臺灣大學化學系
NTU Chemistry

台灣大學開放式課程

有機化學乙

蔡蘊明　教授

Chapter 8
Alkenes and alkynes: addition reactions

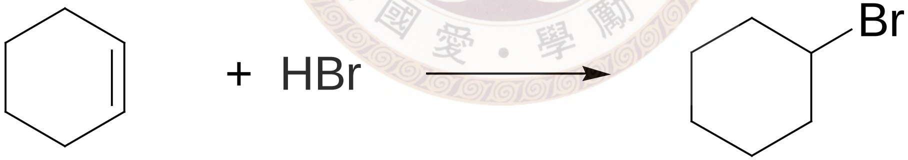
electrophilic

electron rich
nucleophilic

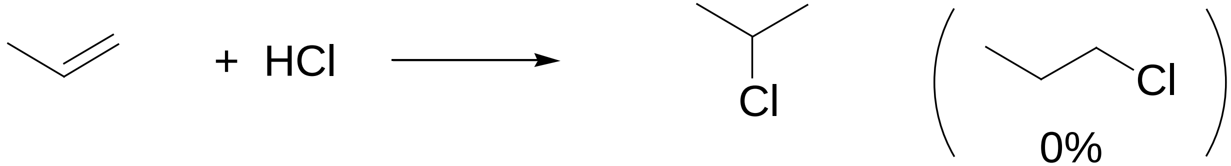
Energetics:
break 1π form 2σ
1σ
In general: exothermic

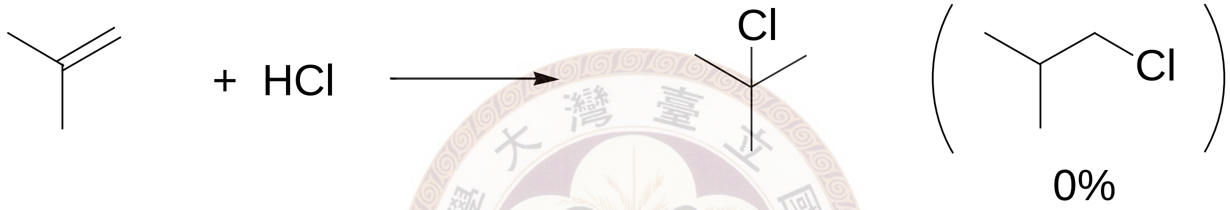
※ Hydrohalogenation: addition of H-X

例



◎ Regioselectivity

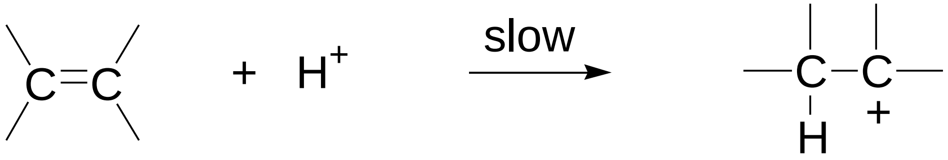




Markovnikov’s rule:

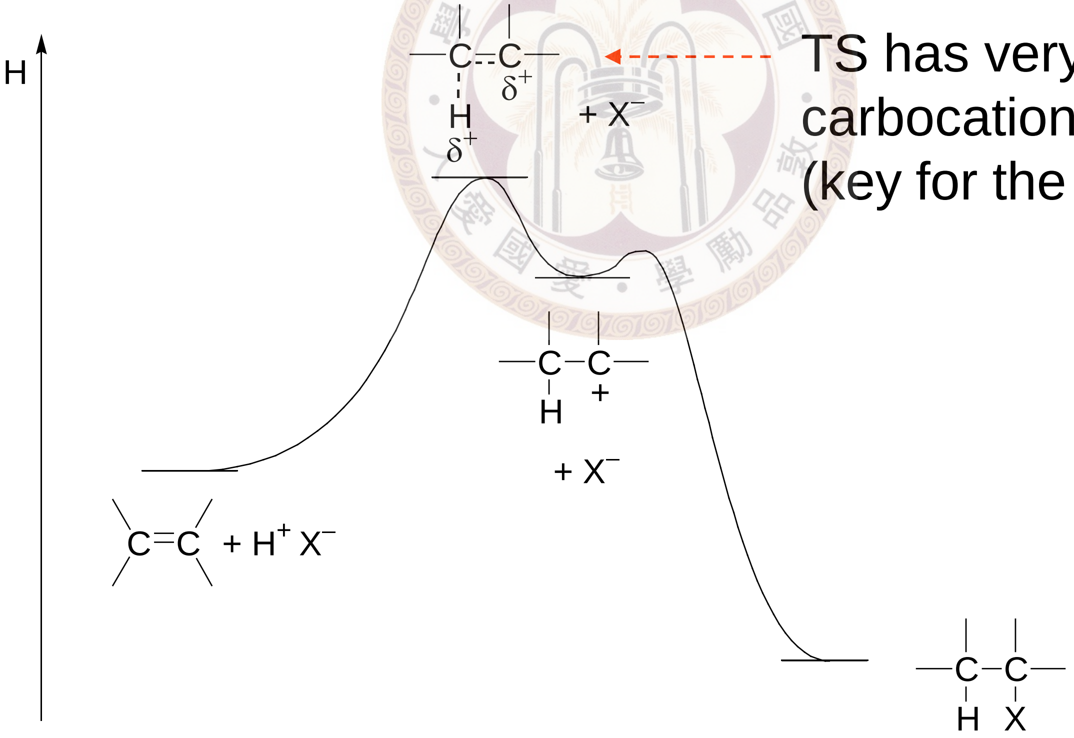
H adds to the C having more H

◎ Mechanism



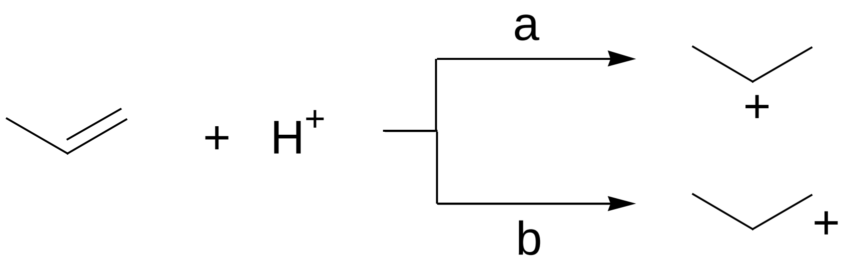
Formation of high E intermediate

Bond formation only

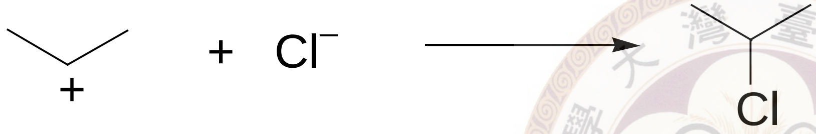


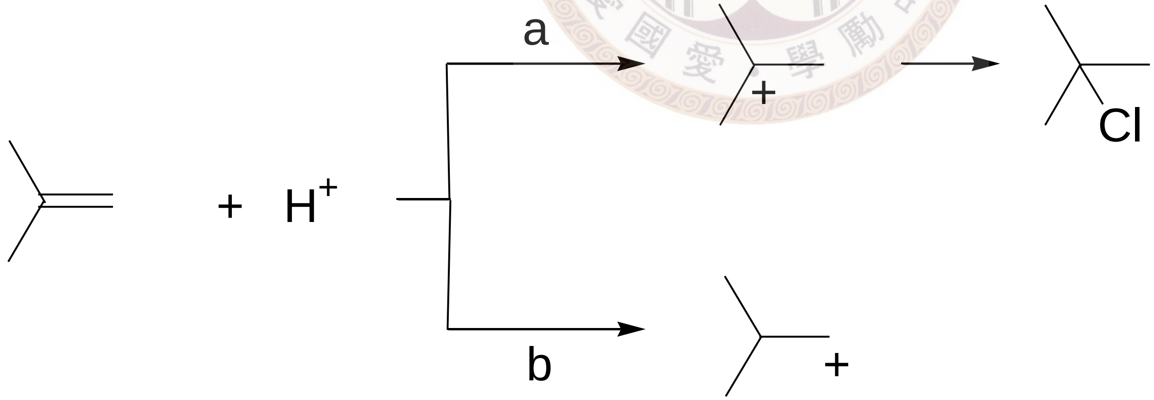
TS has very high carbocation character (key for the regioselectivity)

◎ Reason for the regioselectivity



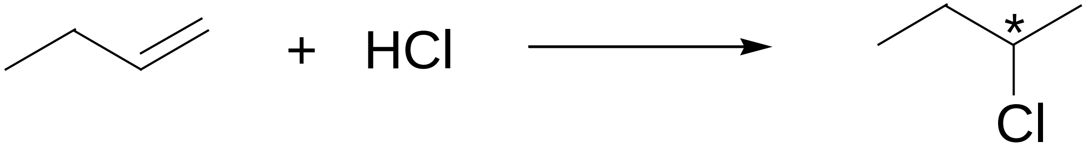
Formation of a more stable carbocation is faster (lower E_a)





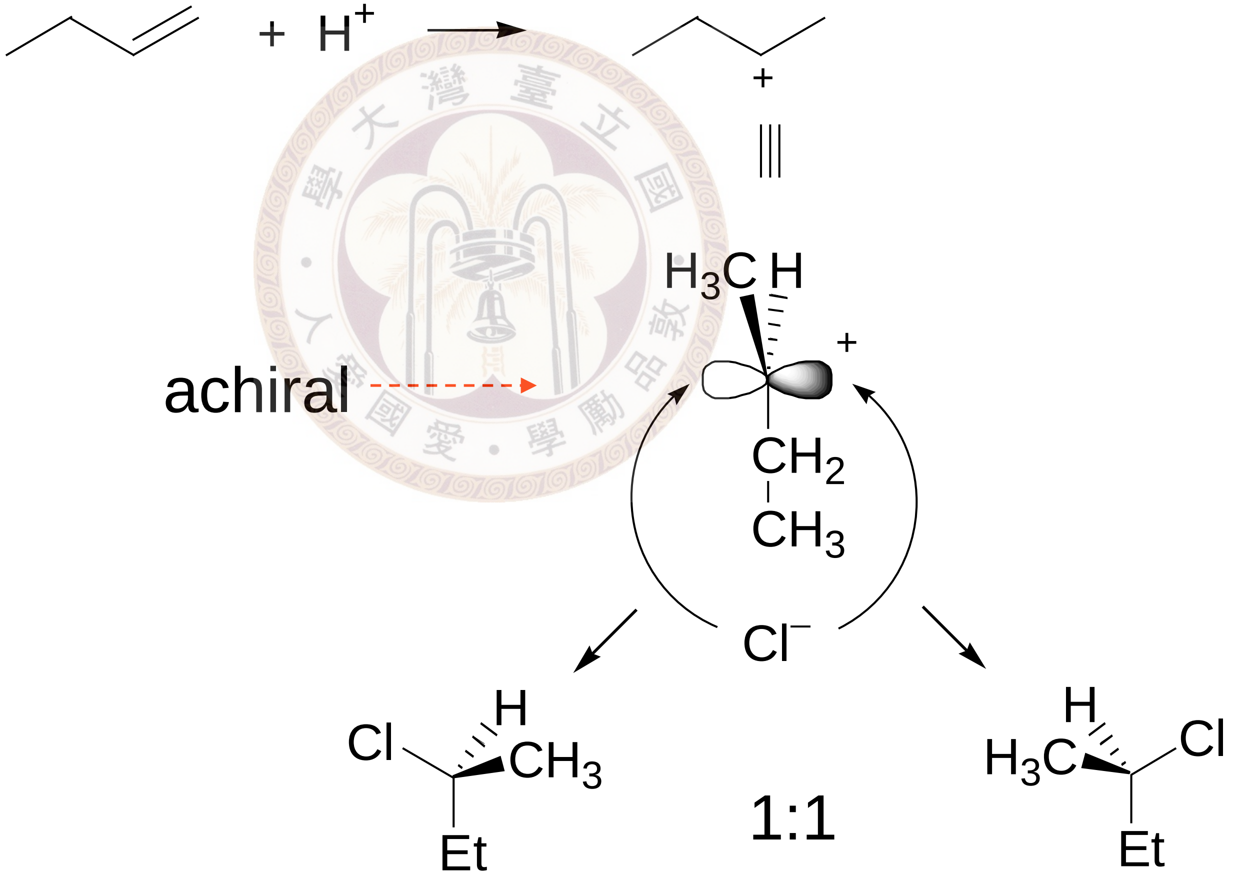
3º carbocation is
very stable:
good selectivity
and very fast rate

◎ Stereochemistry



racemic mixture

Mechanism:

