Aliphatic compounds

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Corey House synthesis of alkanes

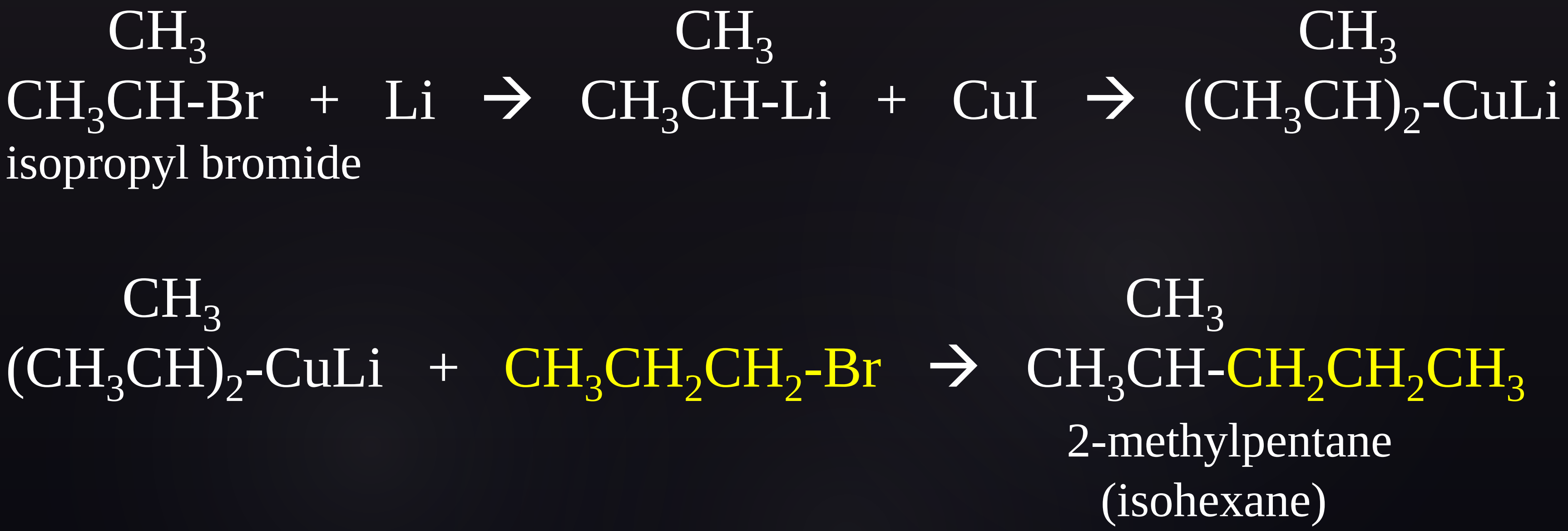
coupling of an alkyl halide with lithium dialkylcopper

$\text{R-X} + \text{Li} \rightarrow \text{R-Li} + \text{CuI} \rightarrow \text{R}_2\text{CuLi}$

$\text{R}_2\text{CuLi} + \text{R}'\text{-X} \rightarrow \text{R—R}'$ (alkane)

(R′-X should be 1° or methyl)

This synthesis is important because it affords a synthesis of a larger alkane from two smaller alkyl halides.



$$\mathrm{CH_3\overset{CH_3}{CH}\text{-}Br + Li \rightarrow CH_3\overset{CH_3}{CH}\text{-}Li + CuI \rightarrow (CH_3\overset{CH_3}{CH})_2\text{-}CuLi}$$

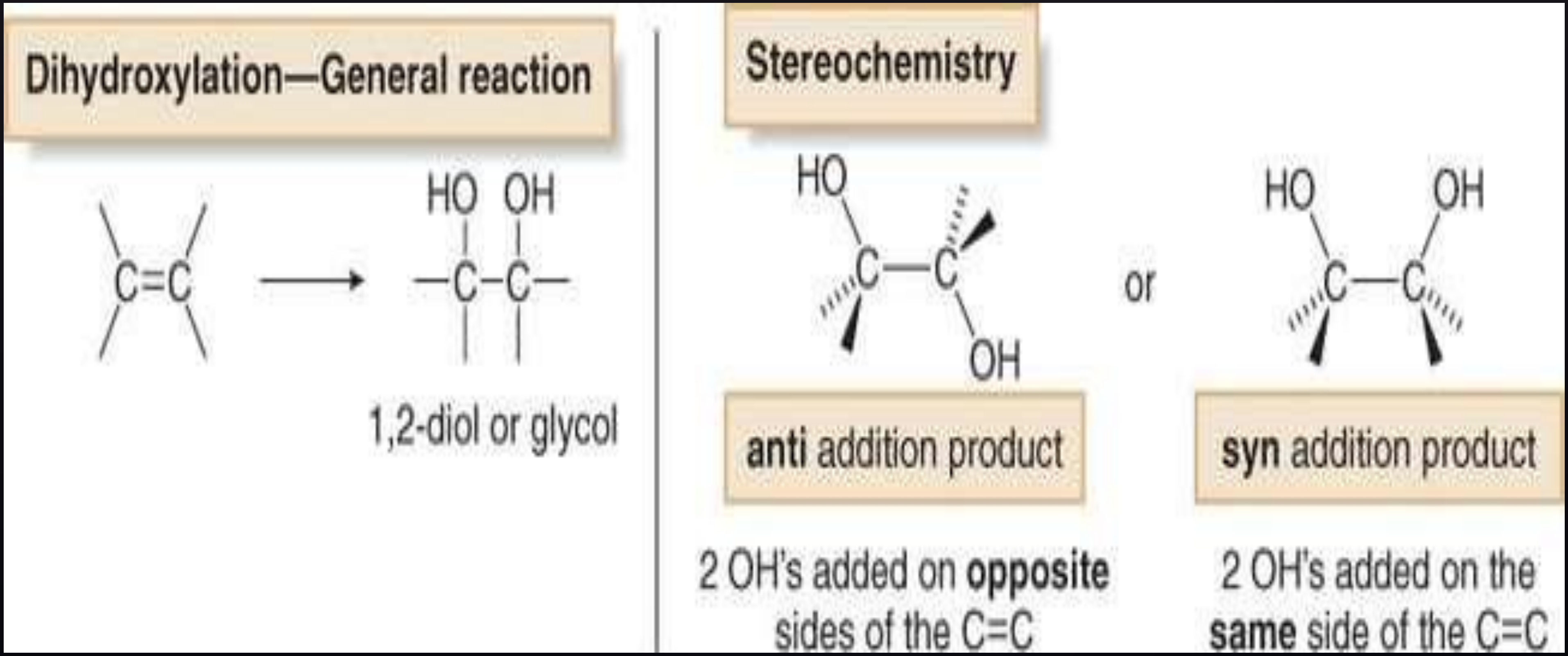
isopropyl bromide

$$\mathrm{(CH_3\overset{CH_3}{CH})_2\text{-}CuLi + CH_3CH_2CH_2\text{-}Br \rightarrow CH_3\overset{CH_3}{CH}\text{-}CH_2CH_2CH_3}$$

2-methylpentane
(isohexane)

Note: the R´X should be a 1° or methyl halide for the best yields of the final product.

Dihydroxylation of alkenes



Dihydroxylation—General reaction

1,2-diol or glycol

Stereochemistry

anti addition product

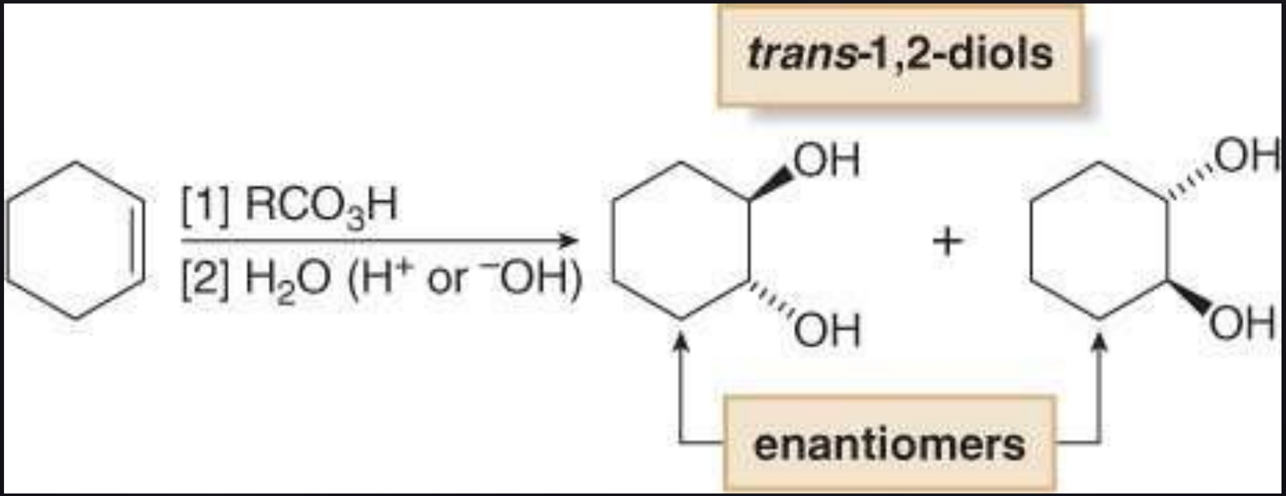
2 OH's added on **opposite** sides of the C=C

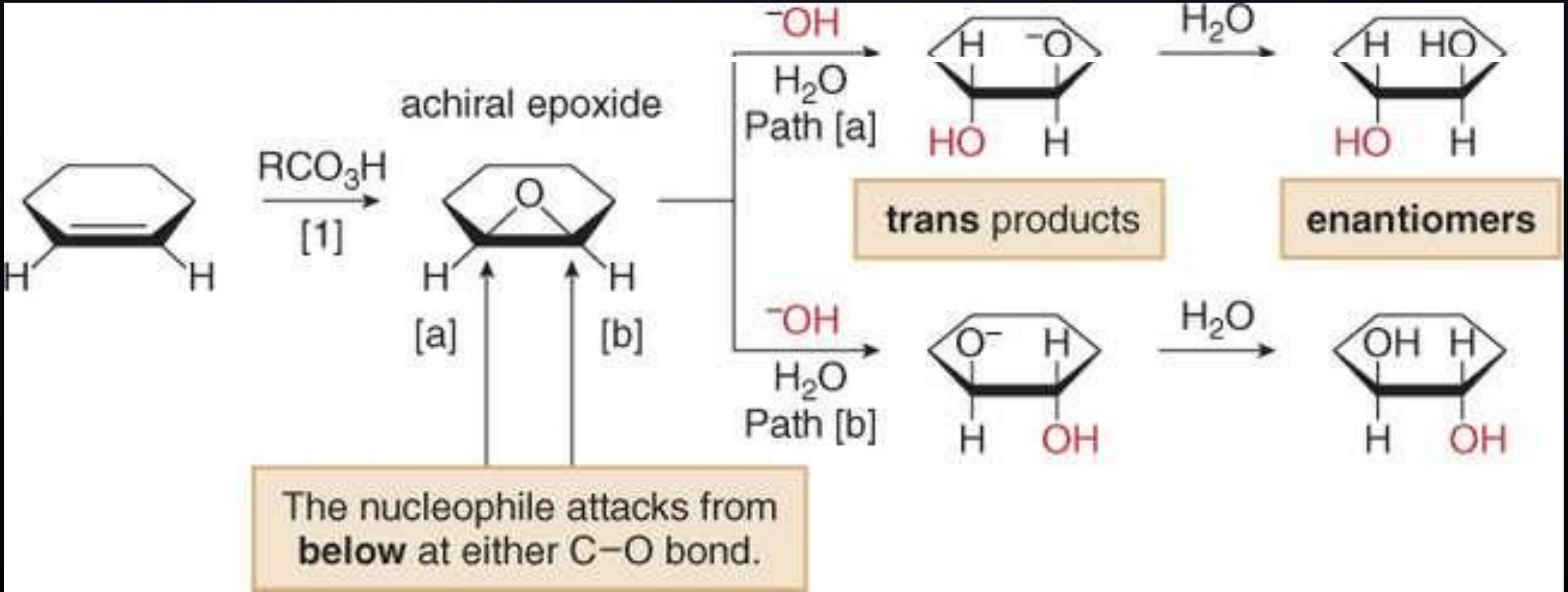
syn addition product

2 OH's added on the **same** side of the C=C

Anti- Dihydroxylation

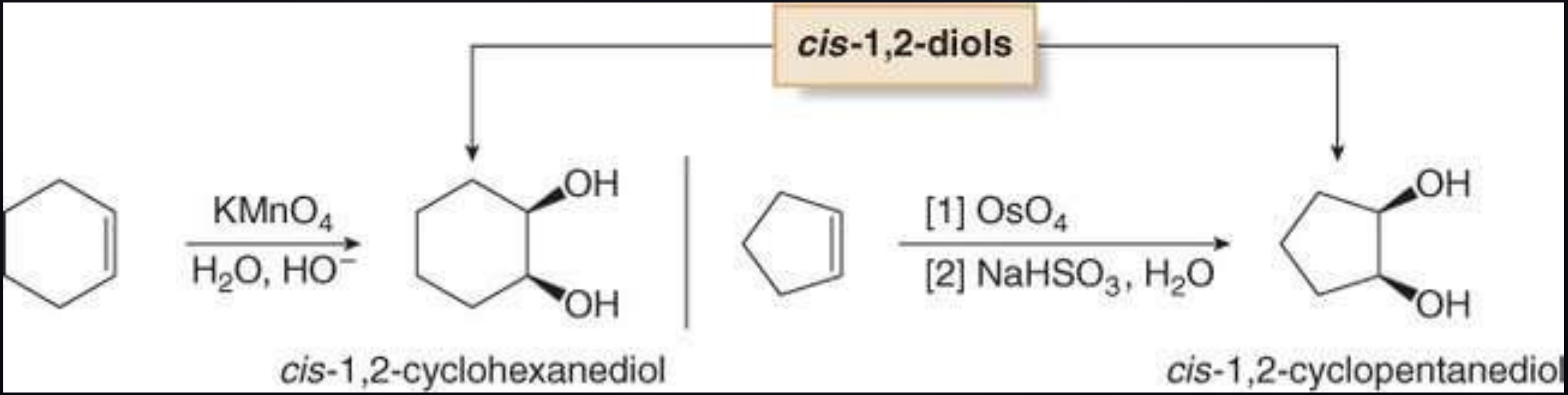
- Anti dihydroxylation is achieved in two steps—epoxidation followed by ring opening with ^{-}OH or H_2O.



