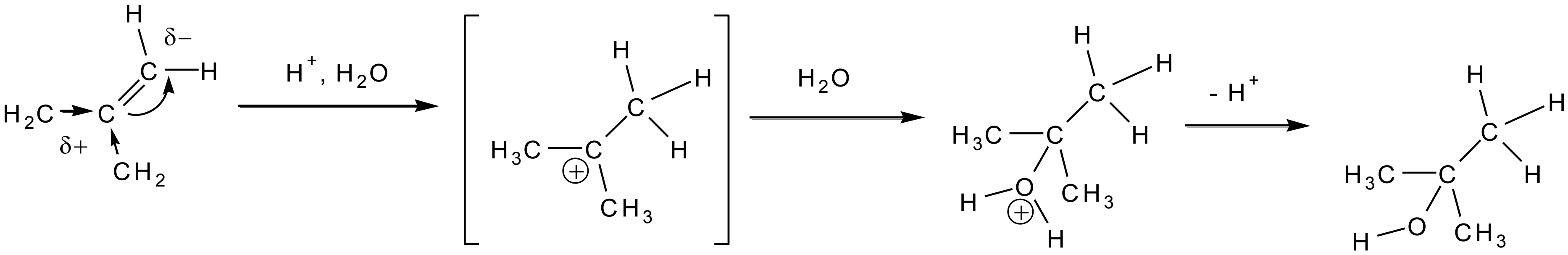
ALKENES AND CYCLOALKENES

Most of the addition reactions is regio a stereospecific, but some of them are not stereospecific.

Addice of H_2O / H^+

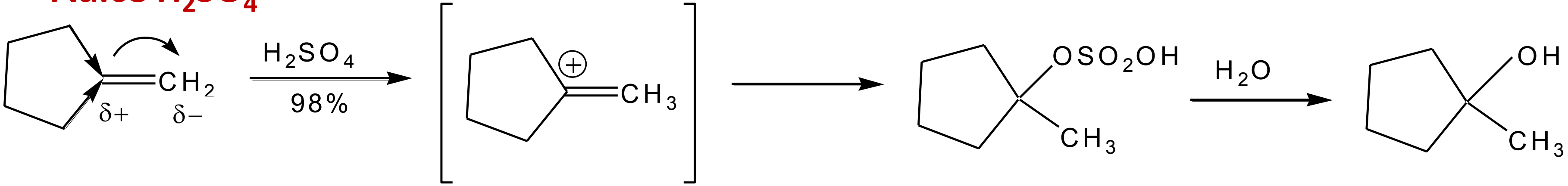
nonstereospecific



Markovnikov rule (regioselective reaction)

nonstereospecific

Adice H_2SO_4



Markovnikov rule (regioselective reaction)

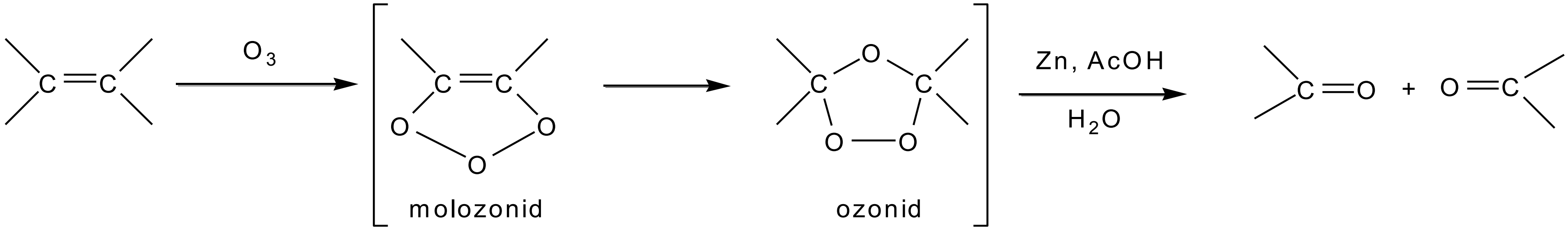
Similarly also addition of hydrohalogenates

