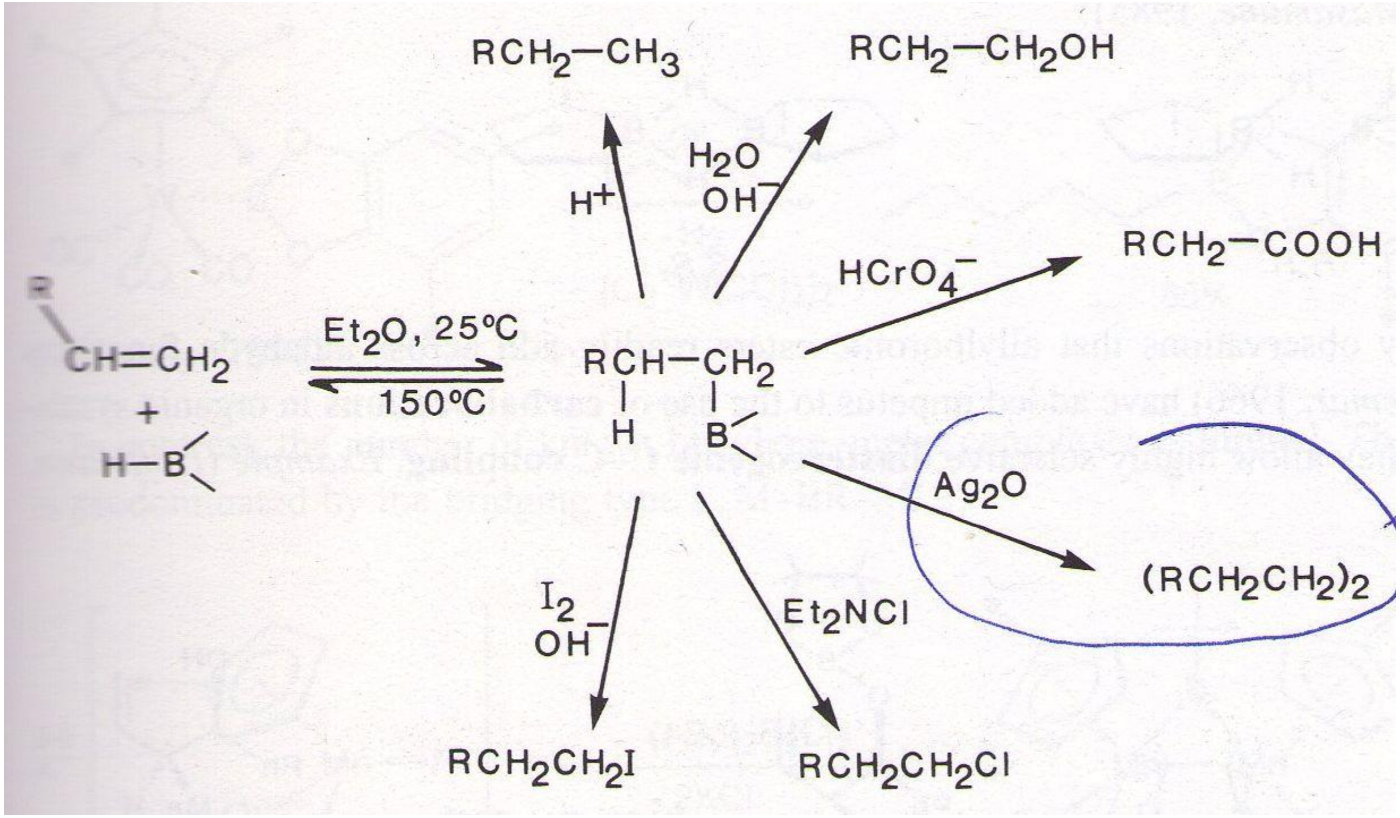
Applications of organoboron compounds

- Synthesis of organometallic compounds (metathesis):

$3HgO + 2BR_3 + 3H_2O \rightarrow 3HgR_2 + 2B(OH)_3$

- <u>Stoichiometric</u> reactions of hydroboration products:

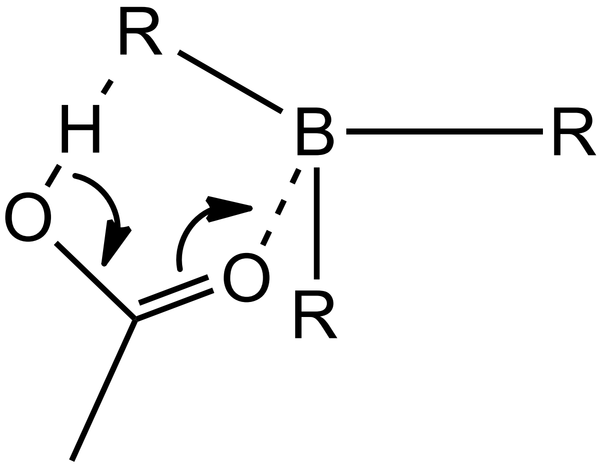


Reactions of hydroboration products

- Protodebororonation: reaction under stoichiometric control (stepwise increasingly difficult protonolysis):

BR_3 + 1 eq. **AcOH** → R-H + R_2BOAc

The reaction operates with retention of configuration at R.



Hydroboration – protodeboronation reaction sequences result in the **formal *cis*-hydrogenation** of double C-C bonds;

Reactions of hydroboration products

- Oxidation: possible with O_2 or with H_2O_2 under basic conditions.

In the first case the reaction is fast, but it often stops after oxidation of two organic residues:

$BR_3 + O_2\text{(exc.)} \rightarrow RB(OR)_2$

Furthermore, the mechanism is radicalic (loss of stereoselectivity):

$BR_3 + O_2 \rightarrow R\bullet + R_2B\text{-}O\text{-}O\bullet$

$R\bullet + O_2 \rightarrow R\text{-}O\text{-}O\bullet$

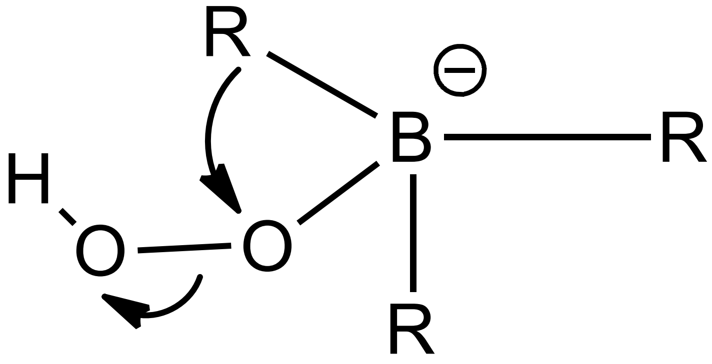
$R\text{-}O\text{-}O\bullet + BR_3 \rightarrow R_2B\text{-}O\text{-}O\text{-}R + R\bullet$