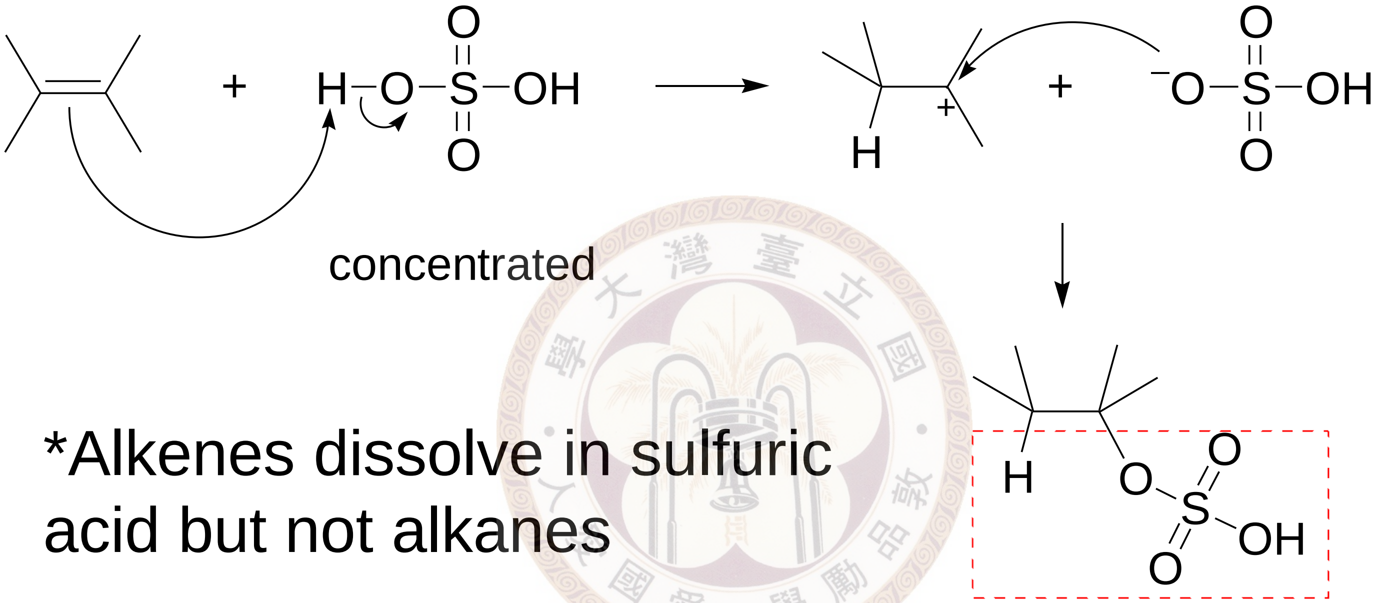


achiral

1:1

equal probability from both side

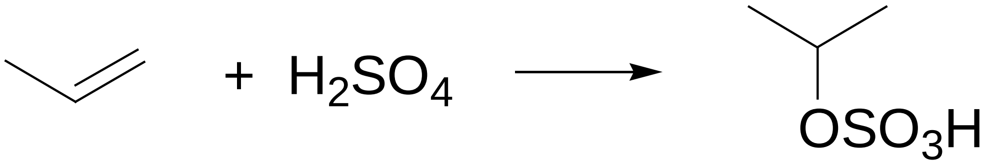
※ Addition of H_2SO_4 (sulfuric acid)



concentrated

an alkyl hydrogen sulfate

*Alkenes dissolve in sulfuric acid but not alkanes

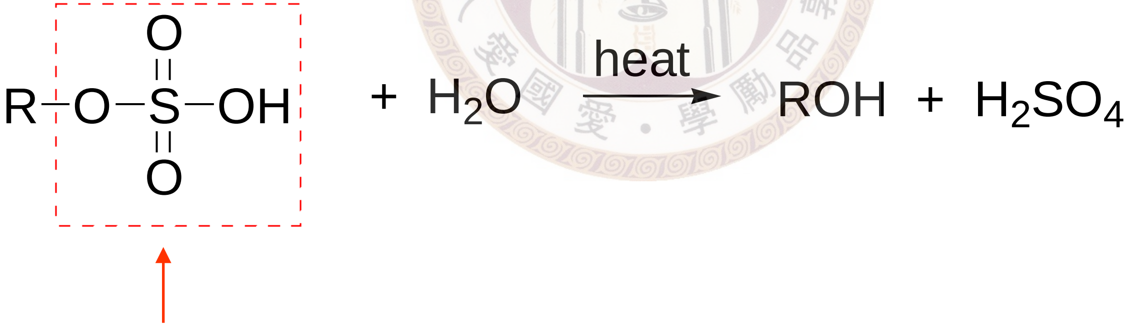


Isopropyl hydrogen sulfate

Markovnikov addition product

Reason: formation of more stable carbocation

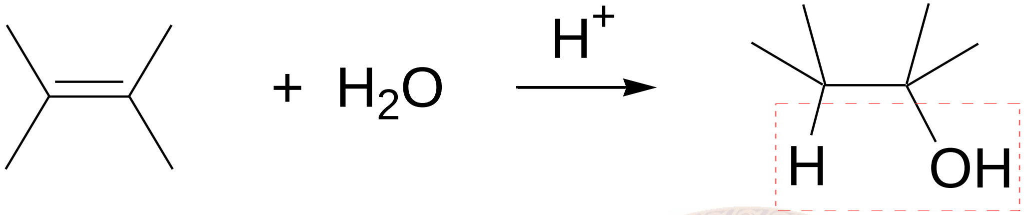
✓ Alkyl hydrogen sulfate hydrolyzes very easily



$$R-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH + H_2O \xrightarrow{\text{heat}} ROH + H_2SO_4$$

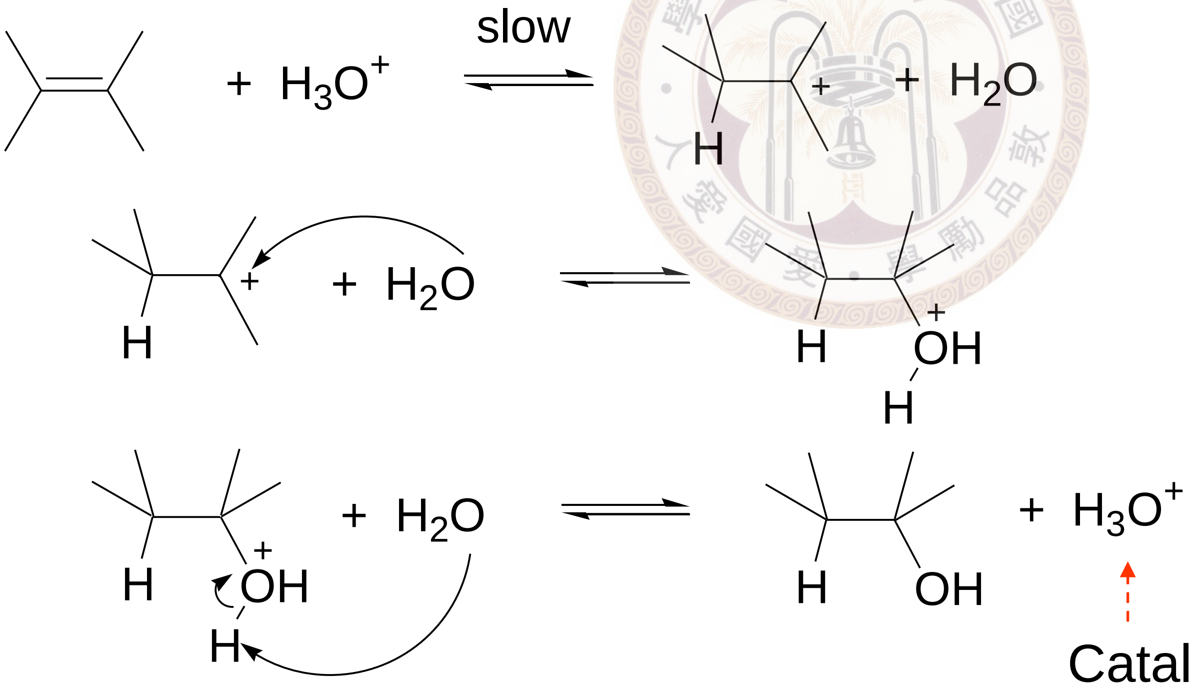
Very good LVG

※ Acid catalyzed hydration



Addition of water:
hydration

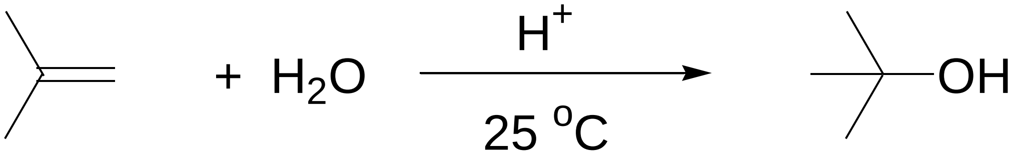
Mechanism:



Catalyst is regenerated

In large amt. of H_2O (solv.) → equilibrium shifts to the right

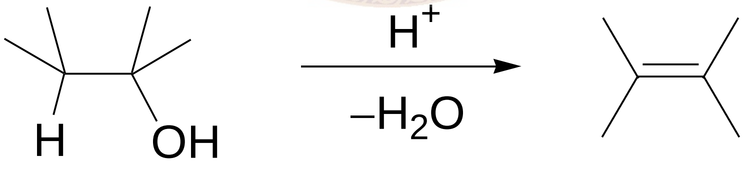
例 $\mathrm{H_2C{=}CH_2} + \mathrm{H_2O} \xrightarrow[300\ ^{o}\mathrm{C}]{\mathrm{H_3PO_4}} \mathrm{CH_3CH_2OH}$



Summary:

- ✓ Formation of more stable cabocation → reacts faster
- ✓ Follow Markovnikov’s rule
- ✓ The reaction is reversible

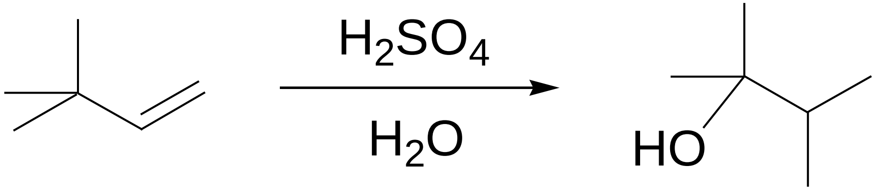
Recall: acid catalyzed dehydration



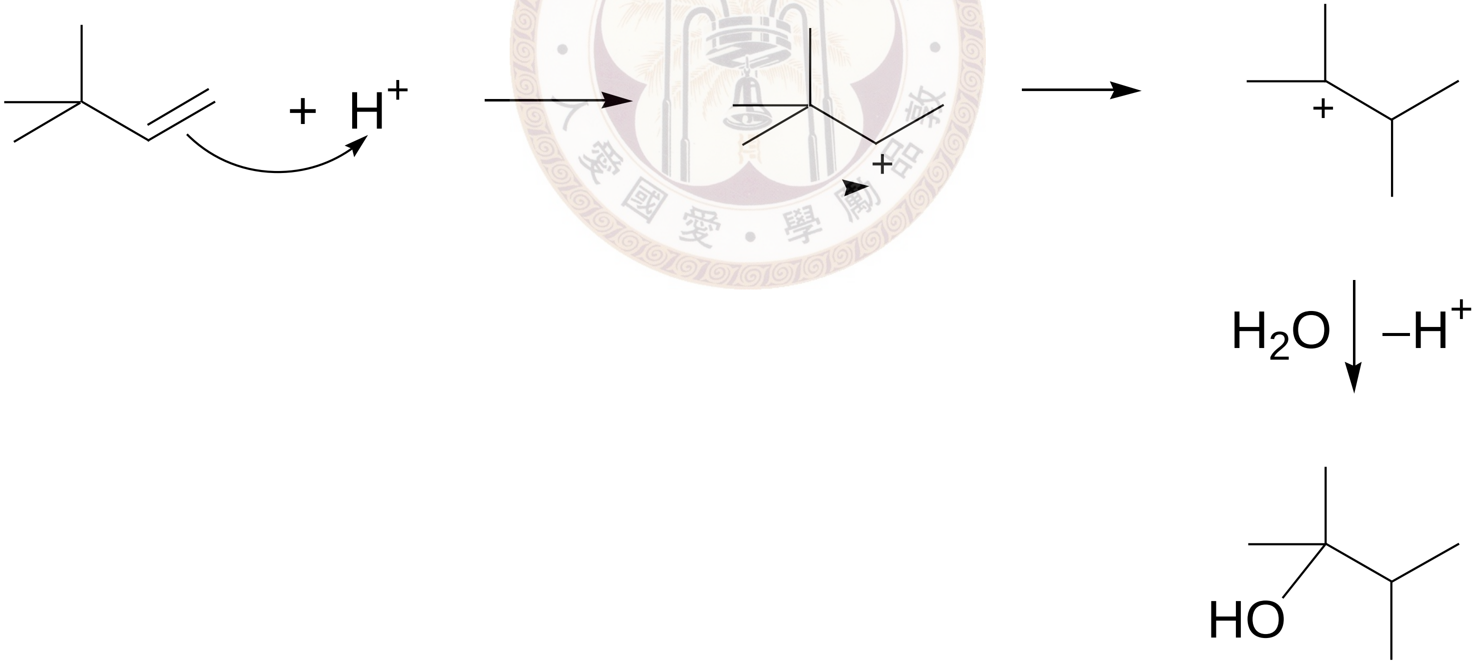
Le Chatelier's principle applies:
removes water → dehydrates