nonstereospecific

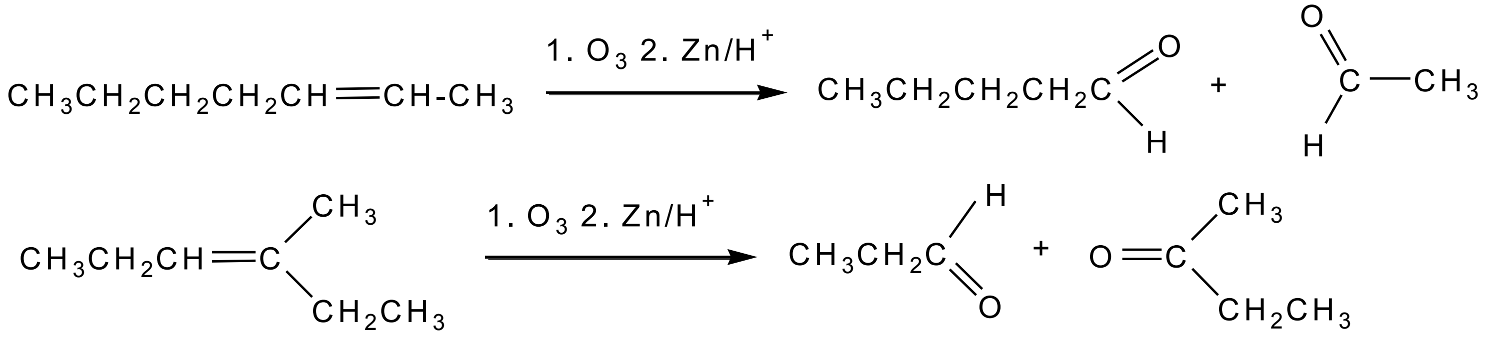
ALKENES AND CYCLOALKENES

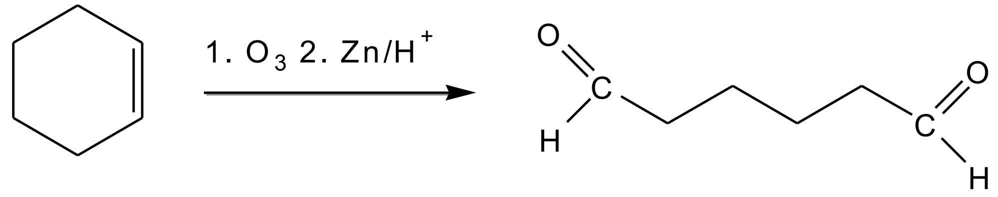
Ozonization

nonstereospecific



Reaction examples:



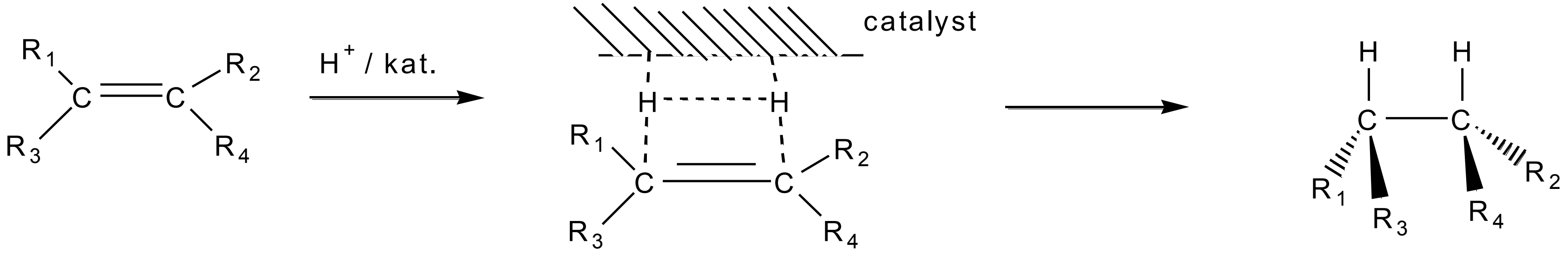


The ozonides are decomposed by catalytic hydrogenation or by treatment by dimethylsufide