$R_2B\text{-}O\text{-}O\text{-}R \rightarrow RB(OR)_2$

Reactions of hydroboration products

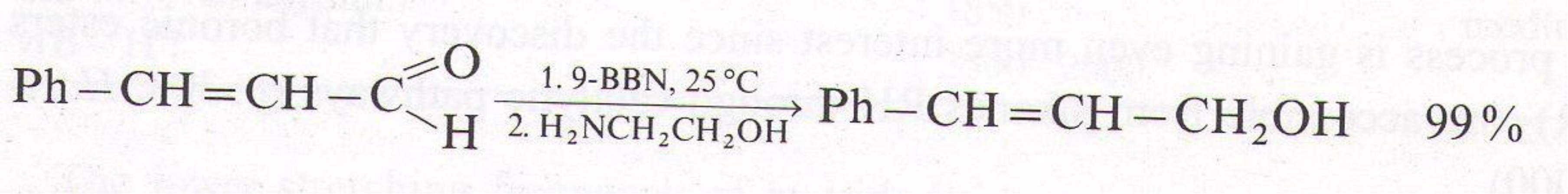
- <u>Oxidation</u>: possible with O_2 or with H_2O_2 under basic conditions.

In the second case, the mechanism is not radicalic, hence reaction with H_2O_2 under basic conditions affords <u>retention of configuration on R</u>, and combined with hydroboration results in a formal <u>*anti*-Markovnikov, *cis*-hydration of double C-C bonds</u>.



Organoboranes as reducing agents

In the presence of carbonyl groups conjugated to double C-C bonds, boranes act as selective reducing agents for the carbonyl:

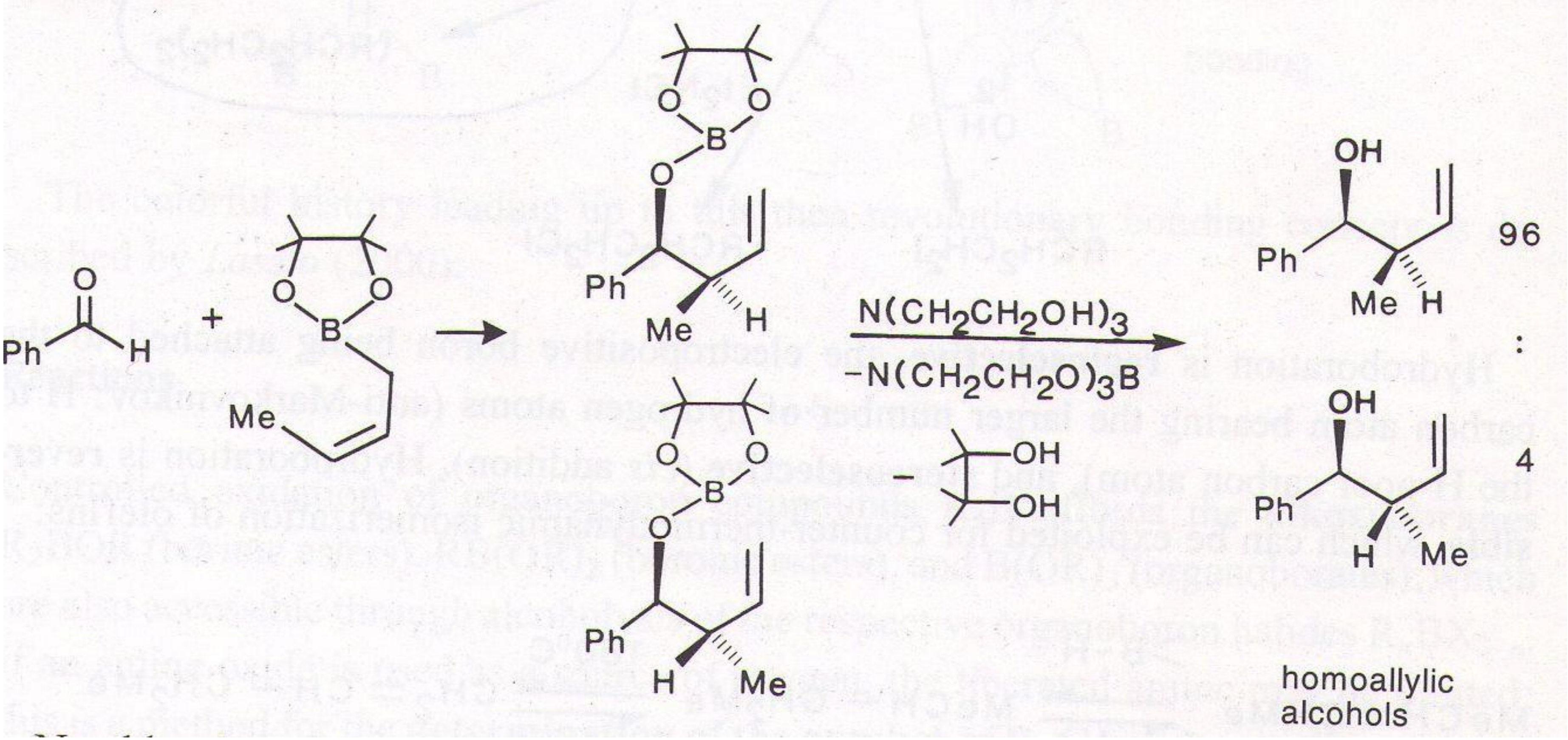


$$\mathrm{Ph{-}CH{=}CH{-}C}\!\begin{smallmatrix}{=}\mathrm{O}\\ \diagdown\mathrm{H}\end{smallmatrix} \xrightarrow[\text{2. } \mathrm{H_2NCH_2CH_2OH}]{\text{1. 9-BBN, 25 °C}} \mathrm{Ph{-}CH{=}CH{-}CH_2OH} \quad 99\,\%$$

Reactions are activated by precoordination of the reagent to B!

Stereoselective reactions with chiral boranes are possible.

