




R = H, *t*-Bu

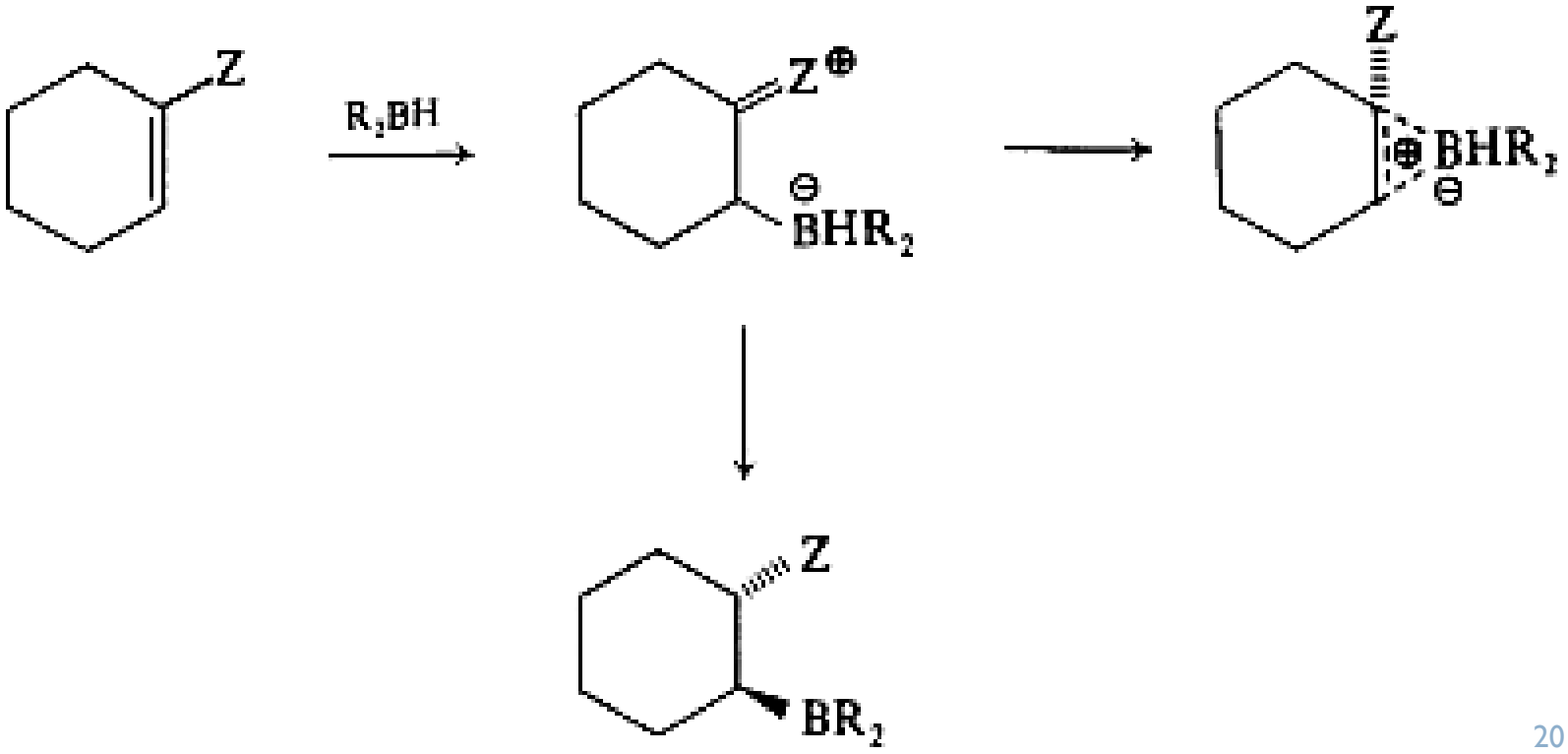
**However, enol ethers and enamines, regardless of the degree of substitution on the original double bond, give 1,2-disubstituted products.**