ALKENES AND CYCLOALKENES

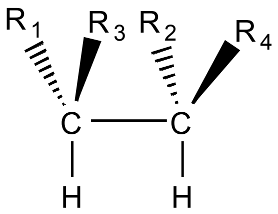
Stereospecific reactions *cis- (syn)-*

Hydrogenation



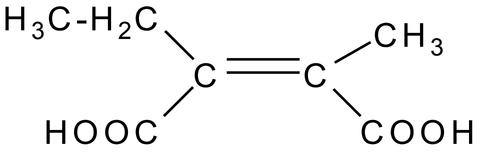
cis-

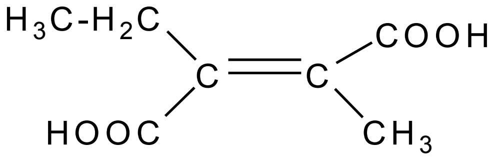
but also



Olefin may attack the catalyst also by the other side

during reaction enantiomers are formed

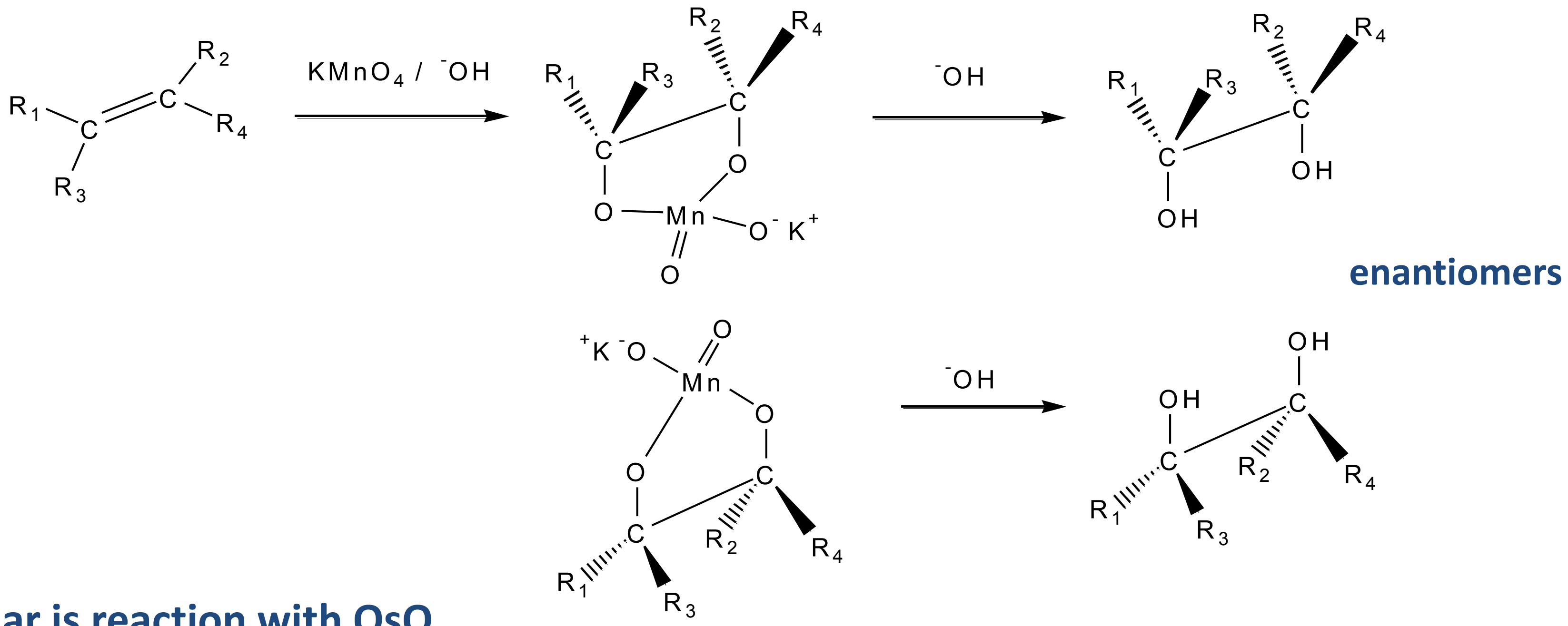




ALKENES AND CYCLOALKENES

Stereospecific reactions *cis- (syn)-*

Oxidation by $KMnO_4$ or OsO_4



Similar is reaction with OsO_4

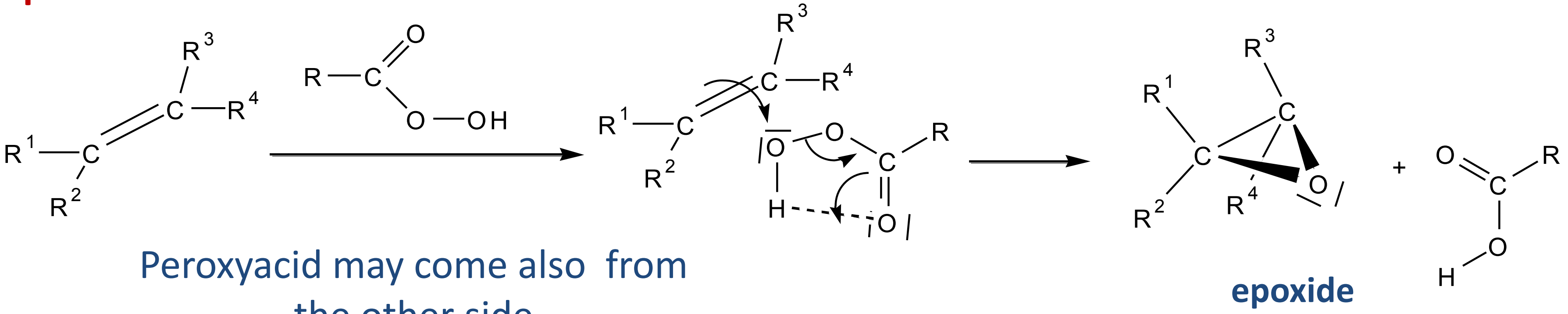
$$\xrightarrow[\text{2. }Na_2SO_3/\ H_2O]{\text{1. }OsO_4}$$

ALKENES AND CYCLOALKENES

Stereospecific reactions *cis- (syn)-*

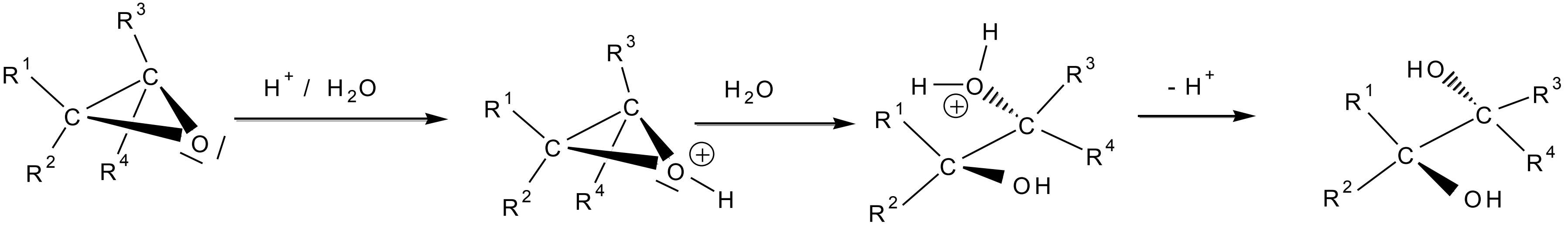
Epoxidation

peroxyacids



Peroxyacid may come also from the other side

Epoxides are not stable = reactive compounds – in an acidic medium we are able to transfer them to dioles