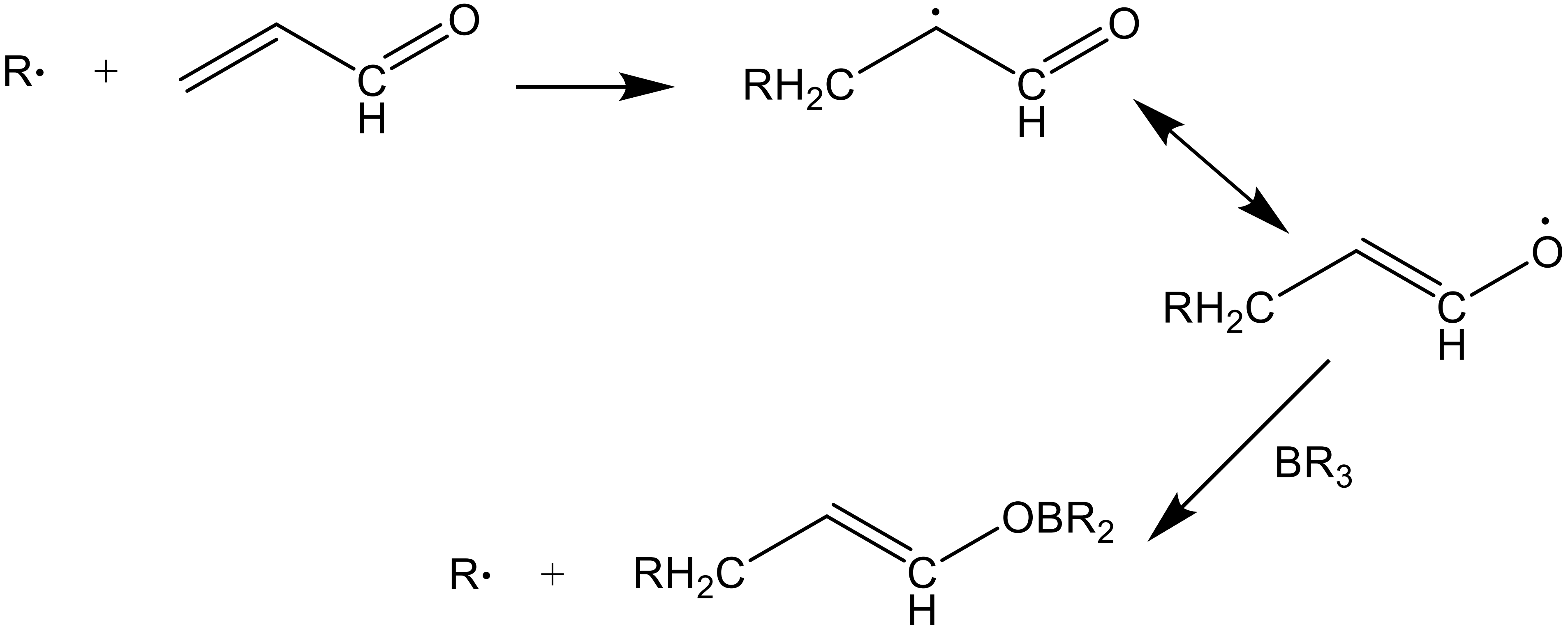
Carbaboration reactions



Radical mechanisms are also possible, in the presence of suitable initiators.

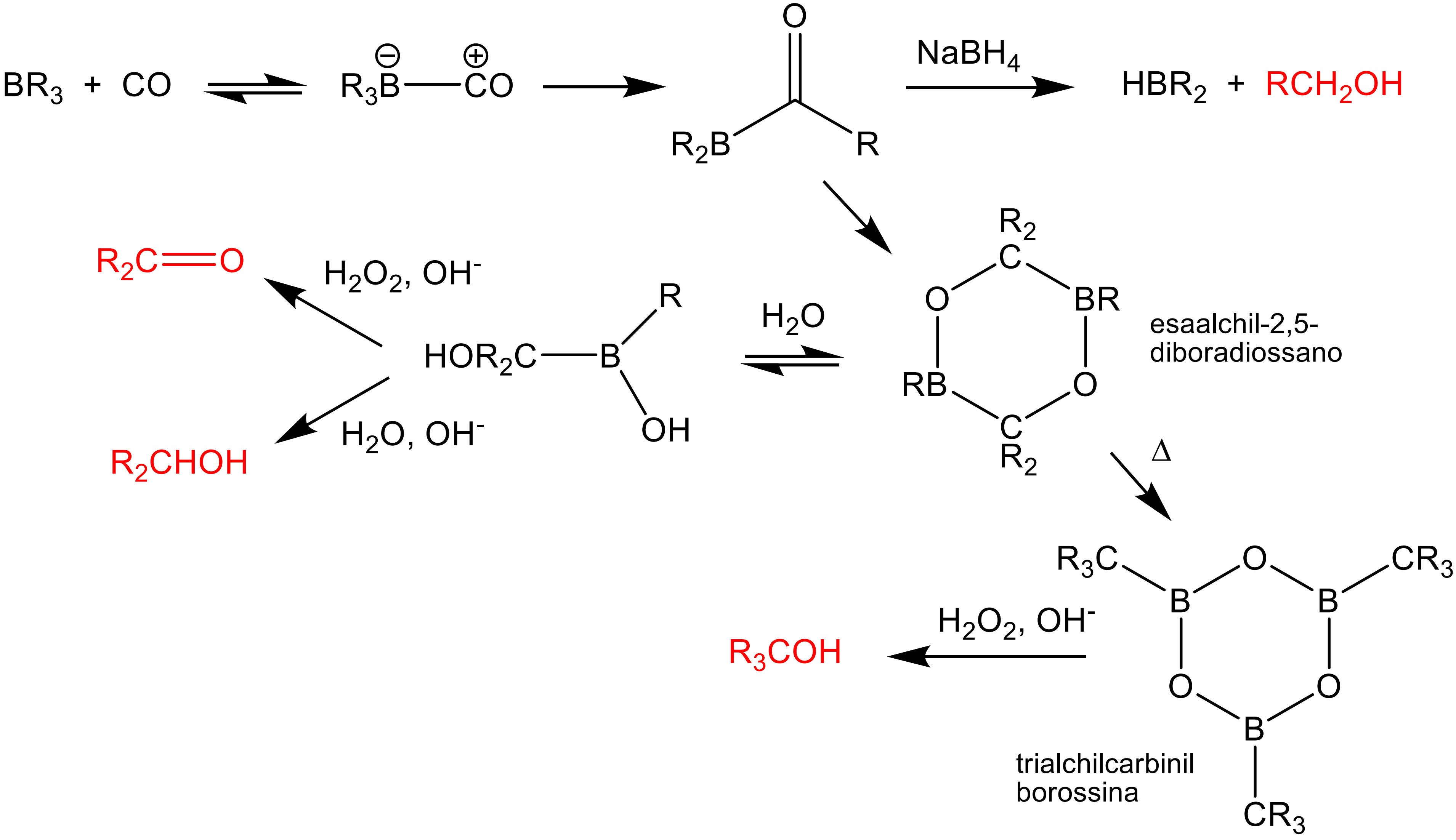
Carbaboration reactions (homologation)

$BR_3 + O_2 \rightarrow R\bullet + R_2B\text{-}O\text{-}O\bullet$



Formal 1,4-carbaboration of acroleine

Reaction of organoboron compounds with CO



Metal catalysed reactions with organoboranes

Numerous examples. The organoboron compound transfers the organic substituent to a transition metal center, which in turn transfers it to an organic substrate.