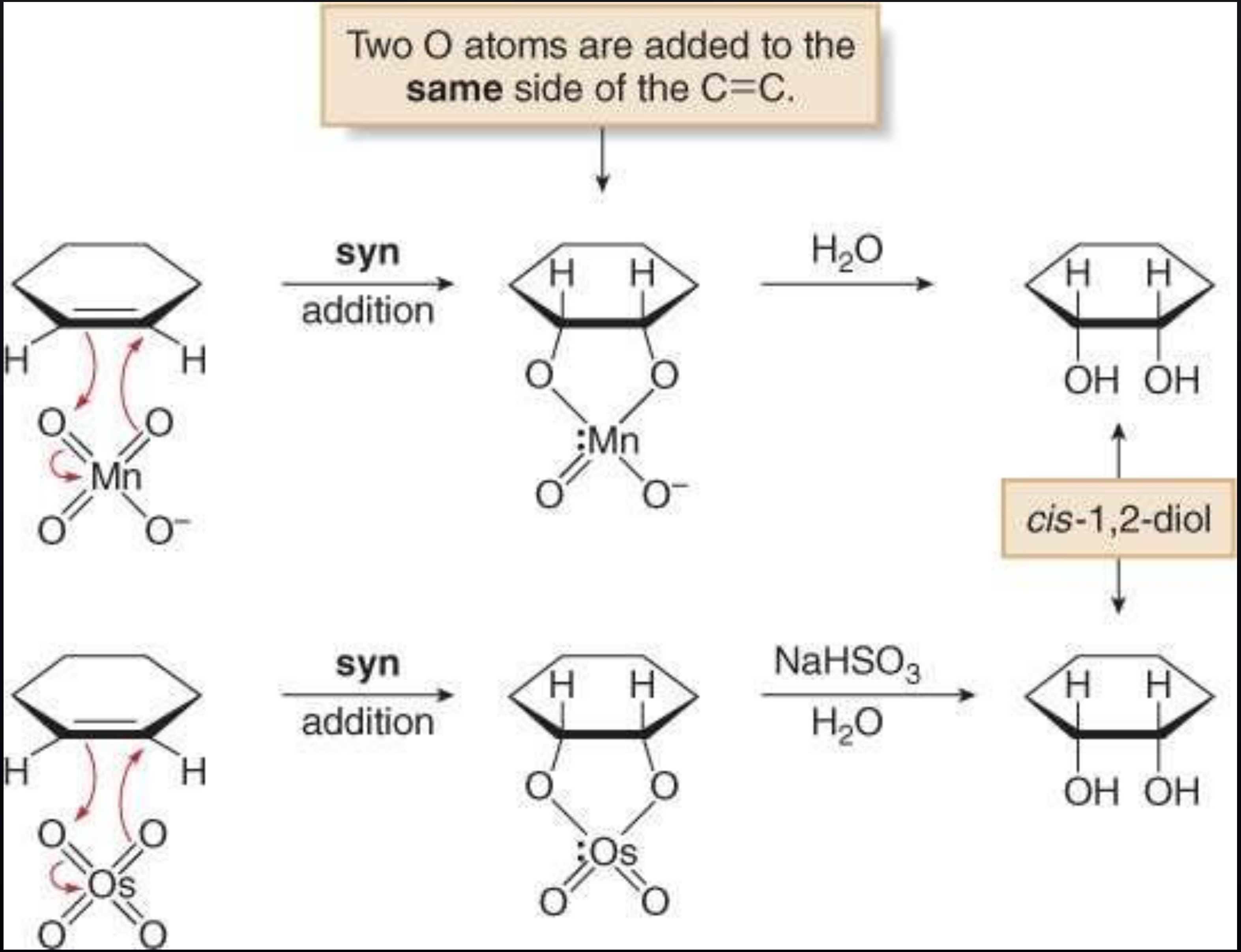


Syn-Dihydroxylation

- Syn hydroxylation results when an alkene is treated with either $KMnO_4$ or OsO_4.



Mechanis of Syn-Dihydroxylation

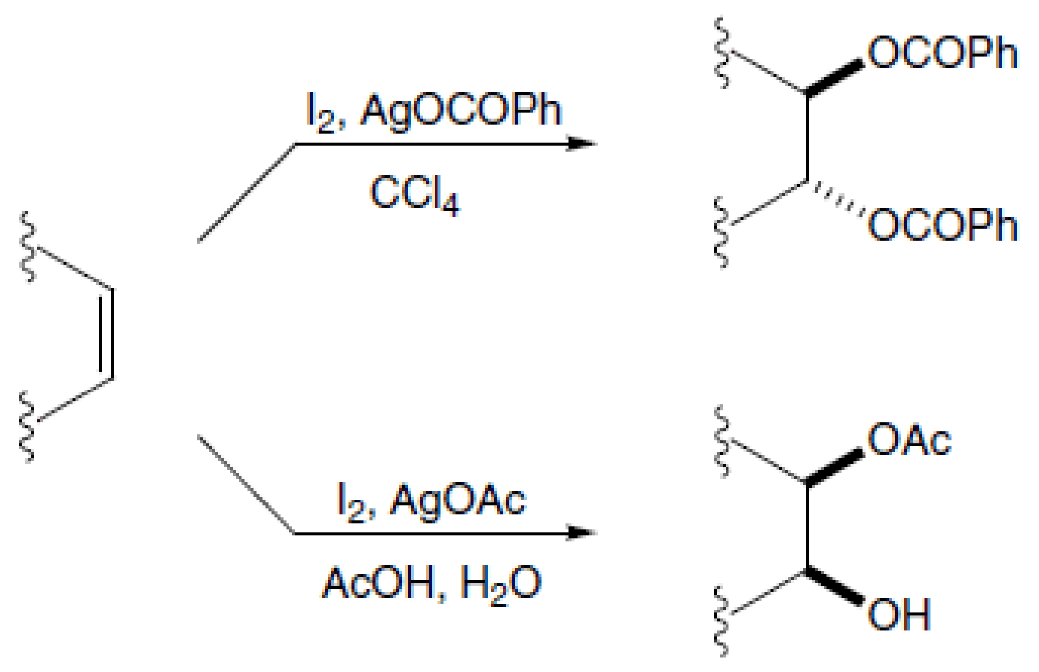


Two O atoms are added to the **same** side of the C=C.

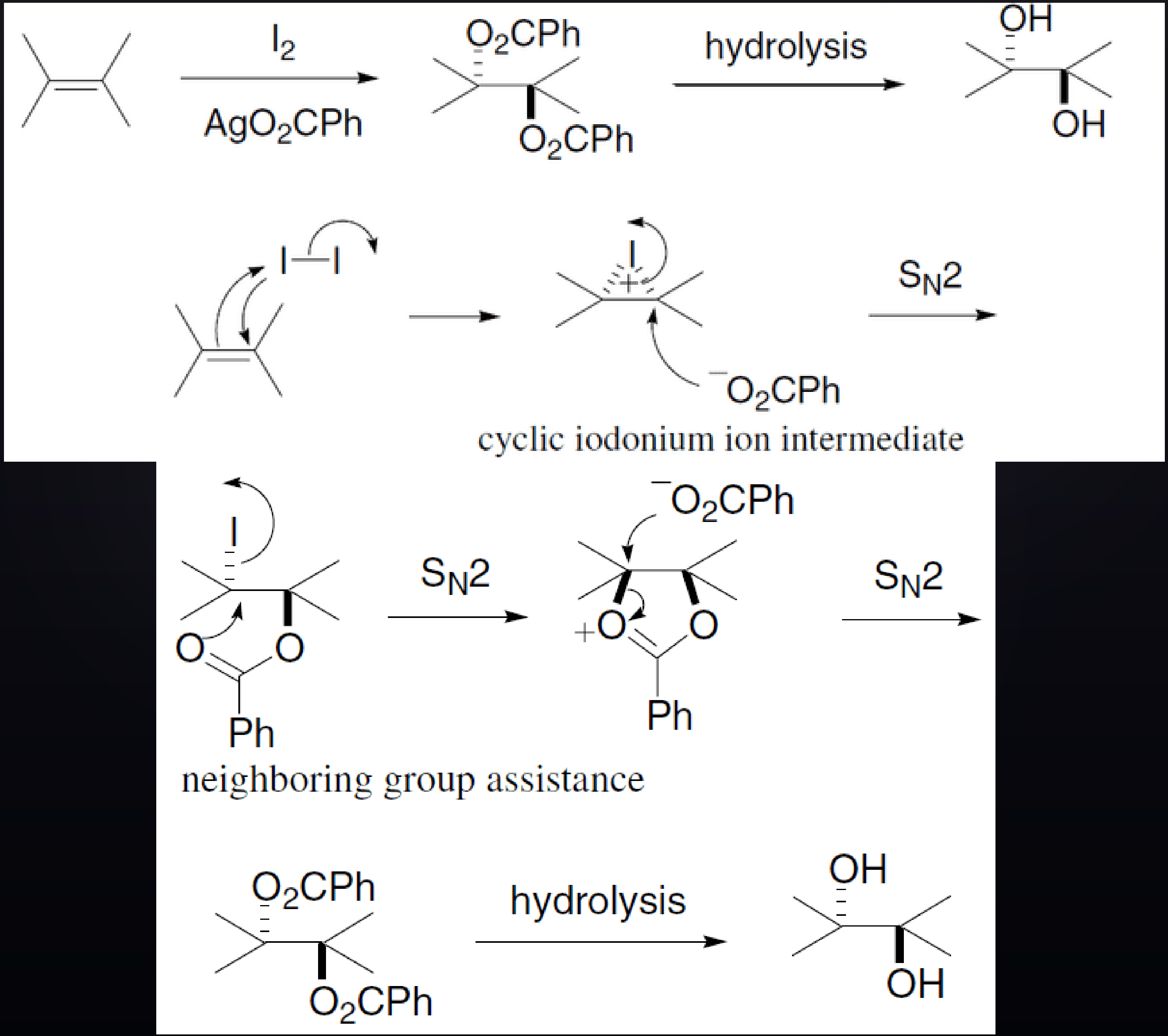
cis-1,2-diol

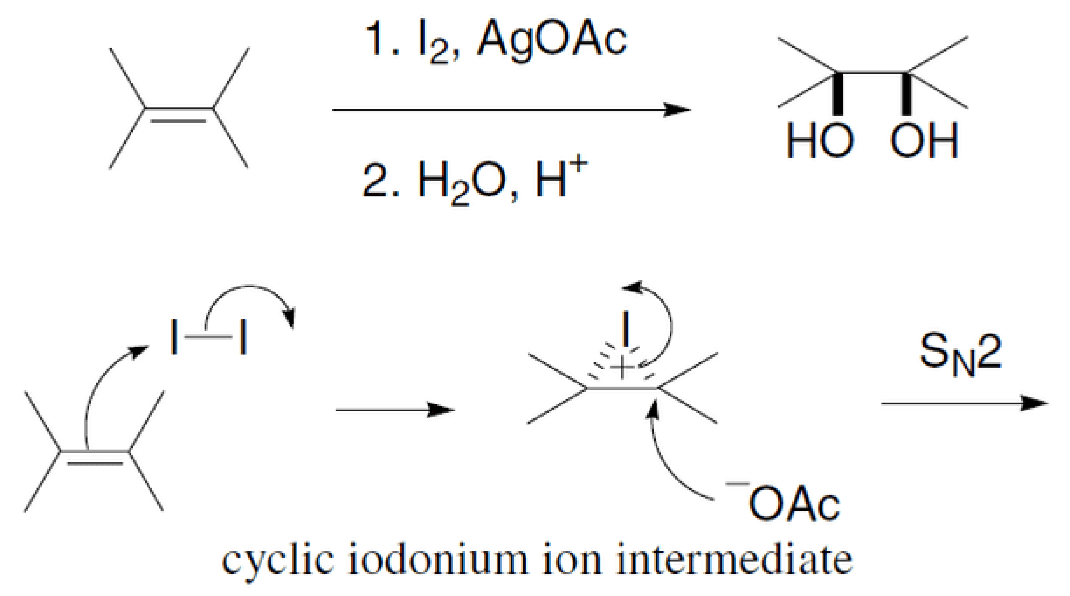
Woodward-prevost hydroxylation

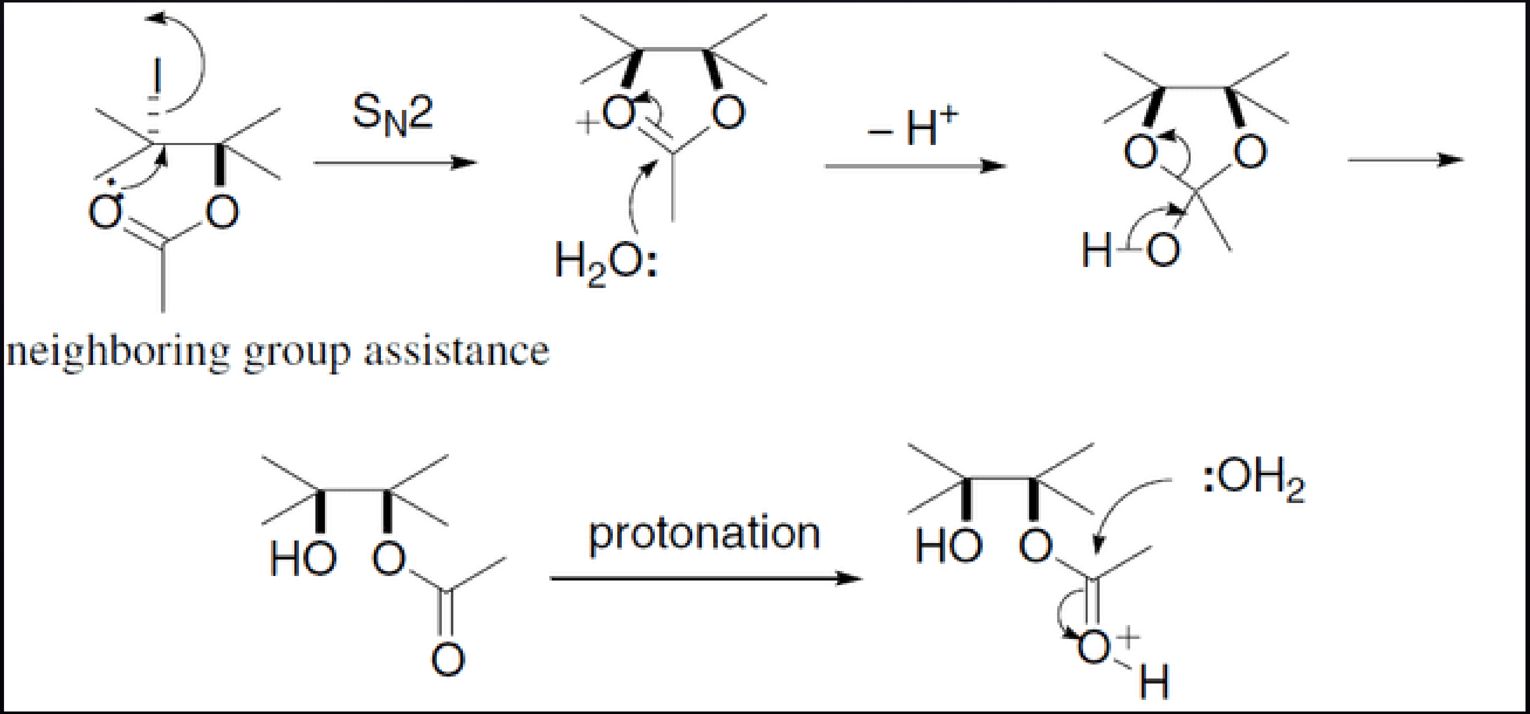
The formation of 1,2-diol products from alkenes can be achieved using Pr´evost's reagent – a solution of iodine in carbon tetrachloride together with an equivalent of silver(I) acetate or silver(I) benzoate. Under anhydrous conditions, this oxidant yields directly the diacyl derivative of the *anti*-diol (Pr´evost conditions), while in the presence of water the monoester of the *syn*-diol is obtained (Woodward conditions).