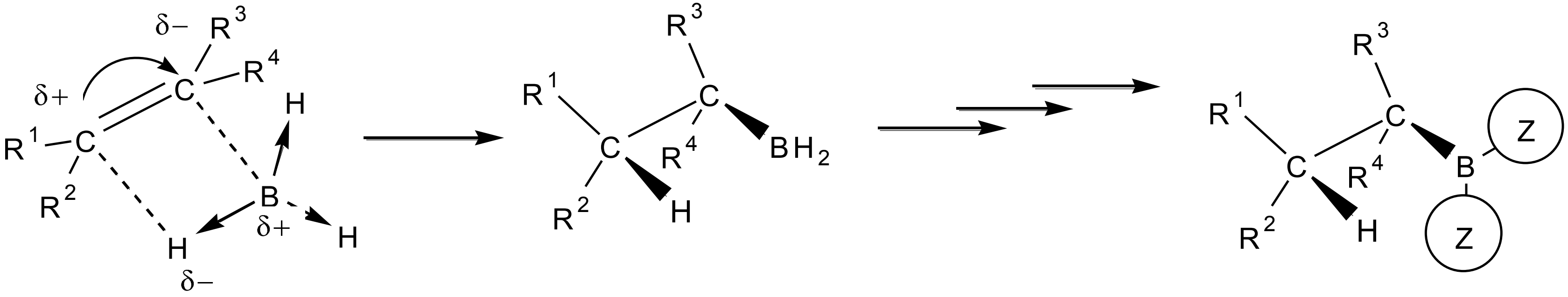
The splitting of the epoxides proceeds under formation of *trans-* dioles

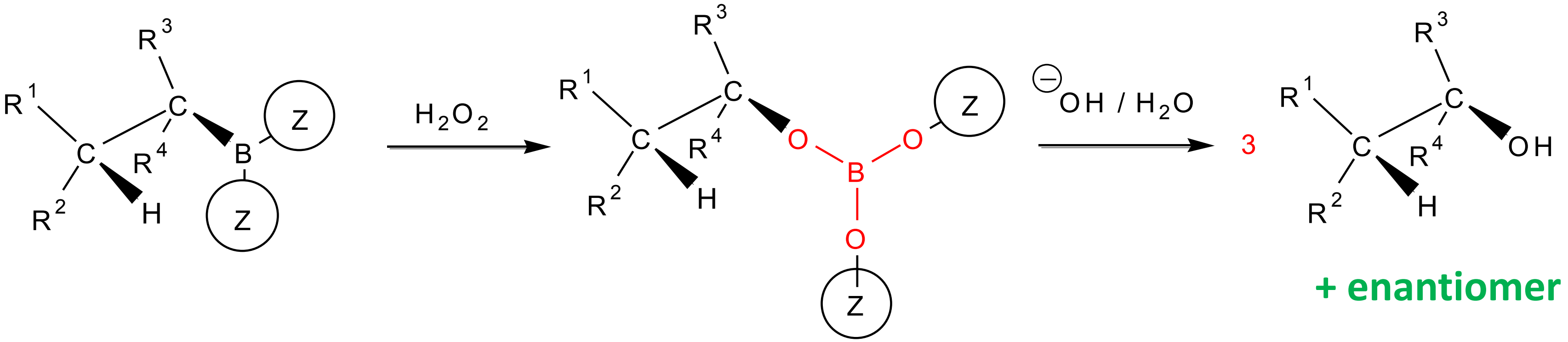
ALKENES AND CYCLOALKENES

Stereospecific reactions *cis- (syn)-*

Markovnikov rule (regioselective reaction)

Hydroboration $B_2H_6 \longrightarrow 2\ BH_3$



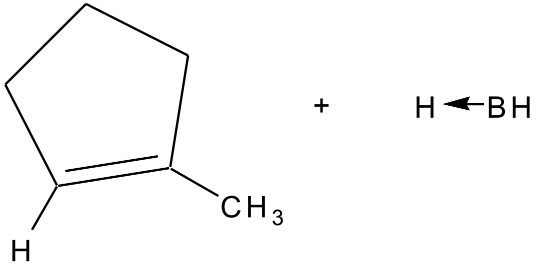


+ enantiomer

The result of the reaction is the same as after addition of water in an acidic medium but the **regioselectivity is contrary**