Very useful reactions, in particular with organic substituents such as aryls, heteroaryls, vinyls (more stable).

Most commonly employed organoboron compounds (all contain and transfer a single R):

R-B$(OH)_2$	organoboronic acids
R-B$(OR')_2$	organoboronic esters
R-BF_3K	organotrifluoroboronates (Molander reagents)

Why organoboron? Organoboron compounds are generally stable, inert towards air/moisture, non-toxic, available in great variety and (relatively) cheap.

Some examples of metal catalysed reactions

- Oxidative homocoupling:

$2RB(OH)_2 \rightarrow R\text{-}R$ cat.= many metals + oxidant (air)

- **Suzuki reaction (cross coupling)**:

$RB(OH)_2 + R'X' + B \rightarrow R\text{-}R' + XB(OH)_2$ cat.= [Pd], [Ni]

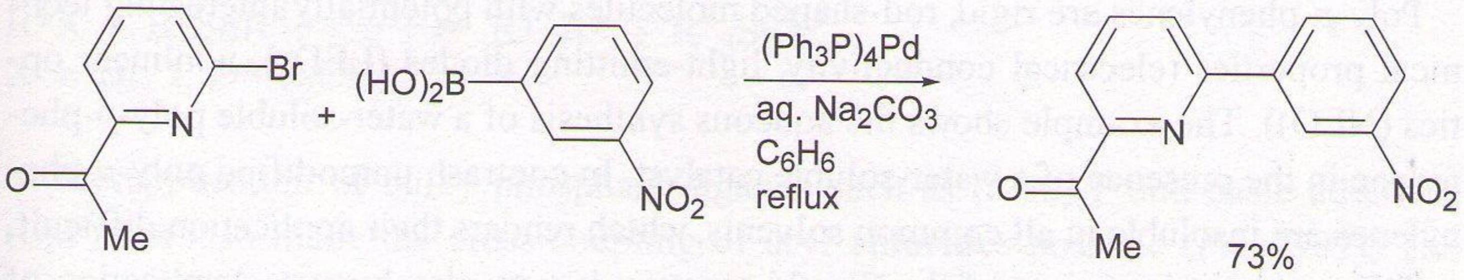
Efficient reaction (fast metathesis in the presence of base);
Very efficient for forming C-C bonds between unsaturated organic fragments.

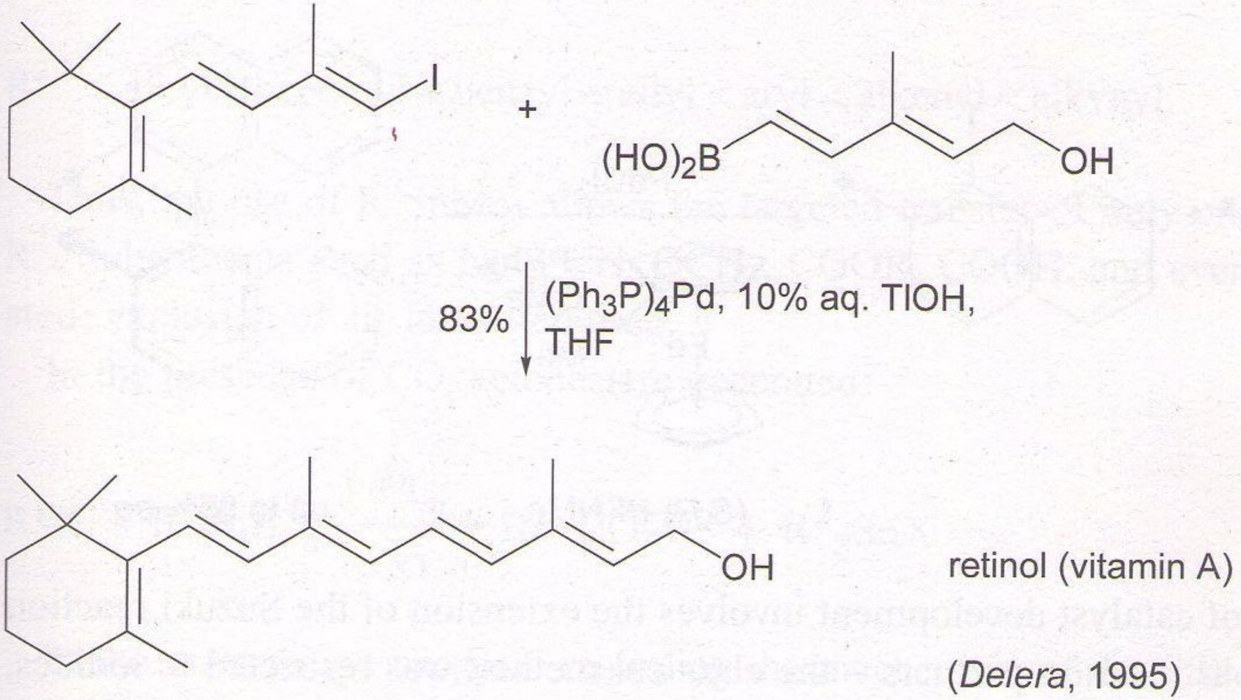
- Oxidative C-O or C-N coupling (Evans-Chan-Lam coupling):

$RB(OH)_2 + Ar\text{-}NH_2 \rightarrow Ar\text{-}NH\text{-}R$ cat.= $Cu(OAc)_2$ + air

