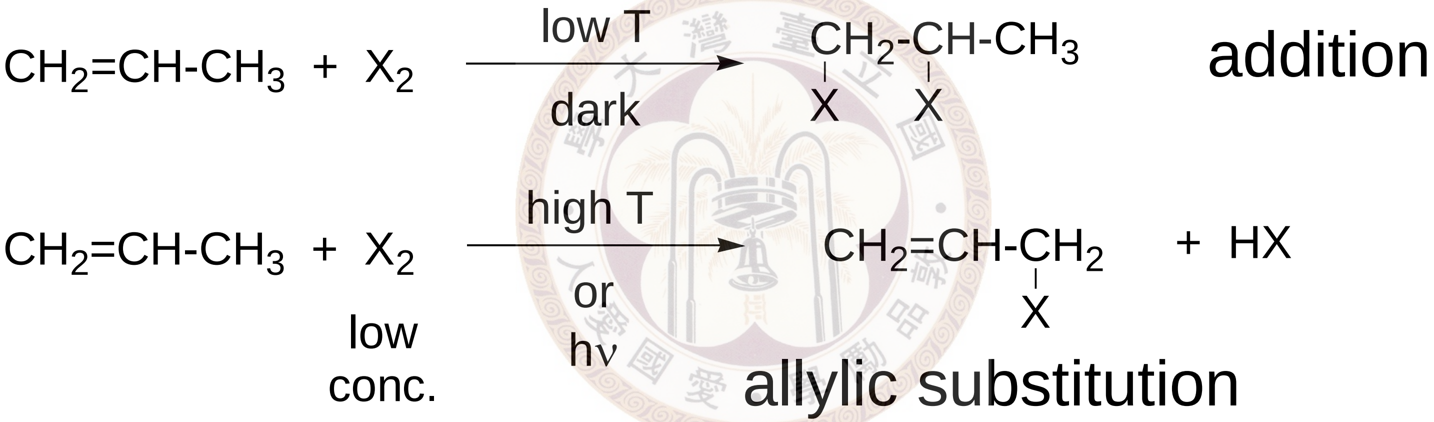
有機化學乙

蔡蘊明　教授

Chapter 13
Conjugated unsaturated system

共軛不飽和系統

※ Allylic substitution



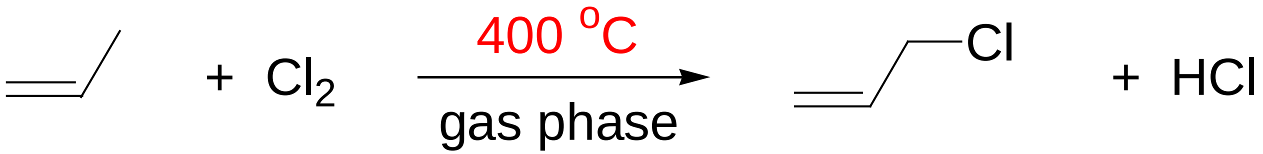
$$CH_2{=}CH{-}CH_3 + X_2 \xrightarrow[\text{dark}]{\text{low T}} \underset{X}{CH_2}{-}\underset{X}{CH}{-}CH_3$$

addition

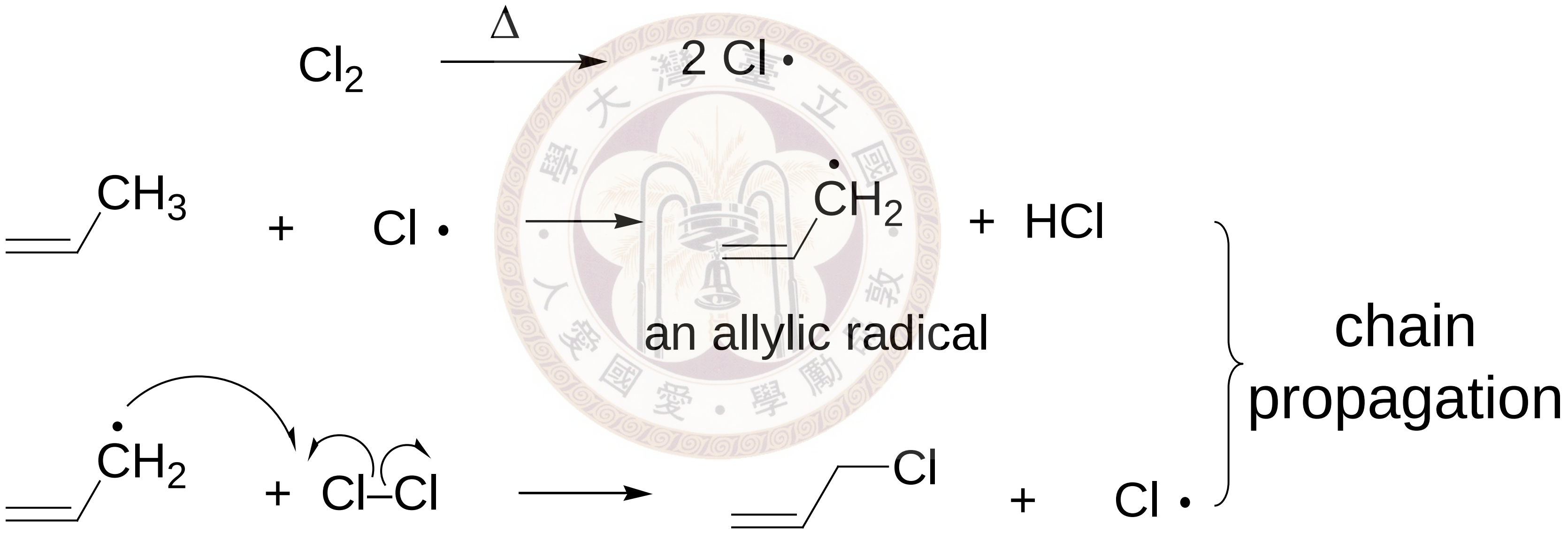
$$\underset{\text{low conc.}}{CH_2{=}CH{-}CH_3 + X_2} \xrightarrow[\text{or } h\nu]{\text{high T}} CH_2{=}CH{-}\underset{X}{CH_2} + HX$$

allylic substitution

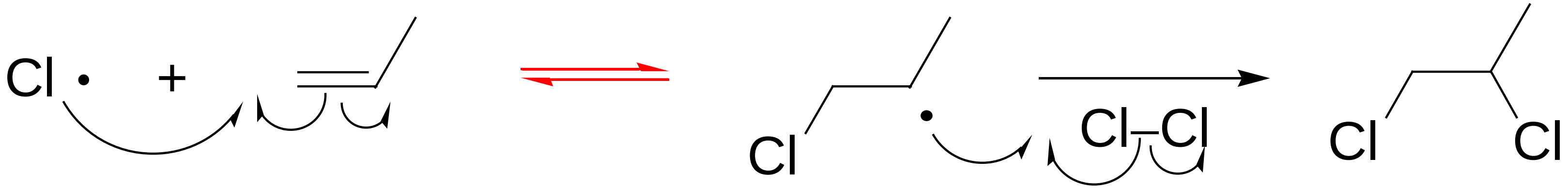
◎ Allylic chlorination



Mechanism:



- ✓ Low concentration of X_2 is important

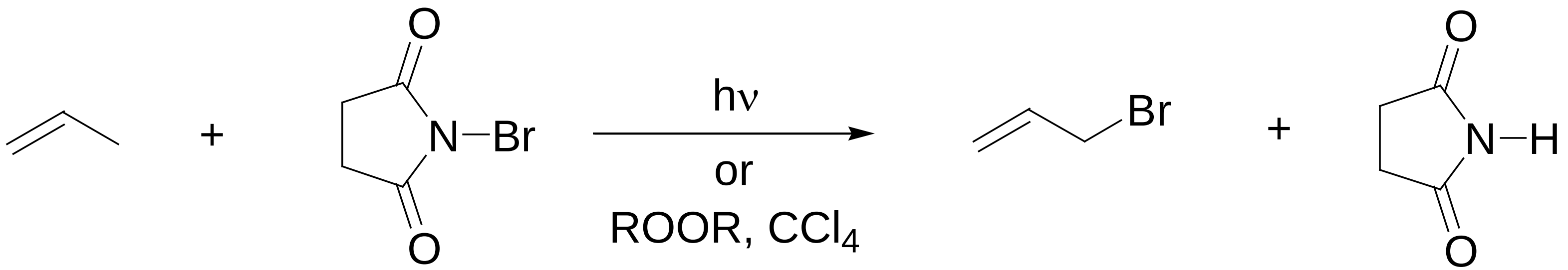


with low $[Cl_2]$
this step is not easy

- ✓ High T for entropic reason

  ionic addition is entropically unfavorable

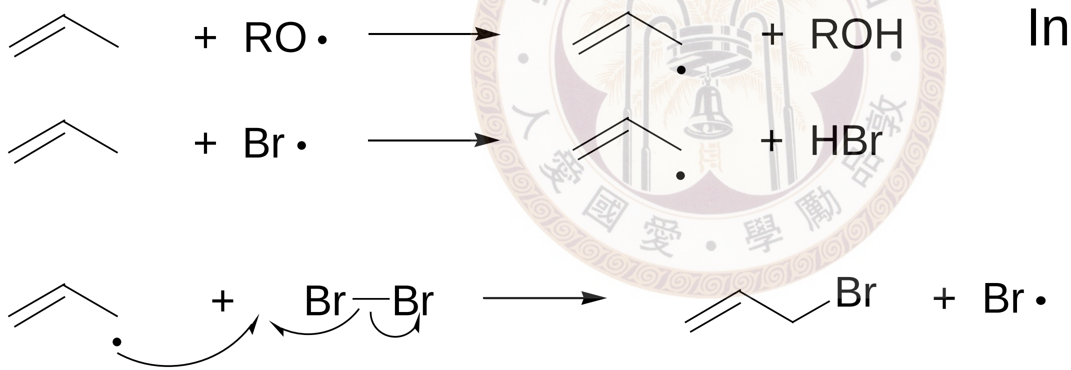
◎ Allylic bromination



N-bromosuccinimide
(NBS)