! Problems:

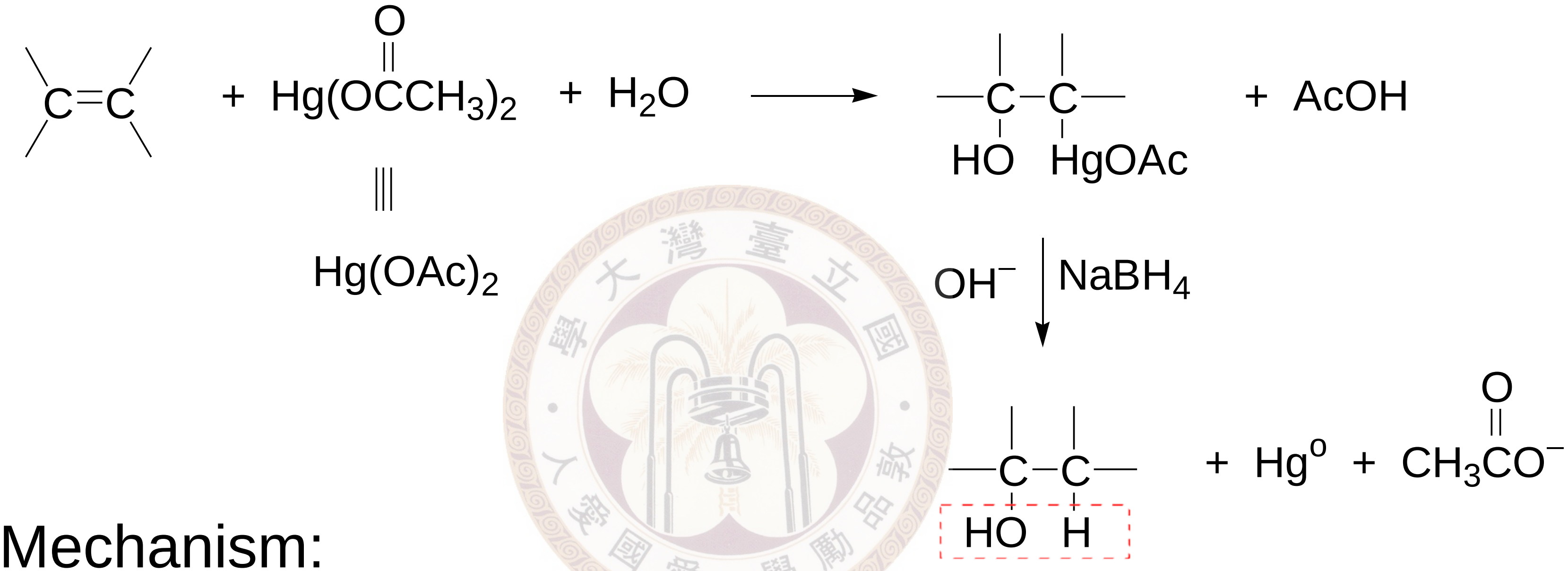
rearrangement of carbocation



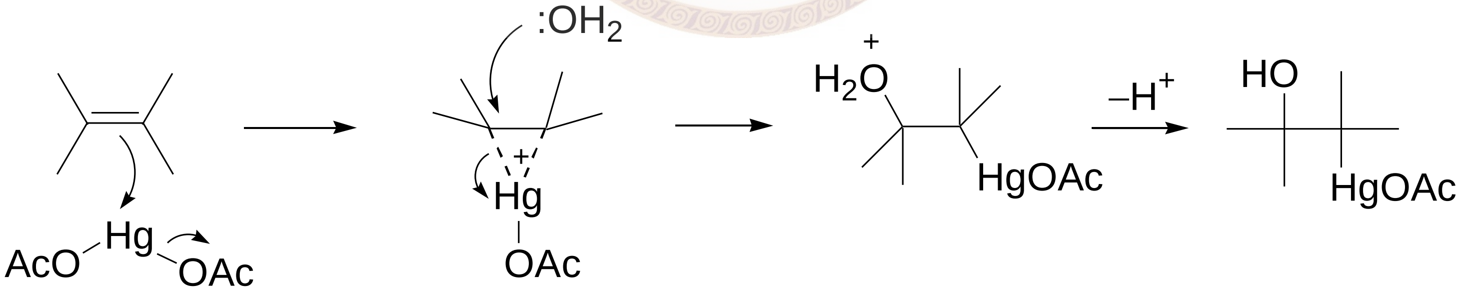
Mechanism:



※ Oxymercuration-demercuration: addition of H_2O without rearrangement



Mechanism:

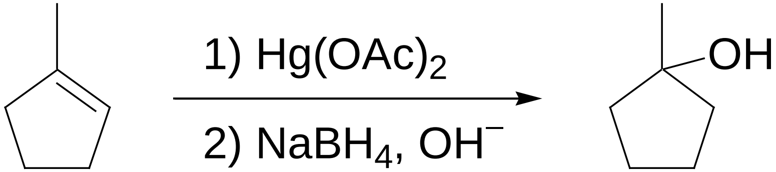


a bridged carbocation

◎ Stereochemistry: anti + syn (lost selectivity at the final step)

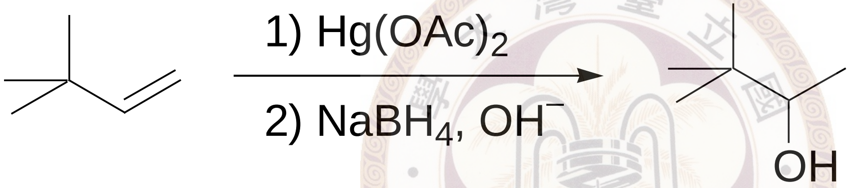
◎ Regiochemistry: follow Markovnikov's rule

例



1) $Hg(OAc)_2$

2) $NaBH_4$, OH^-

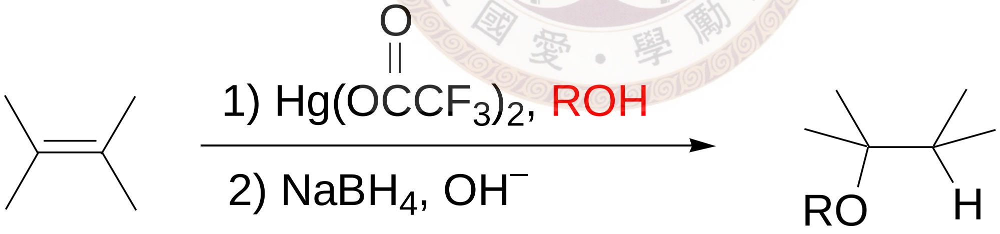


1) $Hg(OAc)_2$

2) $NaBH_4$, OH^-

94%

no rearrangement



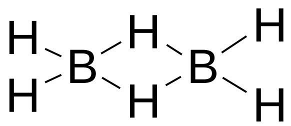
1) $Hg(O\overset{O}{\overset{\|}{C}}CF_3)_2$, ROH

2) $NaBH_4$, OH^-

A method to synthesize ethers

※ Hydroboration-oxidation

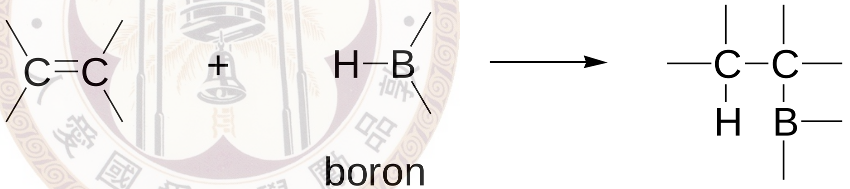
Diborane B_2H_6 ≡



tetrahydrofuran
(THF)

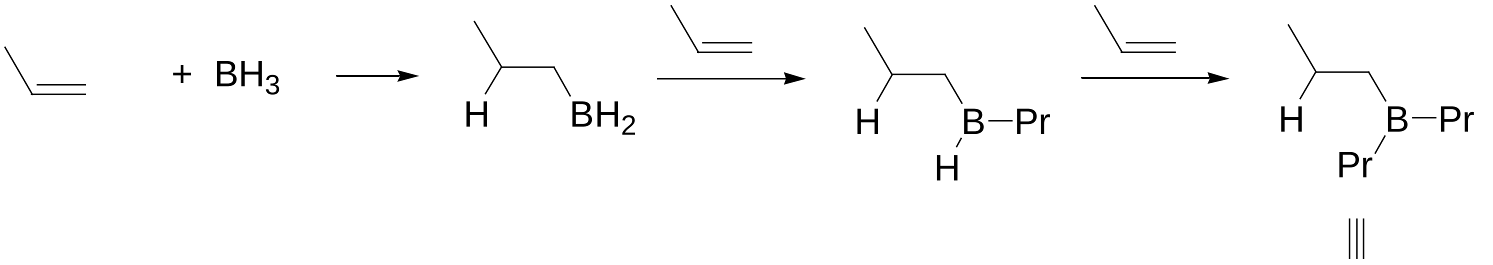
borane THF complex

◎ Hydroboration:



boron
hydide

an organoborane



Pr_3B

tripropyl borane

◎ Regioselectivity

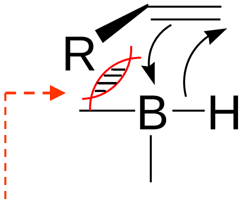
B on less substituted C

Reasons:

1. Steric

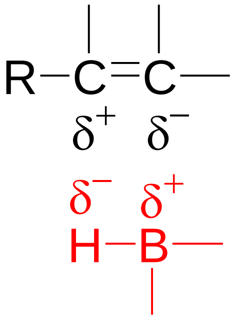
Go through a concerted four center TS (bond breaking and formation in concert)

