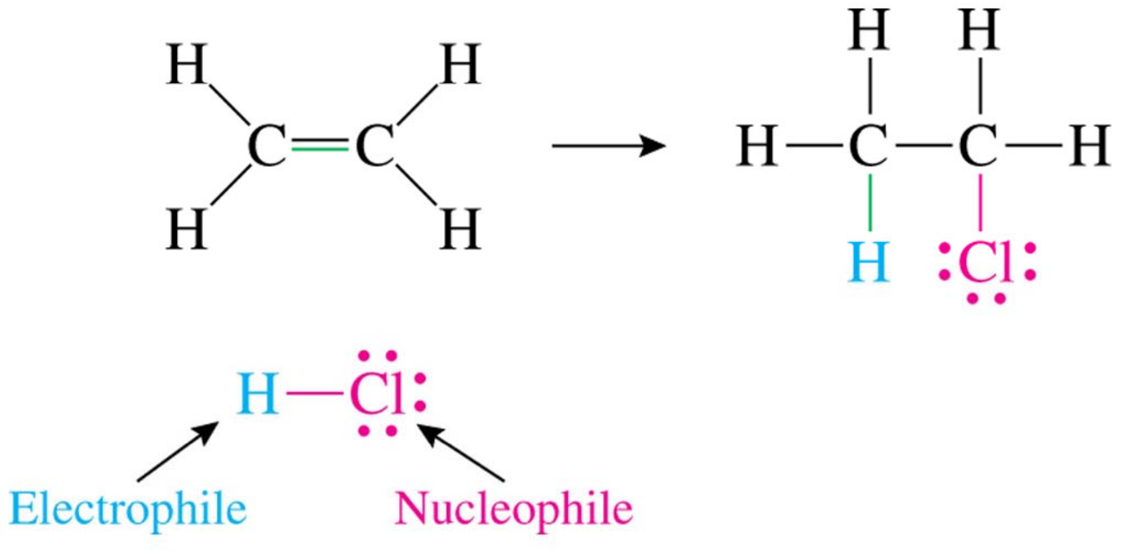
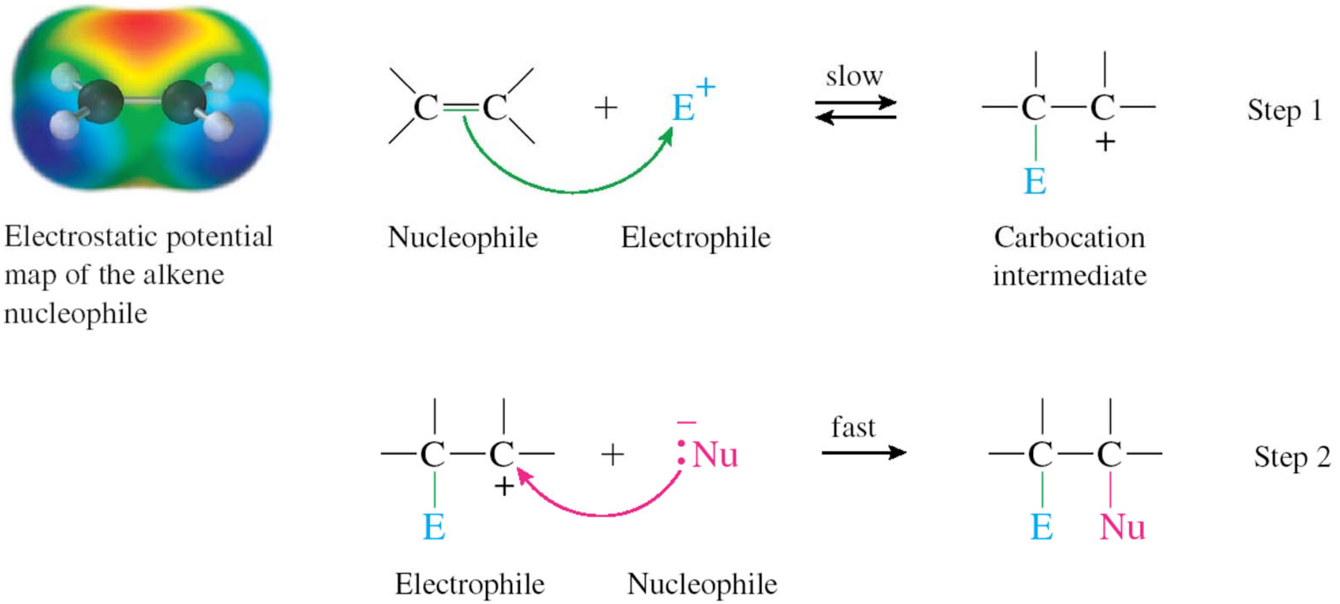
Chapter 11

Additions to Carbon-Carbon Double and Triple Bonds

⇒ **The addition of an electrophile and a nucleophile to a C-C double or triple bonds**



