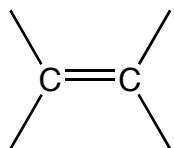
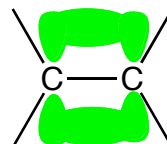


# Alkenes

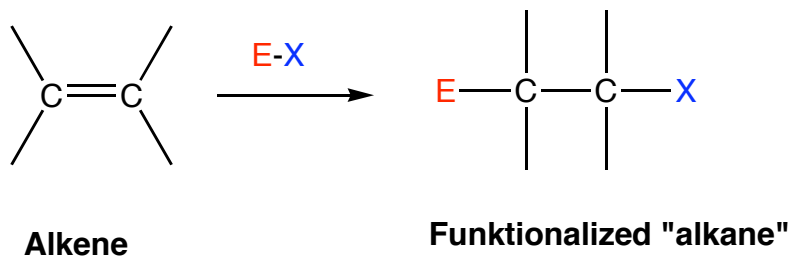


Double bond:  $\pi$  and  $\sigma$

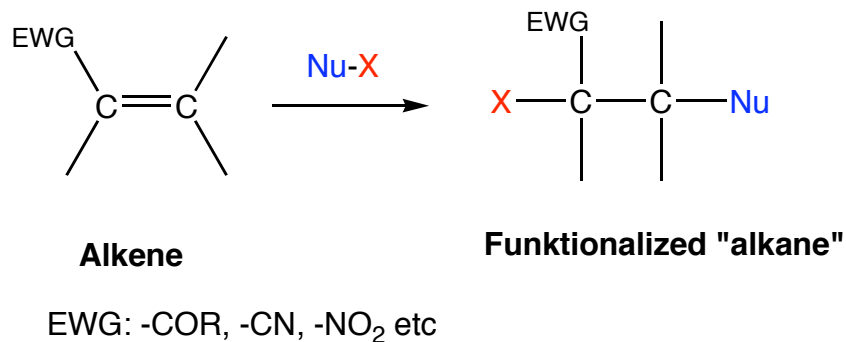


$sp^2$  C  
 $120^\circ$

**Electrophilic** addition to alkenes

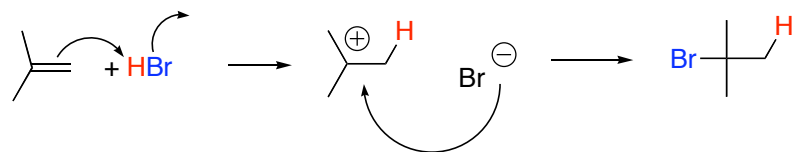


**Nucleophilic** addition to alkenes  
(chapt. 23)



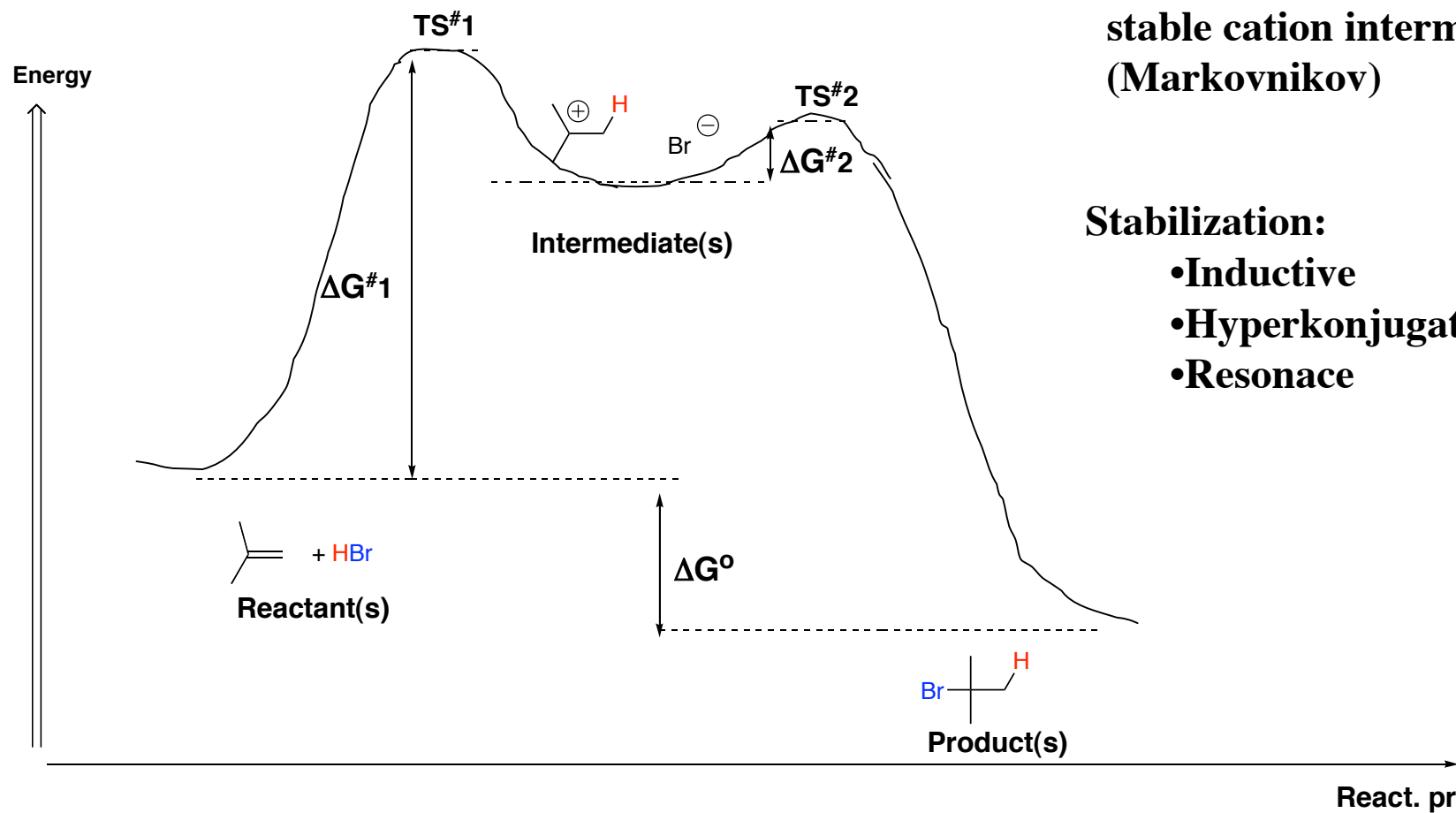
**Radical react.**  
**(Polymerization etc, Chapt 7.10)**

**Conjugate add., 1,4-add., Michael add.**



**1. step. rate limiting**

**Regiosel.: Formation of the most stable cation intermediate (Markovnikov)**

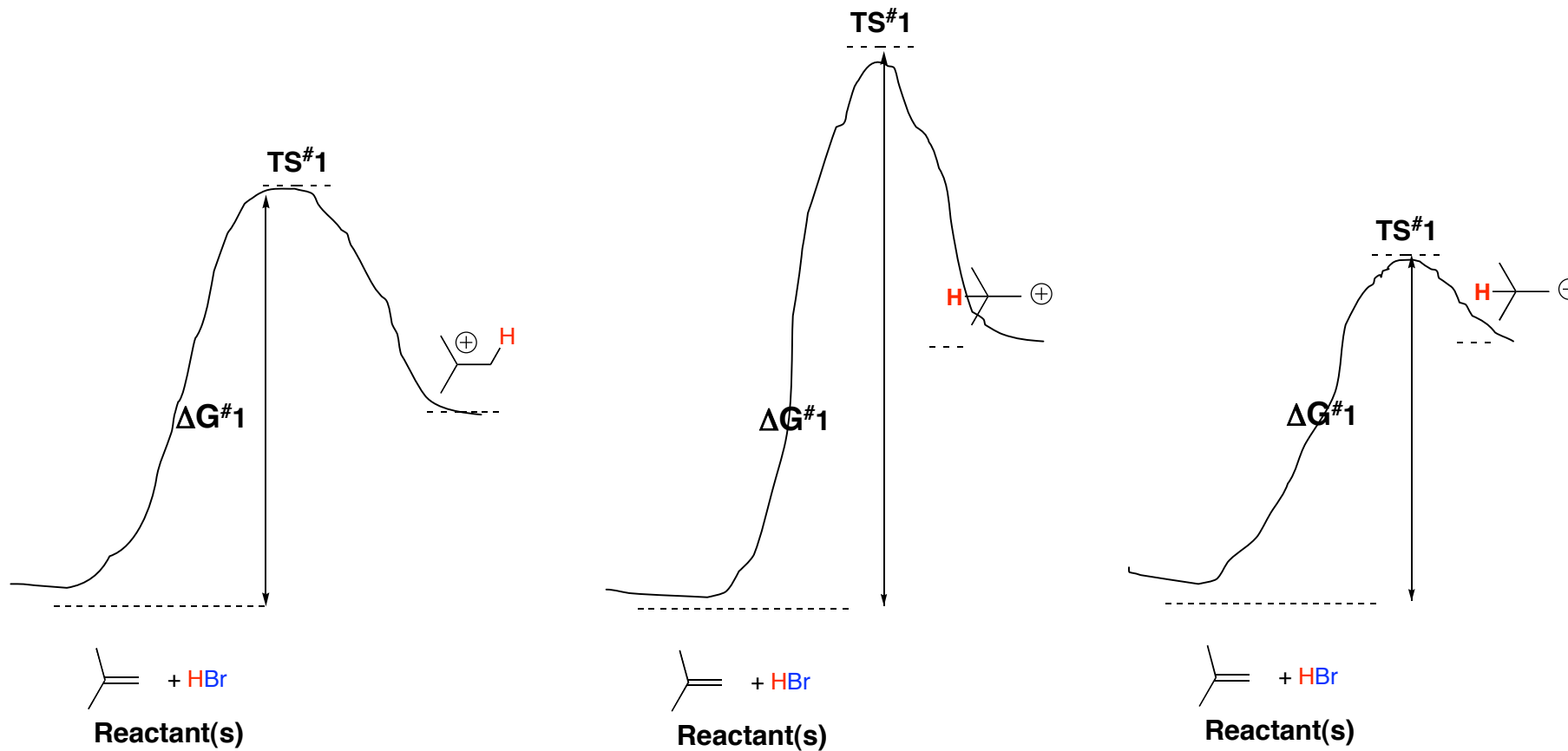
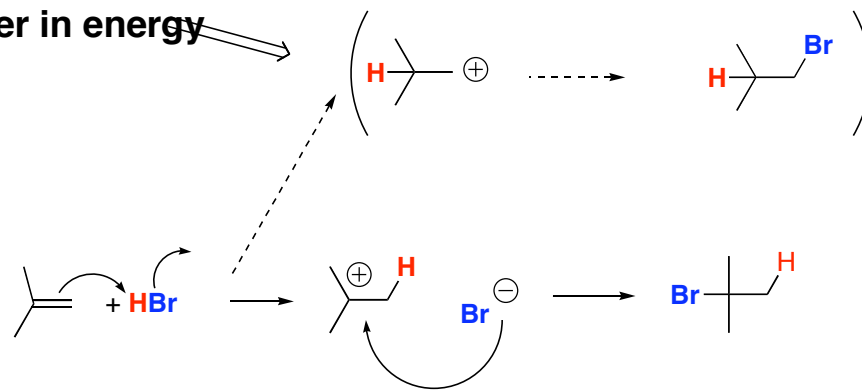