better



steric interaction

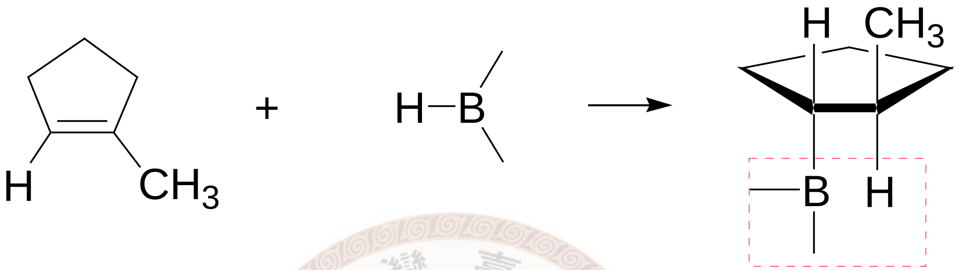
2. Electronic



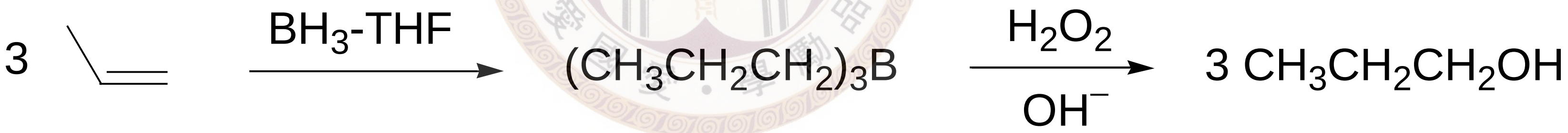
Boron has smaller electronegativity

◎ Stereochemistry

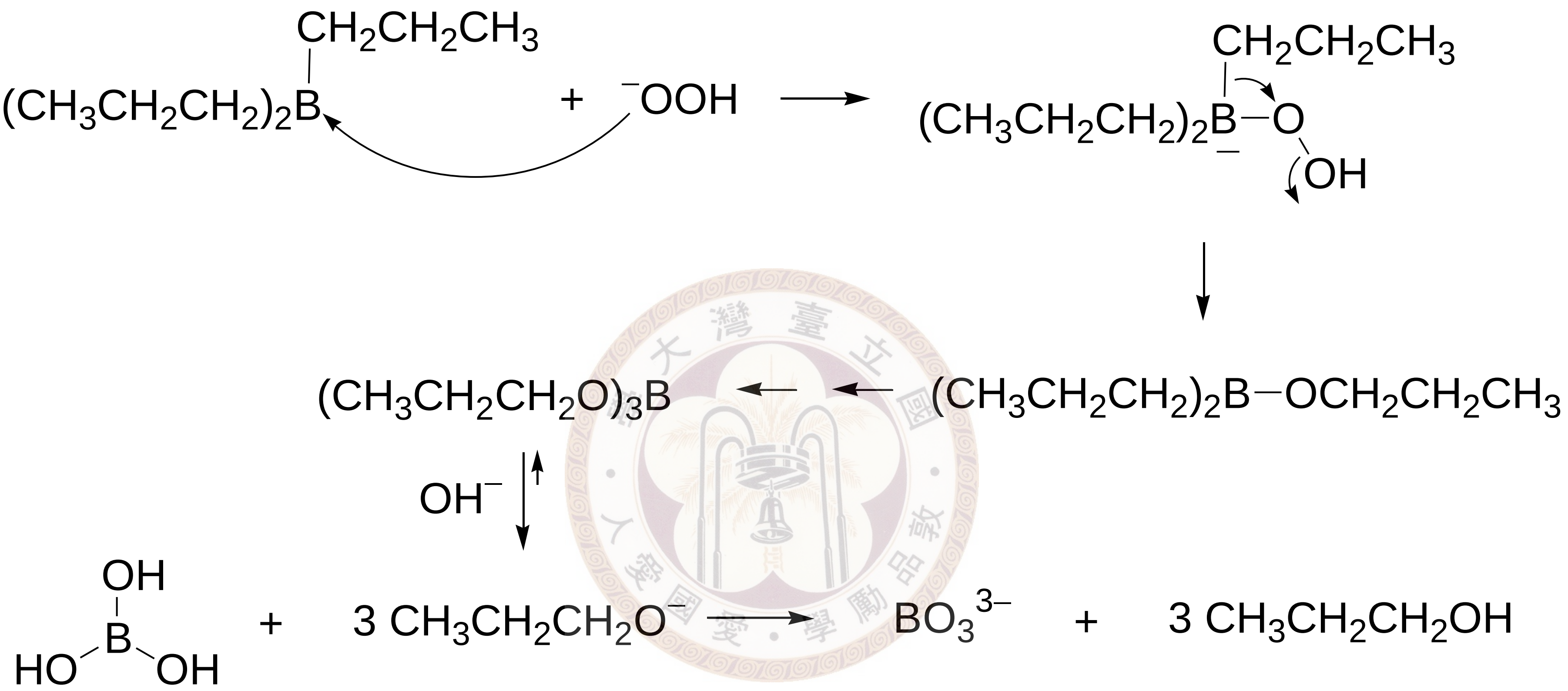
syn-addition



◎ Oxidation



Mechanism:



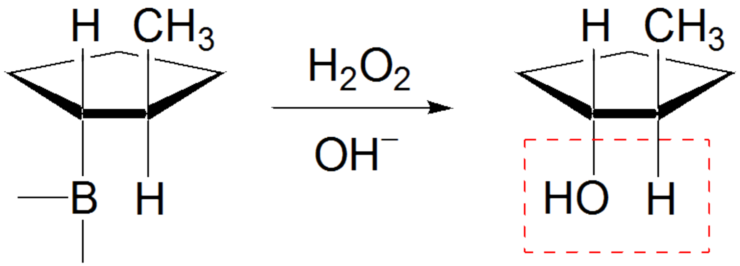
$$(CH_3CH_2CH_2)_2B\text{–}CH_2CH_2CH_3 + {}^{-}OOH \longrightarrow (CH_3CH_2CH_2)_2\underset{-}{B}(CH_2CH_2CH_3)\text{–}O\text{–}OH$$

$$\longrightarrow (CH_3CH_2CH_2)_2B\text{–}OCH_2CH_2CH_3 \longrightarrow\longrightarrow (CH_3CH_2CH_2O)_3B$$

$$(CH_3CH_2CH_2O)_3B \xrightleftharpoons{OH^-} B(OH)_3 + 3\ CH_3CH_2CH_2O^-$$

$$B(OH)_3 + 3\ CH_3CH_2CH_2O^- \longrightarrow BO_3^{3-} + 3\ CH_3CH_2CH_2OH$$

★ The alkyl group migrates with retention



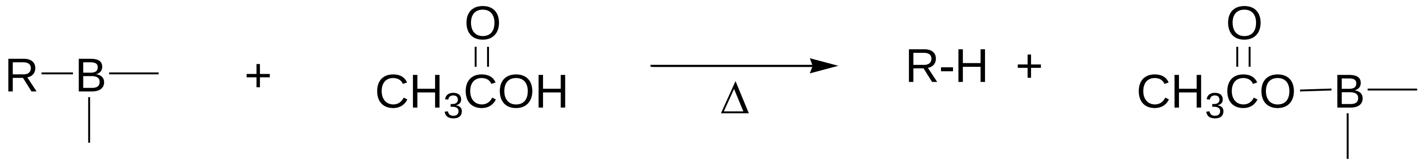
trans

Overall:

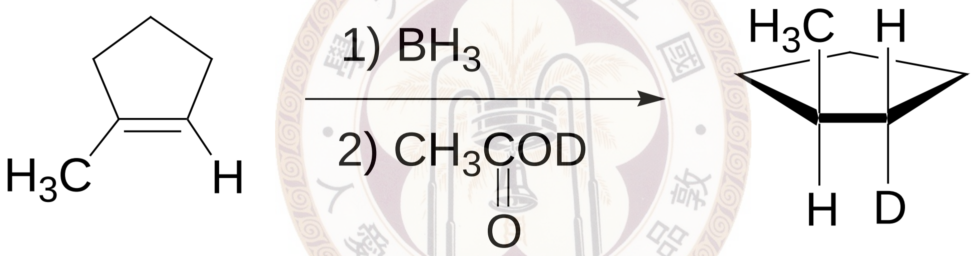
anti-Markovnikov orientation

syn-addition of H_2O

◎ Protonolysis of organoboranes



例



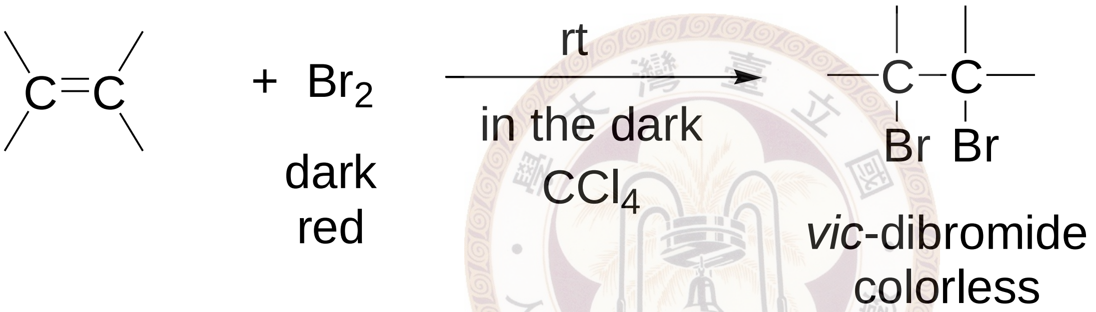
Overall: reduction of alkenes

syn-addition of H_2

※ Halogenation

Addition of bromine and chlorine

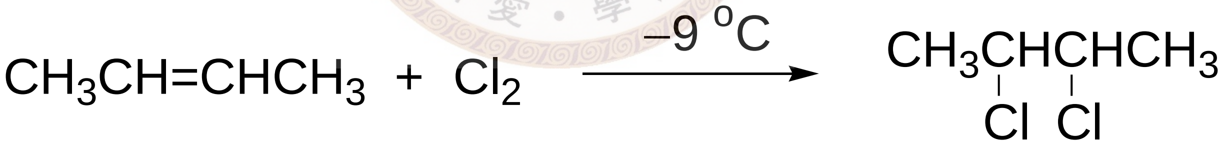
Bromination:



$$C{=}C + Br_2 \xrightarrow[\text{in the dark, } CCl_4]{\text{rt}} \underset{Br}{C}\text{–}\underset{Br}{C}$$

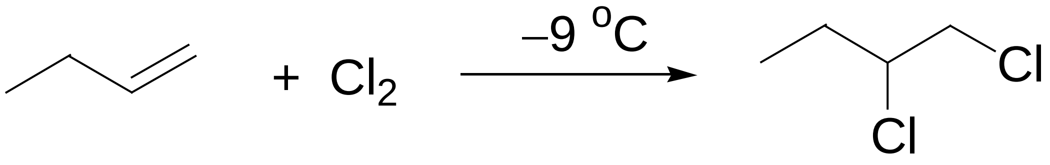
*vic: vicinal

例: chlorination:



$$CH_3CH{=}CHCH_3 + Cl_2 \xrightarrow{-9\ ^oC} CH_3\underset{Cl}{C}H\underset{Cl}{C}HCH_3$$

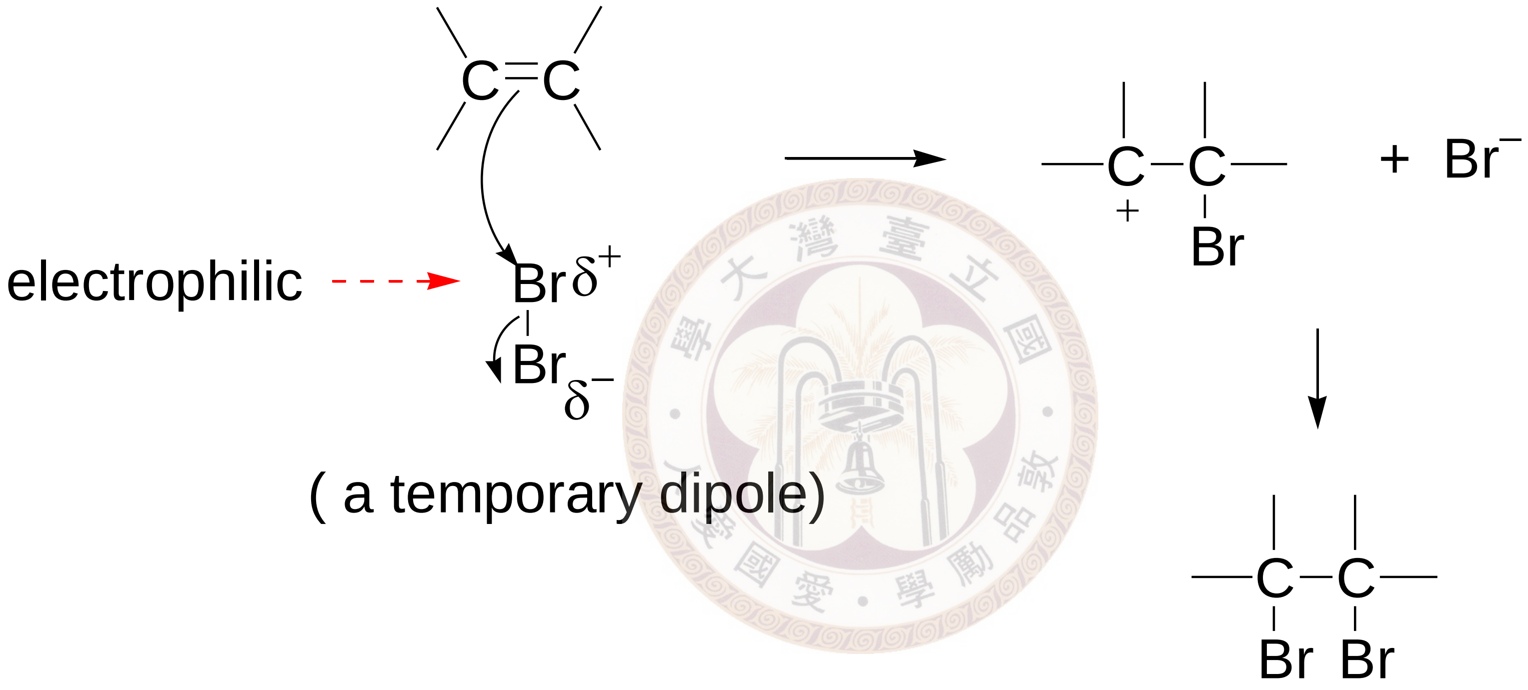
100%



97%

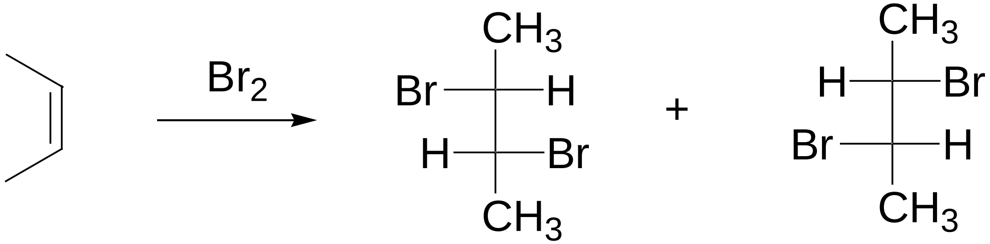
◎ Mechanism

✓One possibility:

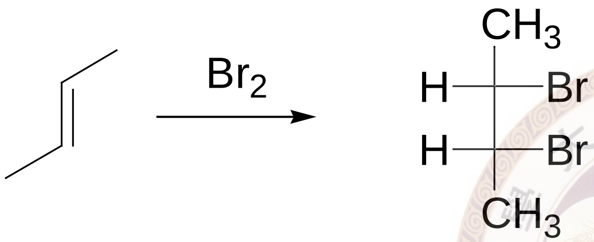


Q: Is this mechanism correct?