11.1 The General Mechanism



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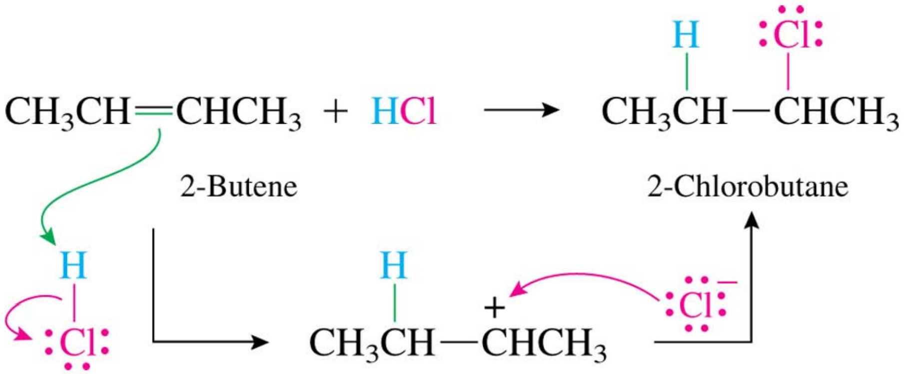
→ **Pi electrons of the double bond is a weak nü**

→ **same as the second step of S_N1**

- ⇒ **electrophilic addition reaction**
- ⇒ **Faster reactions for the compounds with structural features that stabilize the carbocation**
- ⇒ **As weak nü is employed, strong electrophile such as H^+ is needed in the acidic or neural conditions not to destroy the electrophile.**

11.2 Addition of Halogen Halides

- ⇒ **Addition of HF, HCl, HBr, and HI to alkenes to give alkyl halides**



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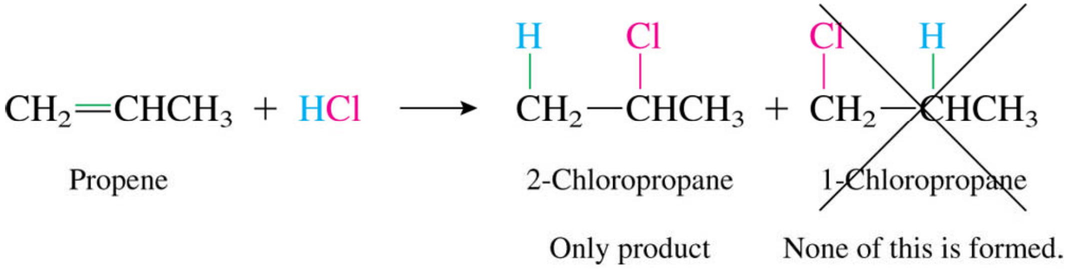
- ⇒ **Symmetric alkene; one product (regioselective rxn)**



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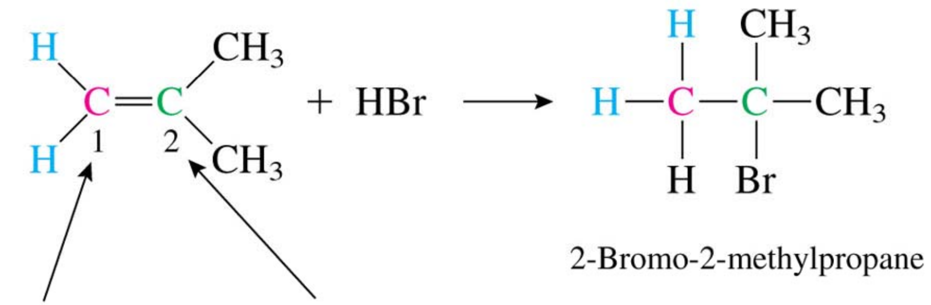
- ⇒ **unsymmetric alkene; still one product**
- ⇒ **Therefore it is regioselective reaction**

why? ⇒ Markovnikov's rule

In addition reactions of HX to alkenes, the H bonds to the carbond with more hydrogens and the X bonds to the carbond with fewer hydrogens

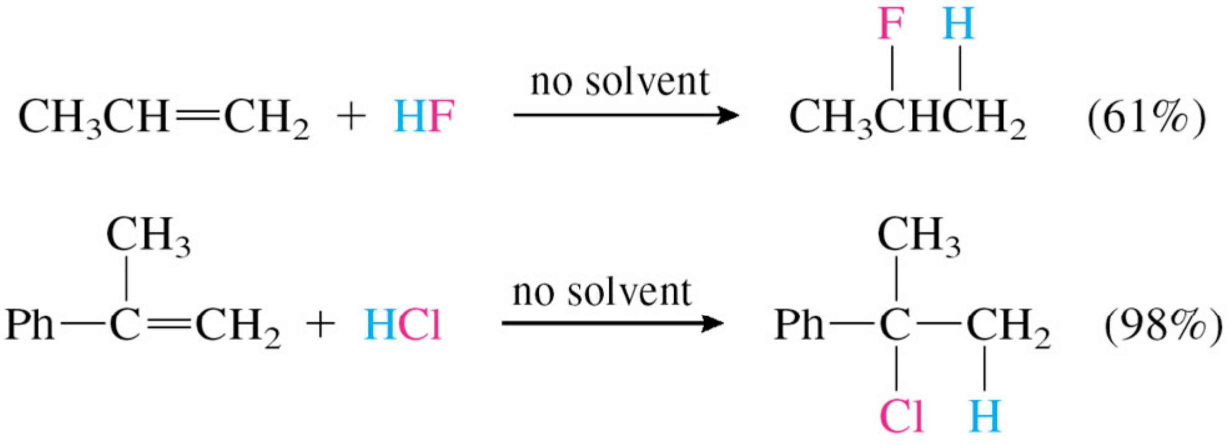


2-Bromo-2-methylpropane

C-1 is bonded to more hydrogens (two), so the H should bond here.