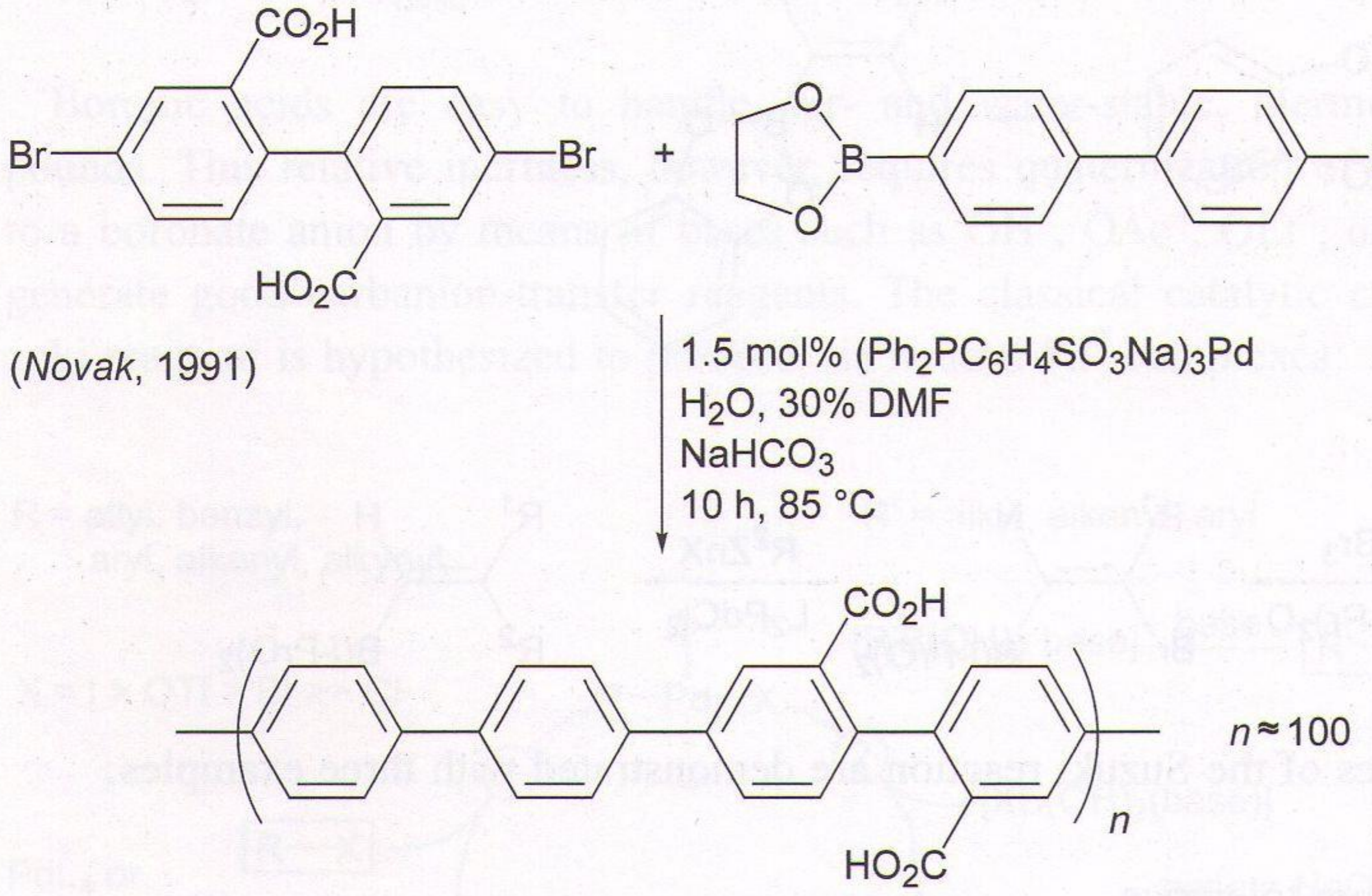
Can be run in water at room temperature….