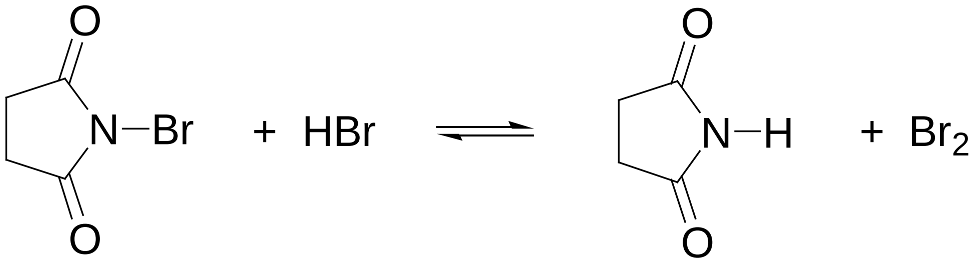
succinimide

Mechanism:



Initiation step

chain propagation

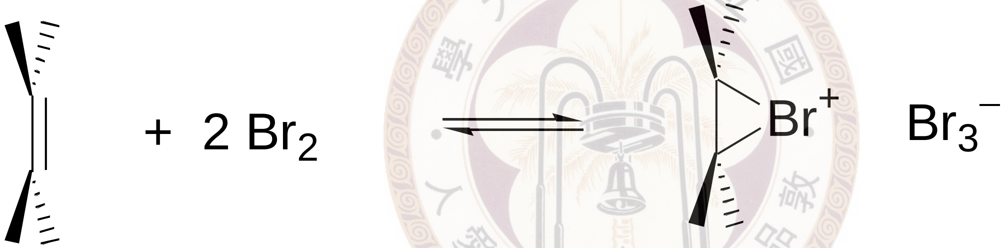


This step provides a low conc. of Br_2

Low solubility in CCl_4

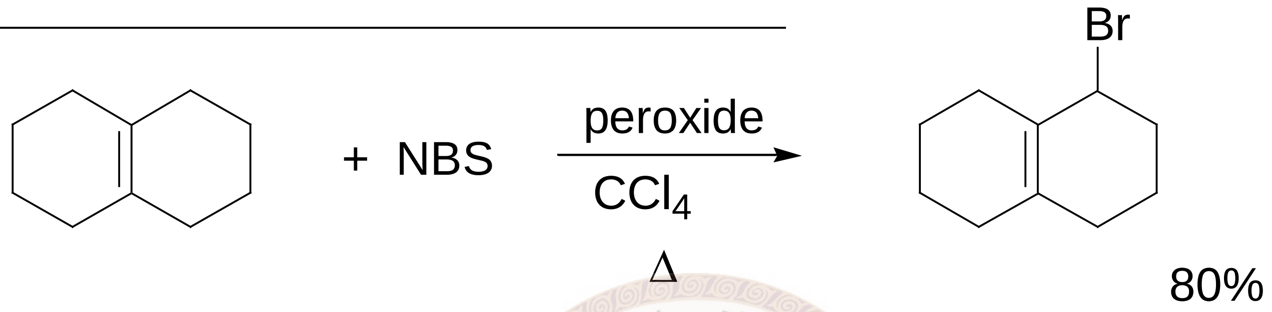
How about ionic addition?

The first step is an equilibrium
→ low $[Br_2]$ favor the left-hand side
Use a nonpolar solvent (e.g. CCl_4)
→Br^- is solvated by Br_2 and forms Br_3^-



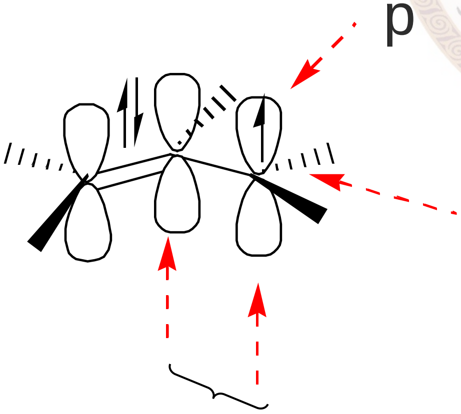
Rate ∝ $[Br_2]^2$
→ slow at low $[Br_2]$

※ The stability of allyl radical



Why is allylic position so special?