ALKENES AND CYCLOALKENES

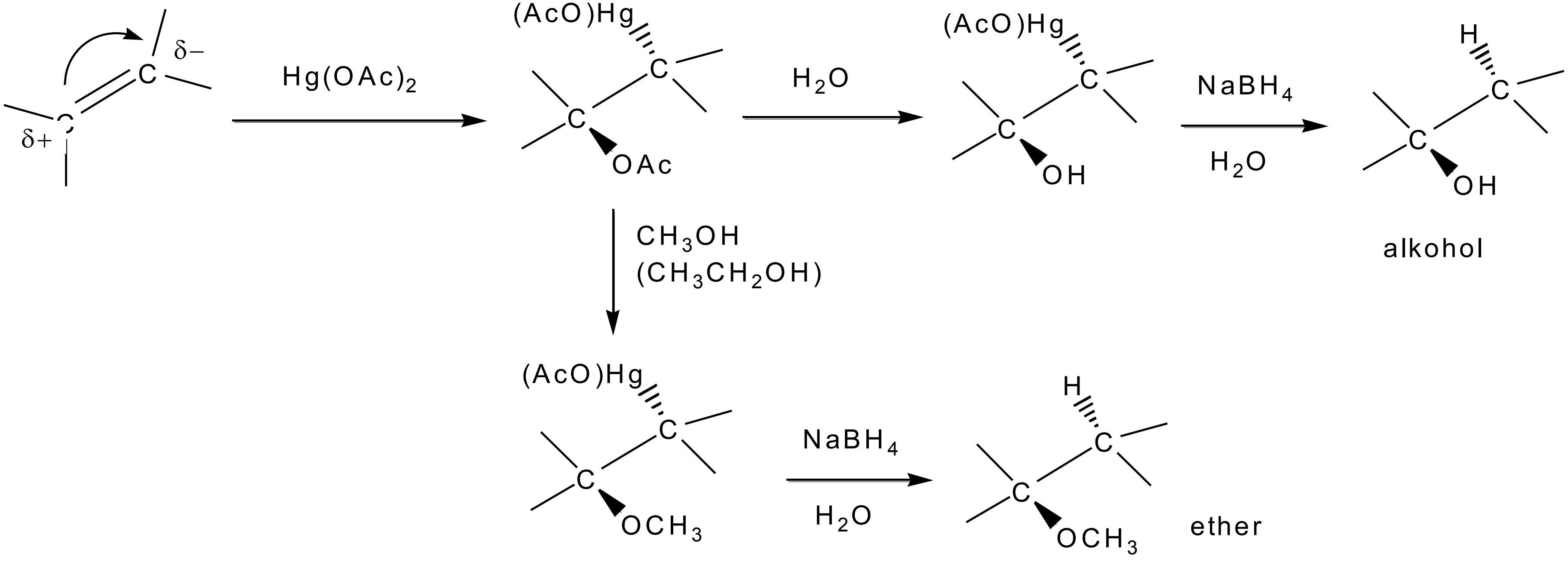
Stereospecific reactions *cis- (syn)-*



ALKENES AND CYCLOALKENES

Stereospecific reaction *cis- (syn)-*

Oxymercuration – demercuration (reaction with mercury acetate, Hg^{2+} is the electrophile)



Demercuration is carried out by $NaBH_4$

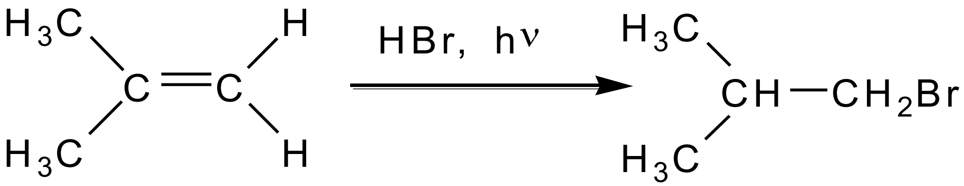
Markovnikov rule (regioselective reaction)

ALKENES AND CYCLOALKENES

!! Under radical conditions the regioselectivity during addition of hydrohalogens is changing!!!

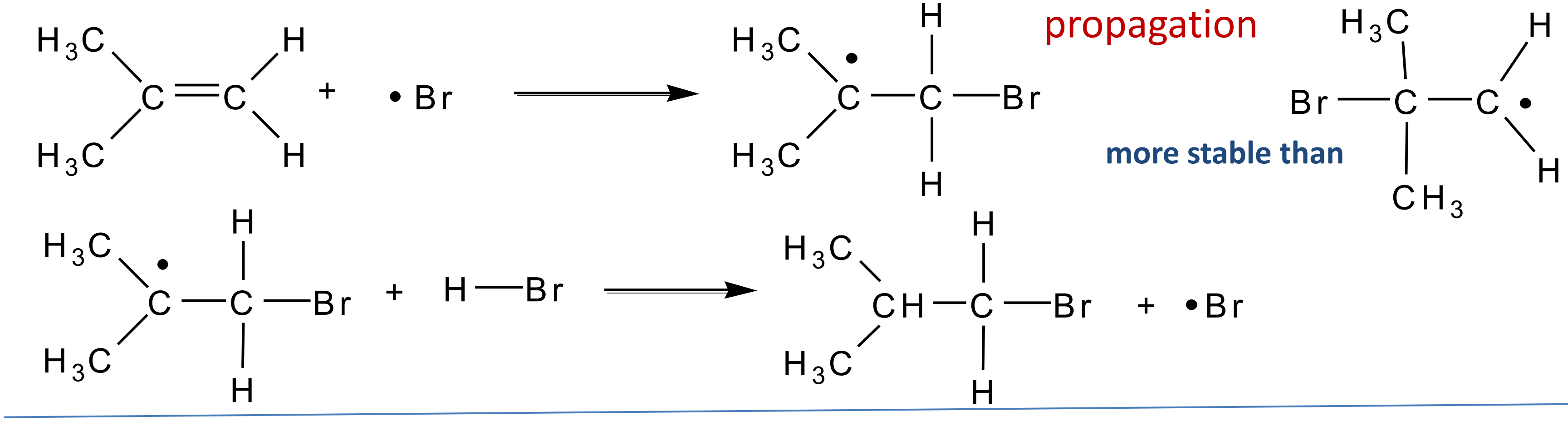
KHARASH phenomenon = antimarkovnikov rule

catalysis by UV light (hν) , radicals, heat



initiation

$$H{-}Br + R\bullet \longrightarrow H{-}R + \bullet Br$$



propagation

more stable than

ALKENES AND CYCLOALKENES

At radical conditions you can expect also additions of :
chlorine, bromine, sulfane, thioles a polyhalogenated alkanes