Some examples of Suzuki reactions

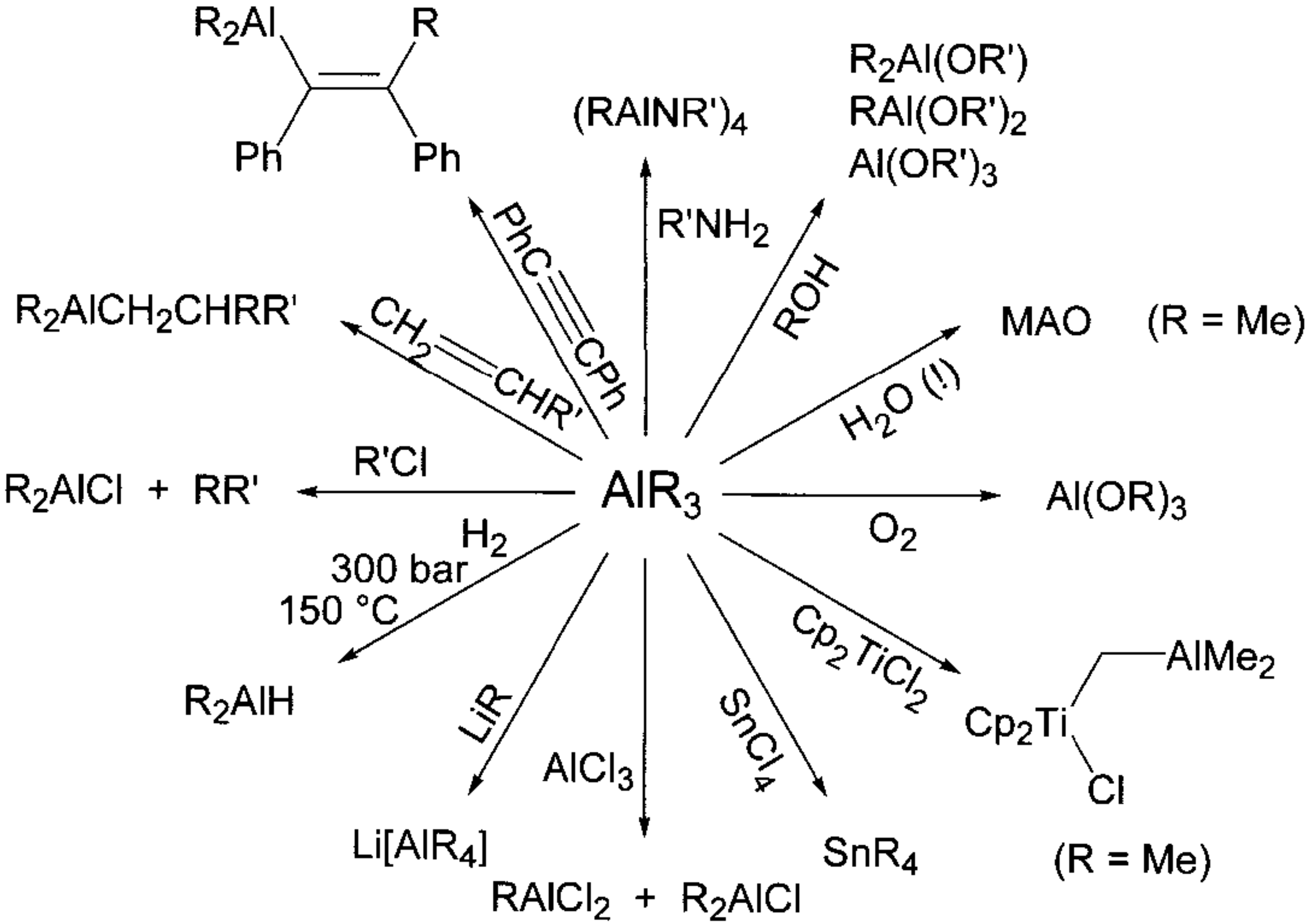




Some examples of Suzuki reactions



Applications in synthesis



Limited use as nucleophiles. Employed in the preparation of other organometallic compounds (metathesis) and as reagents/intermediates in hydroalumination/carboalumination.

Applications in synthesis
Hydroalumination/carboalumination

- Fast reactions, regioselective, stereoselective *cis*, easily reversible in the case of double bonds with more than one substituent;

- Branched AlR_3 are generally employed as hydroalumination reagents (dehydroalumination);

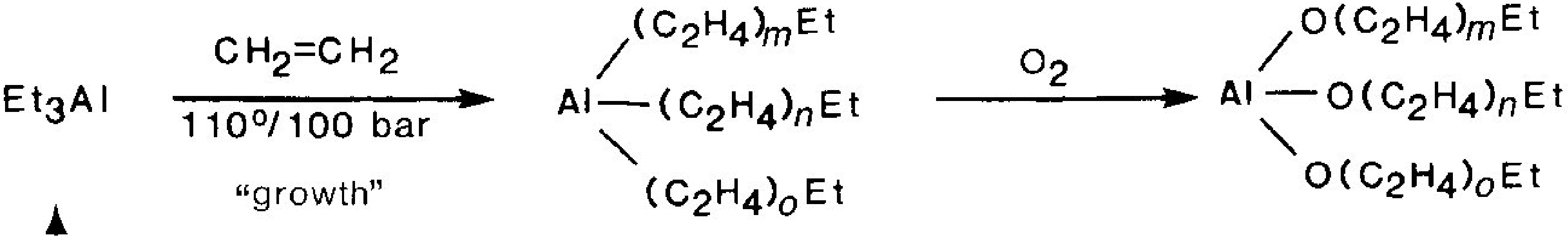
- The kinetic law often evidences an order 0.5 for the organometallic reagent (consequency of the dimerisation):

$$-d(substrate)/dt=k[substrate][AlR_3]^{1/2}$$

The reacting species is the monomer; consequently, monomeric or easily dissociable AlR_3 are more reactive (Et > Me);

- With ethylene, polymeric chains can be formed; with terminal olefins only dimerisation occurs.

Synthesis of long-chain alcohols

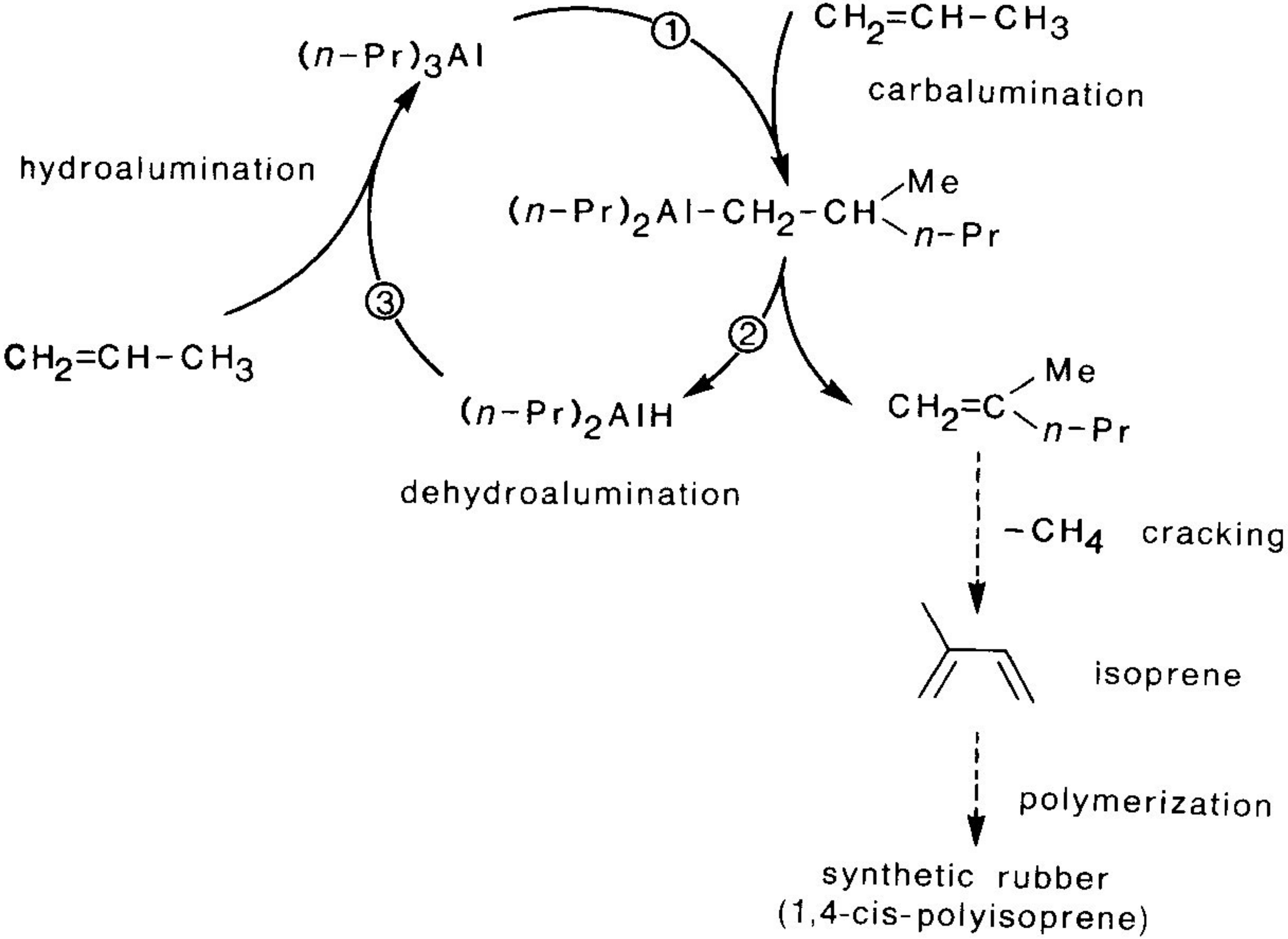


The growth of the chains can be interrupted by dehydroalumination, hydrogenation, solvolysis (H replaces Al) or **oxidation**.