★ Allylic radical is stabilized by conjugation (共軛) with adjacent double bond

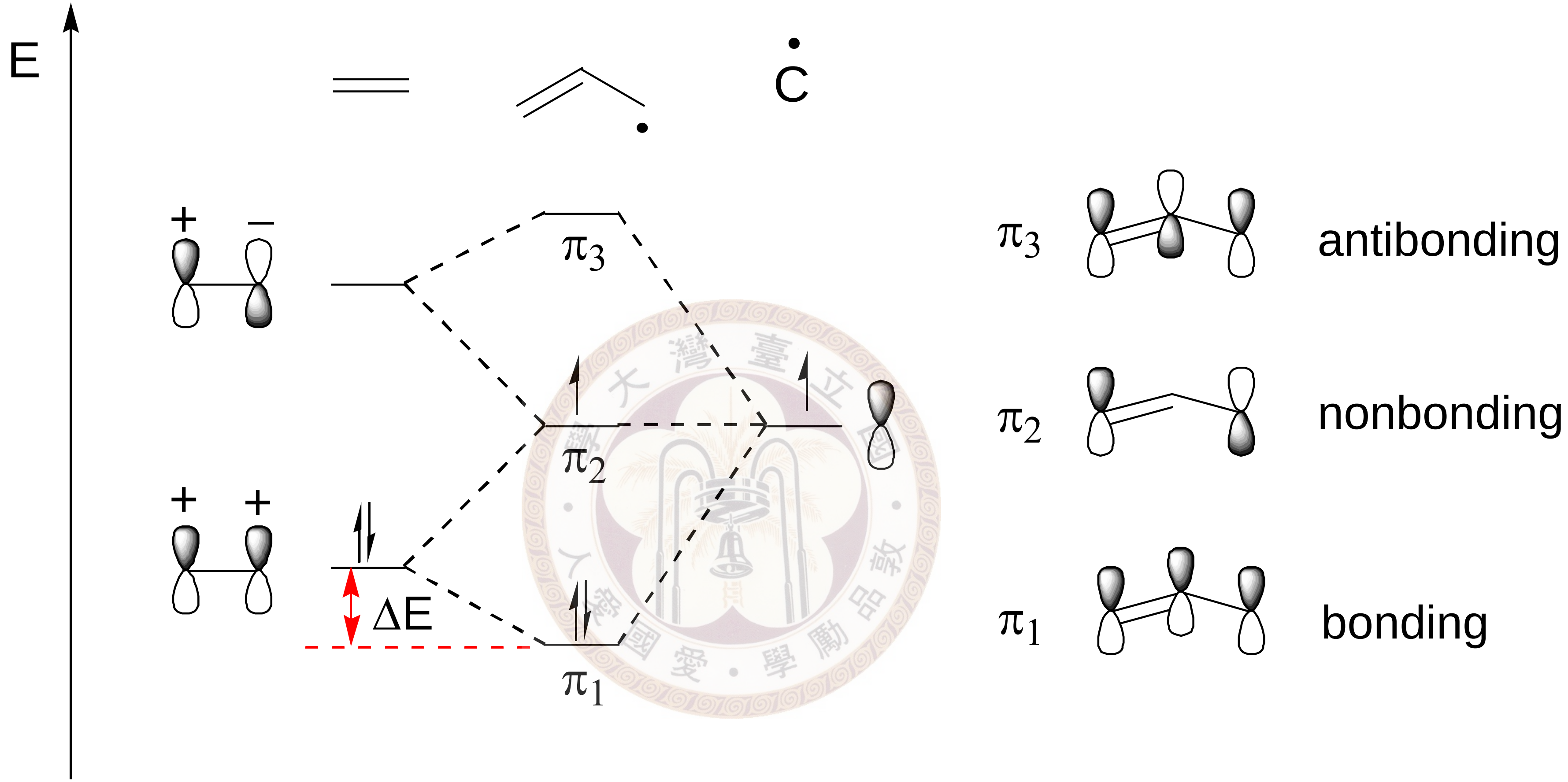


p

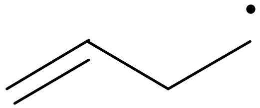
sp^2 for σ bonding

eclipsed → π type bonding occurs

MO view



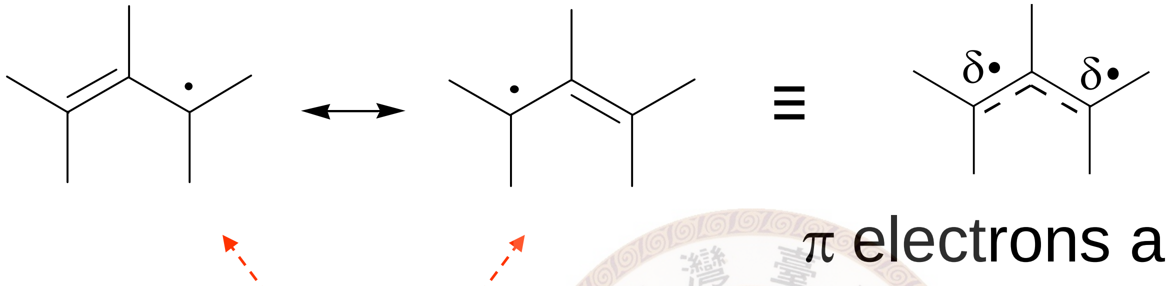
Conjugation resulted in extra stabilization (2 × ΔE)



← This radical is isolated, not conjugated

Valence bond view:

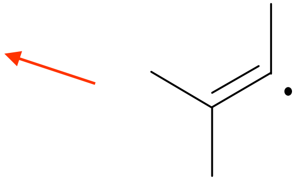
the allylic radical is resonance stabilized



resonance structures
(not equilibrium)

π electrons are delocalized over three carbons (bonded by three atoms instead of two)
→ The gained delocalization E is also called resonance E

★ Relative stability of radicals:
allylic > 3^{o} > 2^{o} > 1^{o} > vinyl



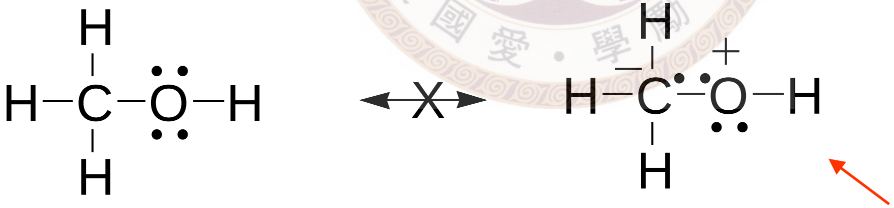
◎ Rules for resonance

- ✓Individual resonance structure does not represent the real structure
- ✓The difference is the arrangement of electrons

$CH_3\overset{+}{C}H\text{-}CH{=}CH_2$ $\overset{+}{C}H_2\text{-}CH_2\text{-}CH{=}CH_2$

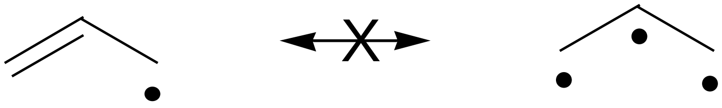
these two are not resonance structures

- ✓Should be correct Lewis structure

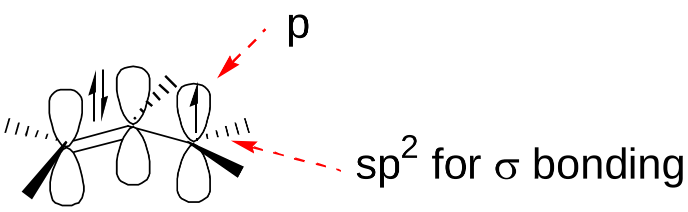


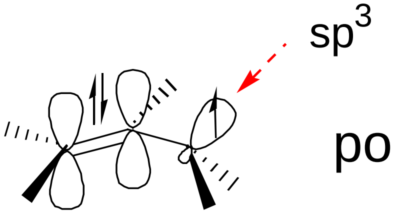
Incorrect Lewis structure

- ✓Same number of unpaired electrons



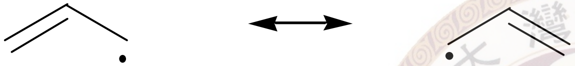
✓Delocalized orbitals must have maximum overlap





poor overlap

✓Resonance structures with equal E → more stabilization



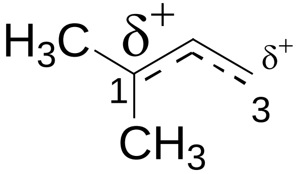
equal energy

✓More stable resonance structure
→ higher contribution to the real structure

more stable (also 3º)

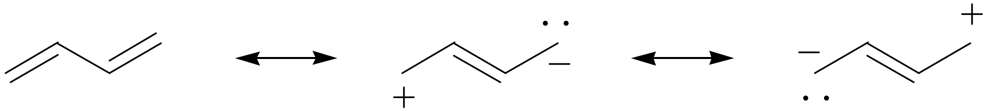
A **B**

real structure:

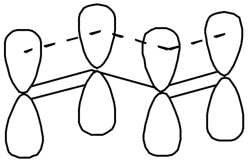


B has higher contribution
→ more **B** like
→ higher partial positive charge at C(1)
→ C(2)-C(3) has more DB character
→ shorter

✓More covalent bond → more stable (more contribution)

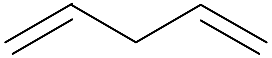


more stable
(more covalent bond)



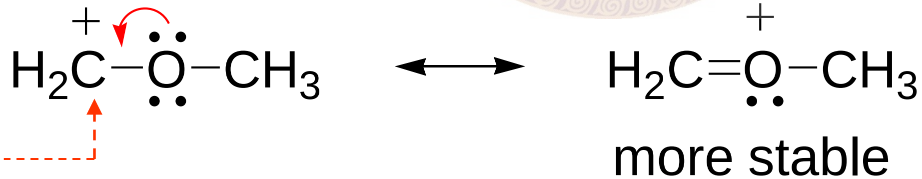
a conjugated diene

more stable than



an isolated diene

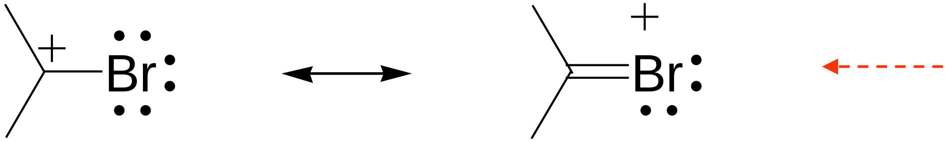
✓Fulfill octect rule → more stable



$$H_2\overset{+}{C}-\ddot{O}-CH_3 \longleftrightarrow H_2C=\overset{+}{O}-CH_3$$

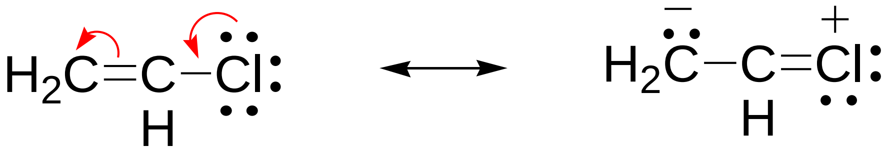
does not
fulfill octect rule

more stable



more stable

✓Charge separation → decreases stability

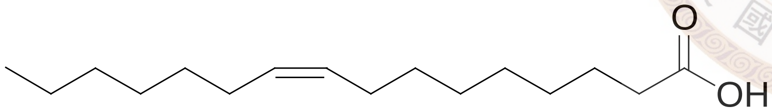


more stable

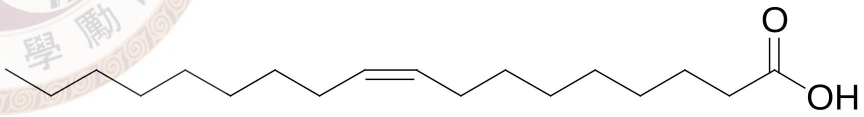
with charge separation
→ lower contribution