Check: Can we explain the stereochemistry?



cis (2*R*,3*R*) (2*S*,3*S*)

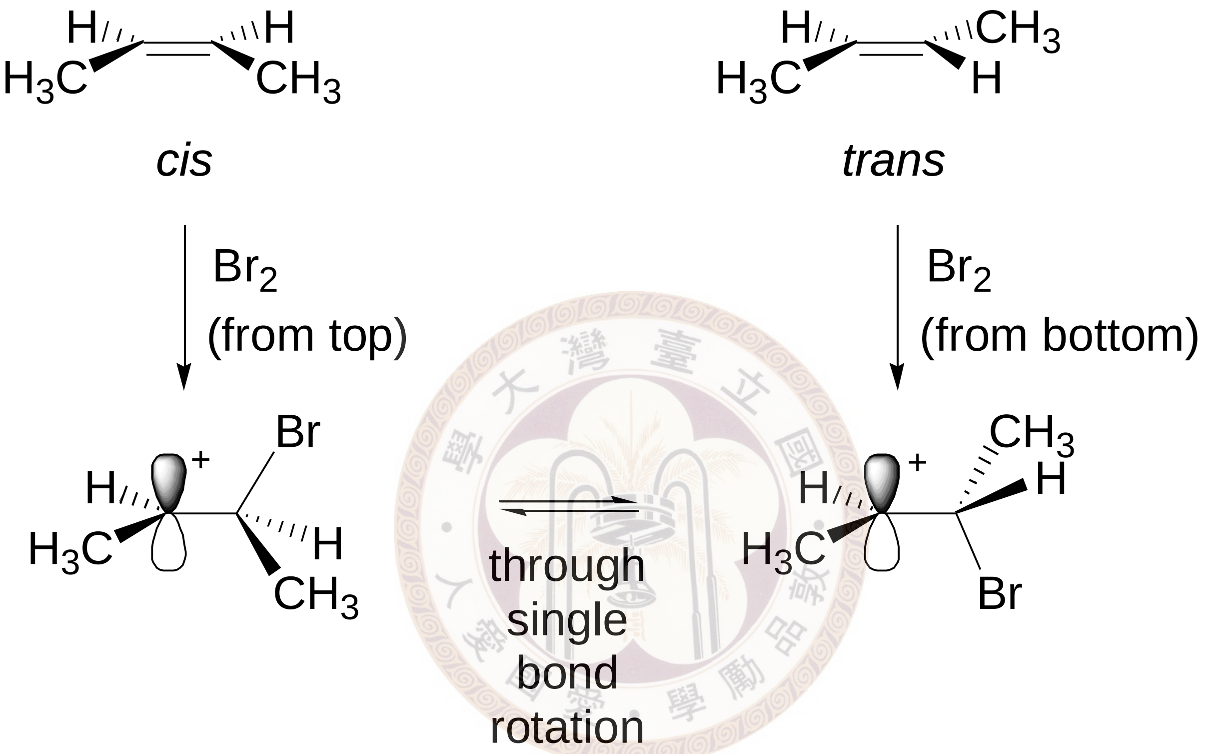


trans meso

A stereospecific reaction:

a particular stereoisomeric starting material gives a specific stereoisomeric product

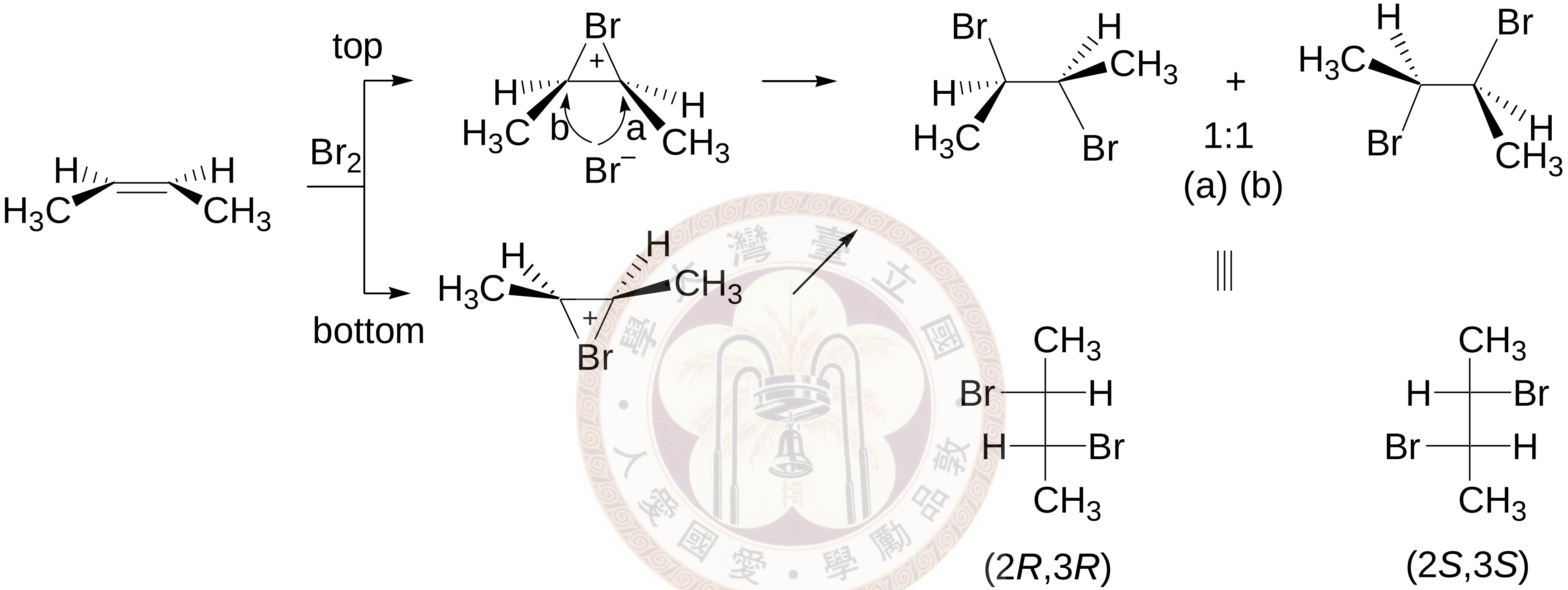
Carbocation mechanism:



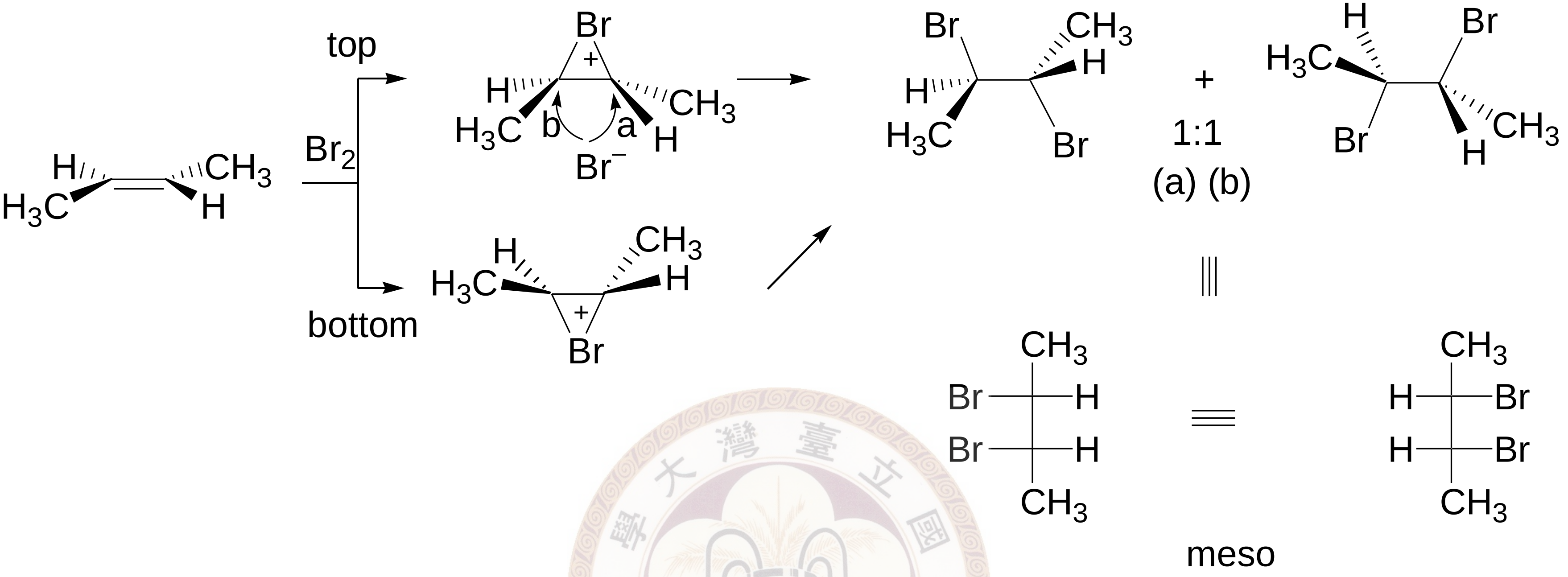
Should give the same product

⇨ The carbocation mechanism can not explain the stereochemistry

★ The real mechanism: formation of a bromonium bridge ion



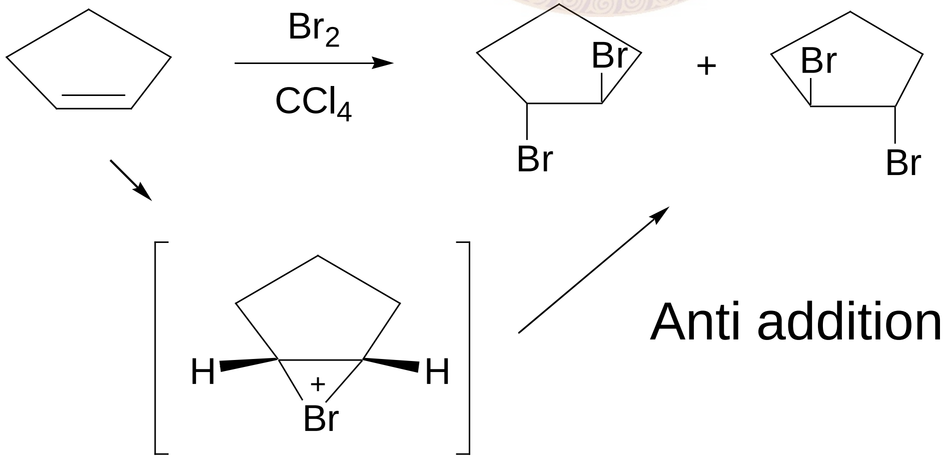
Net anti addition of bromine



Why bromonium bridge ion?

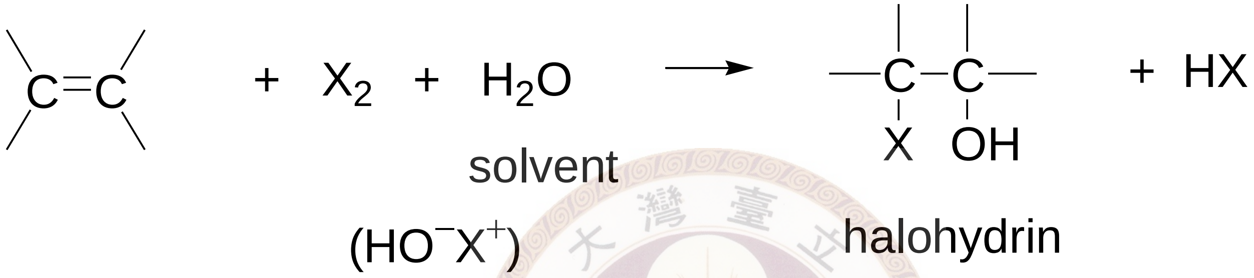
fulfill octet rule with extra bond formation

例

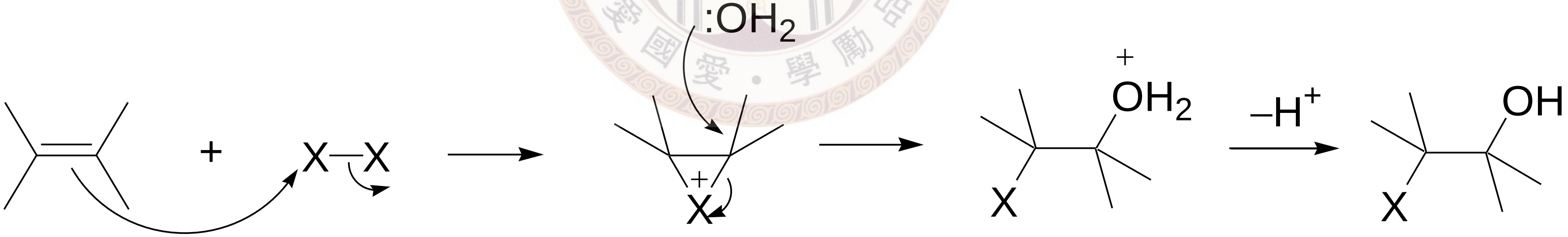


Anti addition of bromine

※ Halohydrin formation



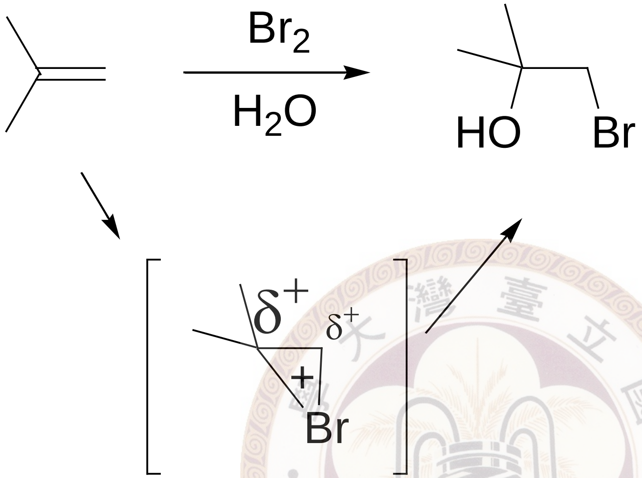
Mechanism:



Stereochemistry:

anti addition of X and OH

◎ Regiochemistry:



More substituted C can stabilize positive charge more

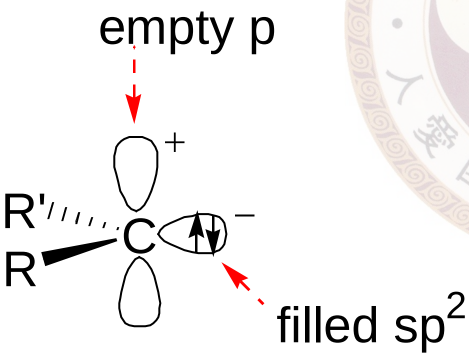
⇒ has higher partial positive charge

※ Carbenes (碳烯)

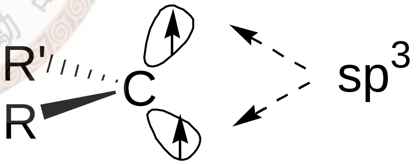
Contain a divalent carbon, do not fulfill octet rule
→ Highly reactive

例 H_2C: (methylene)

✓ Structure:



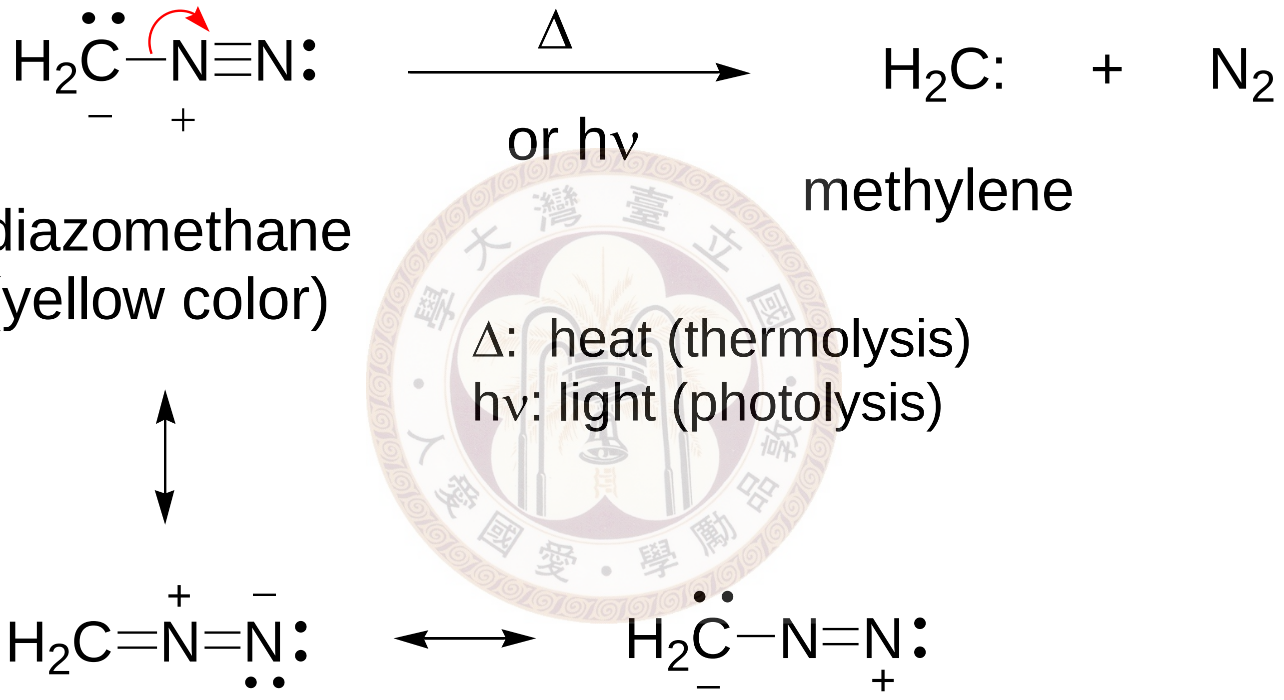
singlet carbene
(spin paired)



triplet carbene
(spin unpaired)

✓ Generation

◆ From diazomethane:



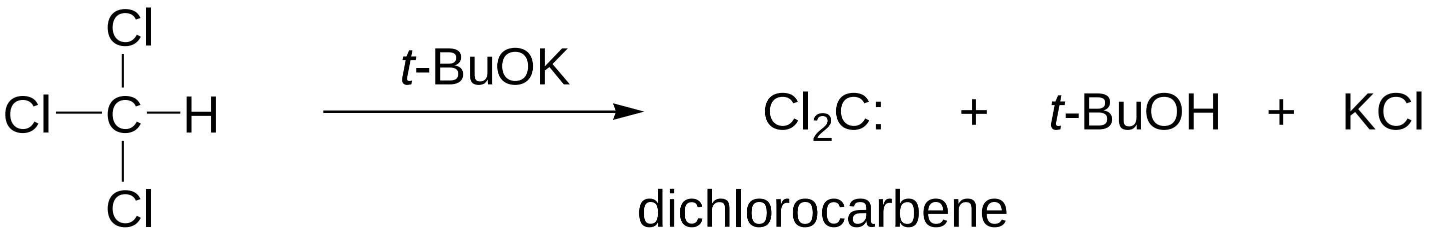
diazomethane
(yellow color)

methylene

Δ: heat (thermolysis)
hν: light (photolysis)

*Carcinogenic (致癌)
*Explosive

◆ From chlorofom: dichlorocarbene

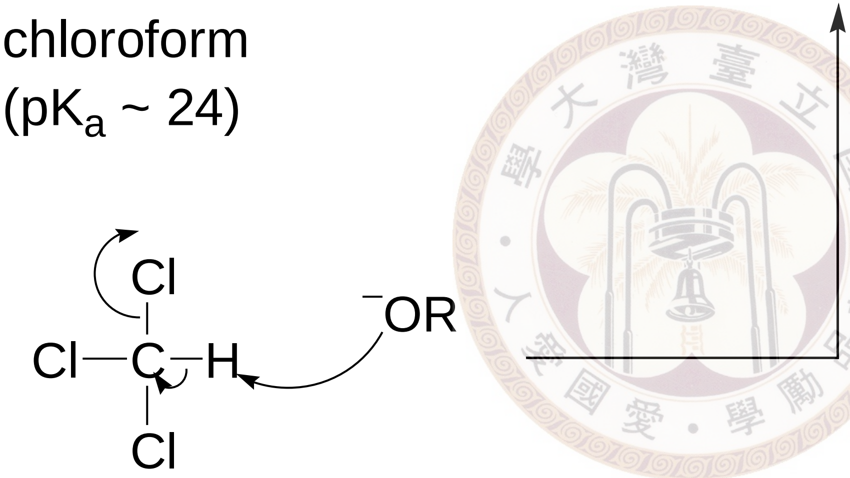


$$CHCl_3 \xrightarrow{t\text{-BuOK}} Cl_2C: \; + \; t\text{-BuOH} \; + \; KCl$$

dichlorocarbene

chloroform

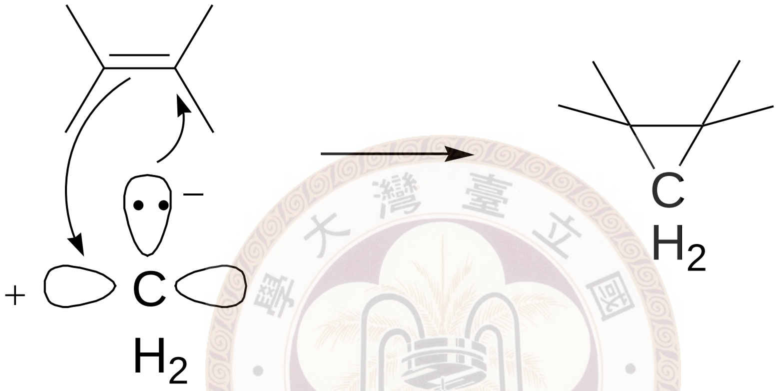
(pK_a ~ 24)



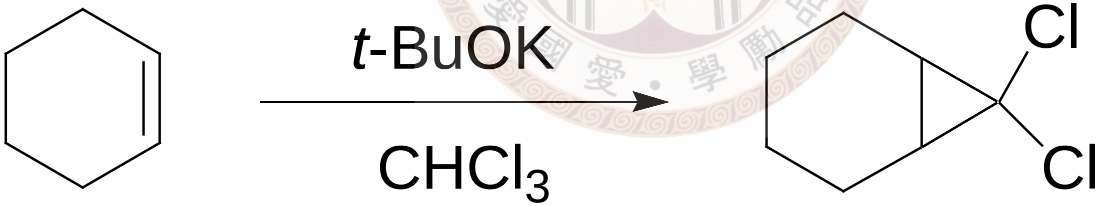
an α-elimination

✓ Reaction

Addition to double bonds: formation of cyclopropanes



例



59%

7,7-dichlorobicyclo[4.1.0]heptane

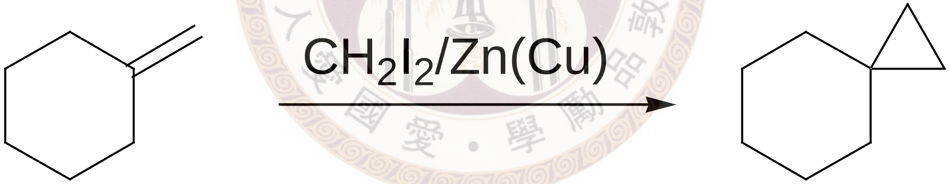
◎ Carbenoids

carbene-like species

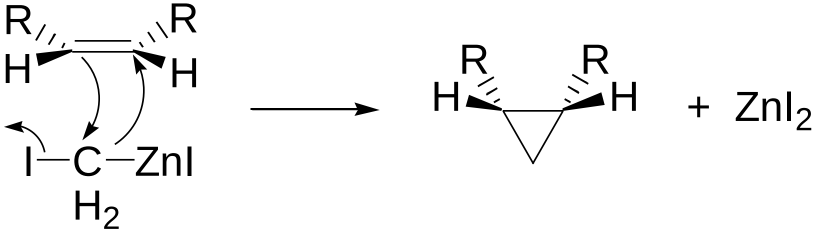
Simmons-Smith cyclopropanation:

$$CH_2I_2 \quad + \quad Zn(Cu) \longrightarrow ICH_2ZnI$$

a carbenoid

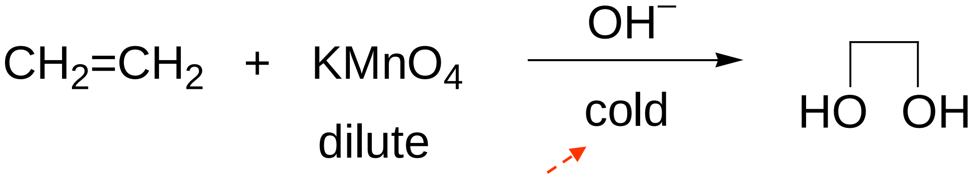


Possible mechanism:



Stereospecific syn-addition

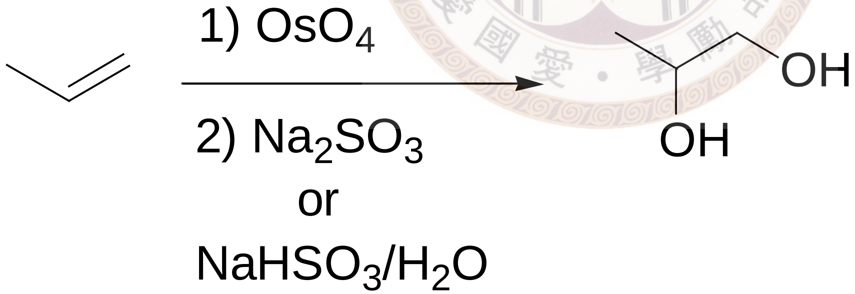
※ Syn 1,2-dihydroxylation: oxidation of alkenes