**Stabilization:**

- Inductive
- Hyperkonjugation
- Resonance

# Energy of TS#1 or intermediate ?

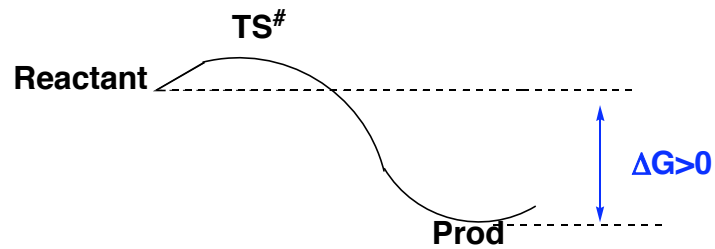
Intermediate  
higher in energy



# The Hammond Postulate

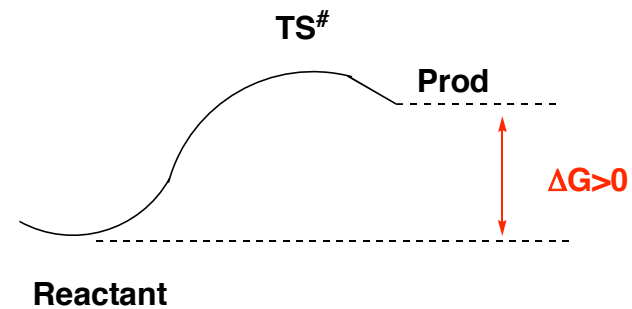
The structure of the  $TS^\ddagger$  resembles the structure of the nearest (in energy) stable species  
(Stable specie = reactant or product / intermediate)