The reaction mechanism of oxidation with O_2 is radicalic, analogous to the one operative with B. In this case, though, complete oxidation of all organic groups on Al is more facile.

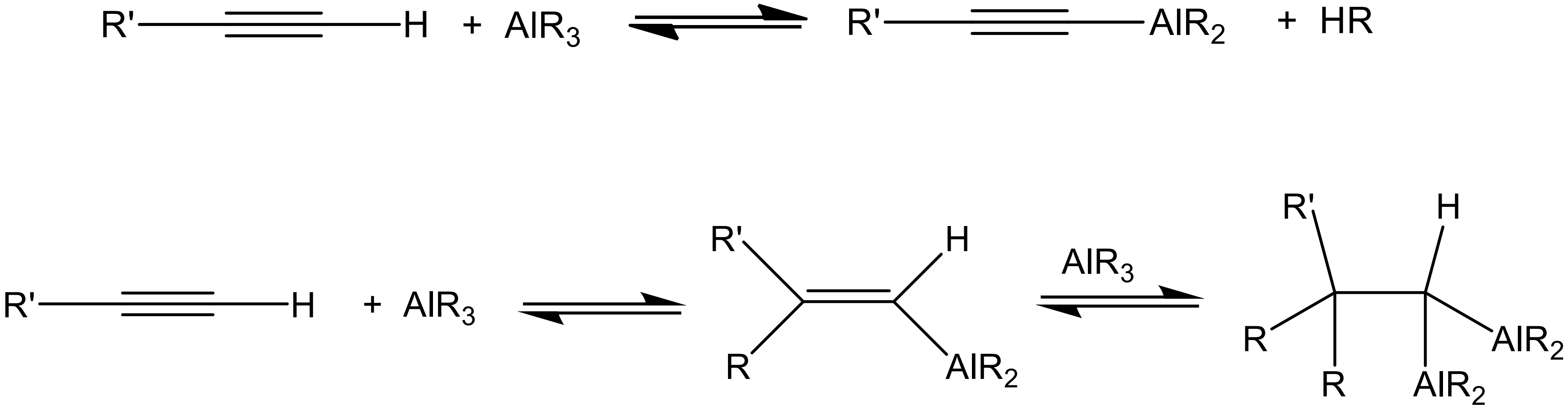
Subsequent hydrolysis furnishes linear alcohols with even or odd numbers of C atoms for use in detergents manufacture.

Goodyear SD process



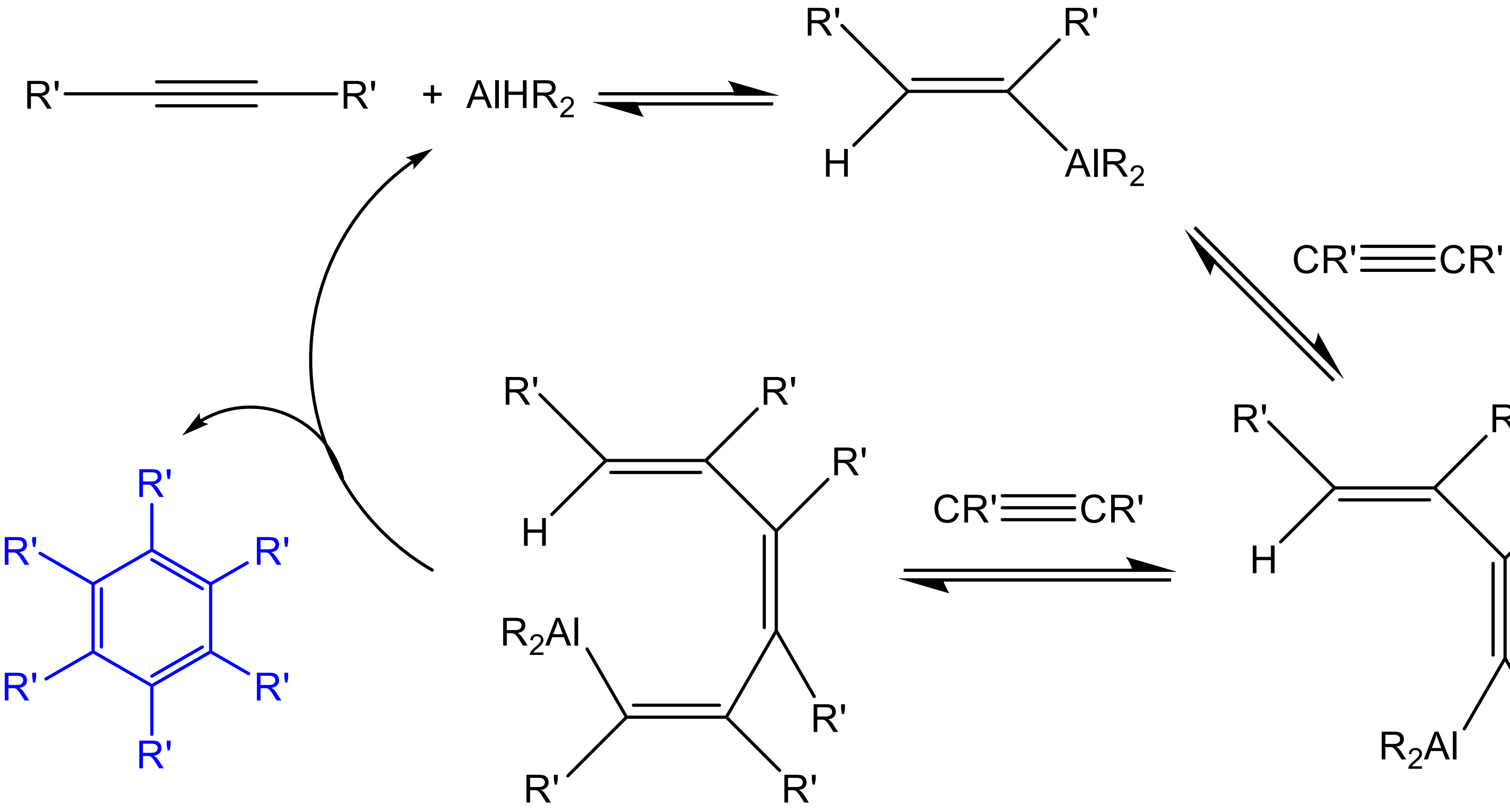
Hydroalumination/carboalumination with alkynes

- Fast reactions, regioselective (with terminal alkynes), stereoselective *cis*. Competition with metallation. With excess AlR_3, the formed vinylaluminum compound can undergo a second addition reaction:



Alkyne ciclotrimerization

With excess alkyne, the carboalumination reaction can yield cyclotrimerisation products (useful with internal, symmetric alkynes).