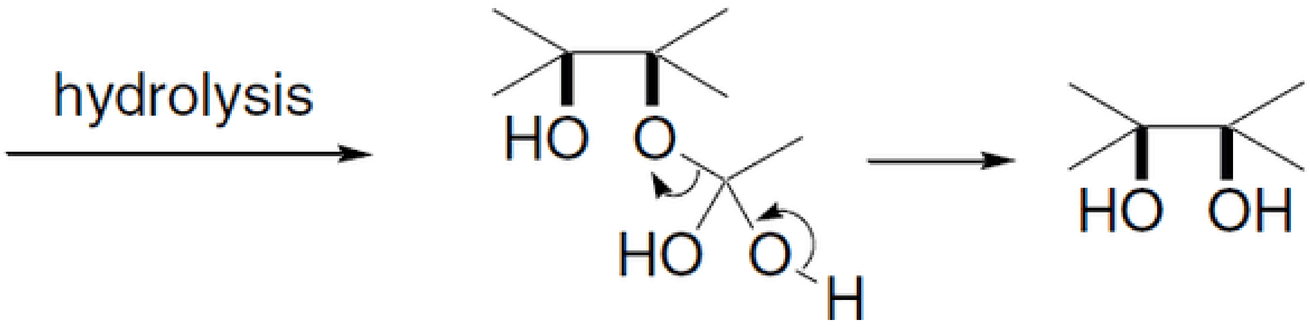


Woodward-prevost hydroxylation

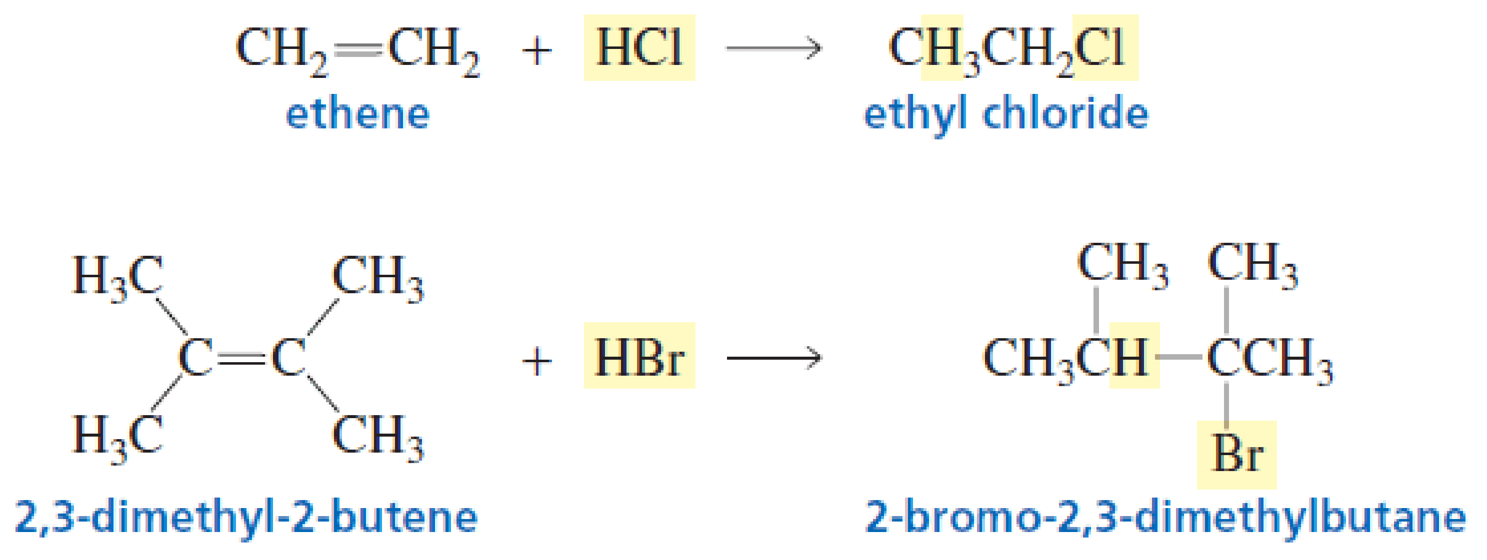



1. I2, AgOAc
2. H2O, H+
HO OH
I—I
SN2
I
+
⁻OAc
cyclic iodonium ion intermediate


I
O
O
neighboring group assistance
SN2
+O
O
H2O:
– H+
O
O
H–O
HO
O
O
protonation
HO
O
:OH2
O+
H


hydrolysis
HO
O
HO
O
H
HO
OH

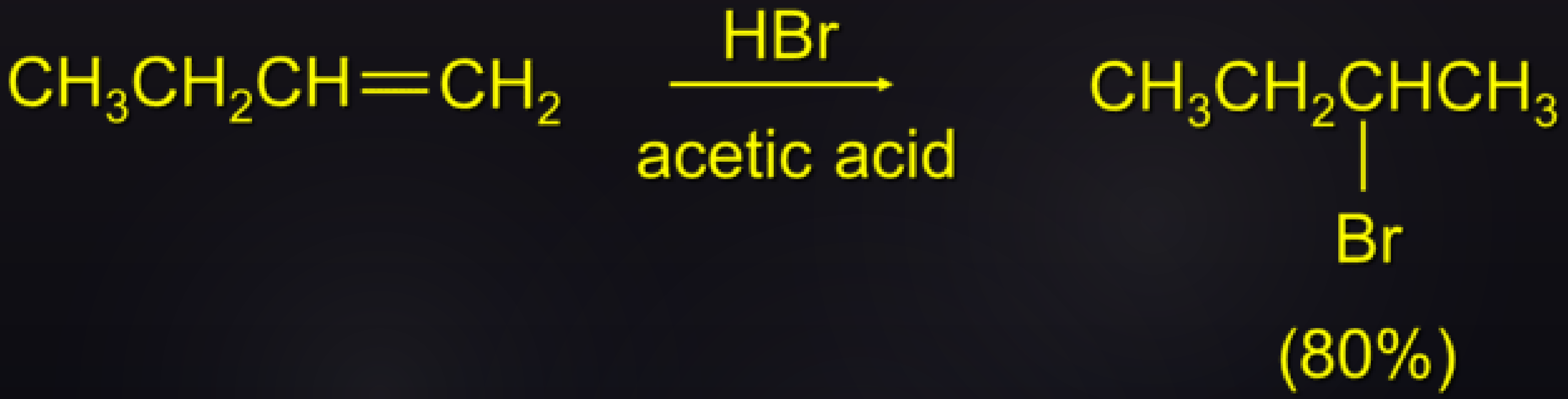
Addition of Hydrogen Halides



Markovnikov's Rule

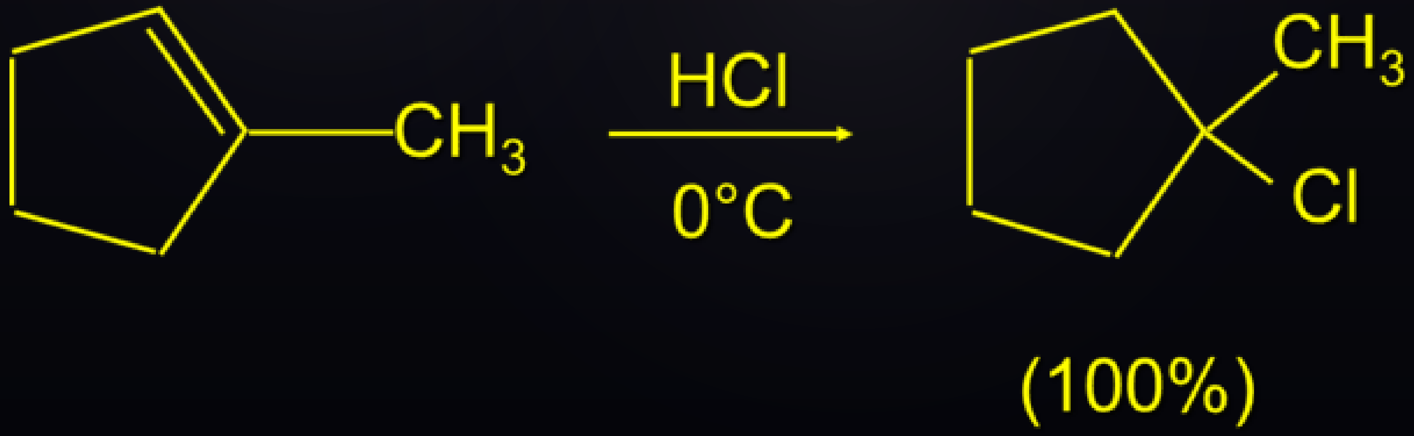
When an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogen substituents, and the halogen adds to the carbon that has the fewer hydrogen substituents.

Markovnikov's Rule



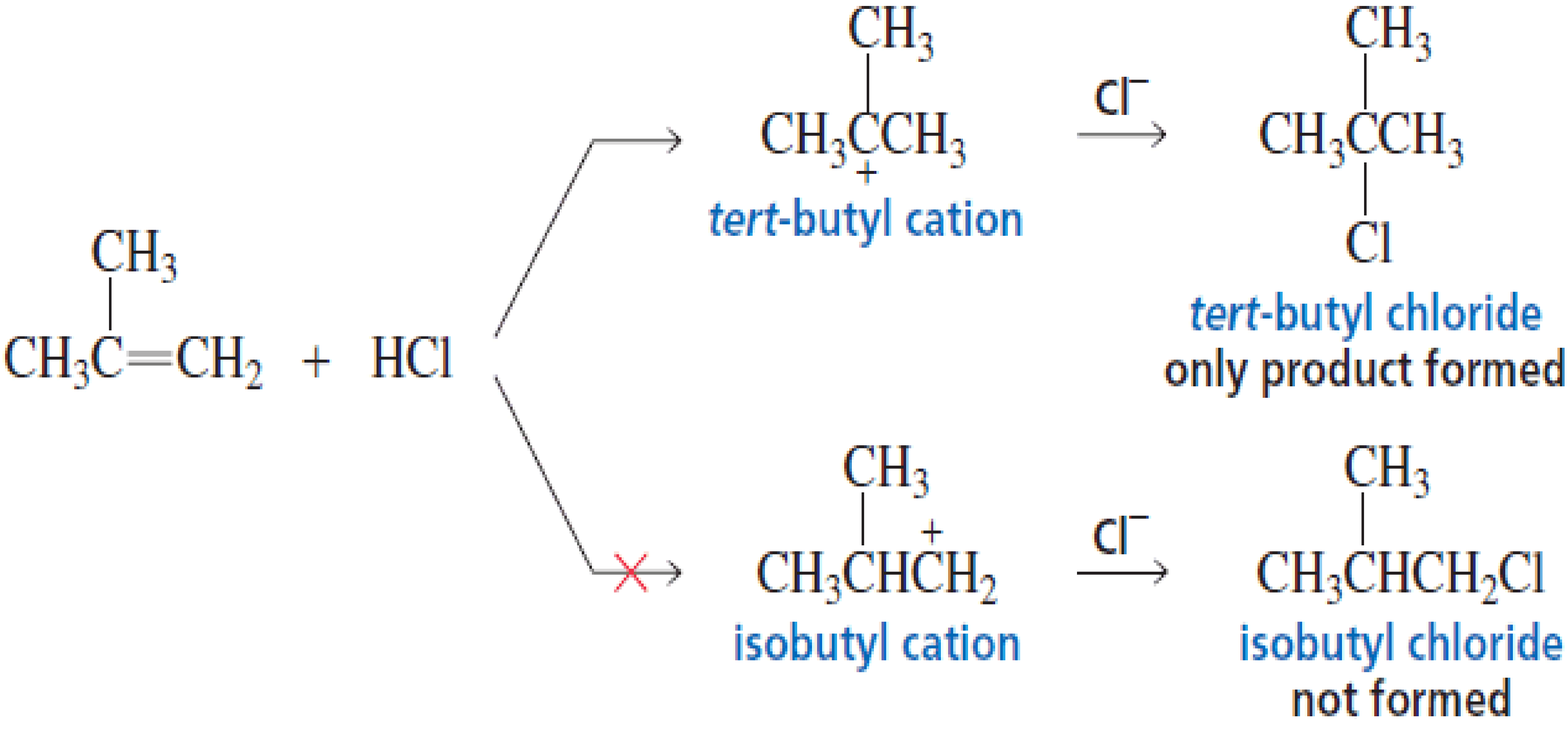
$$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{acetic acid}]{HBr} CH_3CH_2\underset{\substack{|\\ Br}}{CH}CH_3$$

(80%)



(100%)