$CH_2=CH_2$ + $KMnO_4$ dilute $\xrightarrow[\text{cold}]{OH^-}$ HO OH

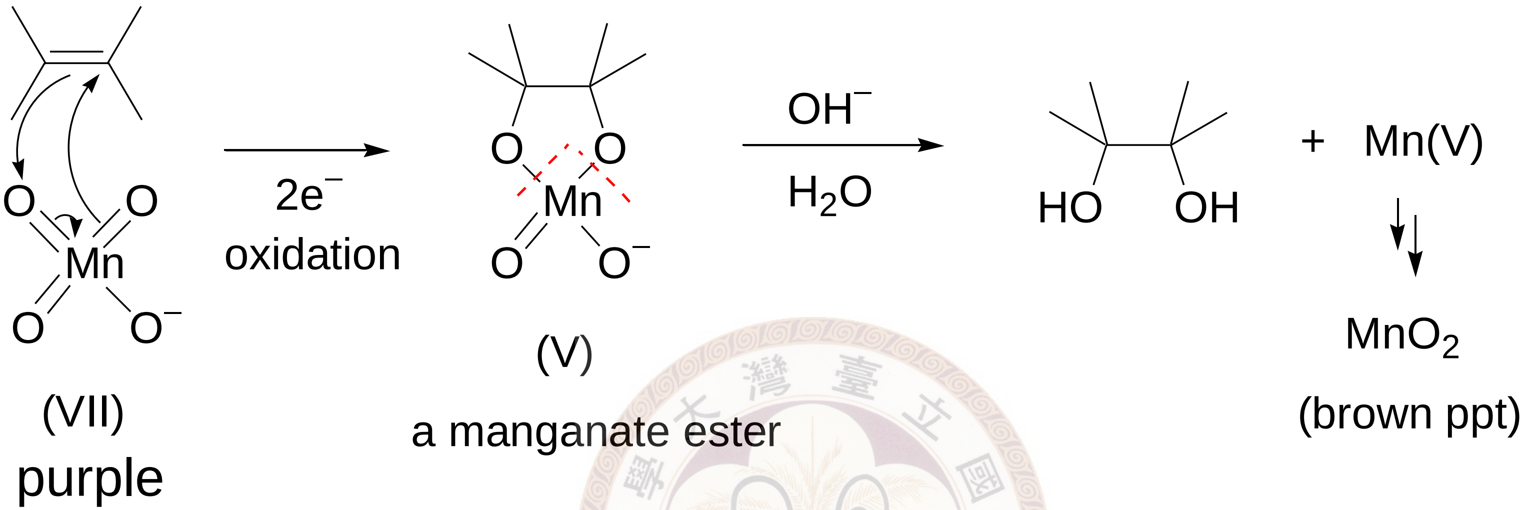
1,2-ethanediol
(ethylene glyol)

At higher T cleavage of diol occurs



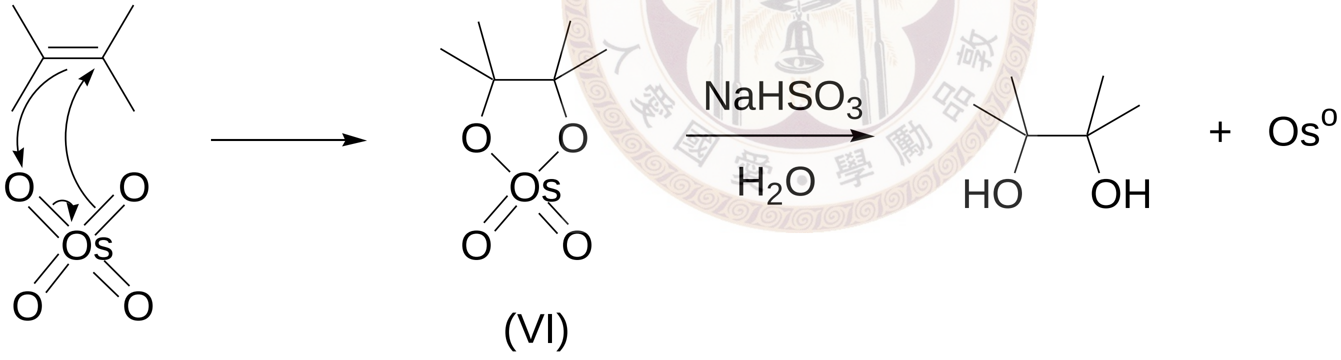
1) OsO_4
2) Na_2SO_3
or
$NaHSO_3/H_2O$

Mechanism:



(VII) purple

(V) a manganate ester



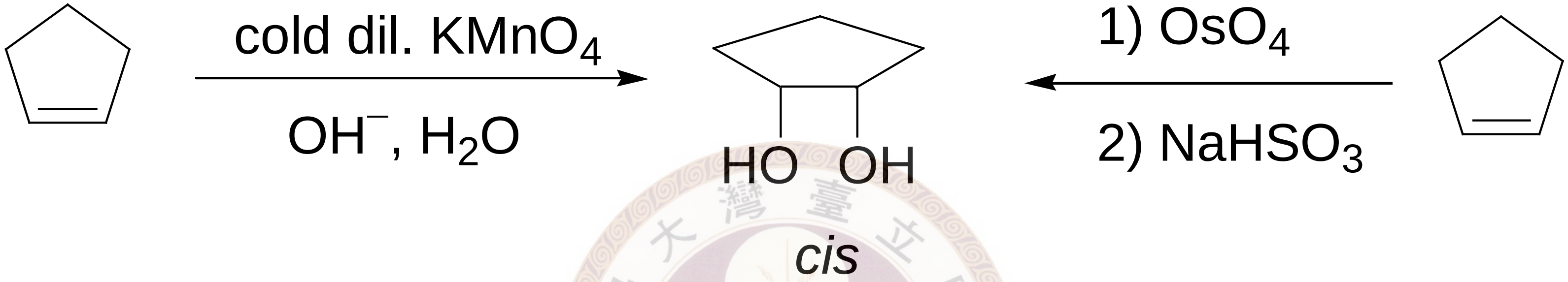
(VIII)

(VI)

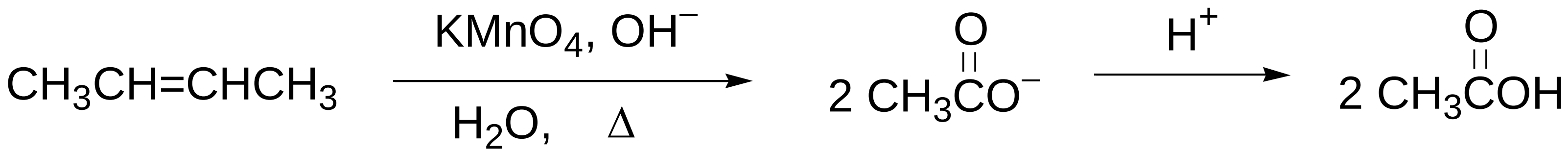
*This mechanism is oversimplified

*OsO_4 is highly toxic (it sublimes) and expensive

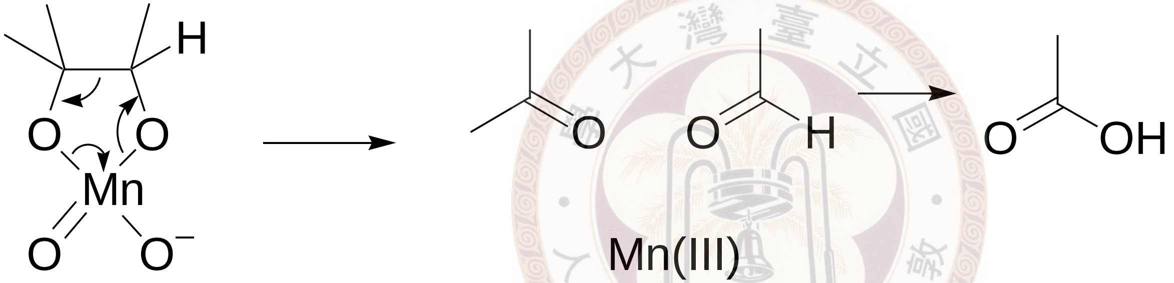
Stereochemistry: syn-addition of the two hydroxyl groups



※ Oxidative cleavage by $KMnO_4$

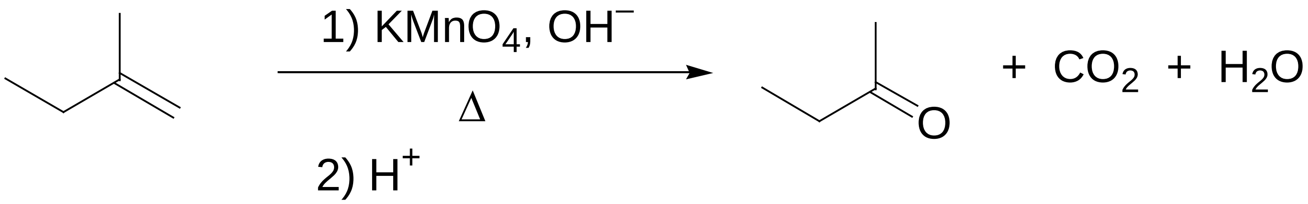


$$CH_3CH{=}CHCH_3 \xrightarrow[H_2O,\ \Delta]{KMnO_4,\ OH^-} 2\ CH_3\overset{O}{\overset{\|}{C}}O^- \xrightarrow{H^+} 2\ CH_3\overset{O}{\overset{\|}{C}}OH$$



(this mechanism is only to help your learning)

例



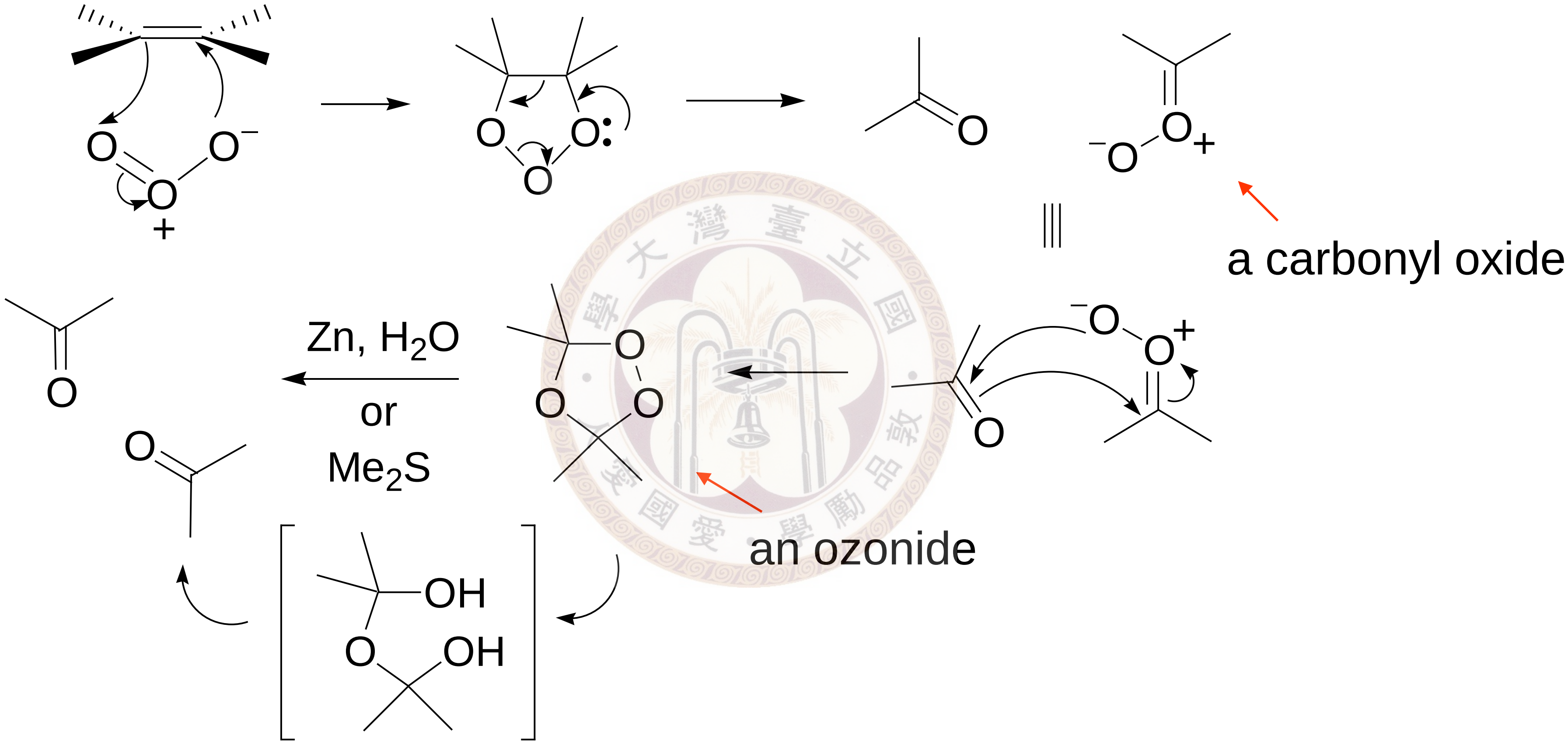
1) $KMnO_4$, OH^-

Δ

2) H^+

$+\ CO_2\ +\ H_2O$

※ Ozonolysis



a carbonyl oxide

an ozonide

Zn, H_2O

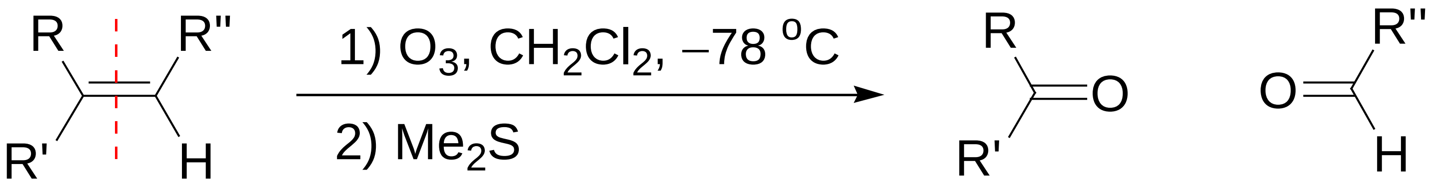
or

Me_2S

hydrolyzes very easily

*When dimethyl sulfide (Me_2S) is used in the reductive work-up, Me_2SO (dimethyl sulfoxide; DMSO) is the side-product