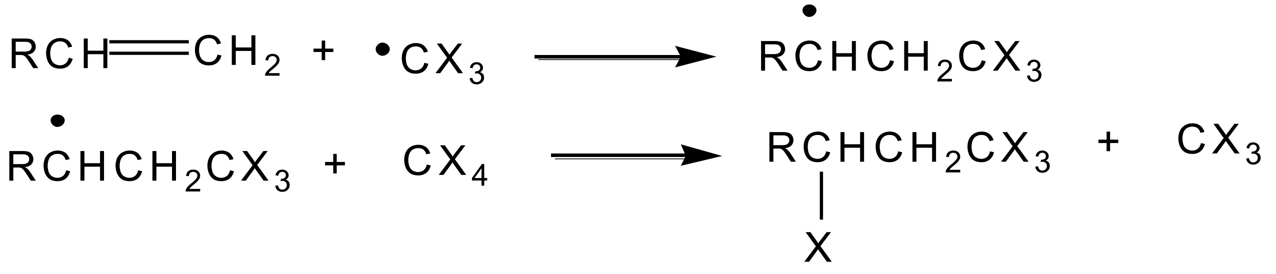
$$CH_3CH_2CH{=}CH_2 + H_2S \xrightarrow[0^{o}]{h\nu} \underset{68\%}{CH_3CH_2CH_2CH_2SH} + \underset{12\%}{(CH_3CH_2CH_2CH_2)_2S}$$

$$(CH_3)_2C{=}CH_2 + CH_3CH_2SH \xrightarrow[O_2]{100^{o}C} \underset{94\%}{(CH_3)_2CHCH_2SCH_2CH_3}$$

$$R\text{-}O\text{-}O\text{-}R \xrightarrow[(h\nu)]{\Delta T} 2\ RO\bullet$$

$$RO\bullet + CX_4 \longrightarrow \bullet CX_3 + ROX$$

iniciation



$$RCH{=}CH_2 + \bullet CX_3 \longrightarrow R\overset{\bullet}{C}HCH_2CX_3$$

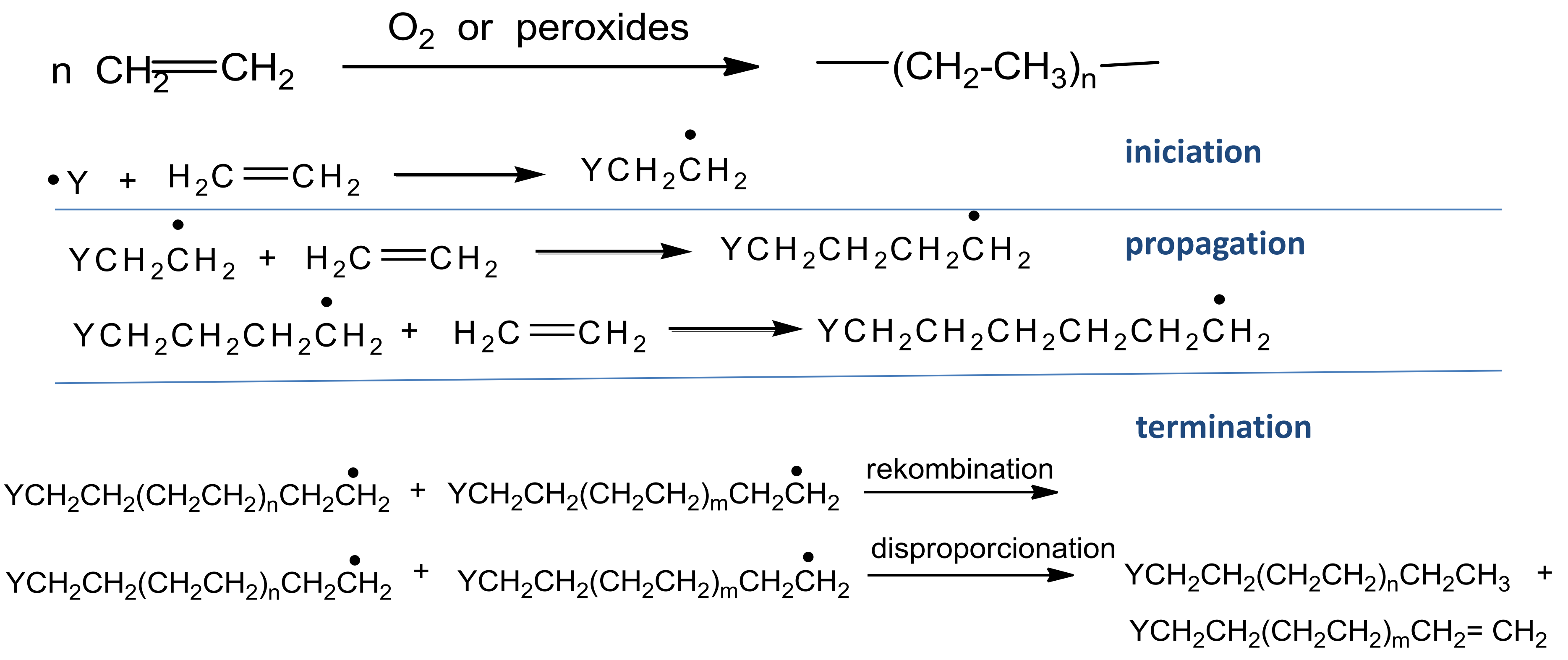
X = Cl , Br

$$R\overset{\bullet}{C}HCH_2CX_3 + CX_4 \longrightarrow R\underset{\underset{X}{|}}{C}HCH_2CX_3 + CX_3$$