Mechanistic Basis for Markovnikov's Rule: Example 1



$CH_3C(CH_3){=}CH_2 + HCl$

$\longrightarrow CH_3\overset{+}{C}(CH_3)CH_3 \xrightarrow{Cl^-} CH_3C(CH_3)(Cl)CH_3$

tert-butyl cation

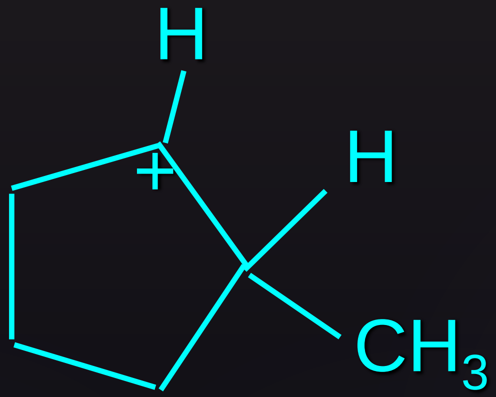
tert-butyl chloride
only product formed

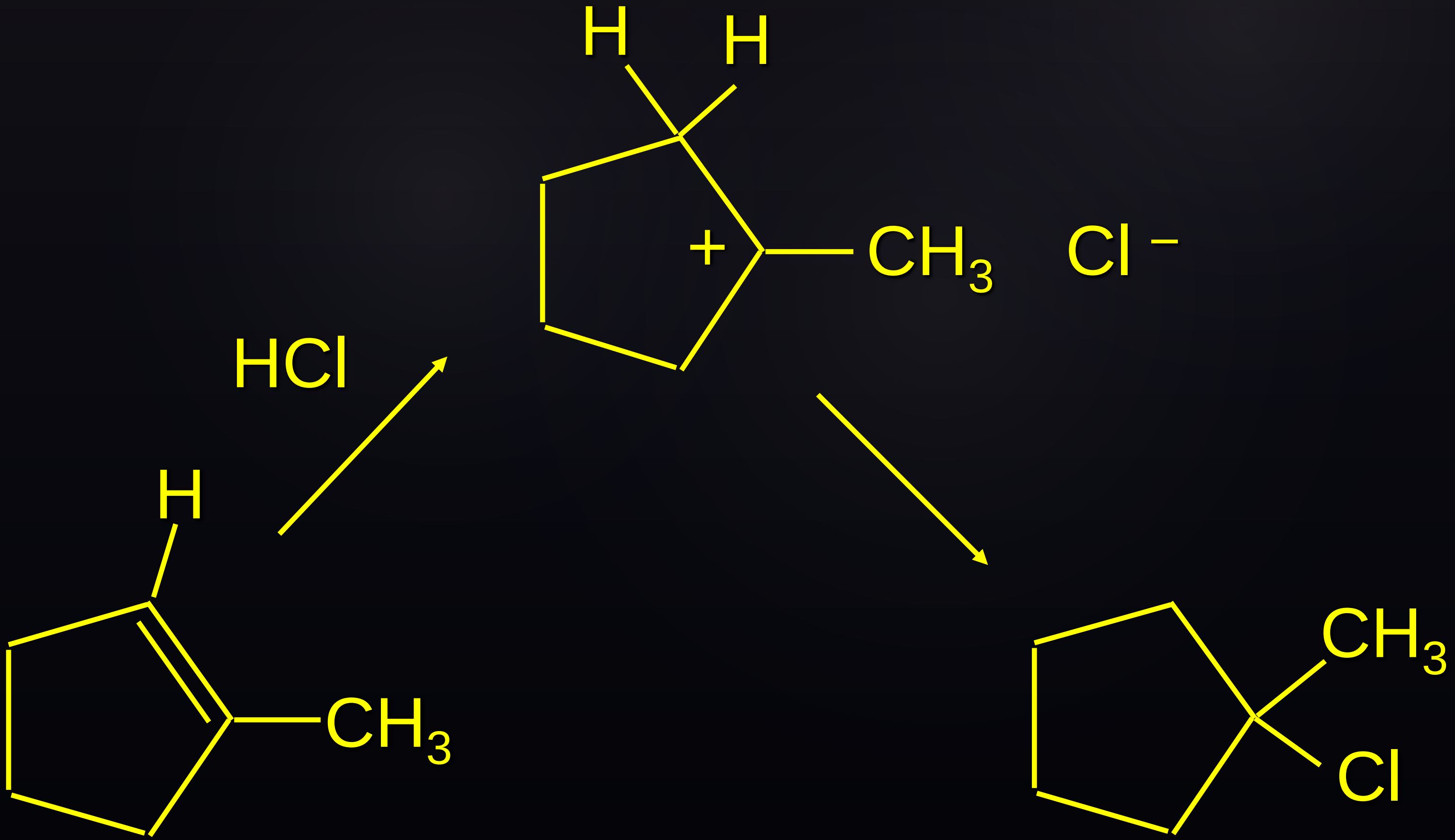
$\not\longrightarrow CH_3CH(CH_3)\overset{+}{C}H_2 \xrightarrow{Cl^-} CH_3CH(CH_3)CH_2Cl$

isobutyl cation

isobutyl chloride
not formed

secondary
carbocation is
less stable:
not formed





Anti Markovnikov's Rule
Or
Peroxide effect

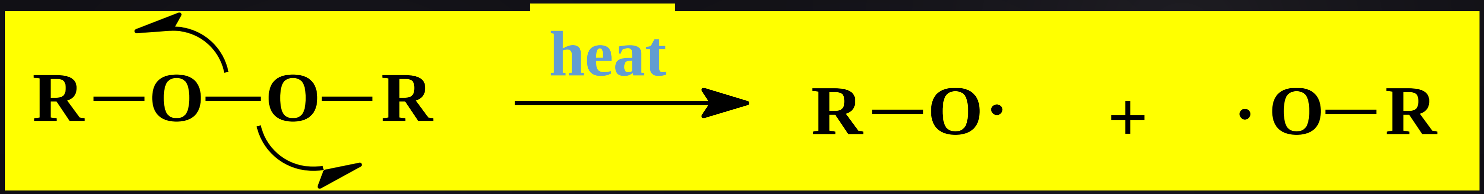
When alkenes are treated with HBr in the presence of *peroxides* (i.e., compounds with the general formula ROOR) the addition occurs in an anti-Markovnikov manner in the sense that the hydrogen atom becomes attached to the carbon atom with fewer hydrogen atoms.

$$CH_3CH{=}CH_2 + HBr \xrightarrow{ROOR} CH_3CH_2CH_2Br$$

This anti-Markovnikov addition occurs *only when HBr is used in the presence of peroxides* and does not occur significantly with HF, HCl, and HI even when peroxides are present.

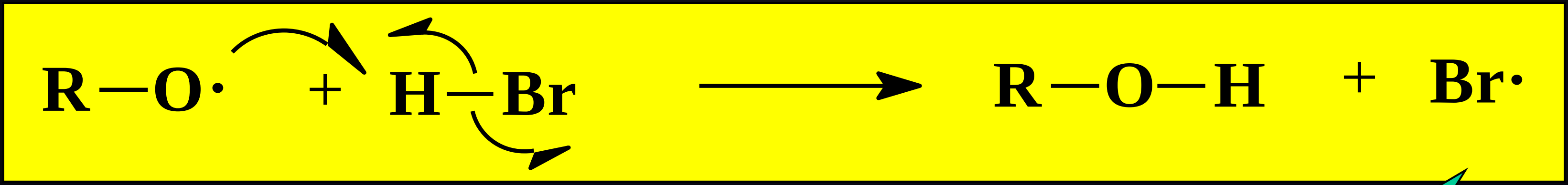
Free Radical Initiation

- **Peroxide O-O bond breaks easily to form free radicals.**



$$R{-}O{-}O{-}R \xrightarrow{\text{heat}} R{-}O\cdot + \cdot O{-}R$$

- Hydrogen is abstracted from HBr.

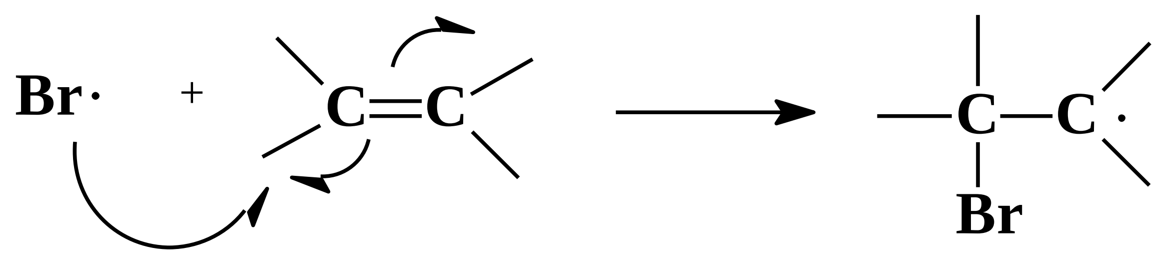


$$R{-}O\cdot + H{-}Br \longrightarrow R{-}O{-}H + Br\cdot$$

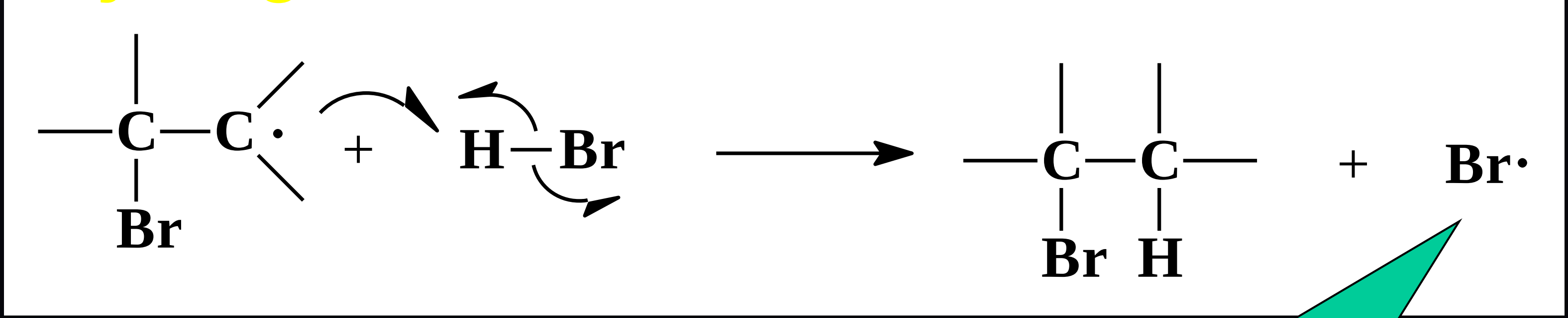
Electrophile

Propagation Steps

- **Bromine adds to the double bond.**

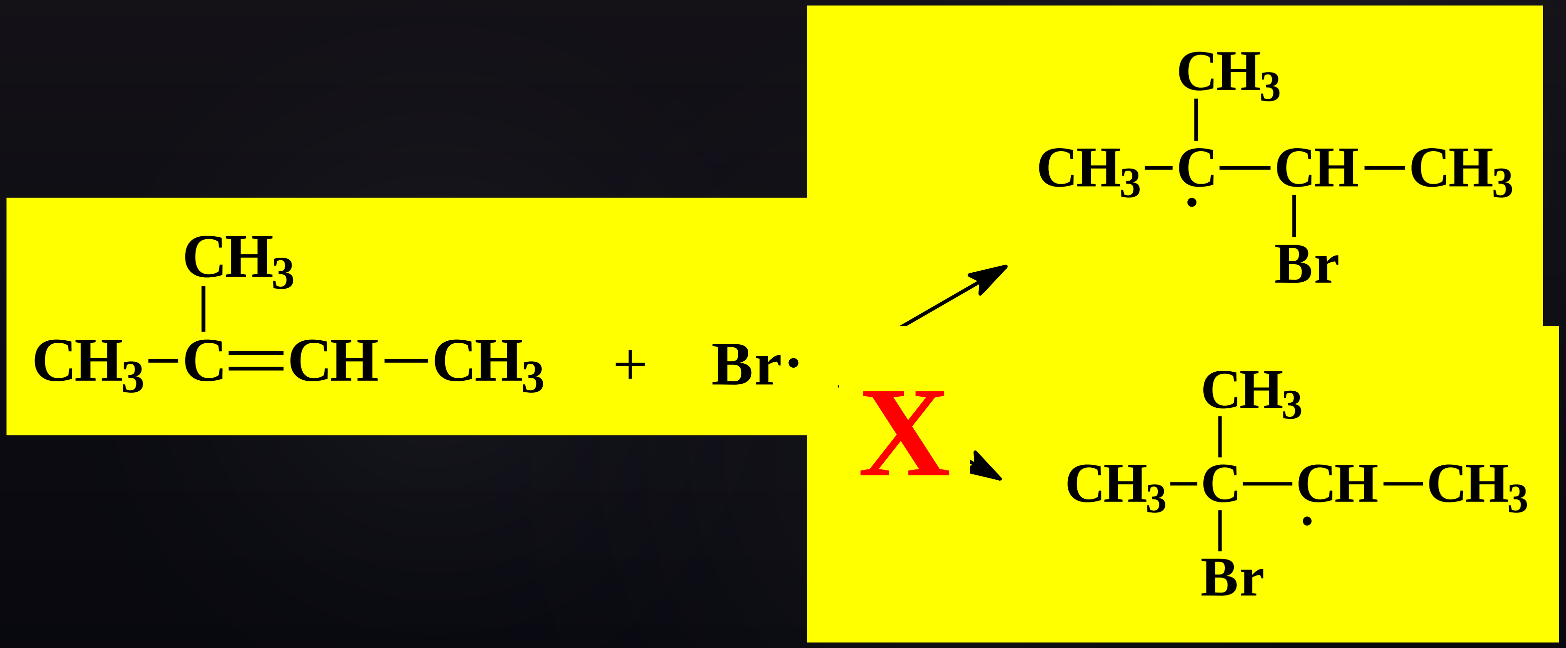


- **Hydrogen is abstracted from HBr.**



Electrophile =>

Anti-Markovnikov ??