◎ Some common fatty acids

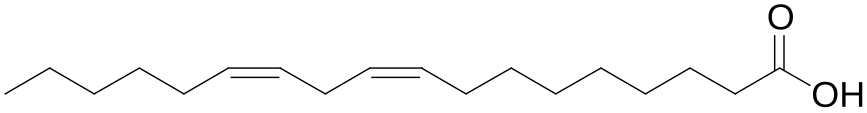
Oil	Saturated (mol%)			Unsaturated (mol%)			
	C_{14}	C_{16}	C_{18}	palmitoleic acid	oleic acid	linoleic acid	linolenic acid
Olive	0-1	5-15	1-4		67-84	8-12	
Corn	1-2	7-11	3-4	1-2	25-35	50-60	
Soybean	1-2	6-10	2-4		20-30	50-58	5-10
Peanut		7-12	2-6		30-60	20-38	



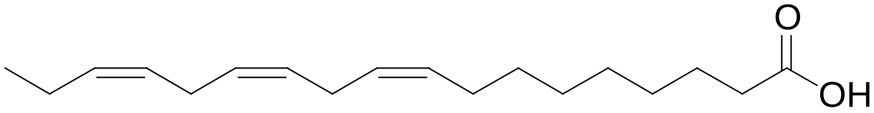
palmitoleic acid (C_{16})



oleic acid (C_{18})

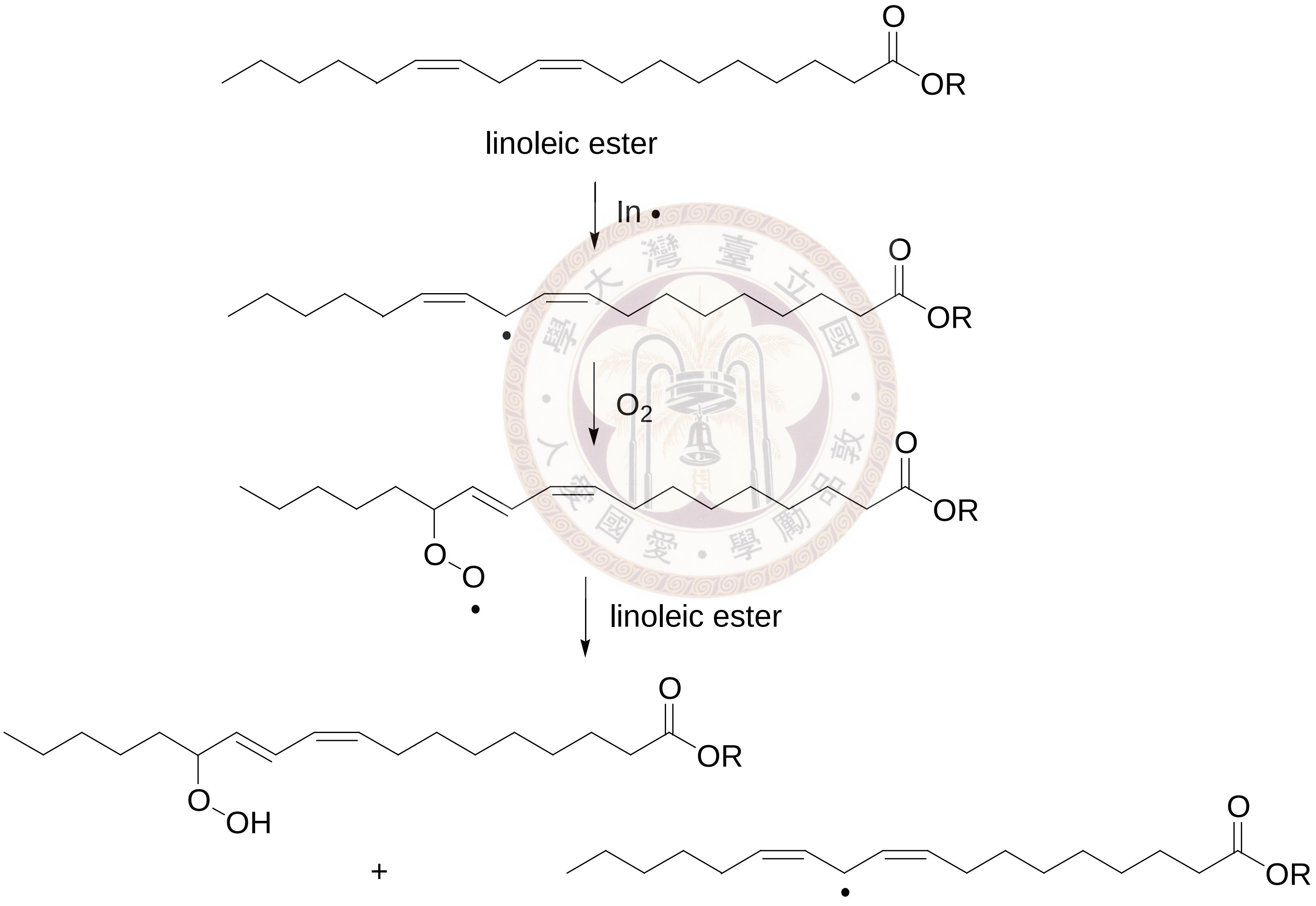


linoleic acid (C_{18})



linolenic acid (C_{18})

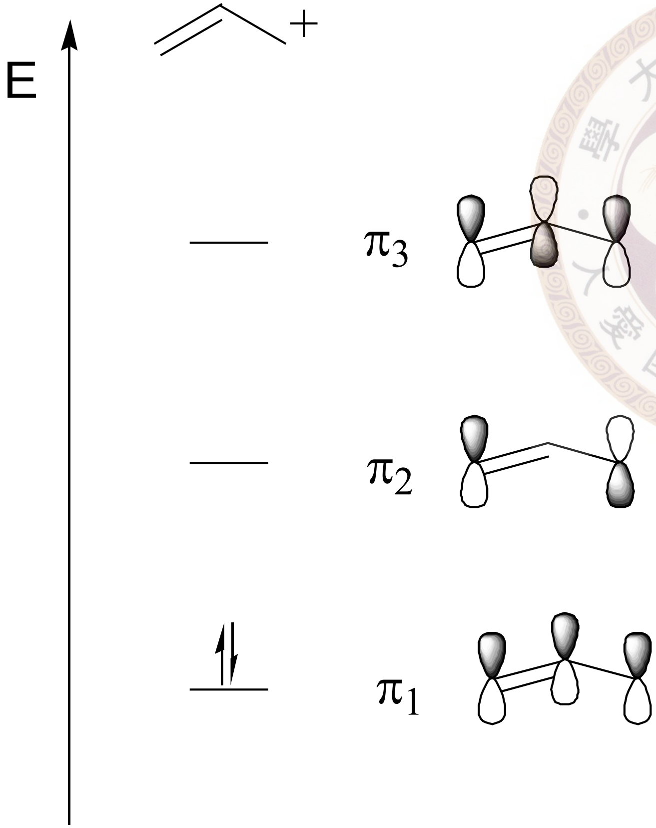
More unsaturation: more unstable



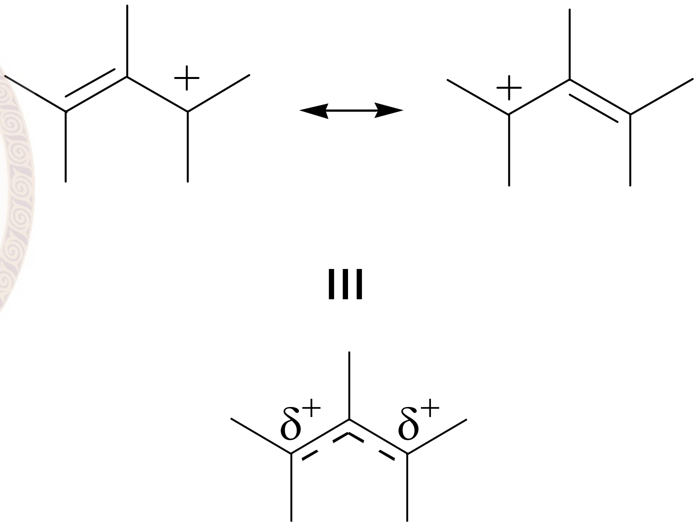
※ Allylic cation

Also stabilized by conjugation with adjacent double bond

MO:

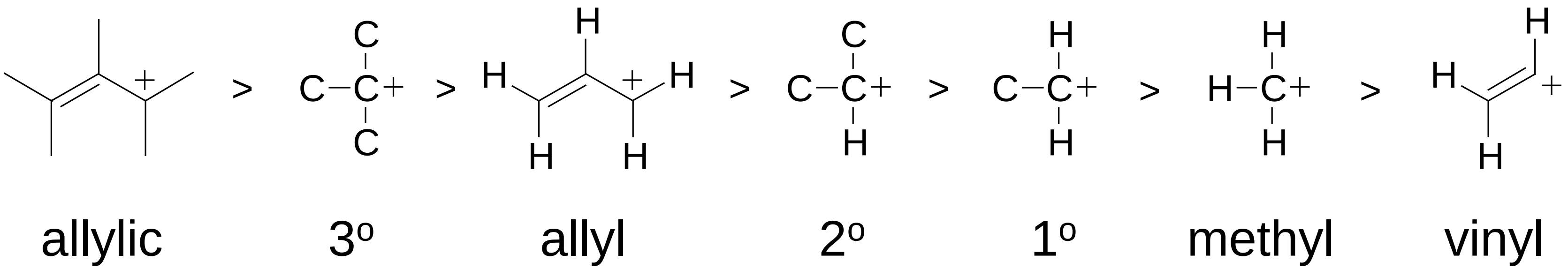


VB:



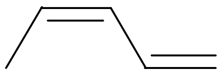
resonance stabilized

Relative stability of carbocations:

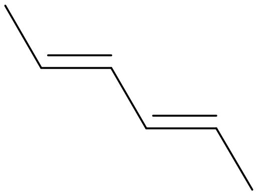


※ Alkadienes and polyunsaturated hydrocarbons

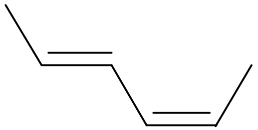
$CH_2=CH-CH=CH_2$ 1,3-butadiene (a conjugated diene)



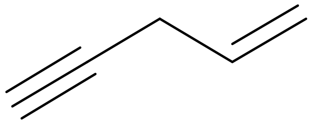
(3*Z*)-1,3-pentadiene
or *cis*-1,3-pentadiene



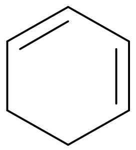
(2*E*,4*E*)-2,4-hexadiene
or *trans*,*trans*-2,4-hexadiene



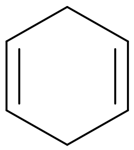
(2*E*,4*Z*)-2,4-hexadiene
or *cis*,*trans*-2,4-hexadiene



pent-1-en-4-yne (an enyne)



1,3-cyclohexadiene



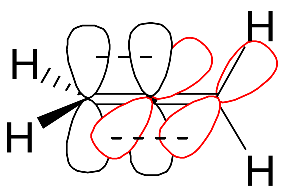
1,4-cyclohexadiene

✓ Cumulene

$H_2C{=}C{=}CH_2$

1,2-propadiene
common name: allene

$\equiv$



Contains two orthogonal π systems
(no overlap, independent to each other)
They are not conjugated

$H_2C{=}C{=}C{=}CH_2$

1,2,3-butatriene

※ 1,3-Butadiene

✓ Structure and bonding

$CH_2=CH-CH=CH_2$

1.34 Å

1.47 Å

cf.

$CH_2=CH_2$

1.34 Å

CH_3-CH_3

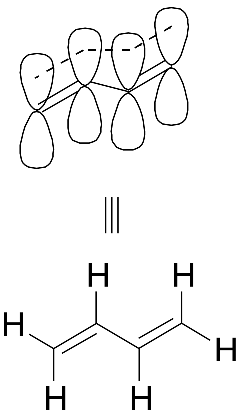
1.54 Å

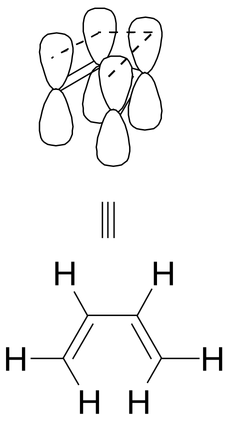
sp^3-sp^3

sp^2-sp^2: more s character → shorter

Planar: to obtain conjugation of π orbitals

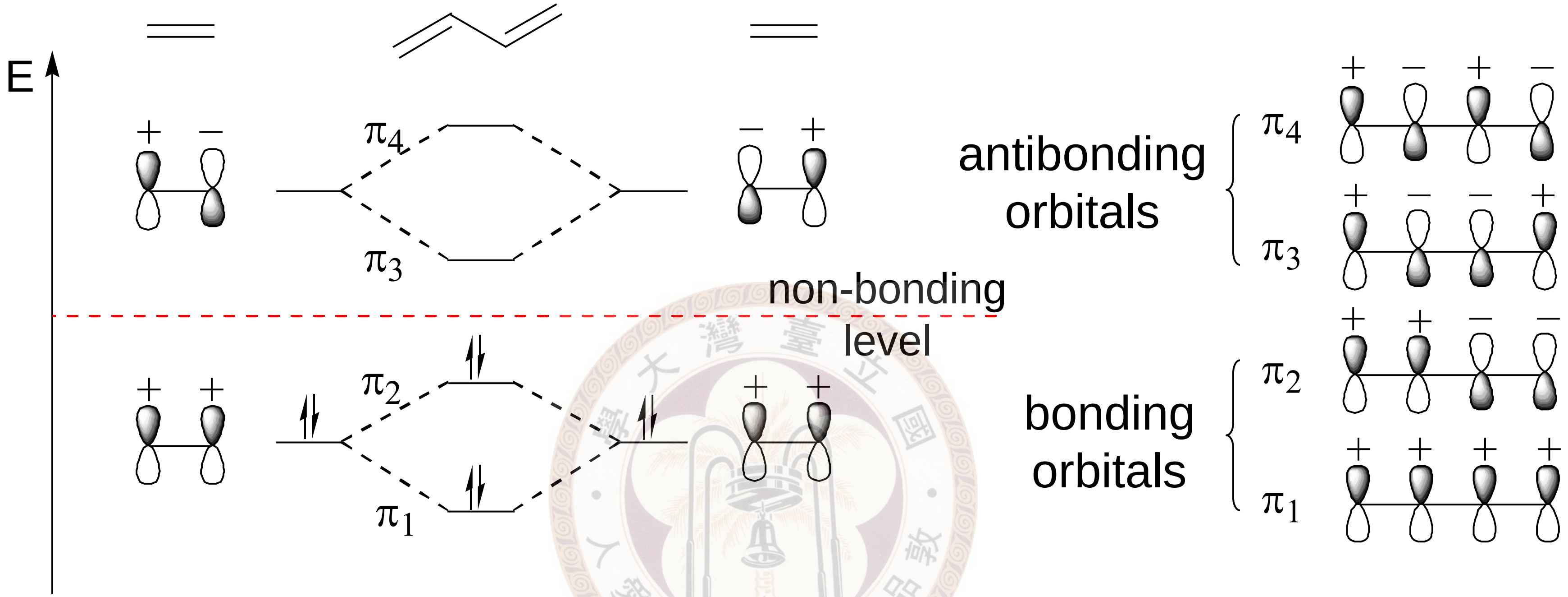
s-trans conformation ←
more stable



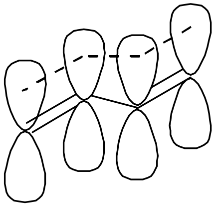


→ s-cis conformation

✓ MO



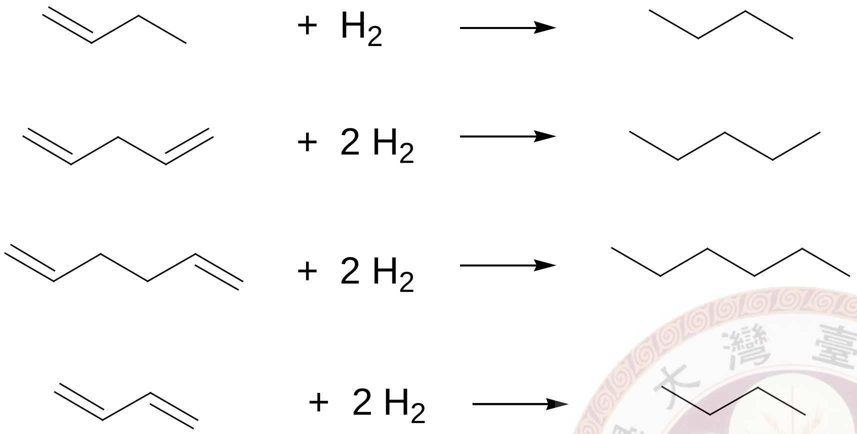
✓ VB



In conjugated dienes, the π electrons are delocalized over the four carbons (非定域化的)