ALKENES AND CYCLOALKENES

POLYMERIZATION

mechanism: **radical polymerization**
ionic polymerization - kationic
- anionic



$$n\ CH_2{=}CH_2 \xrightarrow{O_2\ \text{or peroxides}} -(CH_2\text{-}CH_3)_n-$$

iniciation

$$\bullet Y + H_2C{=}CH_2 \longrightarrow YCH_2\dot{C}H_2$$

propagation

$$YCH_2\dot{C}H_2 + H_2C{=}CH_2 \longrightarrow YCH_2CH_2CH_2\dot{C}H_2$$

$$YCH_2CH_2CH_2\dot{C}H_2 + H_2C{=}CH_2 \longrightarrow YCH_2CH_2CH_2CH_2CH_2\dot{C}H_2$$

termination

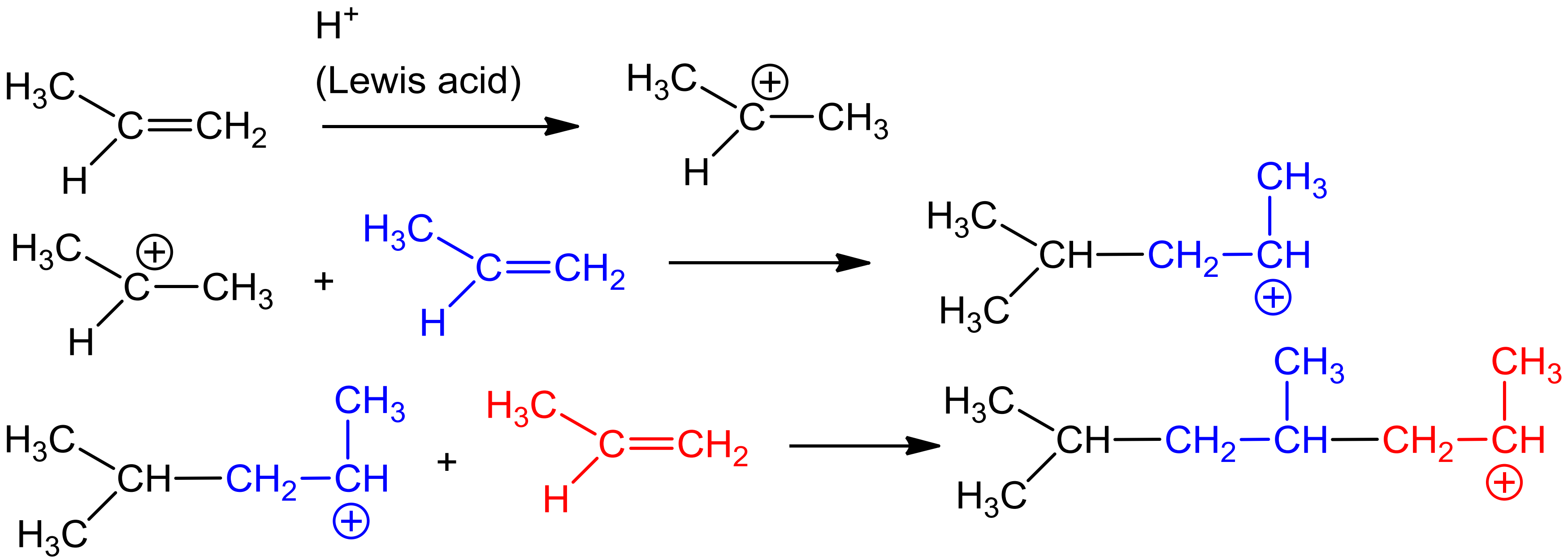
$$YCH_2CH_2(CH_2CH_2)_nCH_2\dot{C}H_2 + YCH_2CH_2(CH_2CH_2)_mCH_2\dot{C}H_2 \xrightarrow{\text{rekombination}}$$

$$YCH_2CH_2(CH_2CH_2)_nCH_2\dot{C}H_2 + YCH_2CH_2(CH_2CH_2)_mCH_2\dot{C}H_2 \xrightarrow{\text{disproporcionation}} YCH_2CH_2(CH_2CH_2)_nCH_2CH_3 + YCH_2CH_2(CH_2CH_2)_mCH_2{=}\ CH_2$$