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \quad + \quad Br\cdot$$

$$\rightarrow CH_3-\underset{\cdot}{\overset{CH_3}{\overset{|}{C}}}-\underset{Br}{\underset{|}{CH}}-CH_3$$

$$\xrightarrow{X} CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{\cdot}{CH}-CH_3$$

- Tertiary radical is more stable, so that intermediate forms faster. =>

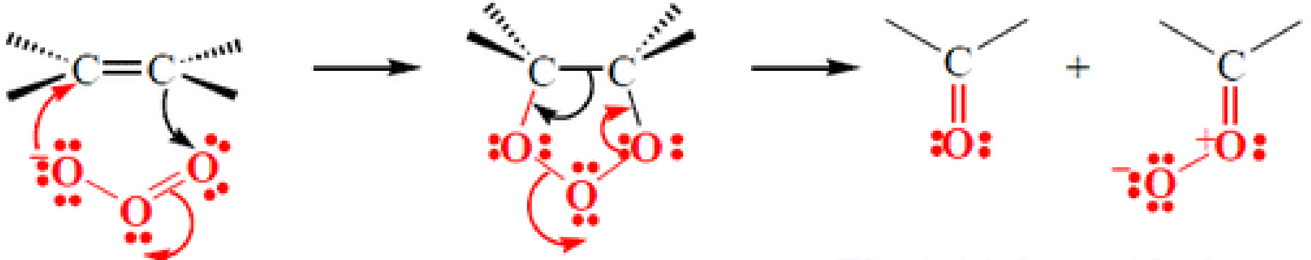
OZONOLYSIS OF ALKENES

- Ozone reacts vigorously with alkenes to form unstable initial ozonides(molozonides) which rearrange spontaneously to form ozonides.

- The rearrangement is thought to go through dissociation of the initial ozonide into reactive fragments that recombine to give the ozonide.

- Ozonides are not usually isolated but are reduced directly by treatment with znic and acetic acid (HOAc).

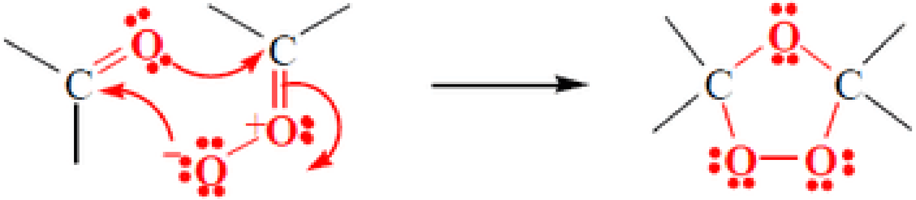
Ozonide Formation from an Alkene



Ozone adds to the alkene to form an initial ozonide.

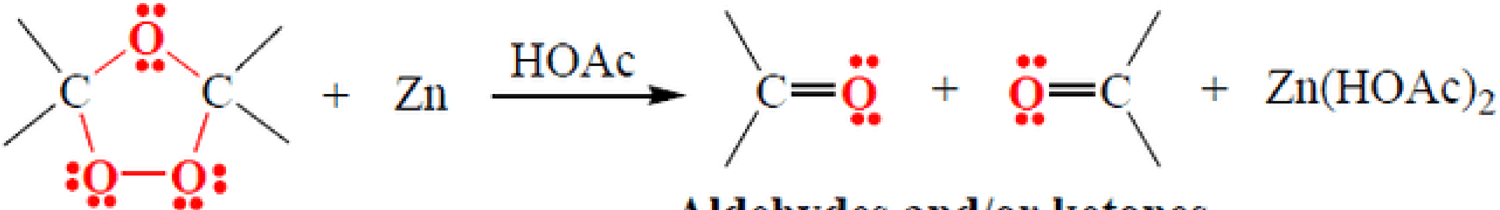
Initial ozonide

The initial ozonide fragments.



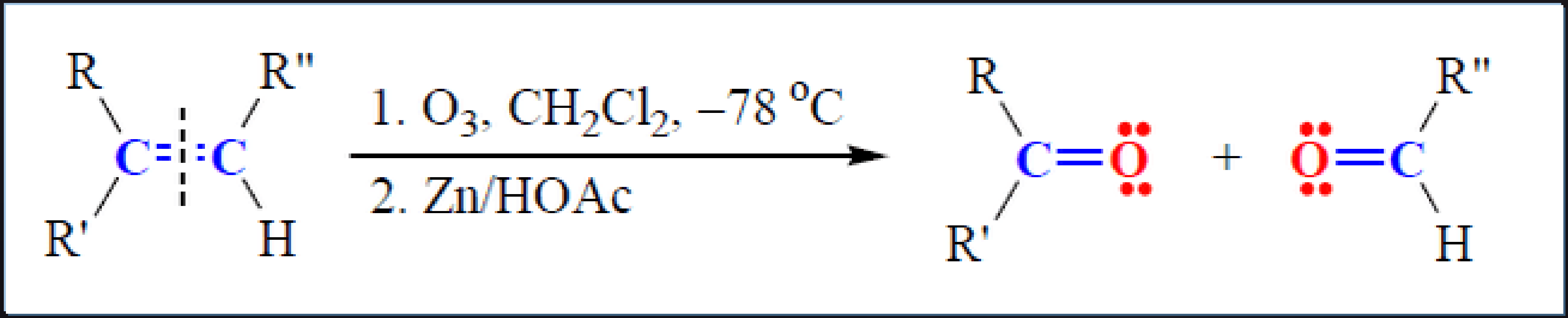
The fragments recombine to form the ozonide.

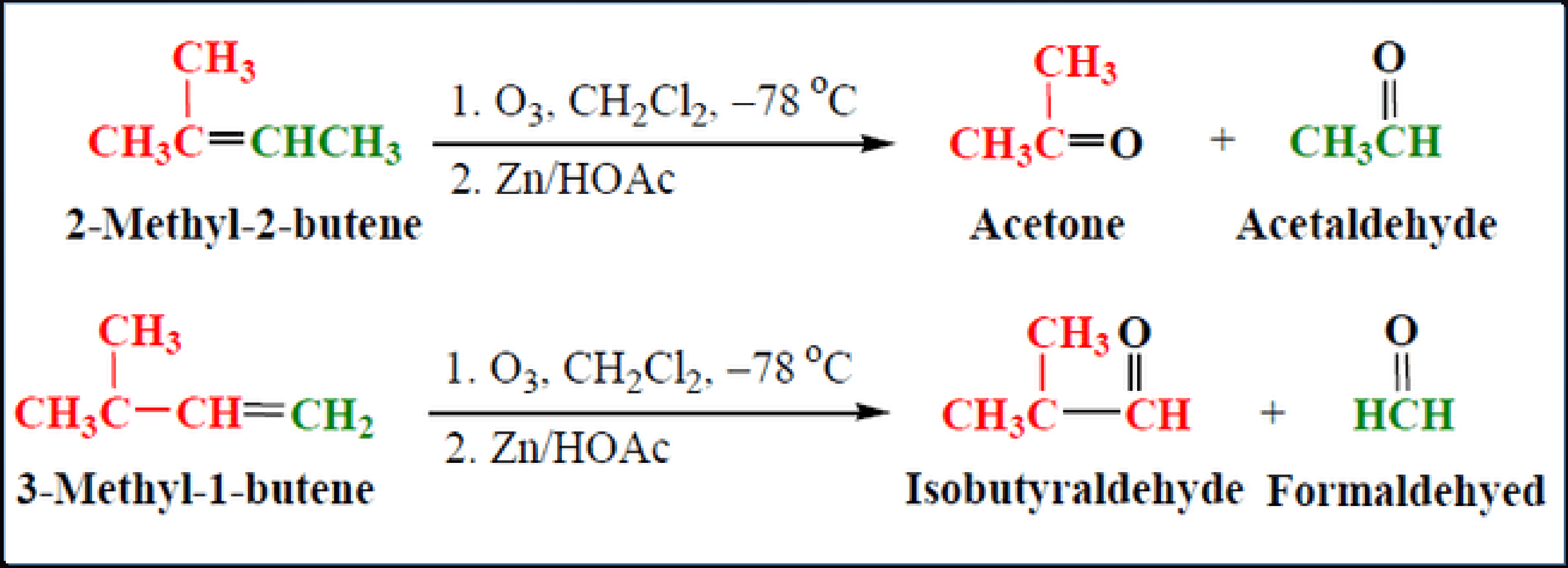
Ozonide



Ozonide

Aldehydes and/or ketones





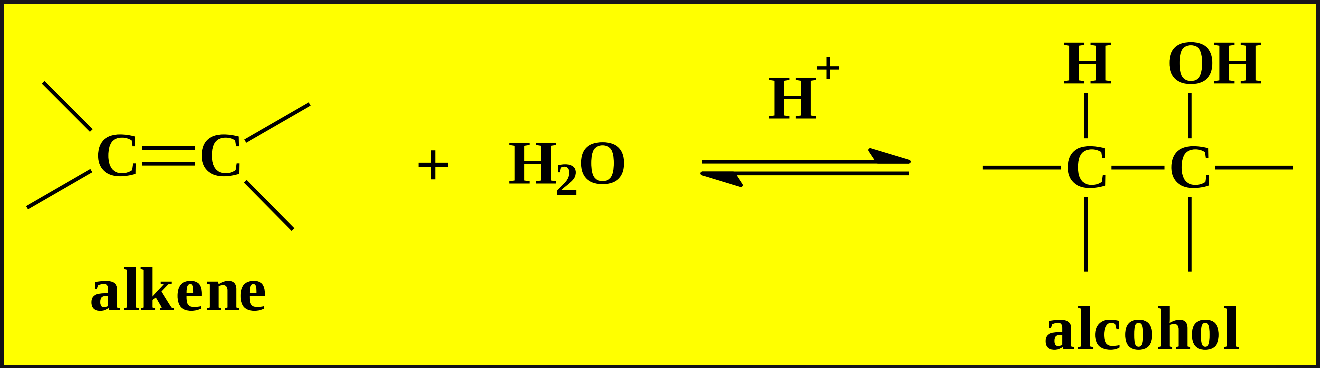
$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_3 \xrightarrow[\text{2. Zn/HOAc}]{\text{1. } O_3\text{, } CH_2Cl_2\text{, } -78\ ^{\circ}C} CH_3\overset{CH_3}{\overset{|}{C}}=O + CH_3\overset{O}{\overset{\|}{C}}H$$

2-Methyl-2-butene Acetone Acetaldehyde

$$CH_3\overset{CH_3}{\overset{|}{C}}-CH=CH_2 \xrightarrow[\text{2. Zn/HOAc}]{\text{1. } O_3\text{, } CH_2Cl_2\text{, } -78\ ^{\circ}C} CH_3\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}H + H\overset{O}{\overset{\|}{C}}H$$

3-Methyl-1-butene Isobutyraldehyde Formaldehyed

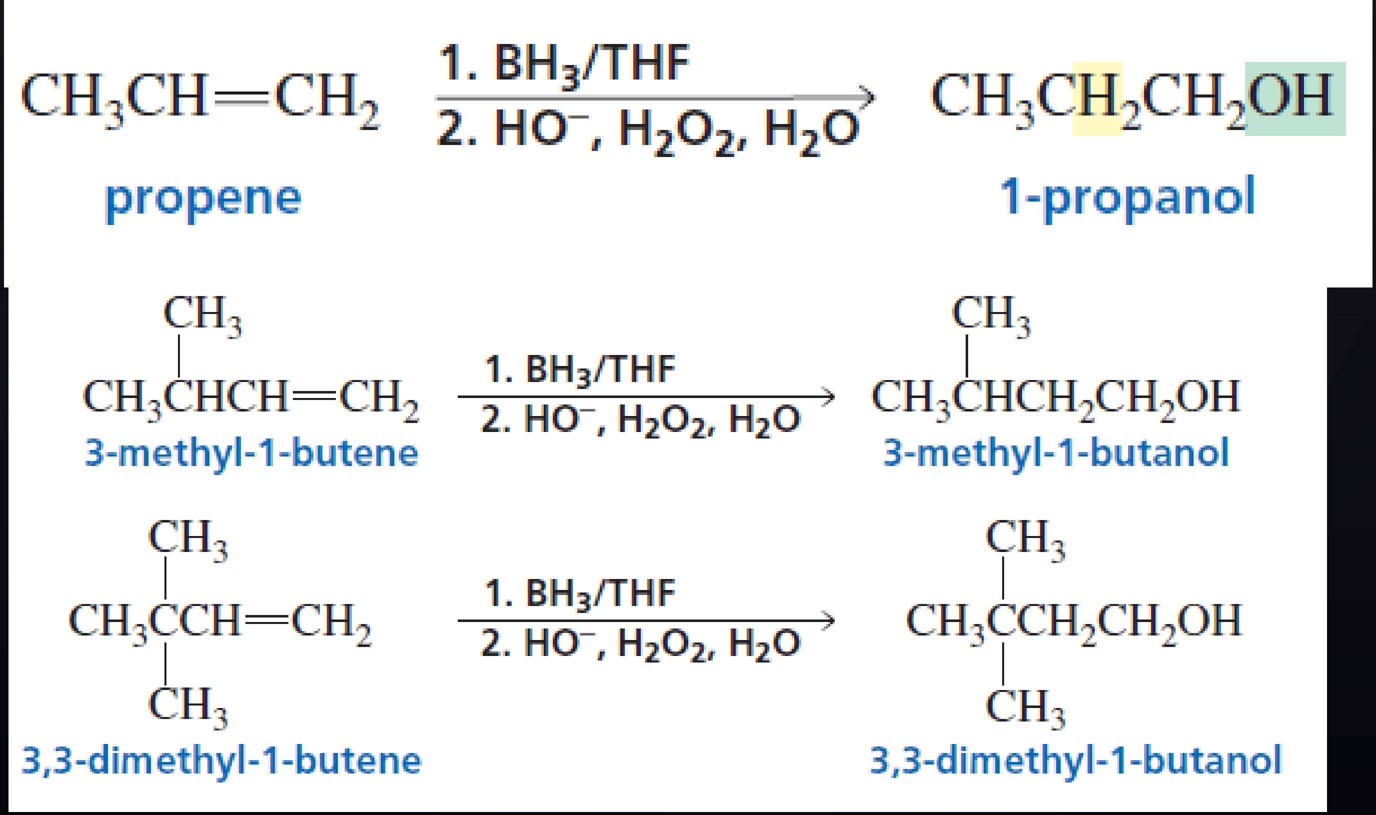
Hydration of Alkenes



- Oxymercuration-Demercuration
  - Markovnikov product formed
  - Anti addition of H-OH
  - No rearrangements
- Hydroboration
  - Anti-Markovnikov product formed
  - Syn addition of H-OH

HYDROBORATION–OXIDATION

The addition of borane to an alkene, followed by reaction with hydroxide ion and hydrogen peroxide, is called **hydroboration–oxidation**.