Reactant like  $TS^\ddagger$

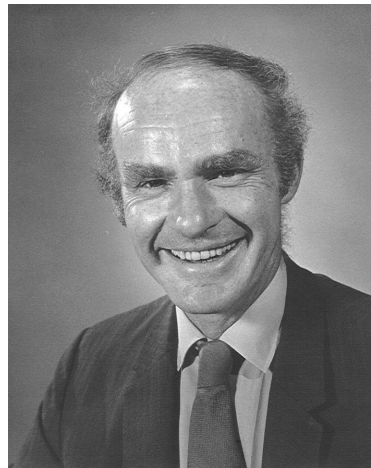


Exergonic step

Product like  $TS^\ddagger$

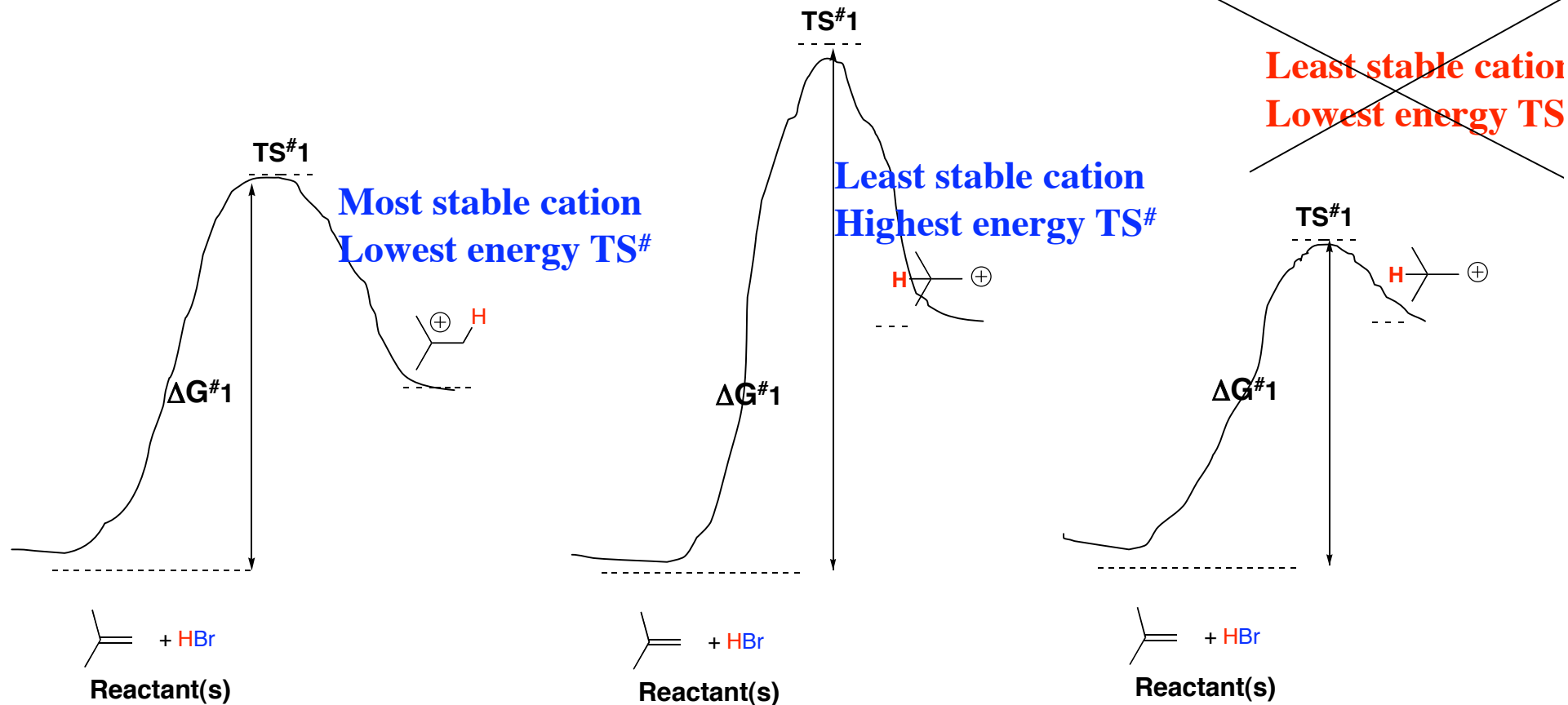


Endergonic step

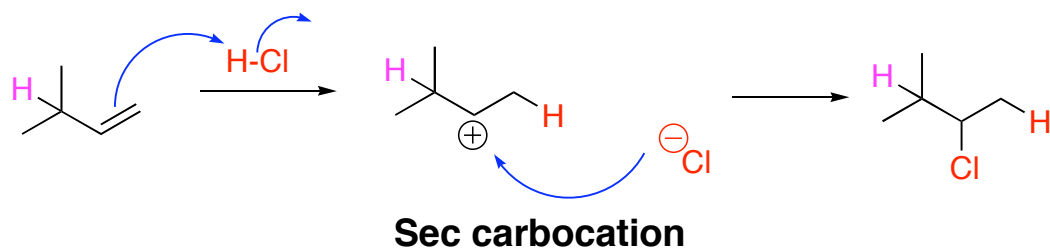


# The Hammond Postulate

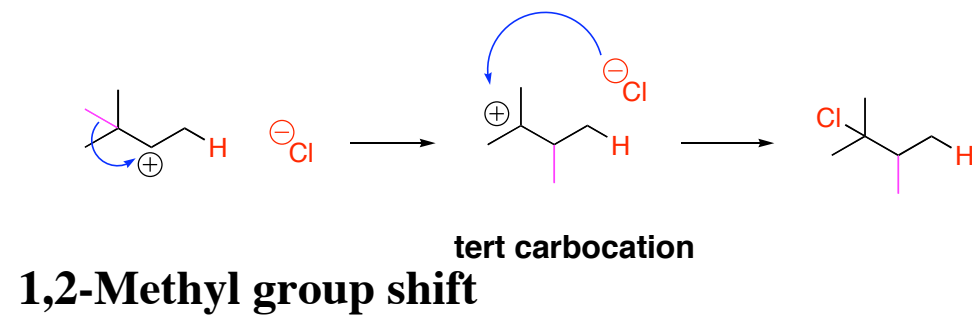
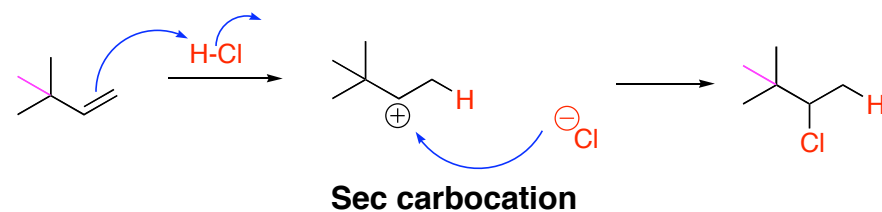
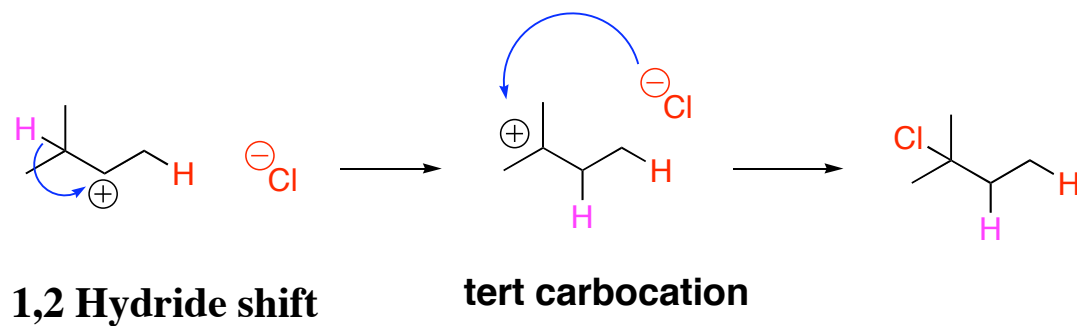
Endergonic react. TS<sup>#</sup> resembles cationic intermed.



# Cation Rearrangement

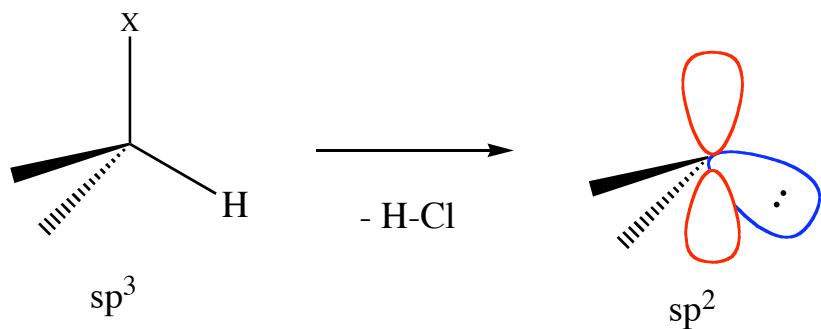
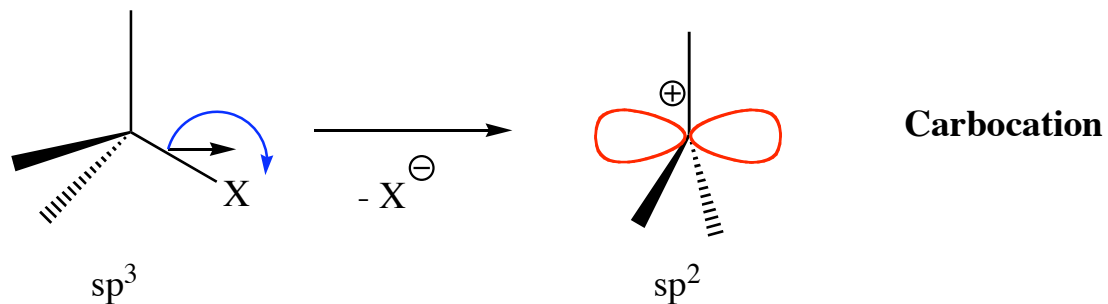
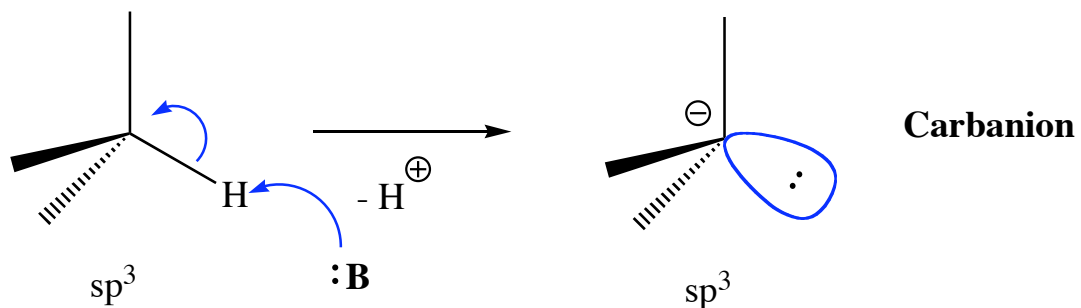


- Hydride shift
- Alkyl shift



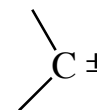
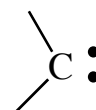
# Carbenes

McM chapt 7.6, lab ex. 7



**Carbene**

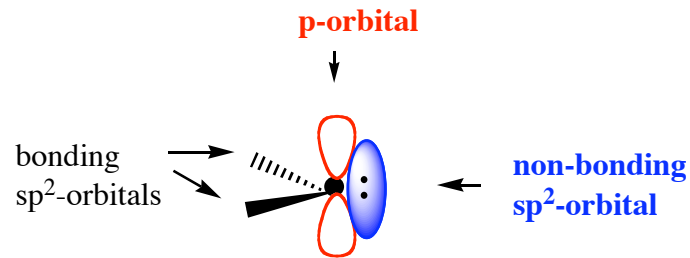
**Neutral  
Divalent**



**6 valence electrons - Highly reactive  $t_{1/2} < 1$  s**

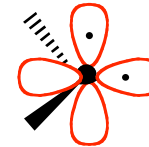
**Electron deficient /electrophilic properties**

### singlet carbene



electron pair, opposite spin  
cation / anion properties

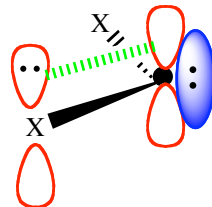
### triplet carbene



2 half-filled p-orbitals  
electrons with parallel spin

diradical properties  
Gives triplet signal in esr spektrum

Triplet normally somewhat more stable than singlet  
Singlets more reactive

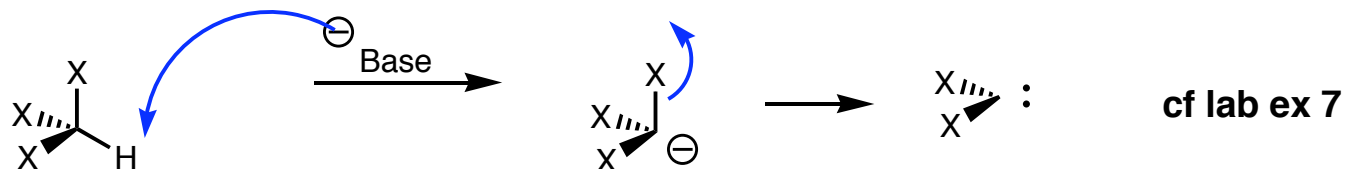


dihalocarbene  
Stabilizing overlap  
in singlet state

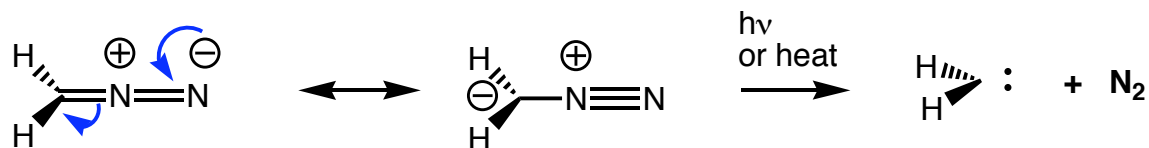


# Carbenes and carbenoids in synthesis

## Generation of carbenes



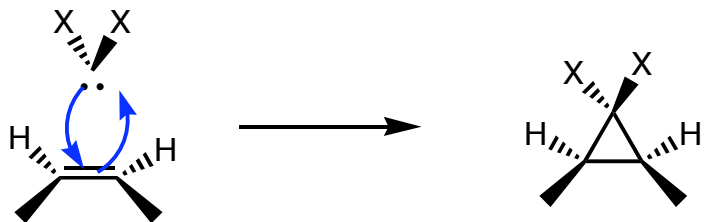
## Not in McM



**Diazomethane**  
(toxic, explosive)

(From Hg-species)

## Reaction with alkenes - Synth. of cyclopropanes

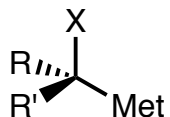


- One-step - Concerted (see also Chapt 30)
- Stereospecific

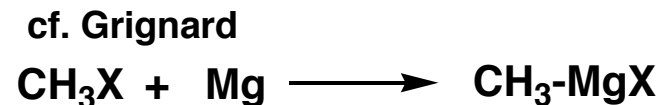
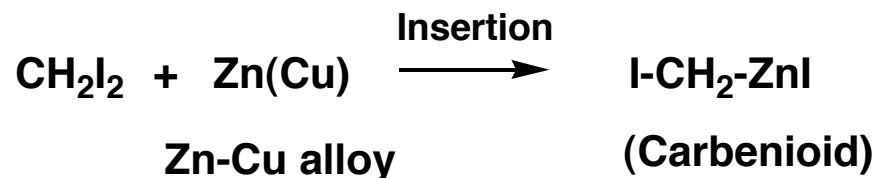
## Carbenoids

Carbenoid  $\approx$  carbene.