→ More stable

✓ The extra stability



$\Delta H^o = -127$ kJ/mol

$\Delta H^o = -254$ kJ/mol

$\Delta H^o = -253$ kJ/mol

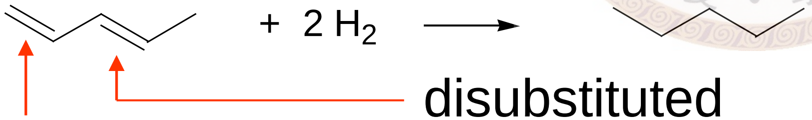
doubled

$\Delta H^o = -239$ kJ/mol

Lower than expected (–254) by 15 kJ/mol

→ Stabilization energy due to conjugation

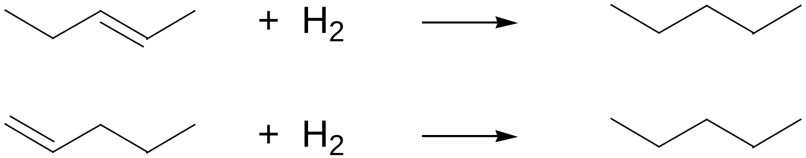
→ Conjugated dienes are more stable



$\Delta H^o = -226$ kJ/mol

disubstituted

monosubstituted



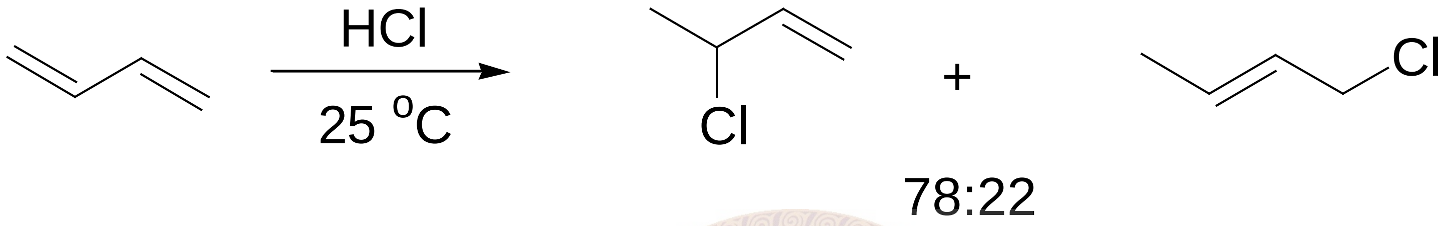
$\Delta H^o = -115$ kJ/mol

$\Delta H^o = -126$ kJ/mol

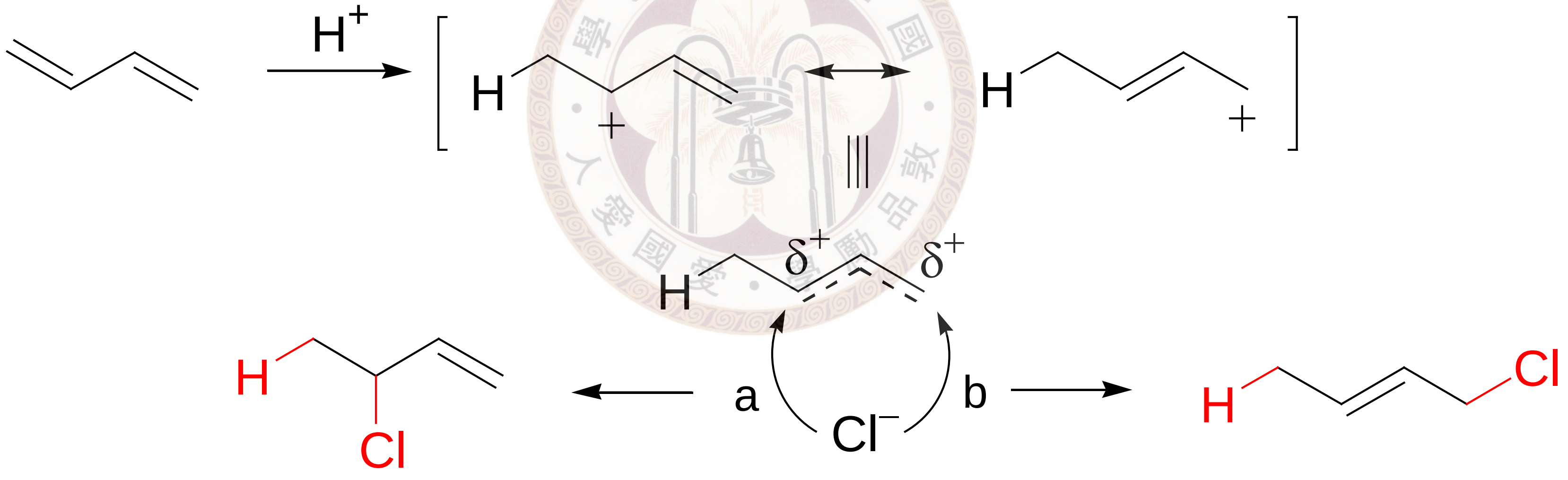
total:
–241 kJ/mol

241 – 226 = 15 kJ/mol → stabilization E due to conjugation

※ 1,4-Addition of conjugated dienes



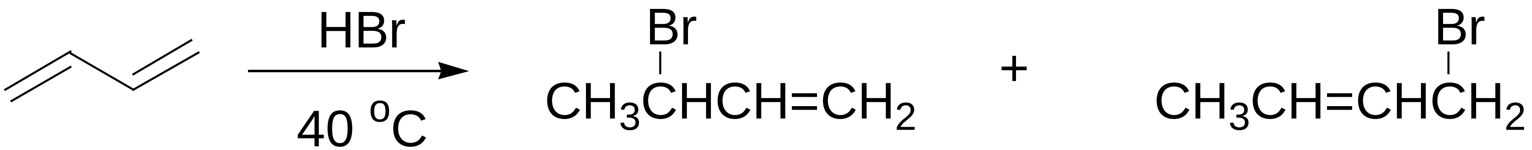
Mechanism:



1,2-addition product

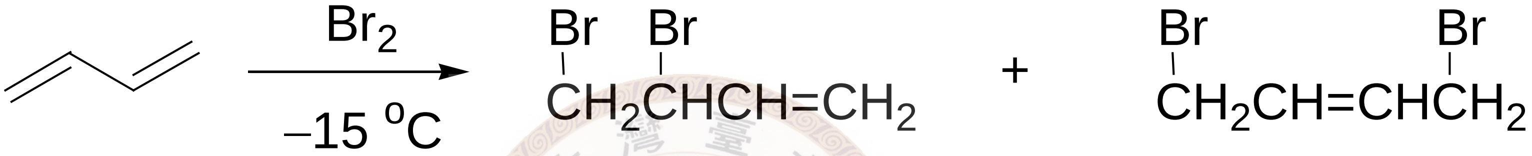
1,4-addition product

例



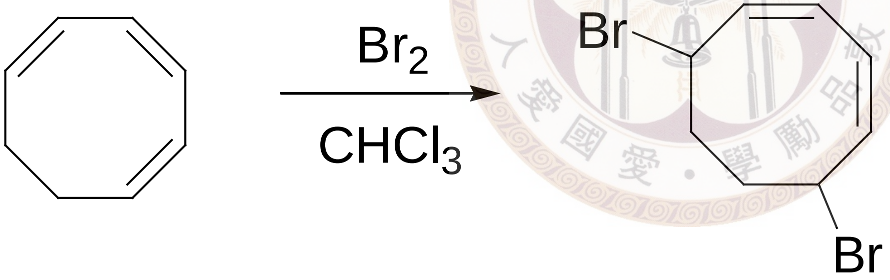
$$\xrightarrow[40\ ^{o}C]{HBr} CH_3\overset{Br}{C}HCH{=}CH_2 + CH_3CH{=}CH\overset{Br}{C}H_2$$

20:80



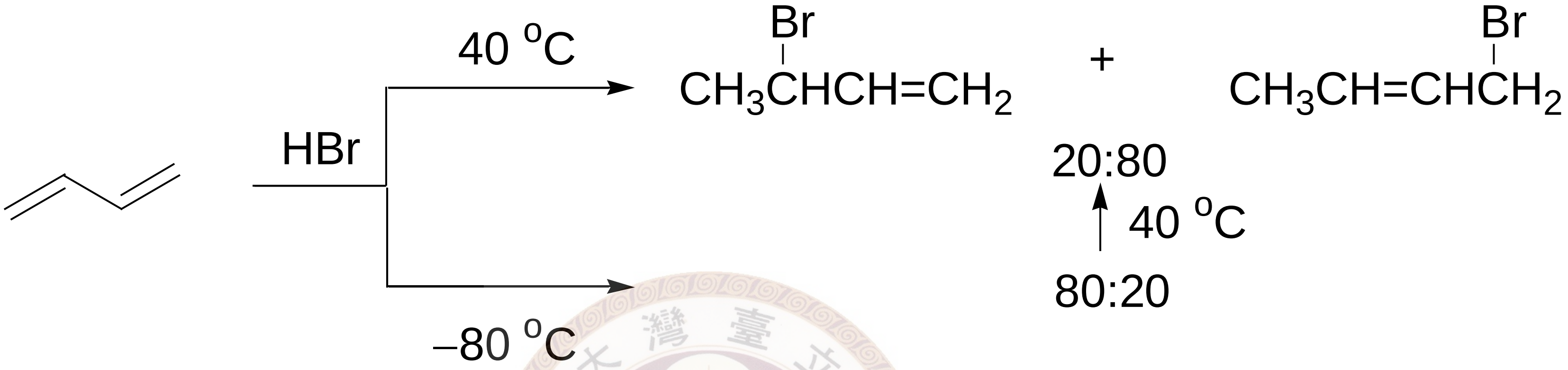
$$\xrightarrow[-15\ ^{o}C]{Br_2} \overset{Br}{C}H_2\overset{Br}{C}HCH{=}CH_2 + \overset{Br}{C}H_2CH{=}CH\overset{Br}{C}H_2$$

54:46



>68%

✓ Regiochemistry?