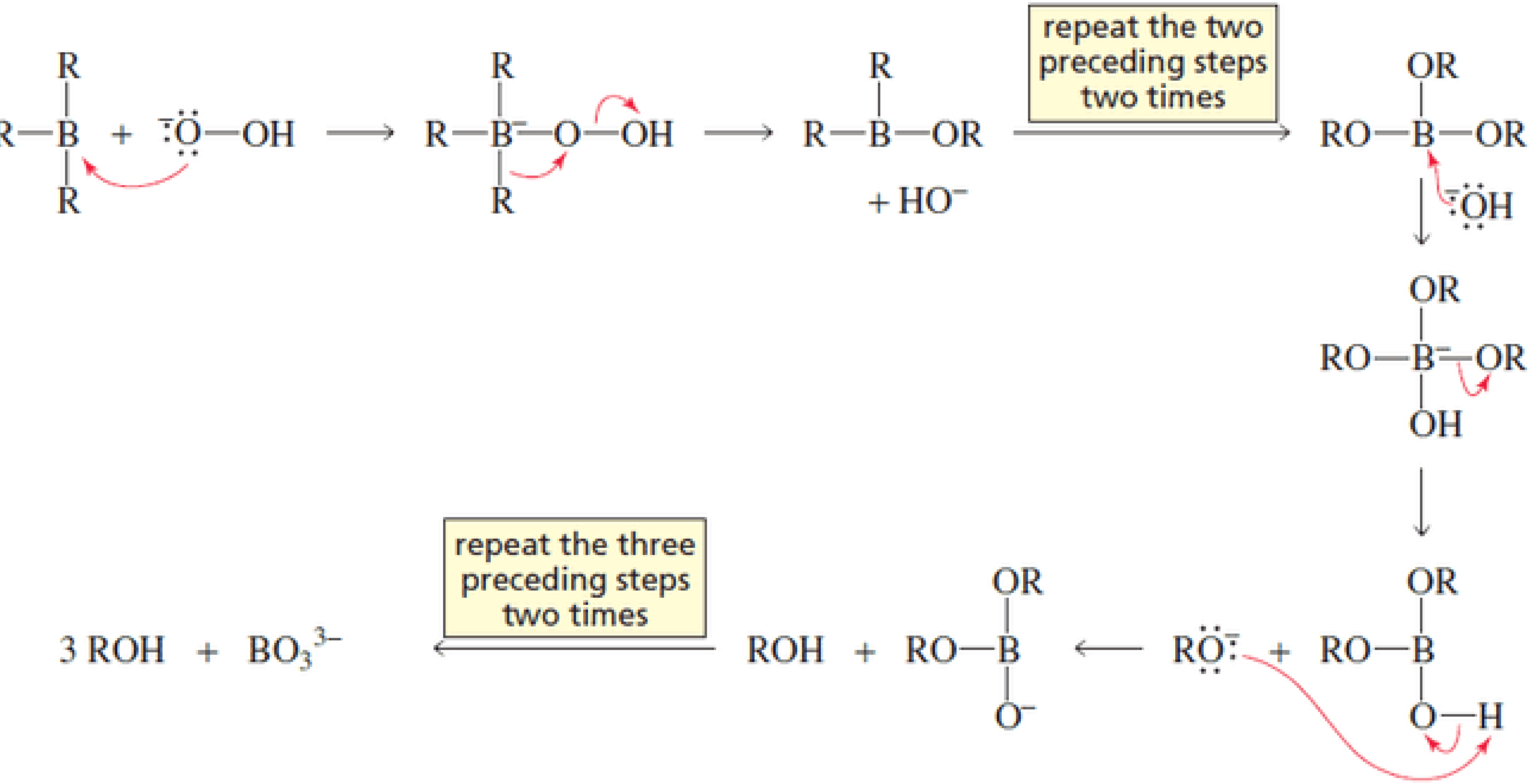
$$\underset{\text{propene}}{CH_3CH{=}CH_2} \xrightarrow[\text{2. } HO^-,\ H_2O_2,\ H_2O]{\text{1. } BH_3/THF} \underset{\text{1-propanol}}{CH_3CH_2CH_2OH}$$

$$\underset{\text{3-methyl-1-butene}}{CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH{=}CH_2} \xrightarrow[\text{2. } HO^-,\ H_2O_2,\ H_2O]{\text{1. } BH_3/THF} \underset{\text{3-methyl-1-butanol}}{CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_2OH}$$

$$\underset{\text{3,3-dimethyl-1-butene}}{CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH{=}CH_2} \xrightarrow[\text{2. } HO^-,\ H_2O_2,\ H_2O]{\text{1. } BH_3/THF} \underset{\text{3,3-dimethyl-1-butanol}}{CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_2CH_2OH}$$

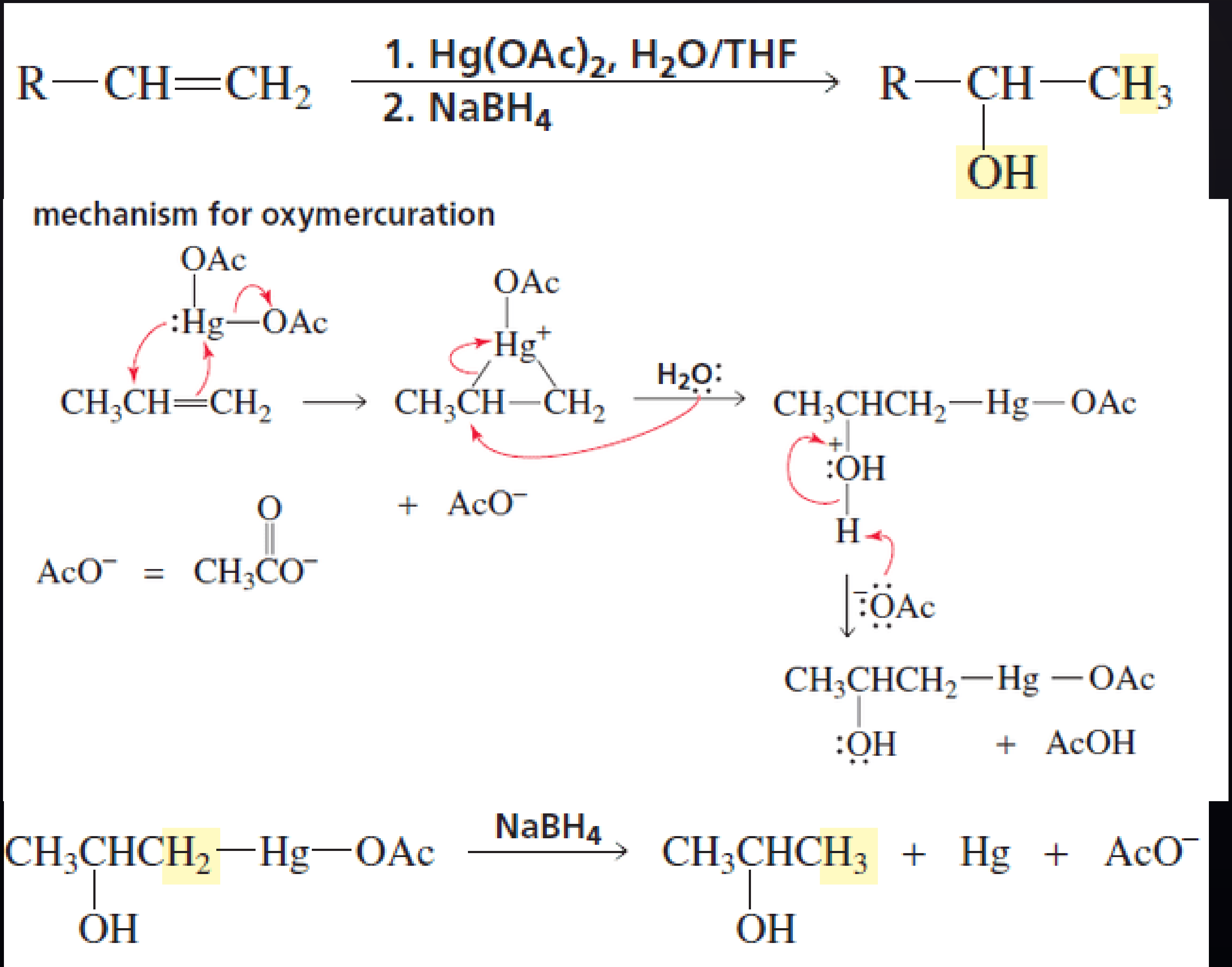
$$3\,CH_3CH{=}CH_2 + BH_3 \xrightarrow{THF} (CH_3CH_2CH_2)_3B \xrightarrow[H_2O]{HO^-,\ H_2O_2} 3\,CH_3CH_2CH_2OH + BO_3^{3-}$$

$$HOOH + HO^- \rightleftharpoons HOO^- + H_2O$$



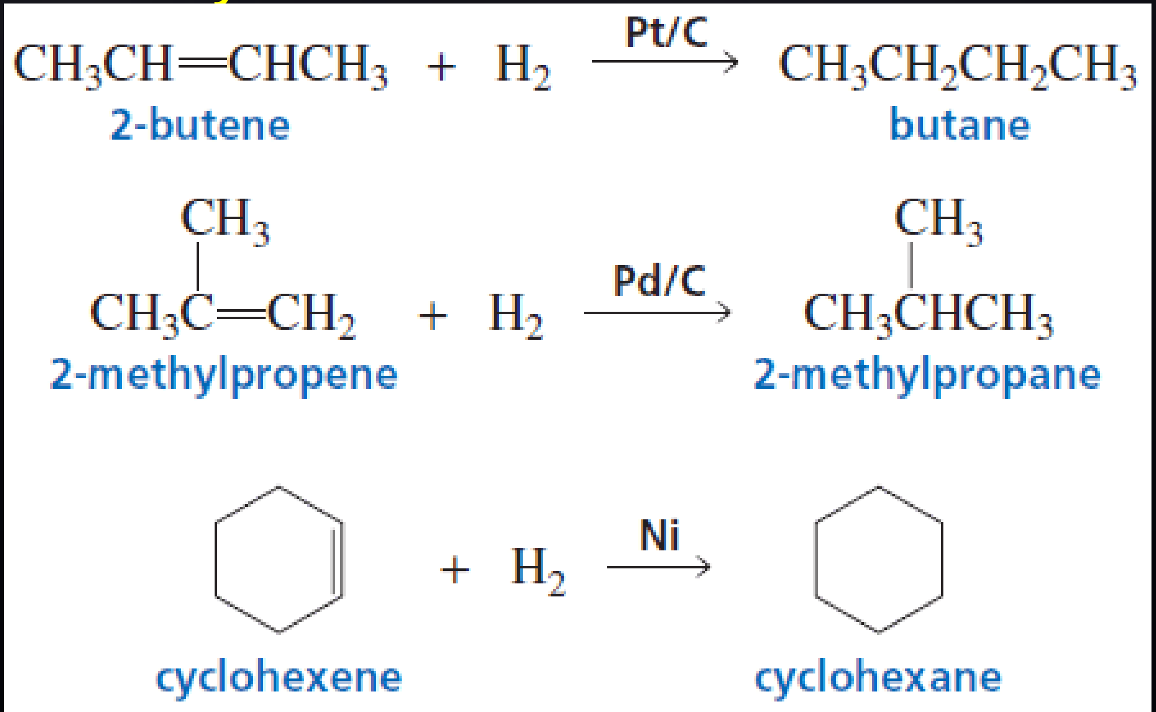
Oxymercuration–demercuration

In oxymercuration, the alkene is treated with mercuric acetate in aqueous tetrahydrofuran (THF). When reaction with that reagent is complete, sodium borohydride is added to the reaction mixture.

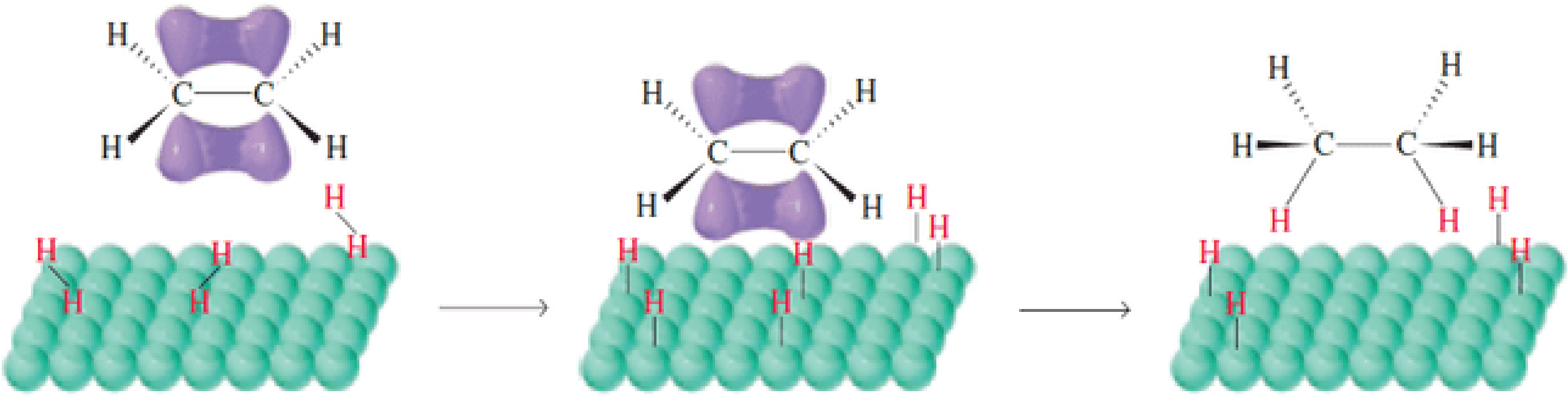


Catalytic hydrogenation of alkenes

In the presence of a metal catalyst such as Pt, Pd, or Ni, H_2 adds to the double bond of an alkene to form an alkane. Without the catalyst, the energy barrier to the reaction would be enormous because the H -H bond is so strong. The catalyst decreases the energy of activation by breaking the H –H bond. Pt and Pd are used in a finely divided state adsorbed on charcoal (Pt/C, Pd/C). The platinum catalyst is frequently used in the form of which is known as Adams catalyst.