Free carbene (probably) not formed, species reacts  $\approx$  carbene

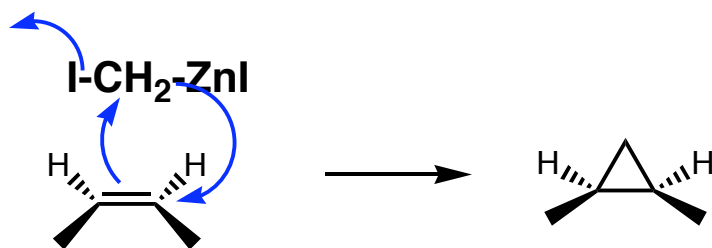


# Carbenoids - Simmons Smith reaction



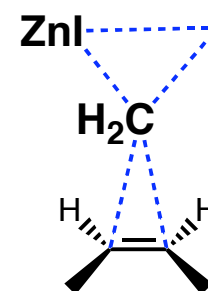
## Other methods

reactants	active reagent
$\Rightarrow$ Et <sub>2</sub> Zn, CH <sub>2</sub> I <sub>2</sub>	EtZnCH <sub>2</sub> I or Zn(CH <sub>2</sub> I) <sub>2</sub>
EtZnI, CH <sub>2</sub> I <sub>2</sub>	I <sub>2</sub> ZnCH <sub>2</sub> I
TFA, Et <sub>2</sub> Zn, CH <sub>2</sub> I <sub>2</sub>	CF <sub>3</sub> COOZnCH <sub>2</sub> I
Sm(Hg), CH <sub>2</sub> I <sub>2</sub>	ISmCH <sub>2</sub> I
R <sub>3</sub> Al, CH <sub>2</sub> I <sub>2</sub>	R <sub>2</sub> AlCH <sub>2</sub> I
ZnX <sub>2</sub> , CH <sub>2</sub> N <sub>2</sub>	Zn(CH <sub>2</sub> I) <sub>2</sub>

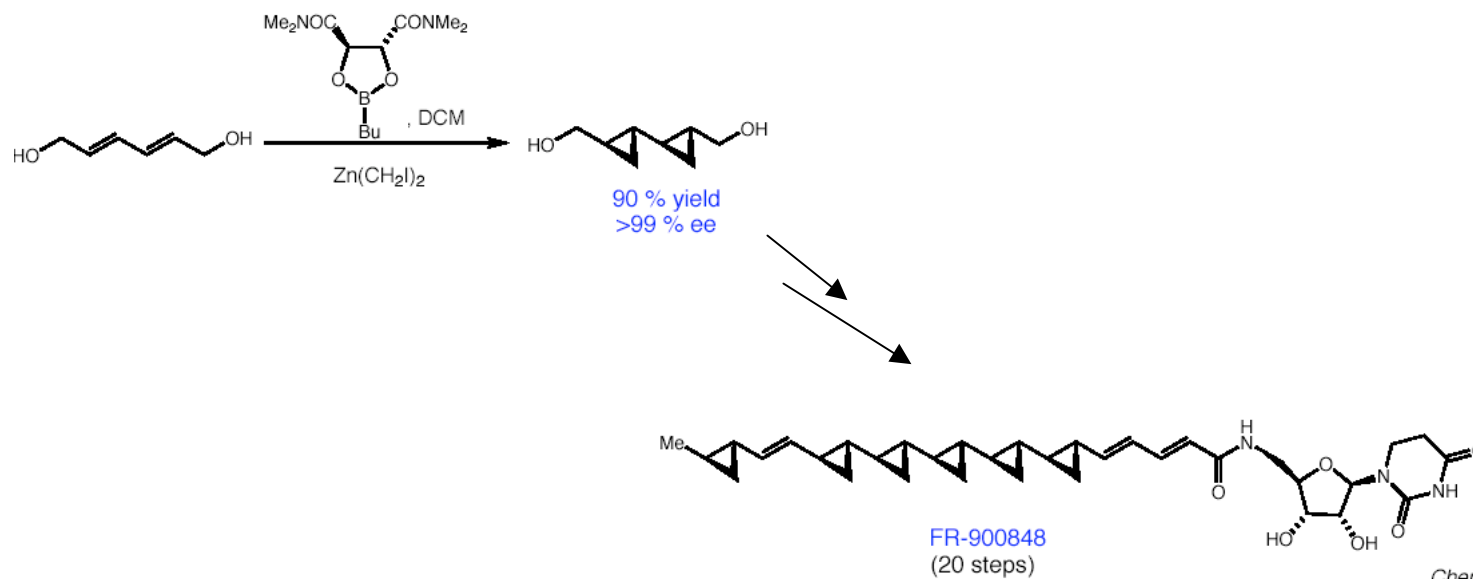


- **One-step - Concerted** (see also Chapt 30)
- **Stereospecific**

TS# ?

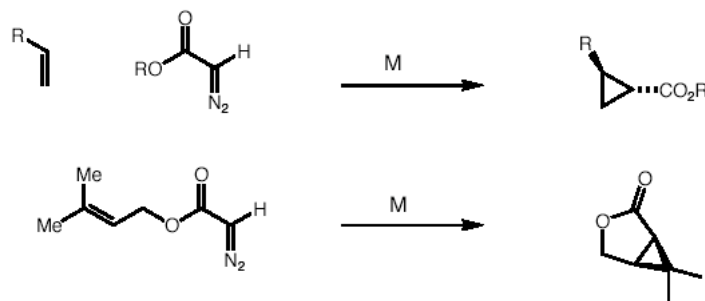


# Enantioselective Simmons Smith Allylic alcohols (Chiral auxiliary or catalyst)



*Chem. Comm.* **1997**, 1693

## Other carbenoids

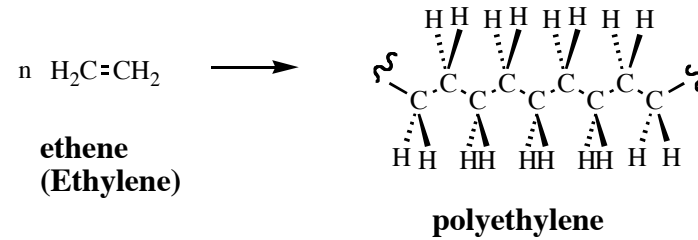


metal carbenoids  
(M = Rh, Pd, Cu...)

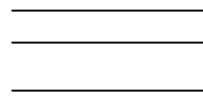
# Polymerization of alkenes (McM 7.10)