X = OEt, $NC_4H_8$

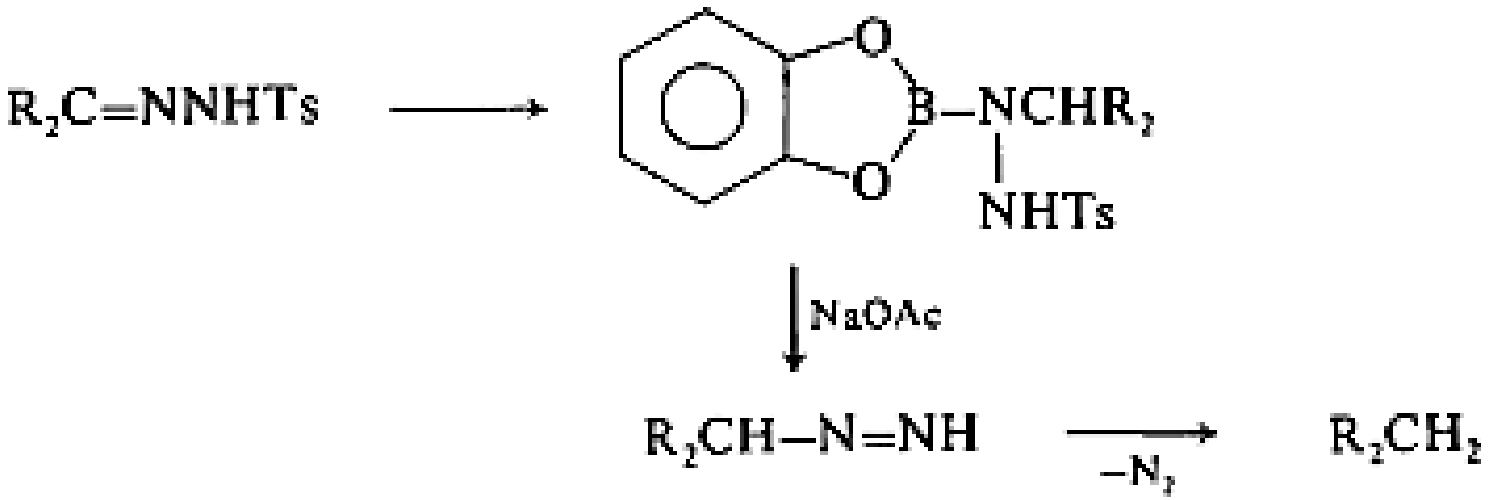
**The halogen and the acetoxy group infuse hardness in the ipso carbon, rendering it a better partner for the boron.**

**Although alkoxy [including intracyclic analogs such as 2,3-dihydrofuran and dihydropyran] and amino substituents should exert a similar inductive effect, this is swamped by the resonance inherent in these systems.**



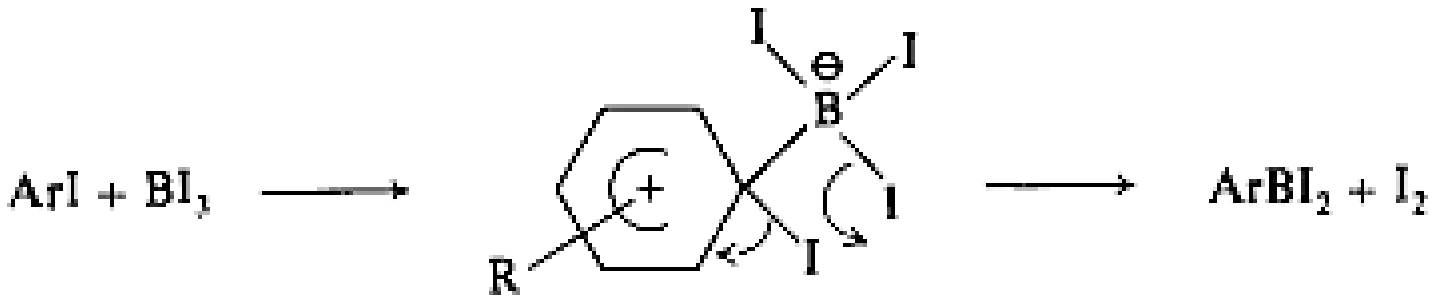
**Chloroborane ($C1BH_2$) is a more regioselective hydroborating agent than borane. This property can be attributed to the heightened hardness of the boron atom.**

**The reaction of organoboranes with carbon-nitrogen multiple bonds always leads to aminoborane derivatives through a hard-hard interaction.**