The addition of hydrogen is called **hydrogenation**. Because the preceding reactions require a catalyst, they are examples of **catalytic hydrogenation**.



hydrogen molecules settle on the surface of the catalyst and react with the metal atoms

the alkene approaches the surface of the catalyst

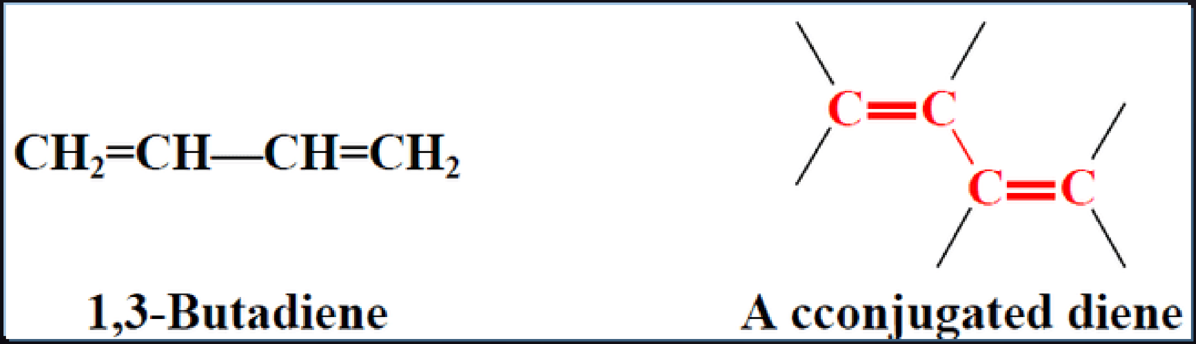
the π bond between the two carbons is replaced by two C—H σ bonds

H_2 is adsorbed on the surface of the metal and that the alkene complexes with the metal by overlapping its own *p* orbitals with vacant orbitals of the metal. Breaking the π bond of the alkene and the sigma bond of H_2 and forming the C-H sigma bonds all occur on the surface of the metal.

Alkadienes

Cumulated, conjugated, and isolated diene.

IN CONJUGATED POLYENES THE DOUBLE AND SINGLE BONDS ALTERNATE ALONG THE CHAIN.

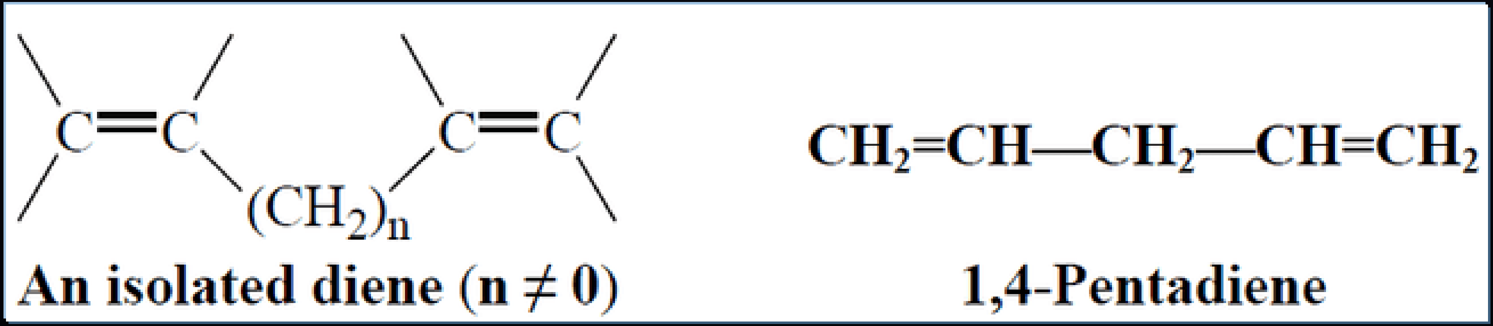


$CH_2{=}CH{-}CH{=}CH_2$

1,3-Butadiene

A cconjugated diene

If one or more saturated carbon atoms intervene between the double bonds of an alkadiene, the double bonds are said to be isolated.



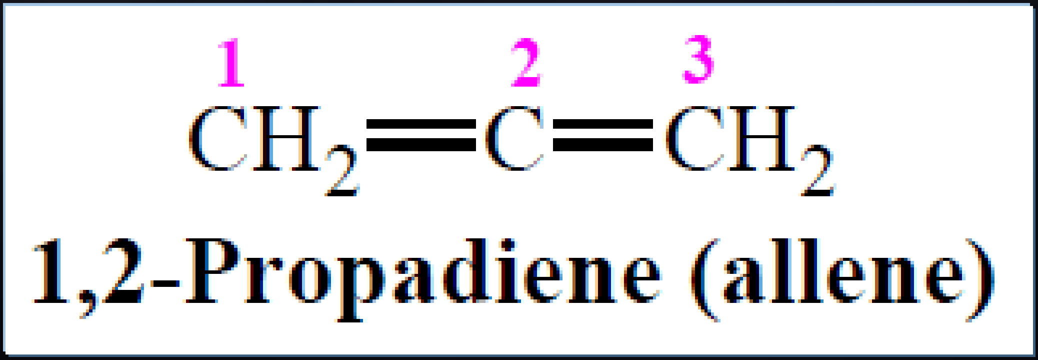
$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

An isolated diene ($n \neq 0$)

1,4-Pentadiene

Conjugated dienes are more stable than isolated dienes.

Cumulated dienes have the double bonds sharing a common atom as in a group of compounds called allenes.

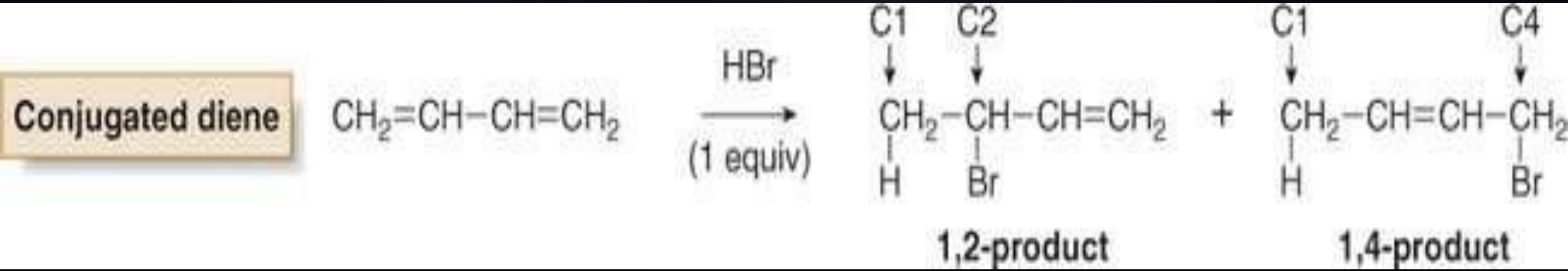


$$\overset{1}{CH_2}=\overset{2}{C}=\overset{3}{CH_2}$$

1,2-Propadiene (allene)

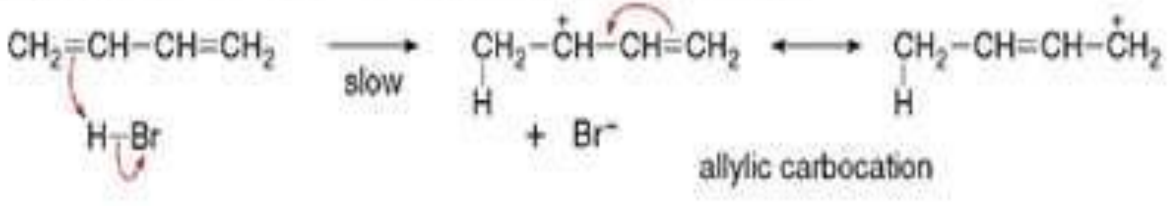
1,2 addition vs 1, 4 addition

- The 1,2-addition product results from Markovnikov addition of HBr across two adjacent carbon atoms (C1 and C2) of the diene.
- The 1,4-addition product results from addition of HBr to the two end carbons (C1 and C4) of the diene. 1,4-Addition is also called conjugate addition.



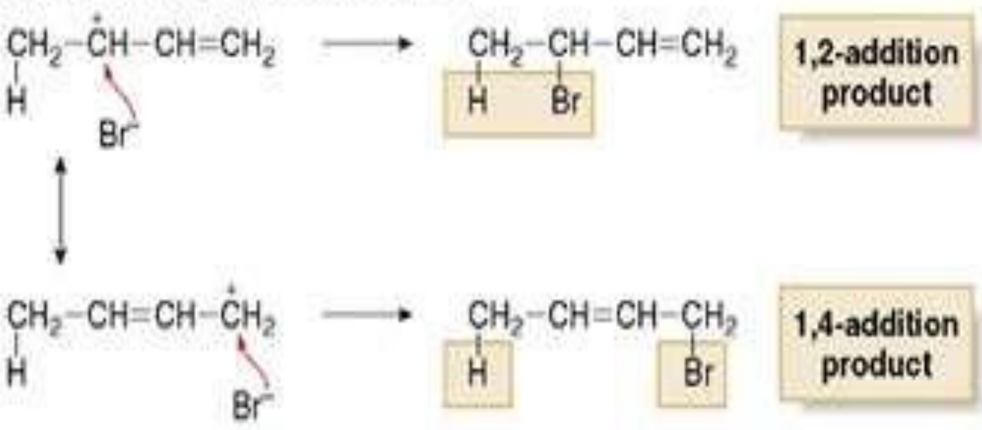
Mechanism 16.1 Electrophilic Addition of HBr to a 1,3-Diene—1,2- and 1,4-Addition

Step [1] Addition of the electrophile (H^+) to the π bond



- Addition of H^+ (from HBr) forms a new C–H bond as the H–Br bond is broken. H^+ always adds to a terminal C of the 1,3-diene to form a resonance-stabilized carbocation. This is the slow step of the mechanism because two bonds are broken and only one is formed.