## Polymers - Synthetic macromolecules


- Radical polymerization
- Cationic polymerization



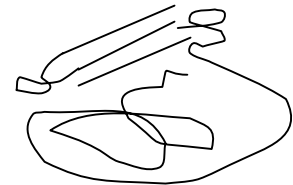
## Conformation of polymer - Properties



linear polymer  
crystalline solid



Amorphous solid



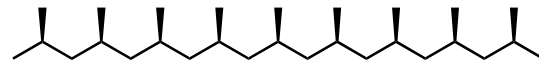
Both linear and amorph areas

hardness - drawn to fibers

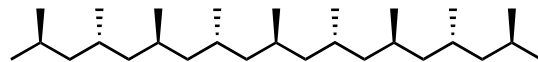
elasticity

# stereochemistry

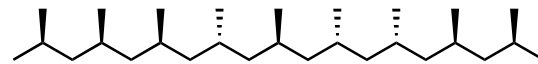
## Polypropylene



**isotactic**



**syndiotactic**

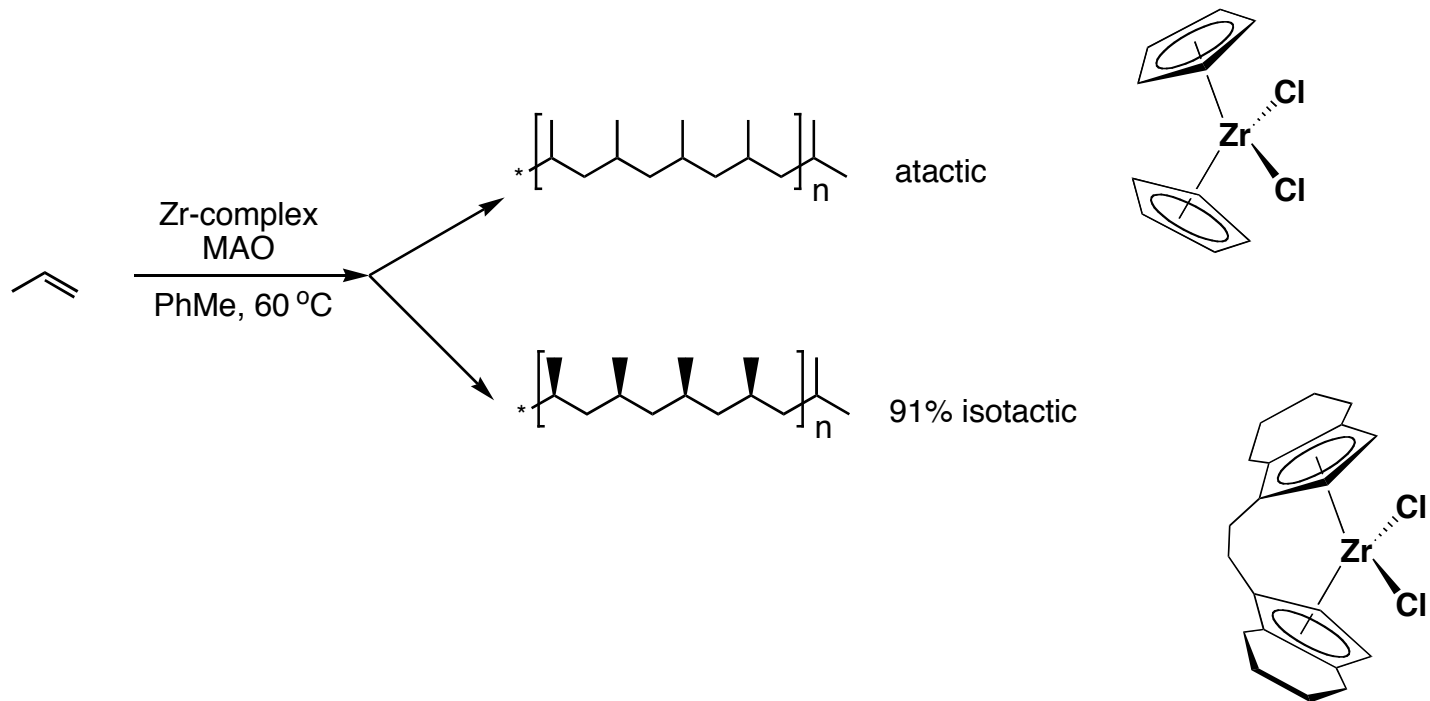


**atactic (random)**

} **more crystalline / harder**

## Chiral zirconocene derivatives

### • Stereoselective polymerisation of alkenes

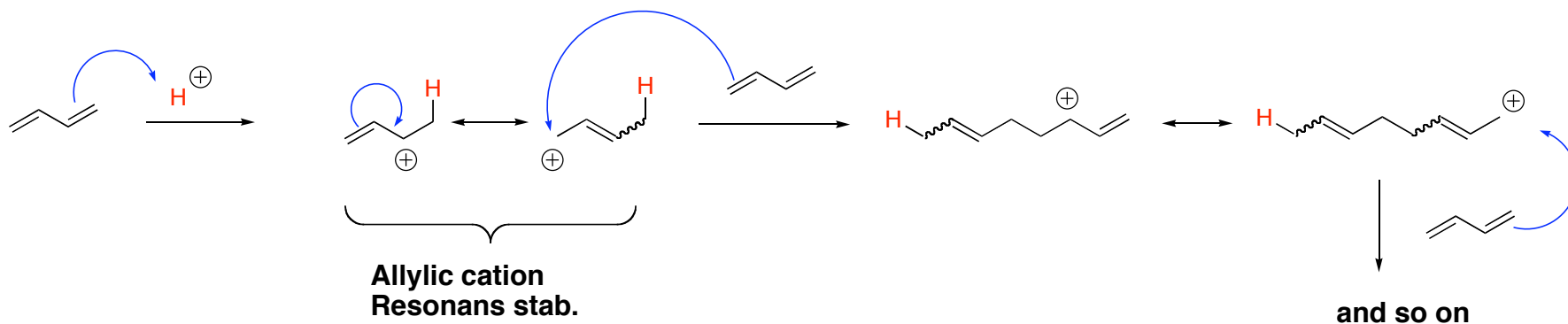


# Polymerization of dienes (McM 14.7)

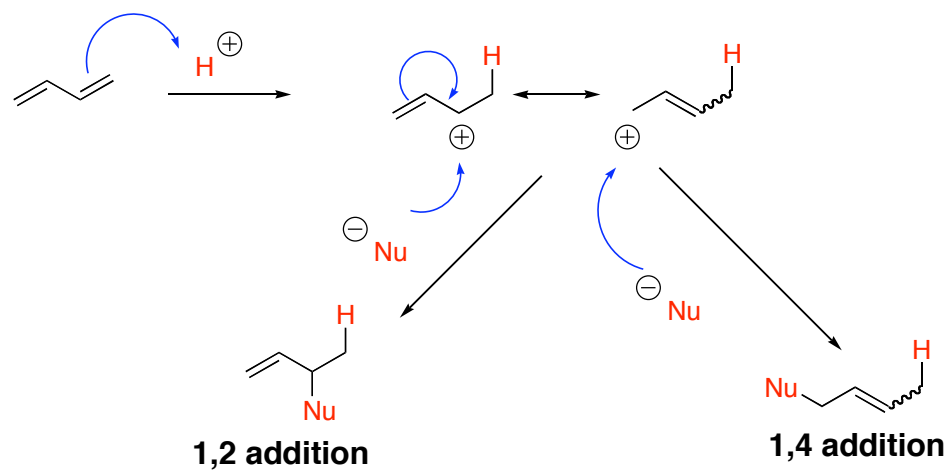
Natural and synthetic rubber

- Radical polymerization
- Cationic polymerization

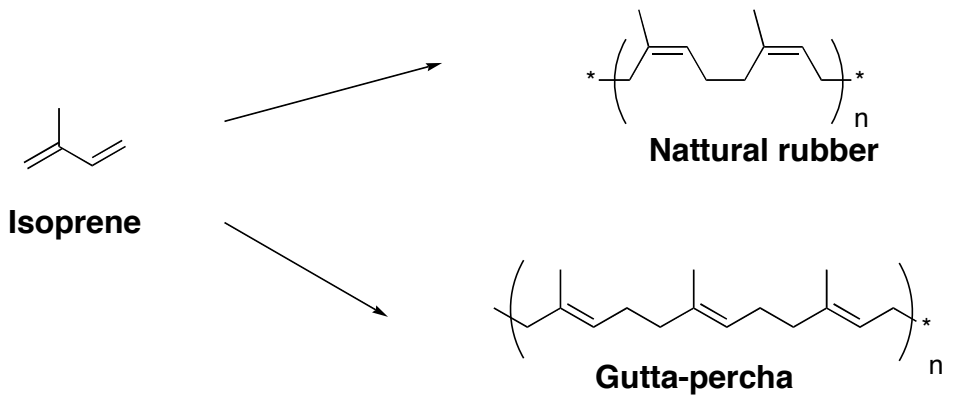
## Acid cat polymerization of 1,3-butadiene



## 1,4-addition







Hevea brasiliensis,  
 tropical Americas.  
 Cautchuc



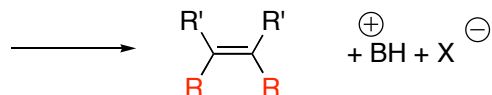
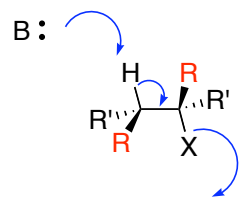
resin from the Isonandra Gutta tree (South east Asia)



**Less elastic than nat. rubber**  
**Isolation under-water cables**  
**Little use today**

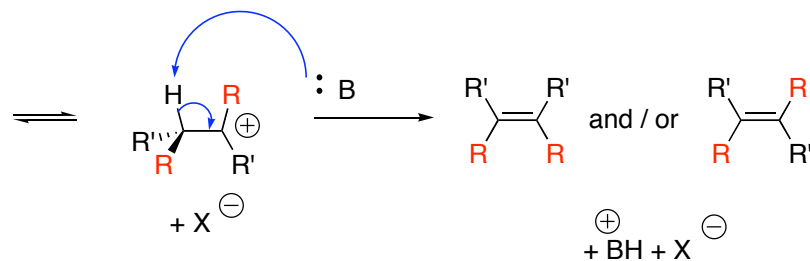
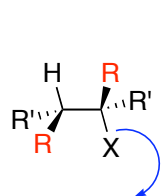
# Elimination reactions - Repetition

## E2: mechanism



- One step
- 2. order
- Stereospecific

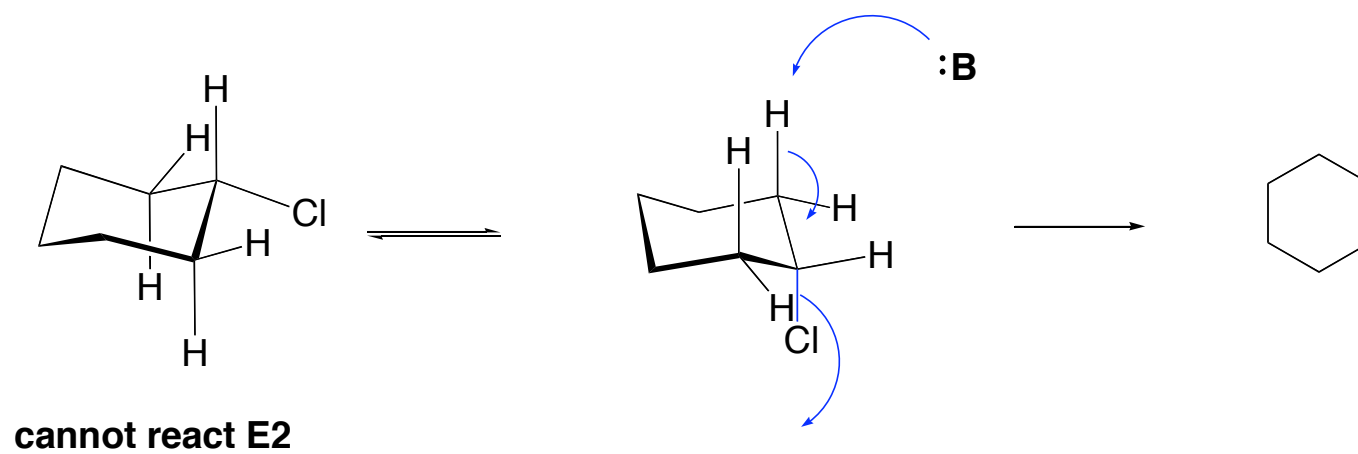
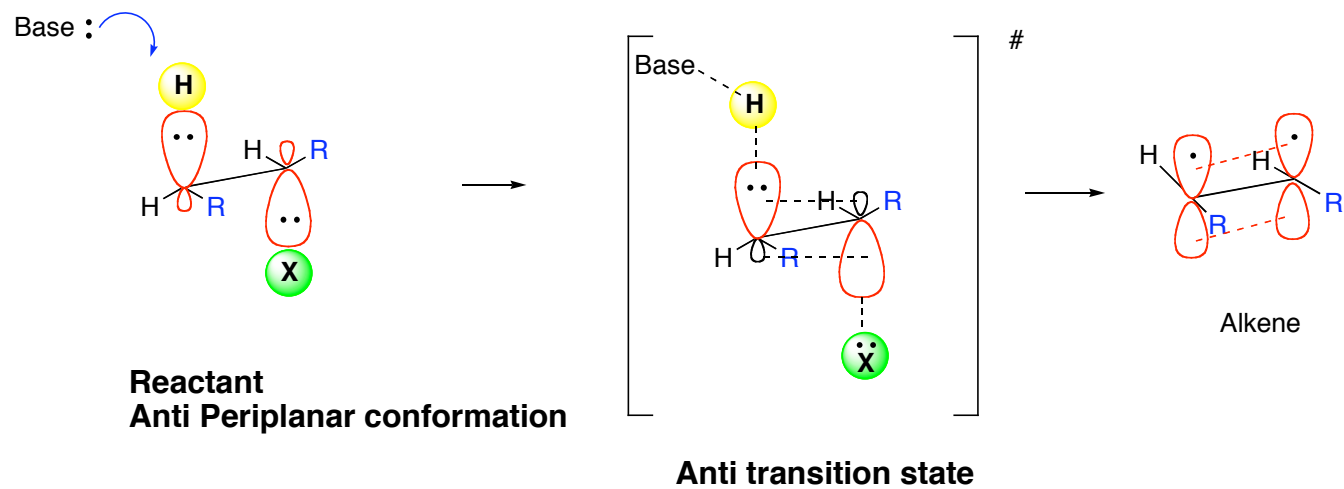
## E1: mechanism