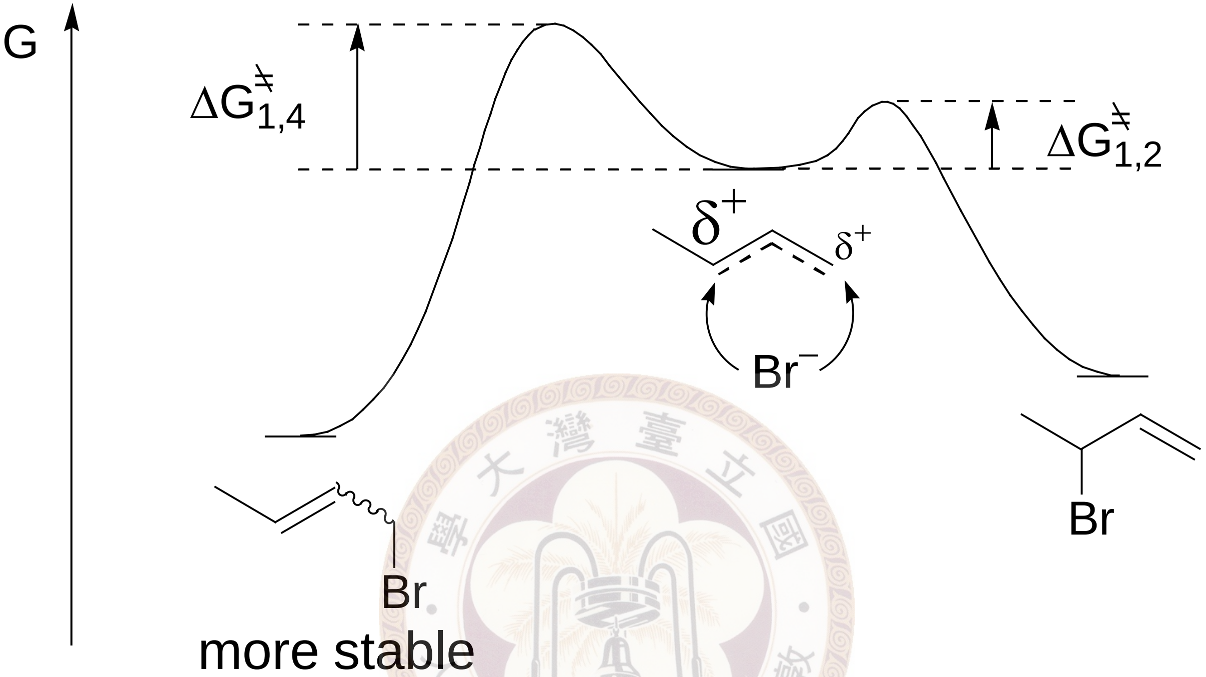
$$CH_3\overset{Br}{C}HCH=CH_2 + CH_3CH=CH\overset{Br}{C}H_2$$

There is an equilibrium at high temperature:

$$CH_3\overset{Br}{C}HCH=CH_2 \overset{40\ ^{o}C,\ HBr}{\rightleftharpoons} CH_3CH=CH\overset{Br}{C}H_2$$

more stable
(disubstituted)

★ Kinetic vs thermodynamic control



Kinetically: Br^- attacking more positive carbon is faster

→ at lower T, the rxn is irreversible

→ product is determined by rate

→ kinetic control

Thermodynamically: 1,4-addition product is more stable

→at higher T, the rxn is reversible

→ product is determined by stability

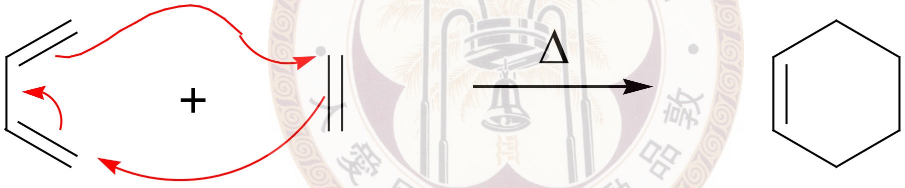
→ thermodynamic control

※ Diels-Alder reaction

A [4+2] cycloaddition reaction (環化加成反應)

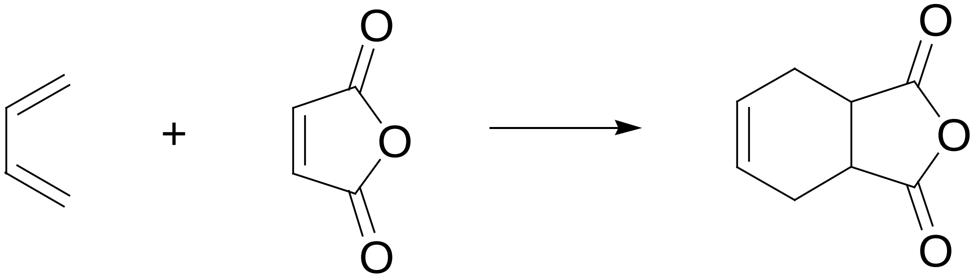
1928 by Diels and Alder → 1950 Nobel prize

Basic pattern:

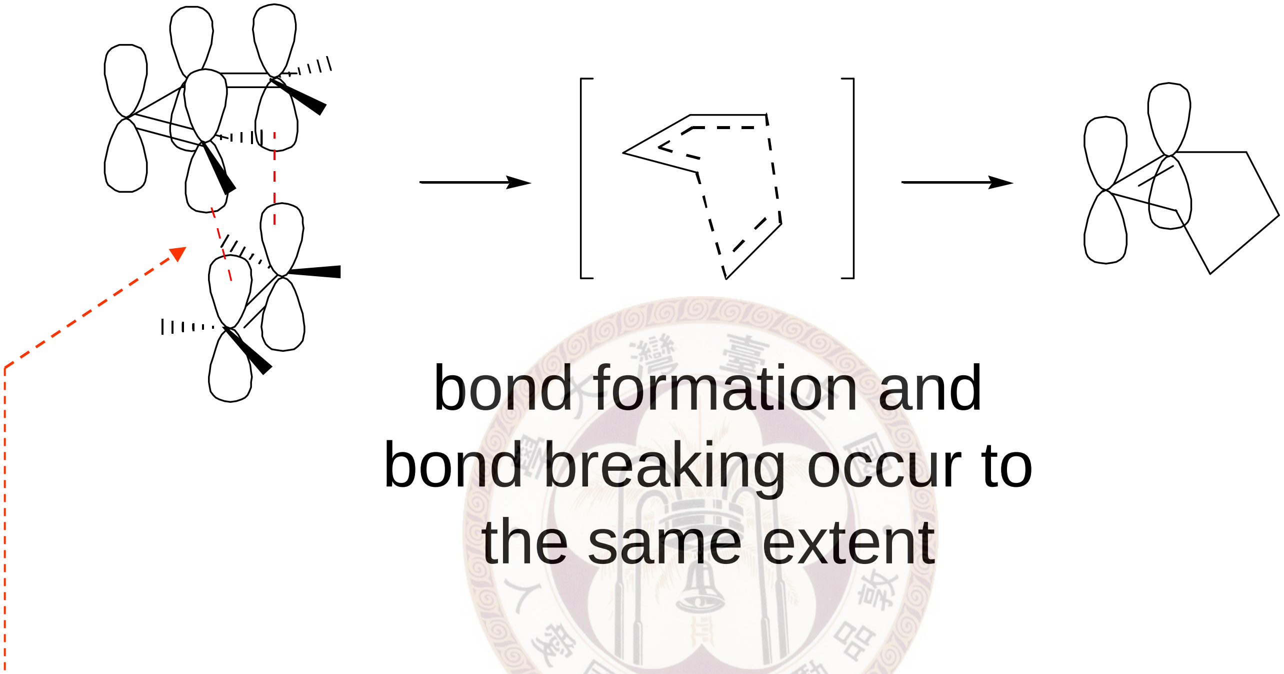


a diene a dienophile cyclohexene

例



✓ The mechanism: a concerted (協同式) process

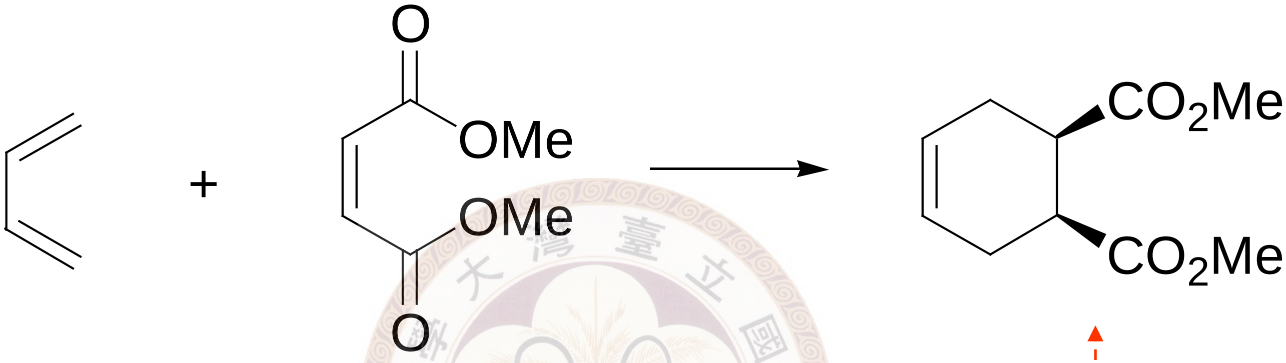


bond formation and bond breaking occur to the same extent

formation of σ bond
head-to head overlap

✓ Stereochemistry

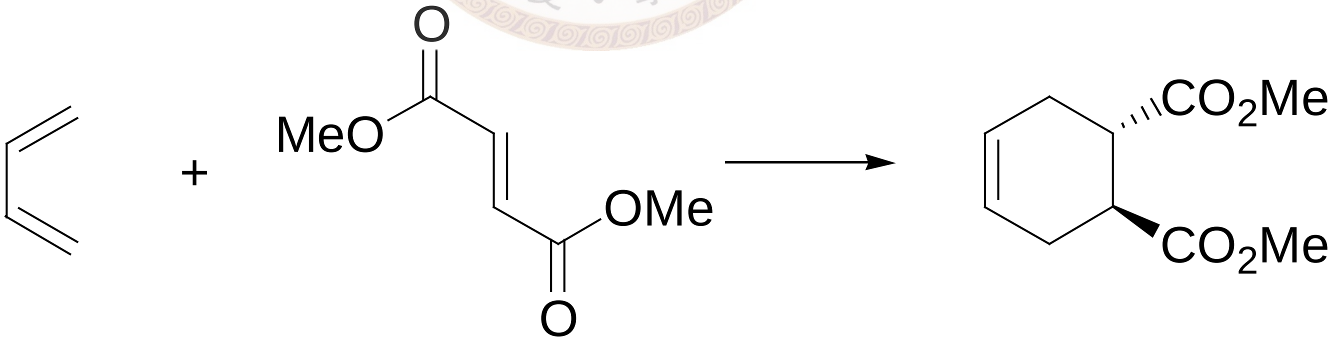
Stereospecifically syn addition to dienophile



dimethyl maleate

cis

cis relationship
is retained



trans

dimethyl fumarate

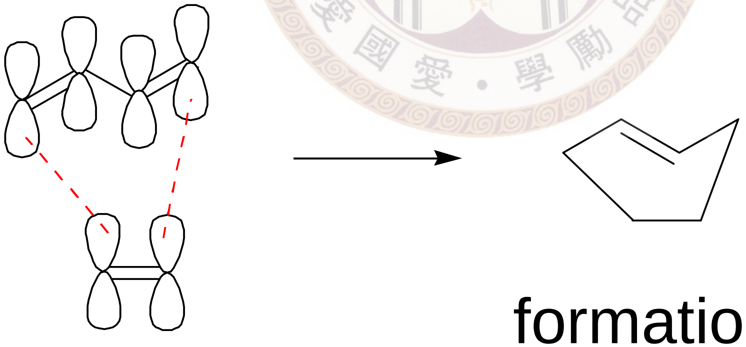
trans

✓ Reactive conformation of diene

⇨ *s*-cis form

s-cis
reactive

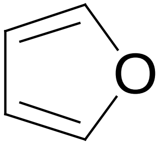
s-trans
unreactive



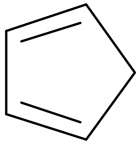
difficult to reach

formation of a
trans-cyclohexene

too strain



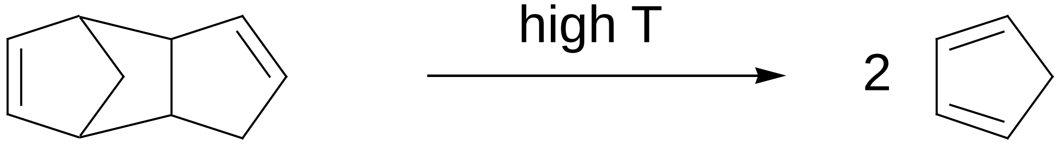
Another reason that furan is a very good diene
→ locked in an *s*-cis configuration



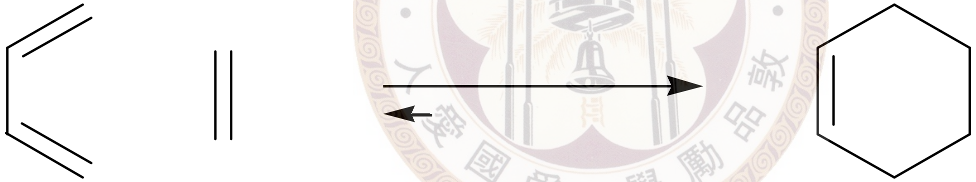
Cyclopentadiene is also a very good diene
→ in fact, it is so good that it dimerizes very easily

dicyclopentadiene

- ✓ Diels-Alder reaction is a reversible reaction

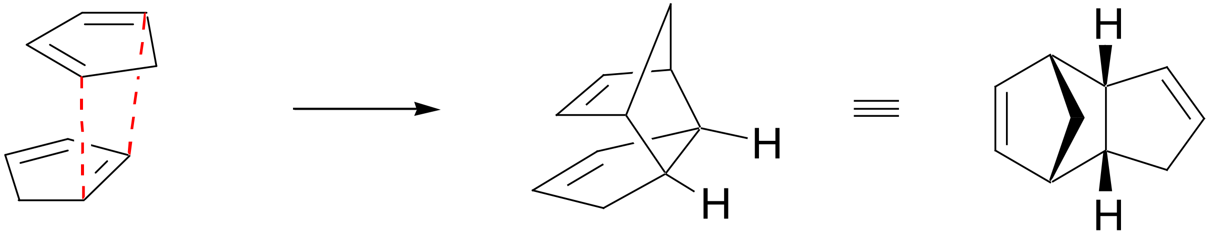


- ✓ Energetics



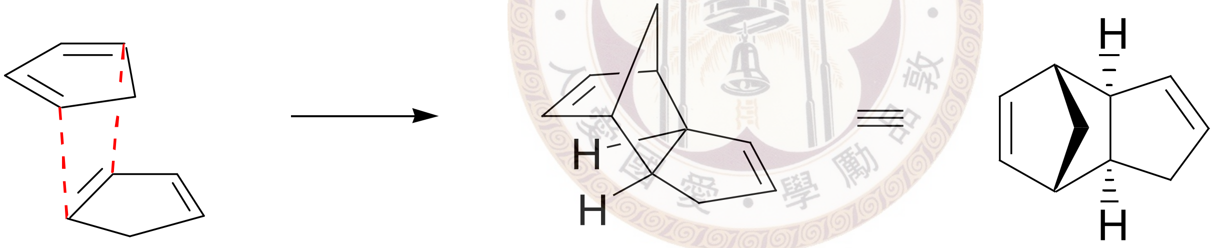
break 3 π
form 2 σ + 1 π
→ usually exothermic
→ the right-hand side is preferred

✓ Follows endo selectivity



preferred

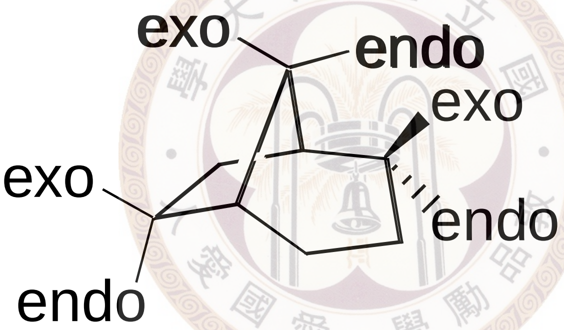
endo-approach



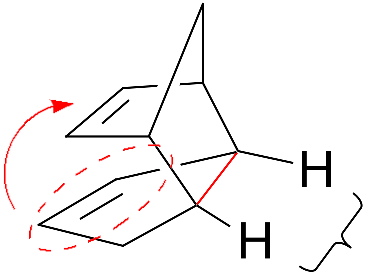
exo-approach

*Definition of endo and exo

Substituent on a bridge of a bicyclic structure:
the group orientated towards the highest numbered bridge
→ endo
the group orientated towards the lowest numbered bridge
→ exo



same side as this bridge
→ endo



exo hydrogens