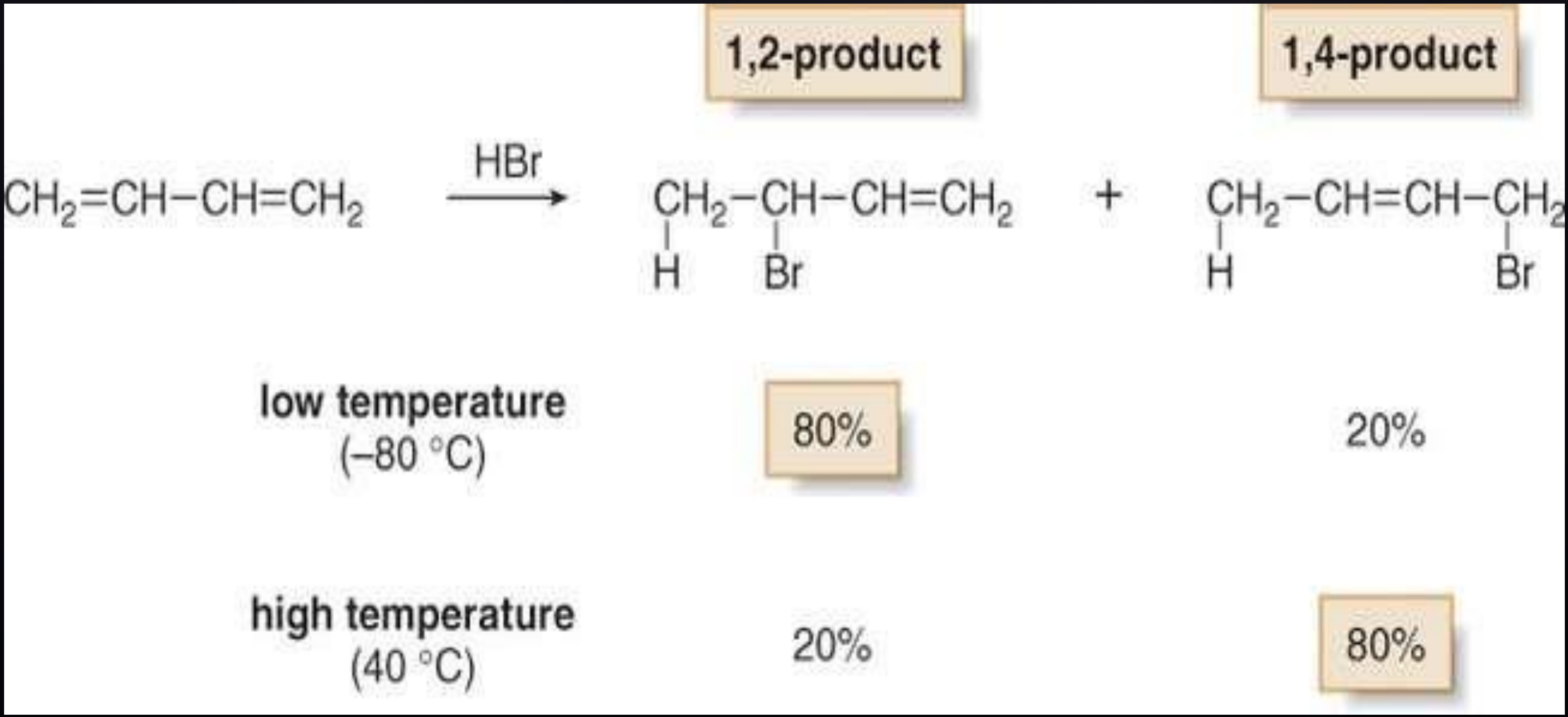
Step [2] Nucleophilic attack of Br^-



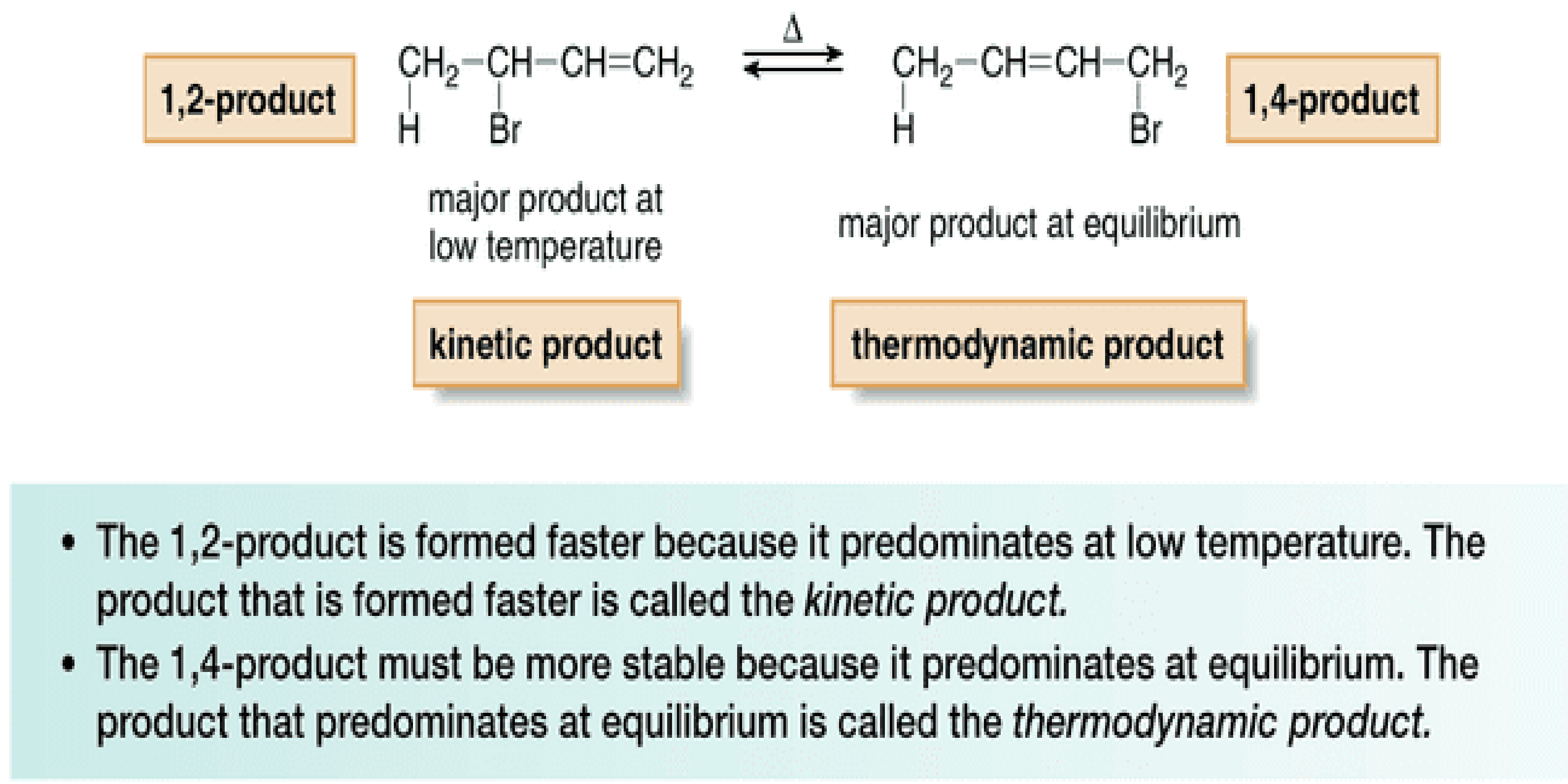
- **Nucleophilic attack of Br^-** can occur at either site of the resonance-stabilized carbocation that bears a (+) charge, forming either the 1,2-addition product or the 1,4-addition product.

Kinetic Vs Thermodynamic Products

- The amount of 1,2- and 1,4-addition products formed in electrophilic addition reactions of conjugated dienes depends greatly on the reaction conditions.



- When a mixture containing predominantly the 1,2-product is heated, the 1,4-addition product becomes the major product at equilibrium.



1,2-product

$$\underset{\text{H}}{\text{CH}_2}-\underset{\text{Br}}{\text{CH}}-\text{CH}=\text{CH}_2 \underset{}{\overset{\Delta}{\rightleftharpoons}} \underset{\text{H}}{\text{CH}_2}-\text{CH}=\text{CH}-\underset{\text{Br}}{\text{CH}_2}$$

1,4-product

major product at low temperature

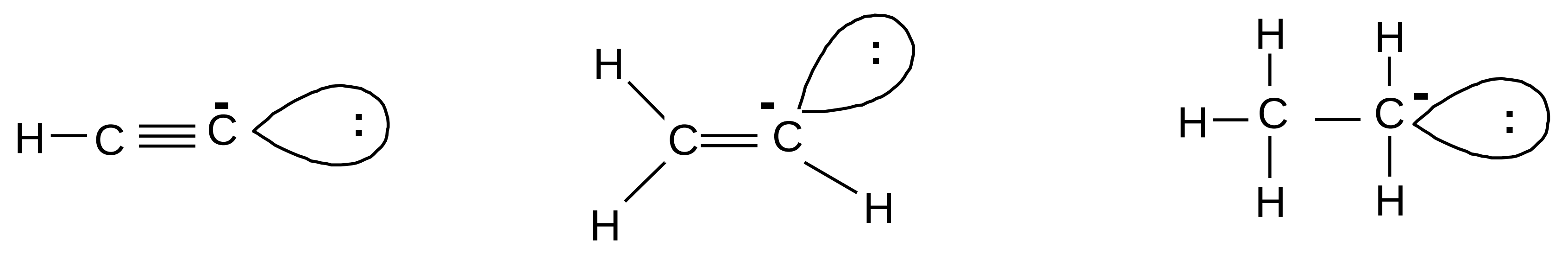
major product at equilibrium

kinetic product

thermodynamic product

- The 1,2-product is formed faster because it predominates at low temperature. The product that is formed faster is called the *kinetic product.*
- The 1,4-product must be more stable because it predominates at equilibrium. The product that predominates at equilibrium is called the *thermodynamic product.*

Alkynes



Acetylide anions

Vinyl anion

Ethyl anion

$$HC \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$$

Acidic nature of alkyne

The hydrogen atoms of ethyne are considerably more acidic than those of ethane or ethane.

The acetylenic hydrogen is weakly acidic (p*K*a ~ 25) and can be removed with a strong base (e.g. NaNH2) to give an anion (called an alkynide anion or acetylide ion).

Acidity of Alkynes

The order of boiling point among hydrocarbons is

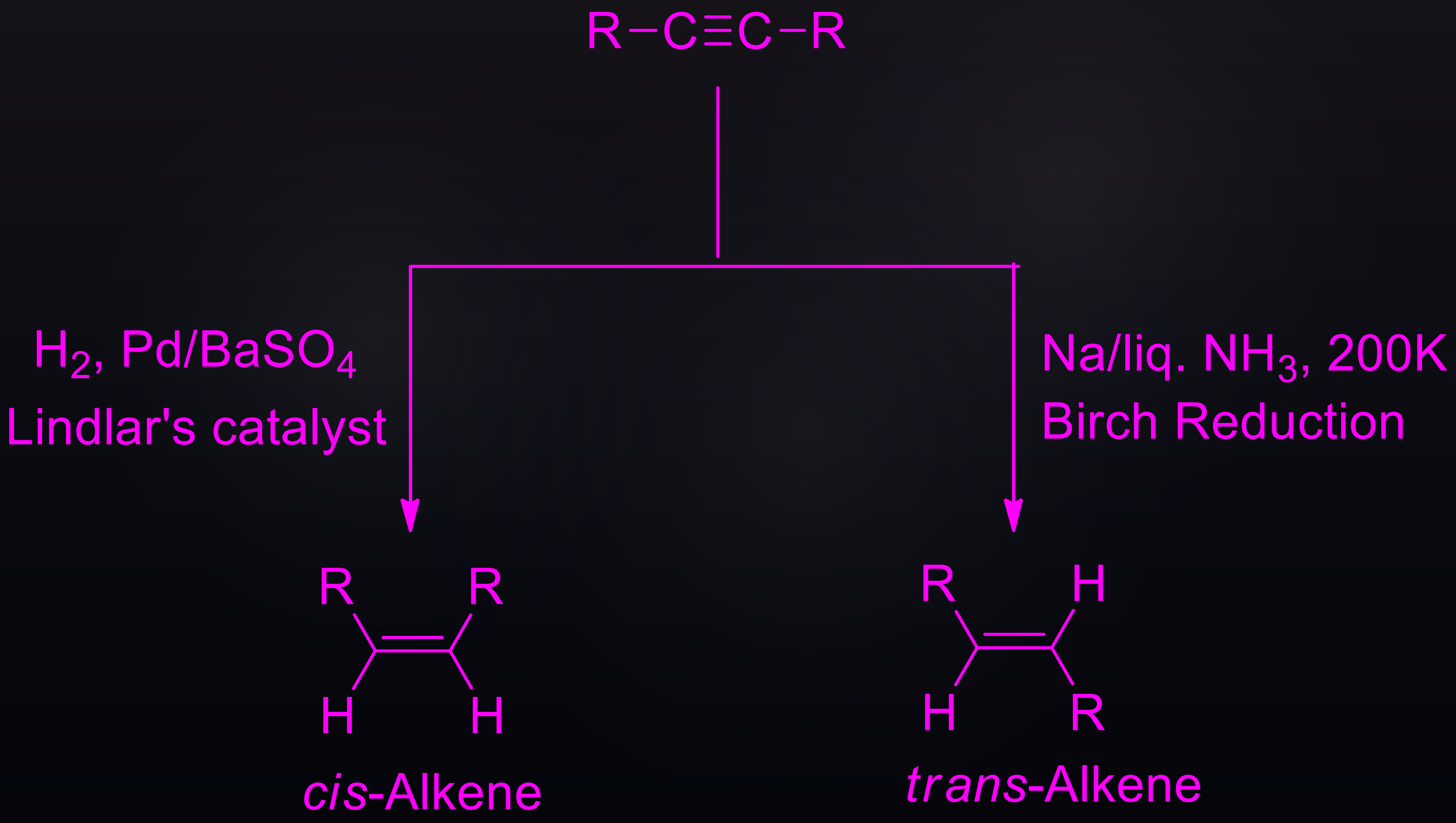
alkynes > alkenes > alkanes.

These hydrocarbons also possess low dipole moment.

$CH_3CH_2C \equiv CH$	$CH_3CH_2CH = CH_2$	$CH_3C \equiv C\ CH_3$
$\mu = 0.80$ D	$\mu = 0.30$ D	$\mu = 0.0$ D

Acetylene having two hydrogen atoms is more acidic than a mono substituted acetylene.

Alkenes via Alkyne Reduction



$R-C\equiv C-R$

H_2, $Pd/BaSO_4$
Lindlar's catalyst

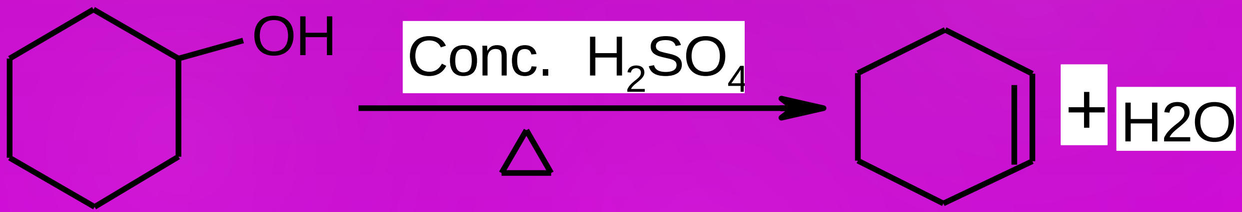
Na/liq. NH_3, 200K
Birch Reduction

cis-Alkene

trans-Alkene

DEHYDRATION OF ALCOHOLS

$$CH_3CH_2CH_2OH \xrightarrow[160°]{Conc.H_2SO_4} CH_3CH = CH_2 + H_2O$$



$$CH_3CH_2CH_2CH_2OH \xrightarrow[300° C]{Al_2O_3} CH_3CH_2CH = CH_2$$

1-butene

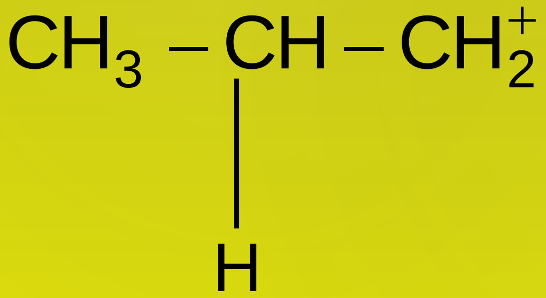
Mechanism

$$CH_3-CH_2-CH_2-OH \overset{H^+}{\rightleftharpoons} CH_3-CH_2-CH_2-OH_2^+$$

Oxonium ion

$$\xrightarrow{-H_2O} CH_3-CH_2-\overset{+}{C}H_2$$

Carbocation

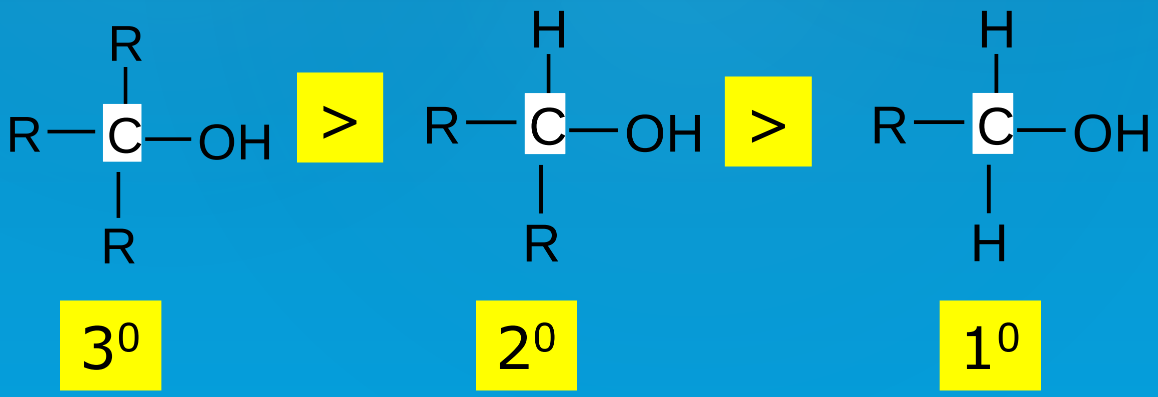


$$CH_3-\underset{\underset{H}{|}}{CH}-CH_2^+ \xrightarrow[-H^+]{} CH_3-CH=CH_2$$

1–propene

Features of dehydration

- A carbocation is formed as an ntermediate.
- The ease of dehydration of alcohols is 3° > 2° > 1°
- 3° carbocation is most stable



$$\mathrm{R-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-OH} \;>\; \mathrm{R-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-OH} \;>\; \mathrm{R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$

3^0 2^0 1^0

Features of dehydration

The stability of alkenes is governed by Saytzeff's rule

$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 \sim RCH=CHR > RCH=CH_2$