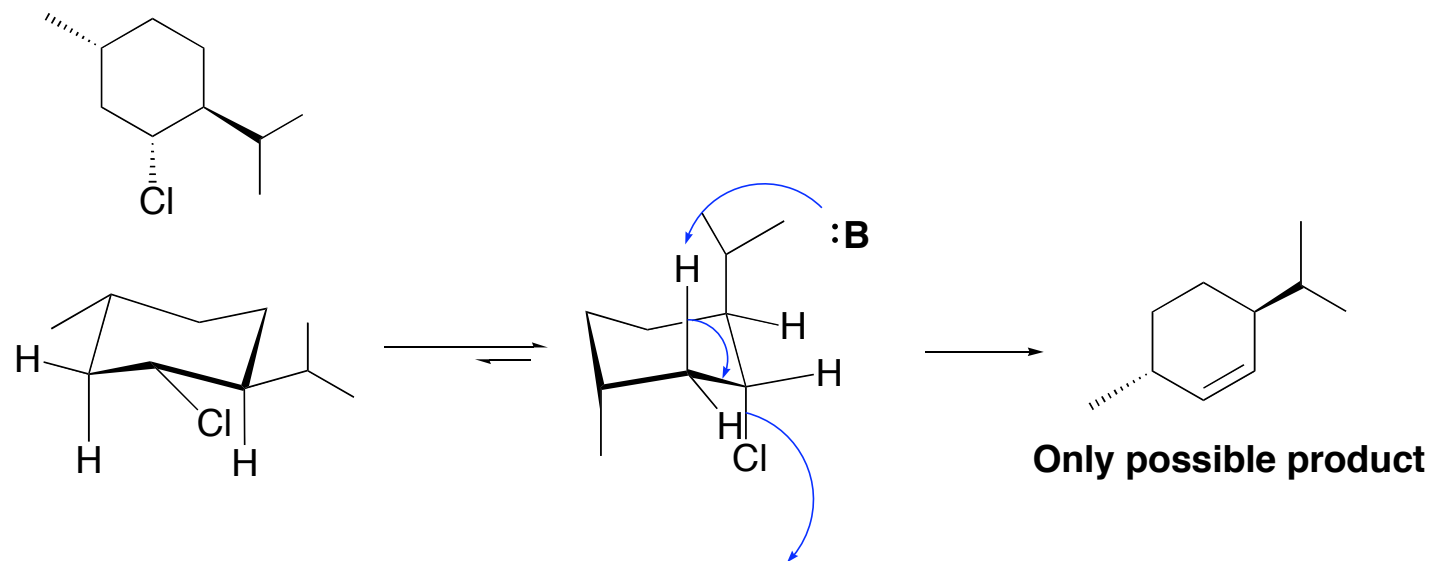
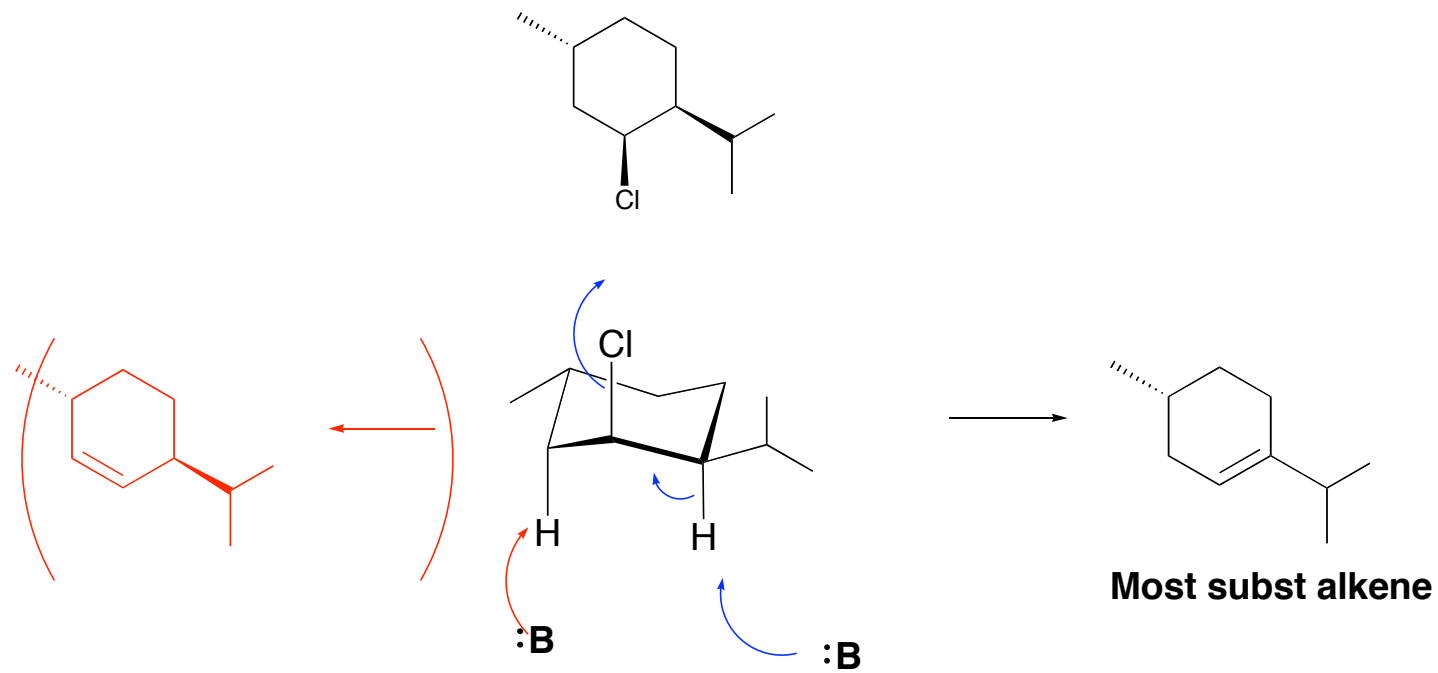


- Two steps
- 1. order
- 1. step rate limiting
- 1. step = 1. step in  $S_N1$
- Not stereospecific

**Elimination in competition with substitution**

# E2 and stereochemistry





# Deuterium Isotope Effect (McM 11.14)

## (Kinetic Isotope Effect)

- Important in elucidation of reaction mechanisms
- Cleavage of C-H and C-D requires different amount of energy

Hookes Law, Stretching frequencies, IR

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f(m_1+m_2)}{m_1 m_2}}$$



$$\bar{\nu} \text{ C-H: ca } 3000 \text{ cm}^{-1}$$

$$\bar{\nu} \text{ C-D: ca } 2200 \text{ cm}^{-1}$$

Relationship between Stretching frequency ( $\nu$ ) and zero-point energy ( $E^0$ )