Overall:

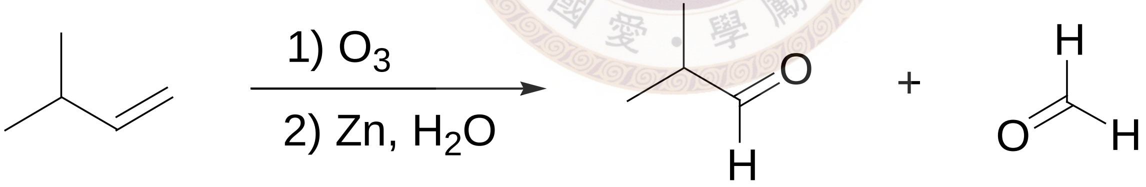


✓A popular method for degradation

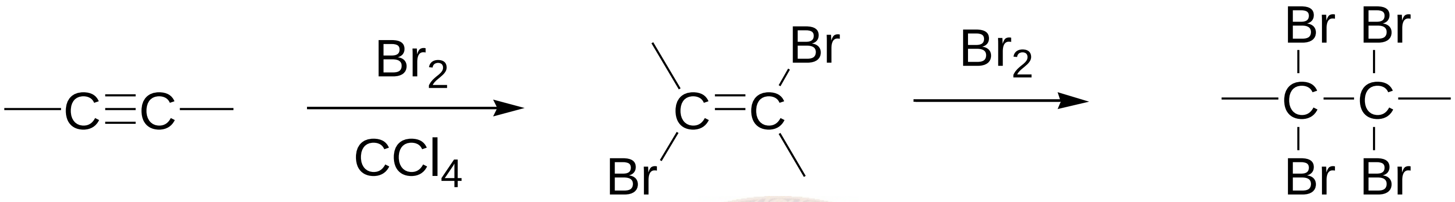
✓Preparation of aldehydes or ketones

✓Useful in structure determination

例



※ Halogenation of alkynes

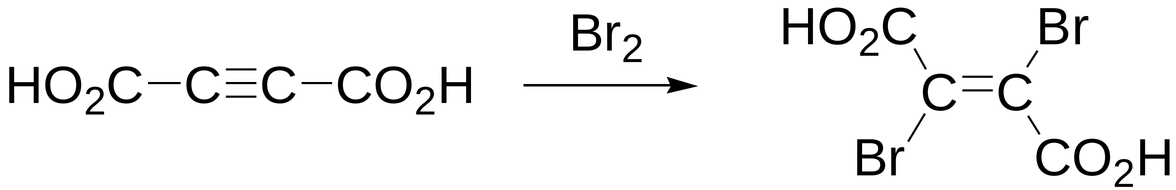


anti-addition

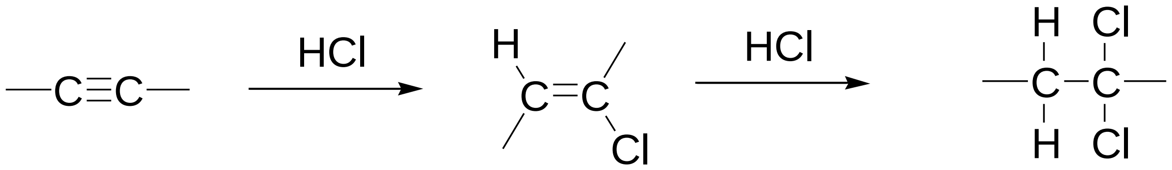
possible to stop here
with 1 eq. of Br_2

Same for Cl_2

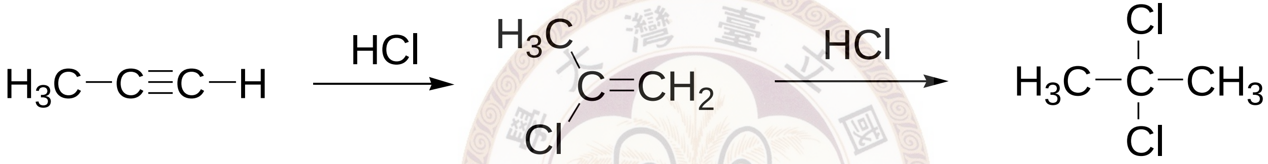
例



※ Hydrohalogenation of alkynes

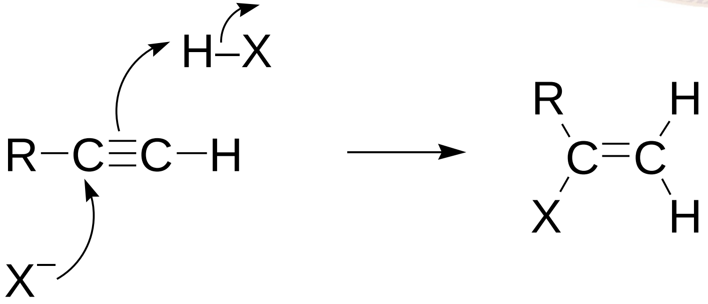


例

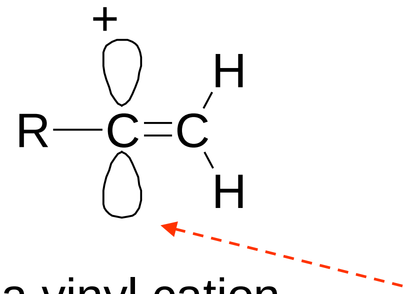


Markovnikov's orientation

Mechanism:

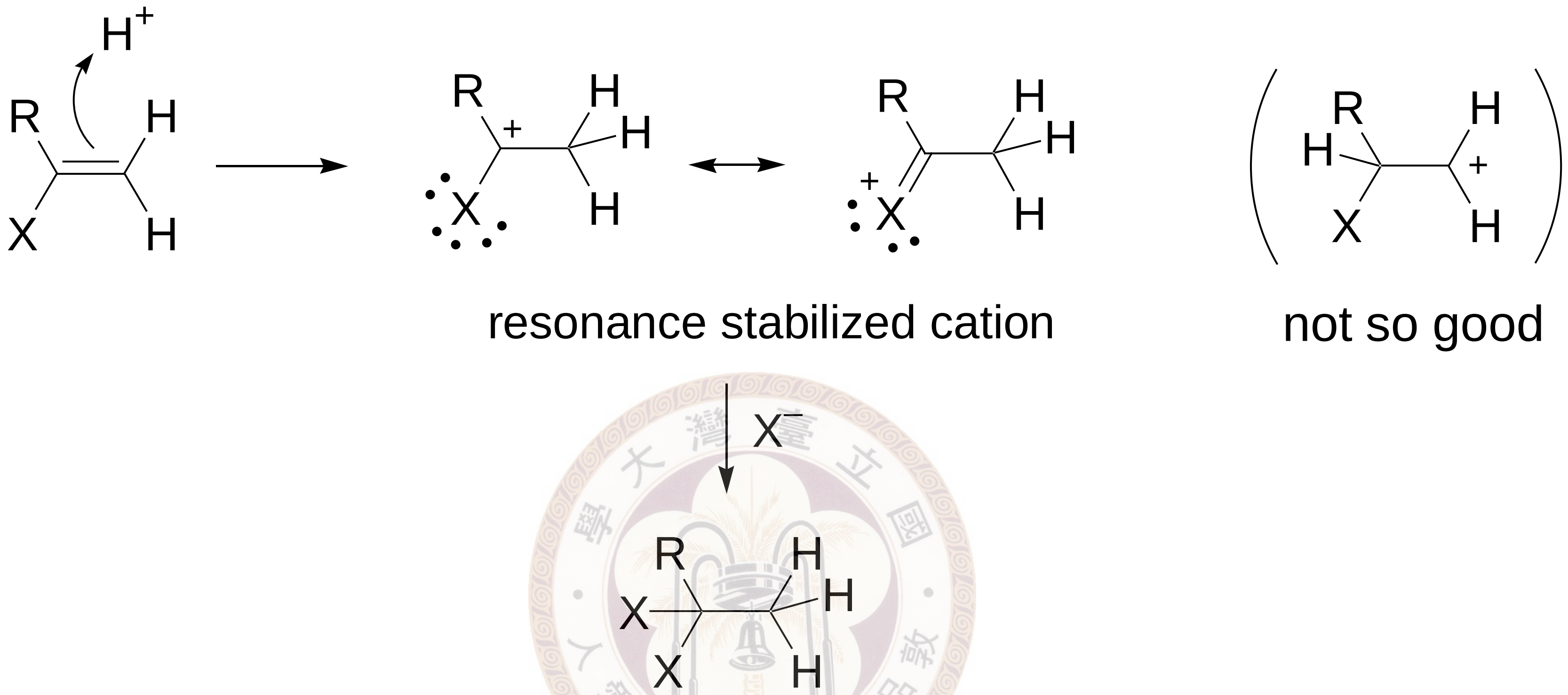


go through:



a vinyl cation

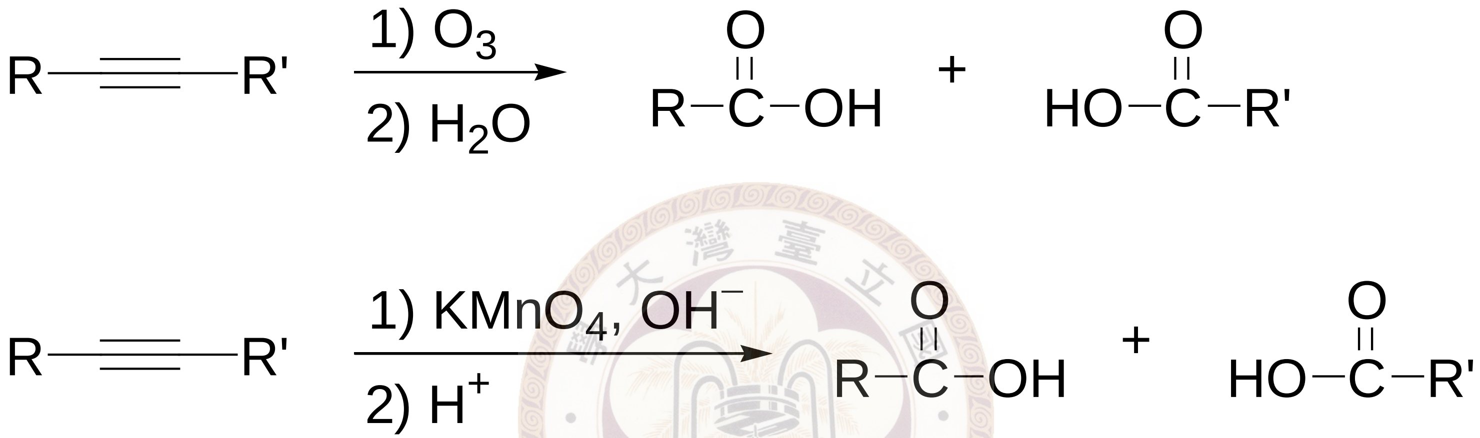
empty p



resonance stabilized cation

not so good

※ Oxidative cleavage of alkynes



$$R-C\equiv C-R' \xrightarrow[\text{2) } H_2O]{\text{1) } O_3} R-\overset{\displaystyle O}{\overset{\|}{C}}-OH + HO-\overset{\displaystyle O}{\overset{\|}{C}}-R'$$

$$R-C\equiv C-R' \xrightarrow[\text{2) } H^+]{\text{1) } KMnO_4,\ OH^-} R-\overset{\displaystyle O}{\overset{\|}{C}}-OH + HO-\overset{\displaystyle O}{\overset{\|}{C}}-R'$$