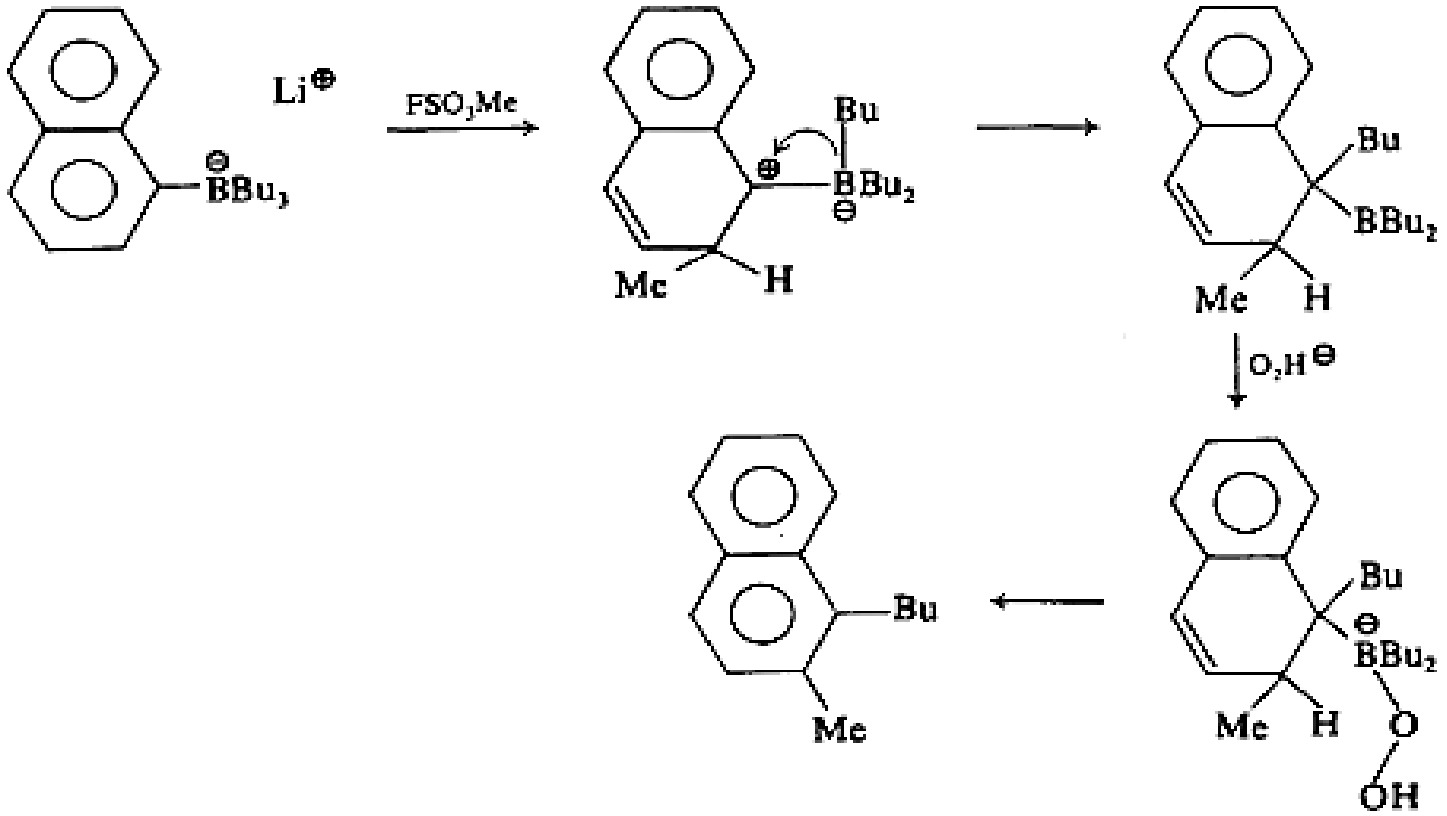


# REACTIONS OF ARYLBORON COMPOUNDS

**Arylboron compounds are susceptible to nucleophilic attack which often results in the cleavage of the $C_{Ar—B}$ bond. On the other hand, the introduction of a boron substituent into the aromatic ring may be performed by the interaction of aryl iodides with boron triiodide.**



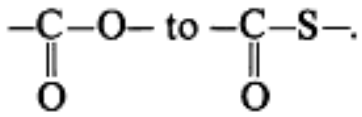
**Ortho-disubstitution of aromatics via aryltrialkylboranides has been studied. Reaction of the boranides with alkyl fluorosulfates affords dihydroarene derivatives which rearomatize on treatment with alkaline hydrogen peroxide. The hydroperoxyboranides may decompose in either of two ways according to the HSAB concept.**