AlR_3 as polymerisation initiators

In classic Ziegler-Natta polmerisation (with Ti(IV) salts) the triorganoaluminum:

1) Reduces Ti(IV) to Ti(III);
2) Trasfers a residue R on Ti (metathesis);
3) Forms species with a free coordination site on Ti.

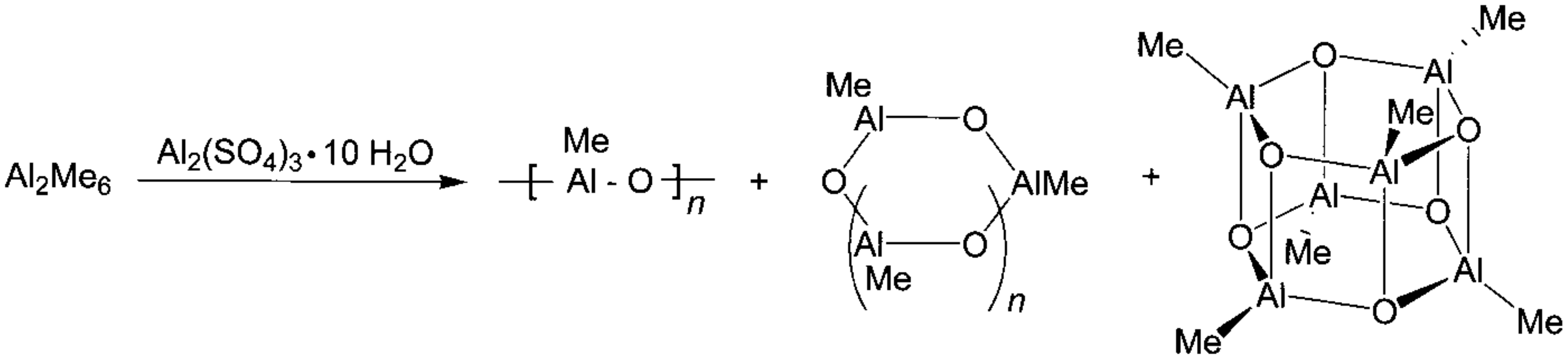
NB The catalyst is heterogeneous!

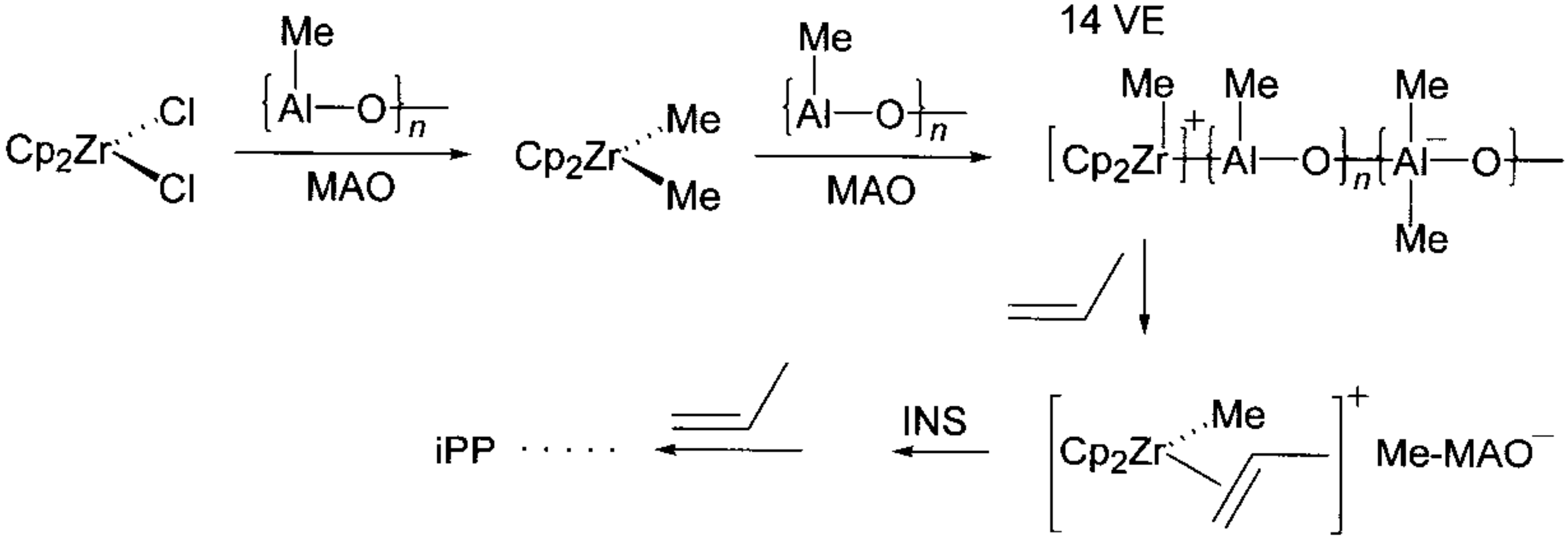
In metal catalysed, single-site polymerisations (i.e. on well defined complexes as homogeneous catalysts) the triorganoaluminum:

1) Transfers a residue R on M (metathesis)
2) Renders the complex cationic upon removal of X^-

Concerning the second point, much more efficient than simple organoaluminum compounds is the so called **methylaluminoxane (MAO)**:

Methylaluminoxane (MAO)





Applications of borates

BPh_4^-: is employed for the selective precipitation of K^+ in the presence of Na^+; its salts with monovalent cations, apart the smallest ones (Li^+, Na^+) are all sparingly soluble in water or protic solvents.

$B(C_6F_5)_4^-$: together with similar anions of formula $RB(C_6F_5)_3^-$ or $B(3,5\text{-bis-trifluoromethylphenil})_4^-$ (BArF) form a family of bulky, very poorly coordinating anions, often employed e.g. as counteranions of transition metal complexes in the catalytic polymerisation of olefins.