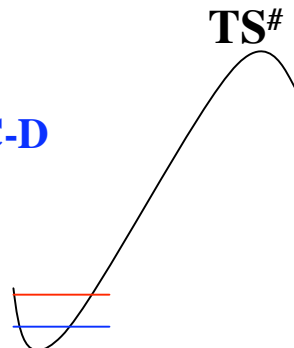
$$E^0 = 1/2 h\nu$$

$$E^0 \text{ C-H } 18 \text{ kJ/mol}$$

$$E^0 \text{ C-D } 13 \text{ kJ/mol}$$

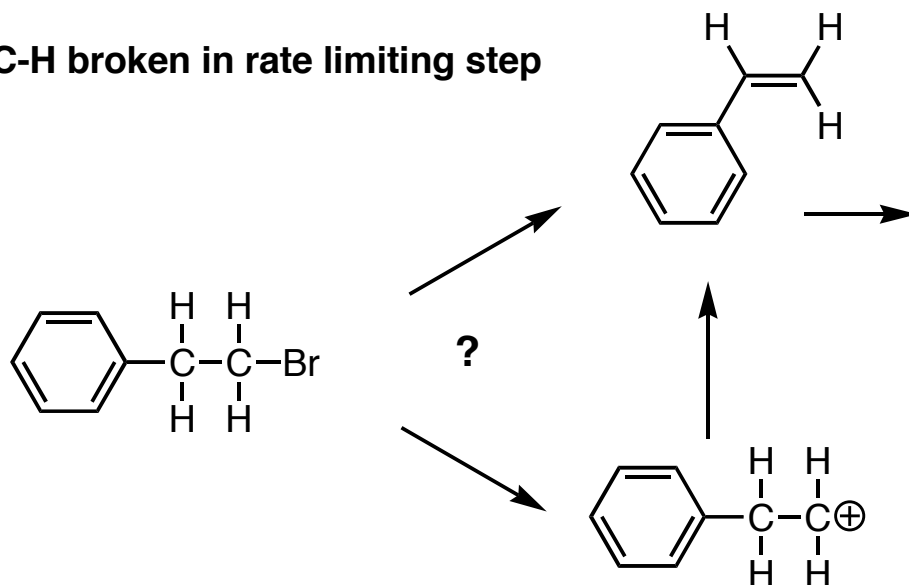
Higher activation energy for cleavage of C-D

Cleavage of C-H will be faster

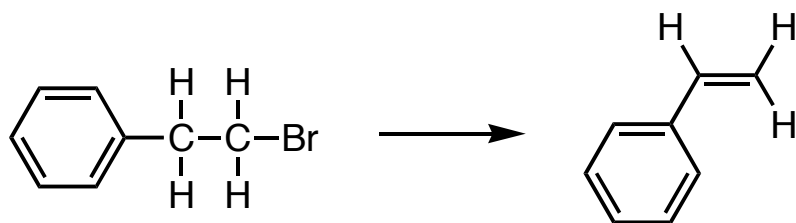


# Mechanistic Information from Deuterium Isotope Effect

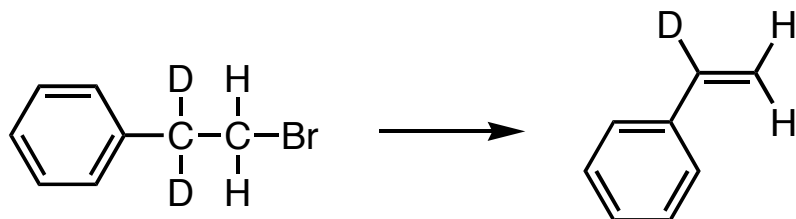
E2 C-H broken in rate limiting step



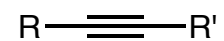
Same prod. no info from regio / stereosel.



Fastest if E2, C-H more easily broken



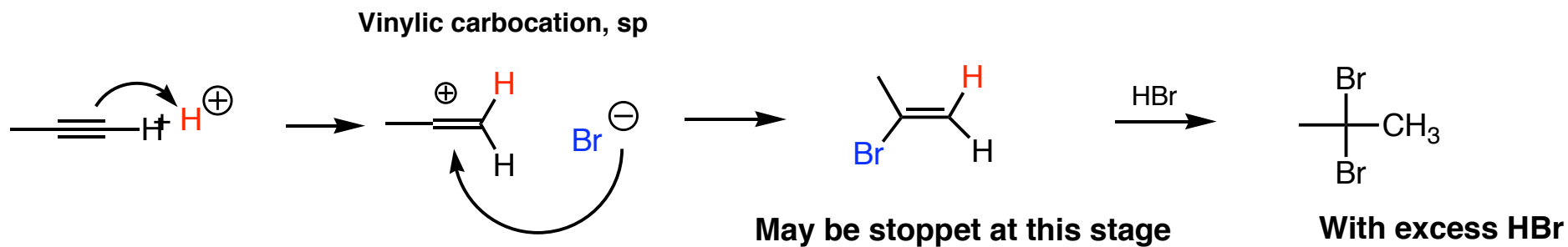
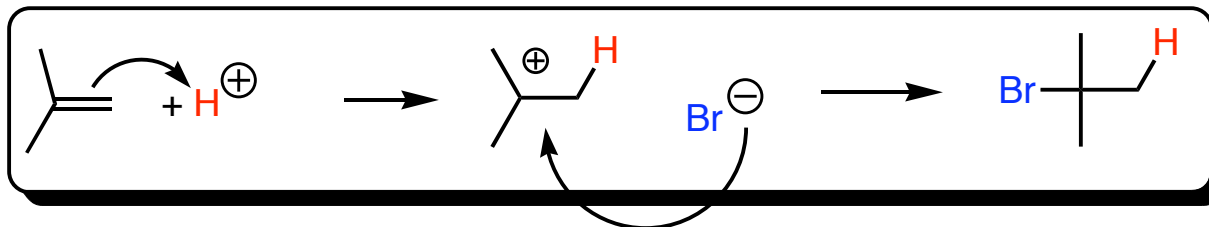
# Alkynes



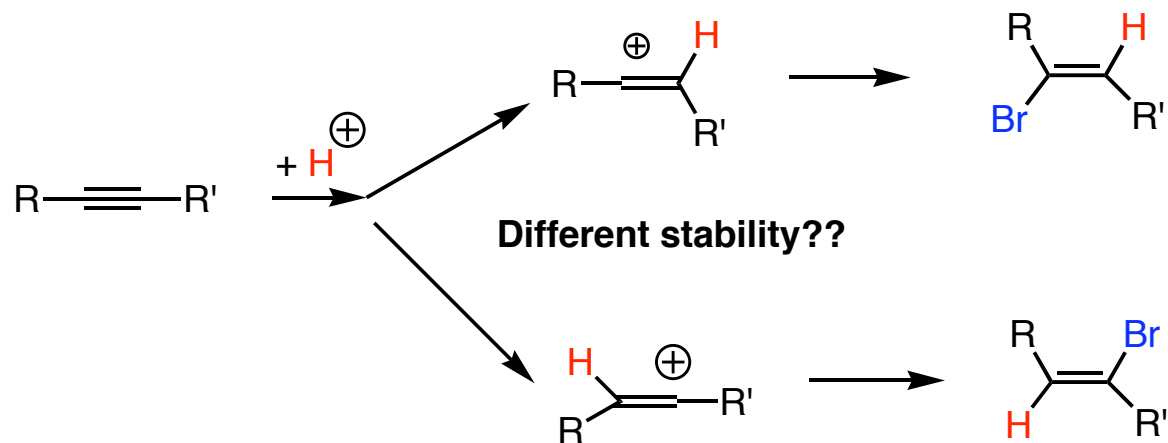
Addition react. on alkynes:

- Add of HX etc
- Hydratization
- Hydrogenation / reductions

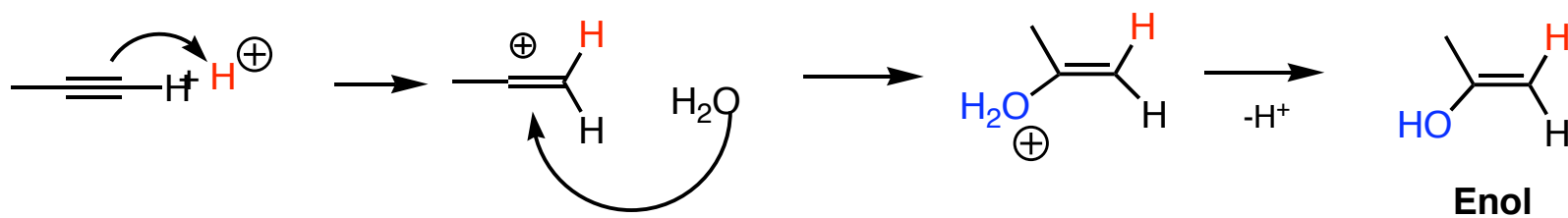
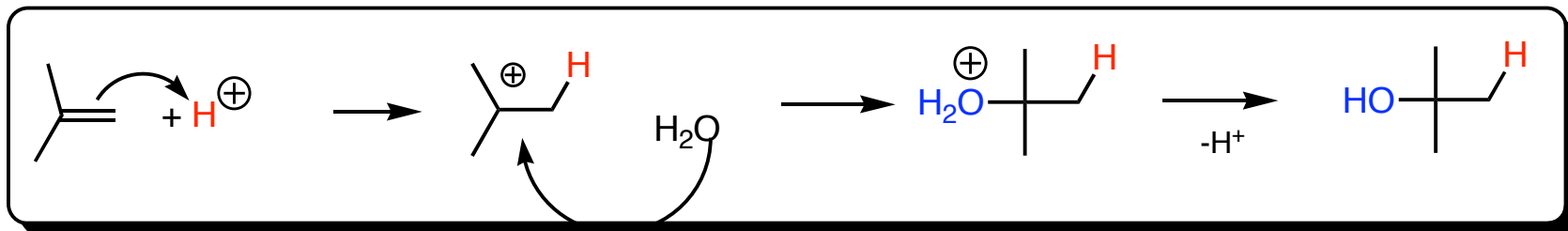
Oxidative cleavage