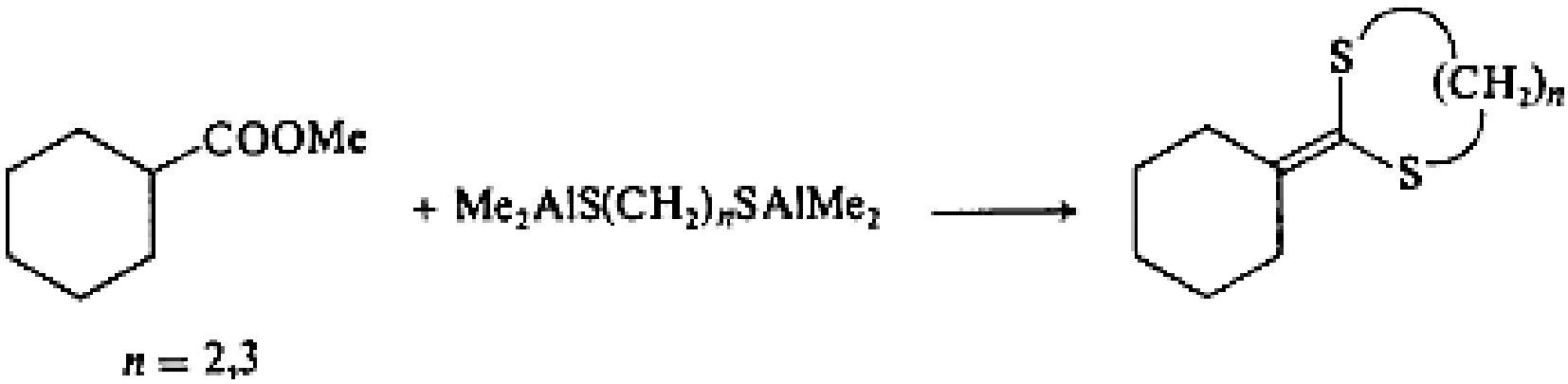


## SOME ASPECTS OF ORGANOALUMINUM REACTIONS

**Aluminum and boron display similar chemical characteristics. One important difference is that boron is a metalloid, whereas aluminum is a bonafide metal.**

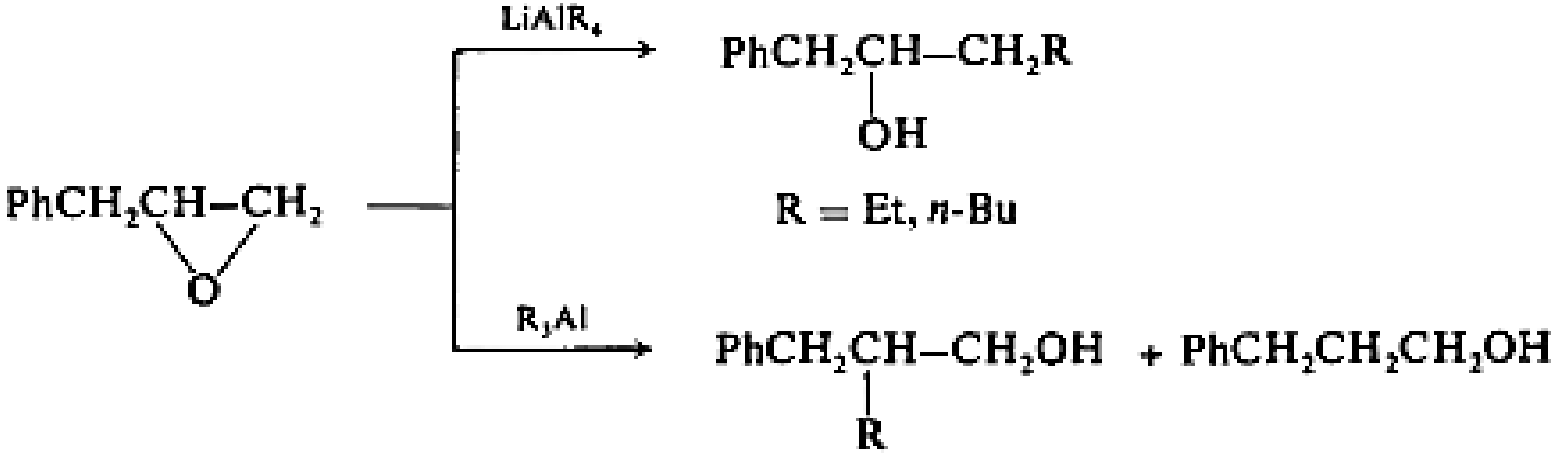
**As a consequence, the boron center shows soft or hard characteristics depending on the ligands it carries; the aluminum center is hard most of the time.**
**Thioesters are synthesized from methyl esters by treatment with alkylthiodimethylalanes.**

**Functional reagents transform esters and lactones into ketene thioacetals and dithio orthoesters, respectively. In these reactions, the alkoxide moiety attaches to the hard Al atom. That the carbonyl C is left to combine with a soft sulfide represents a compromise as the hard-hard Al-O interaction far outweighs the loss in stability resultant from the change of** 


$n = 2,3$

**Unsymmetrical epoxides are cleaved differently by lithium tetraalkylaluminate and trialkylaluminum. Alkyl transfer from the softer "ate“ complexes takes place at the softer (less substituted) carbon atom, whereas the harder $R_3A1$ reacts at the alternative position. It can also be shown that "ate“ complexes effect opening of epoxides with inversion of configuration, whereas $R_3A1$ gives alcohols in which the configurations are retained.**




| | | |
|---|---|---|
| R = *n*-Bu | 90% | 10% |
| R = Et | 80% | 20% |

**The conversion of epoxides to allylic alcohols can be accomplished by dialkylamide anions, but the treatment with N-diethylalanyl-2,2,6,6-tetramethylpiperidine is more efficient. A cyclic syn-elimination pathway is indicated. A perfect match of hard interactions is provided by such combinations.**