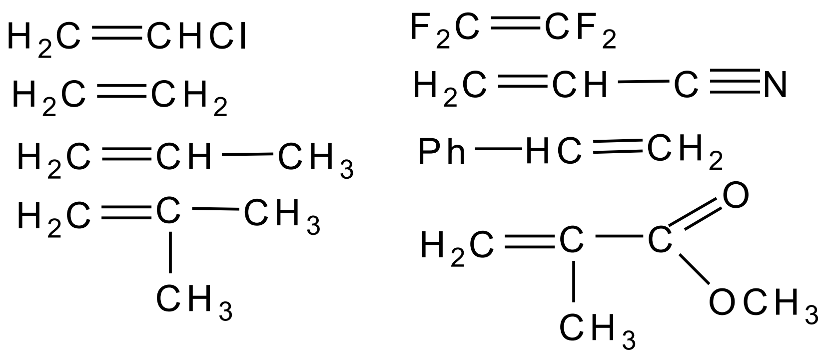
ALKENES AND CYCLOALKENES

POLYMERIZATION

Kationic polymerizations, catalysis by BF_3, $TiCl_4$, R_3Al ……



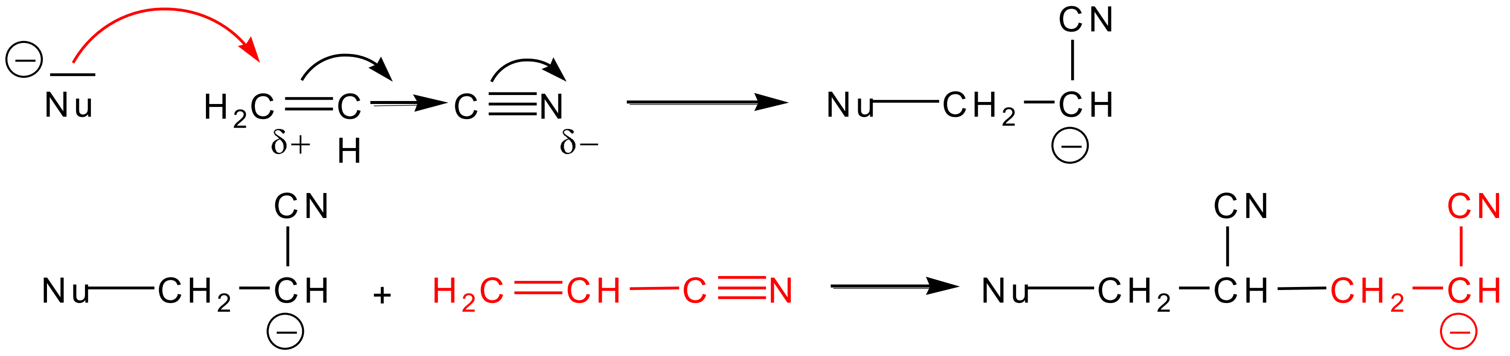
Monomers for the most important polymers



ALKENES AND CYCLOALKENES

POLYMERIZATION

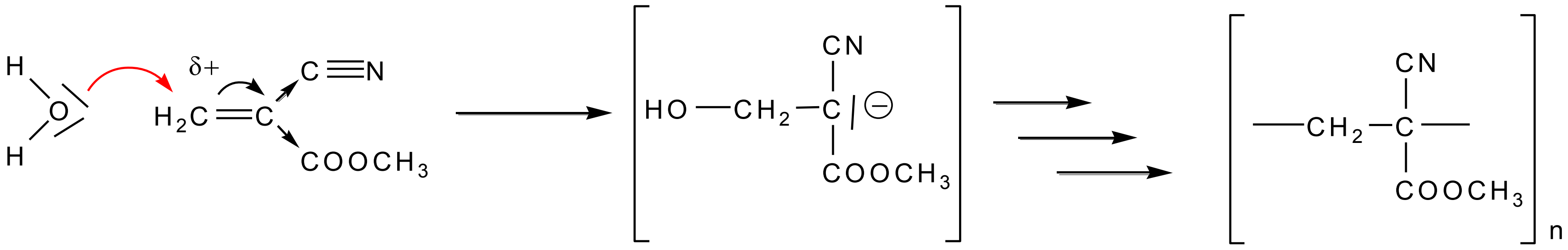
Anionic polymerizations, catalysis by strong bases: BuLi, $NaNH_2$...



$$Nu^{-} + H_2C{=}CH{-}C{\equiv}N \longrightarrow Nu{-}CH_2{-}\underset{\ominus}{C}H{-}CN$$

$$Nu{-}CH_2{-}\underset{\ominus}{C}H{-}CN + H_2C{=}CH{-}C{\equiv}N \longrightarrow Nu{-}CH_2{-}CH(CN){-}CH_2{-}\underset{\ominus}{C}H{-}CN$$

This method is suitable for alkenes with electronwithdrawing groups, where that group enables entrance of the base and stabilisation of formed anion.



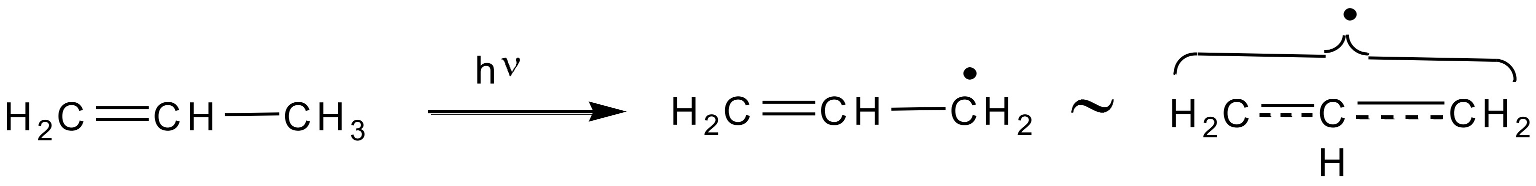
$$H_2O + H_2C{=}C(C{\equiv}N)COOCH_3 \longrightarrow \left[HO{-}CH_2{-}\overset{\ominus}{C}(CN)(COOCH_3)\right] \longrightarrow \longrightarrow \longrightarrow \left[{-}CH_2{-}C(CN)(COOCH_3){-}\right]_n$$

mechanism of the second glue action

ALKENES AND CYCLOALKENES

Notice higher reactivity of hydrogenatoms at Csp^3 in neighbourghood of double bond

Hydrogen atoms at **allylic position** are reactive in radical reactions (the formed radical is stabilized by the double bond next to it)



$$H_2C{=}CH{-}CH_3 \xrightarrow{h\nu} H_2C{=}CH{-}\dot{C}H_2 \sim \overbrace{H_2C\cdots\underset{H}{C}\cdots CH_2}^{\bullet}$$

In allylic position you can realize halogenation without loss of double bond (without addition)

The suitable halogenation agent is NBS (NCS)