Internal alkynes may not be so selective

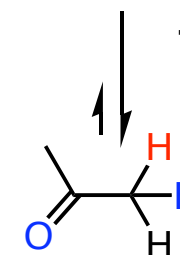






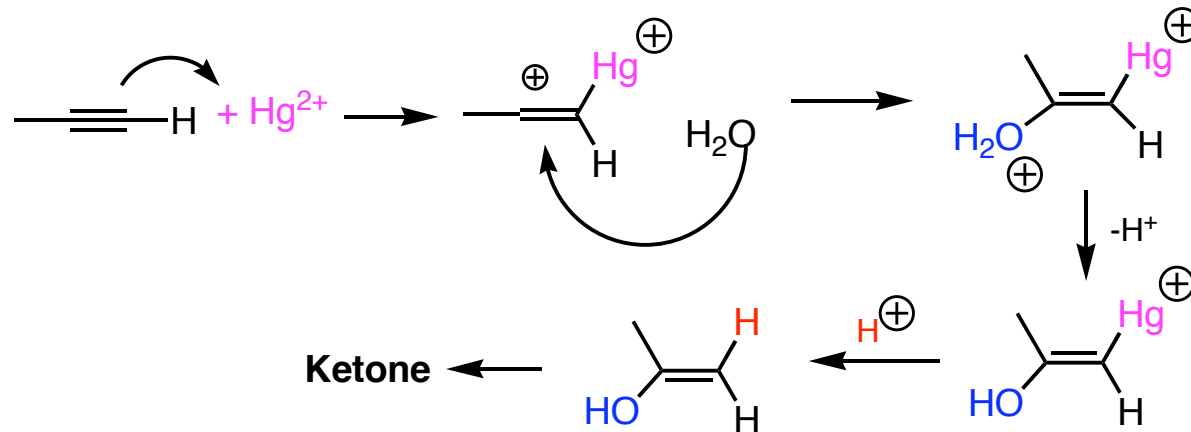
Enol

Taut.

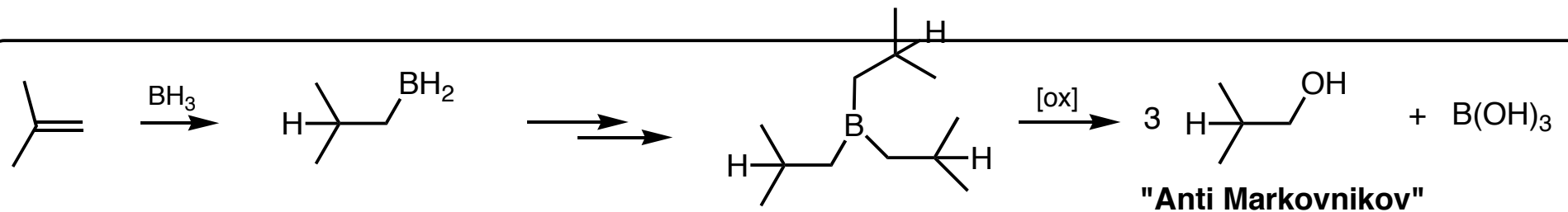


keto  
No second add.

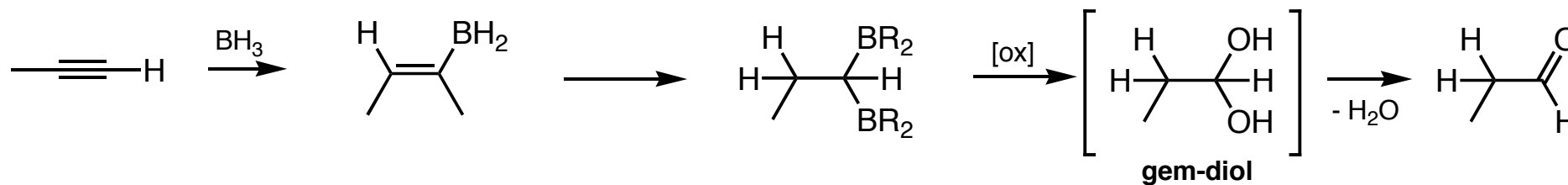
**Hg(II)-cat, required with internal alkynes  
(see also Fig 8.3)**



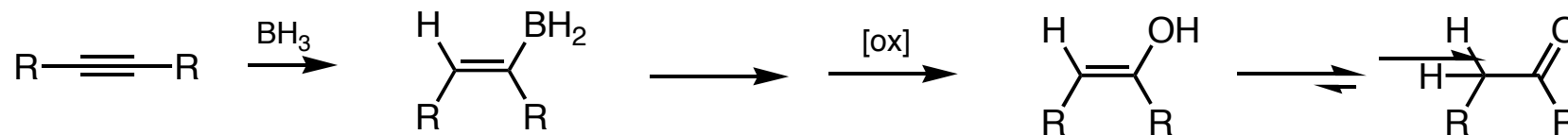
Ketone



### Terminal alkyne - aldehyde



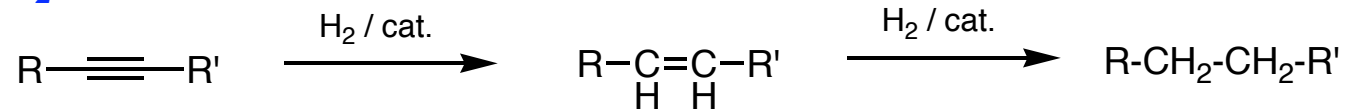
### Internal alkyne - ketone



**Sel. probl. if not symmetrical**

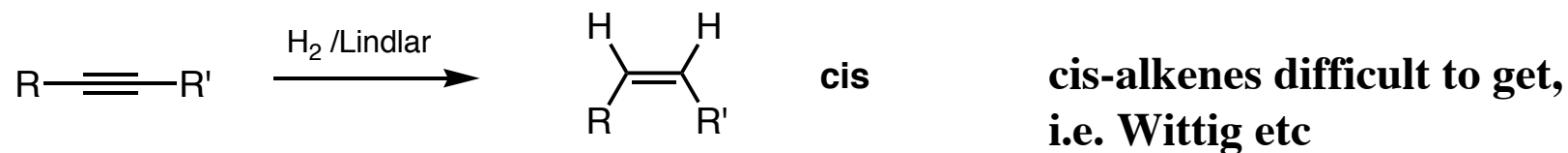
# Reduction of alkynes

**H<sub>2</sub> / cat.**

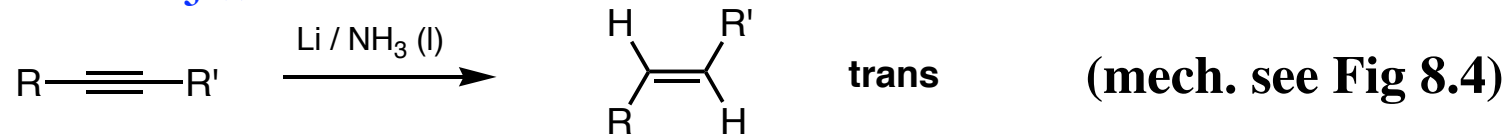


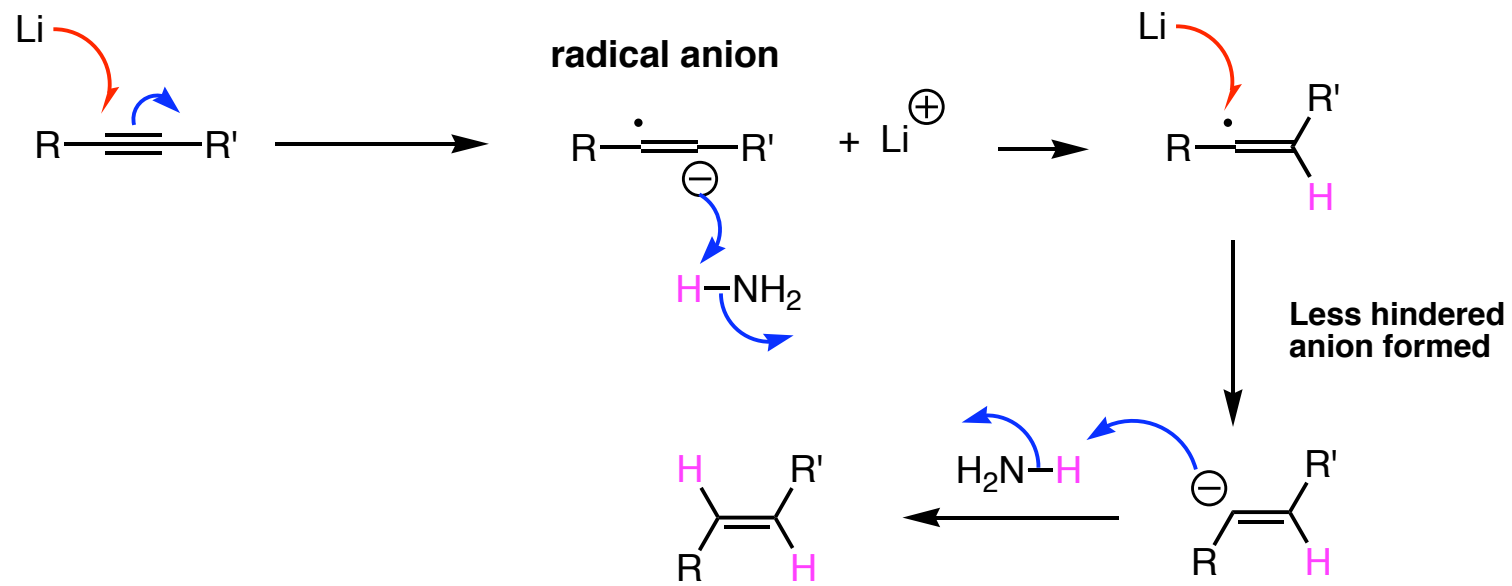
Difficult to stop here,  
cf. hydrogenation of alkenes

**Lindlar (deactivated Pd-cat.)**



**Li / NH<sub>3</sub> (l)**





# Oxidative cleavage of alkynes