C-2 is bonded to fewer hydrogens (none), so the Br should bond here.

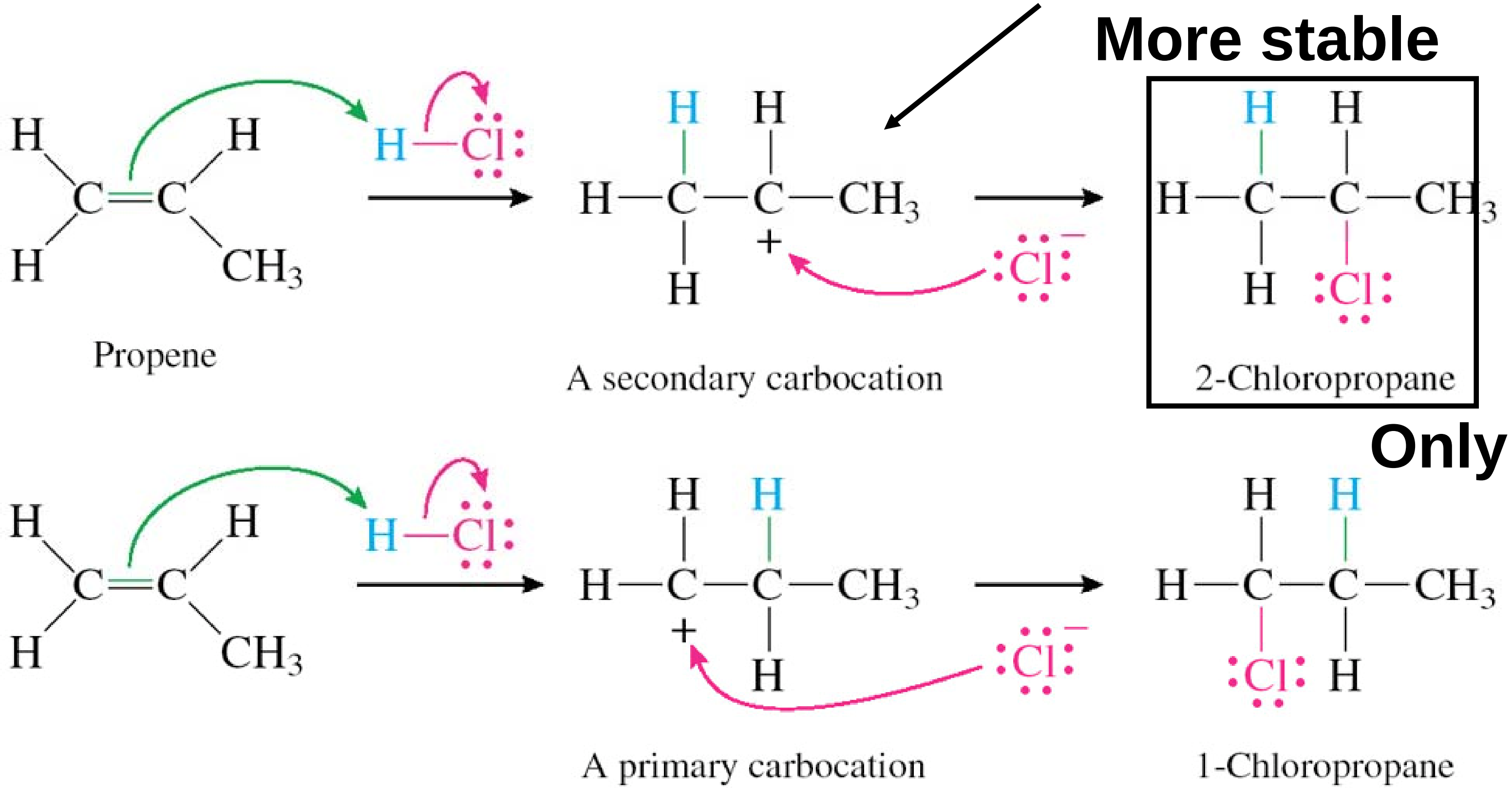
examples



$$CH_3CH{=}CH_2 + HF \xrightarrow{\text{no solvent}} CH_3\overset{F}{C}H\overset{H}{C}H_2 \quad (61\%)$$

$$Ph{-}\overset{CH_3}{C}{=}CH_2 + HCl \xrightarrow{\text{no solvent}} Ph{-}\overset{CH_3}{\underset{Cl}{C}}{-}\underset{H}{C}H_2 \quad (98\%)$$

why? ⇒ **the stability of the carbocation in the intermediate state**

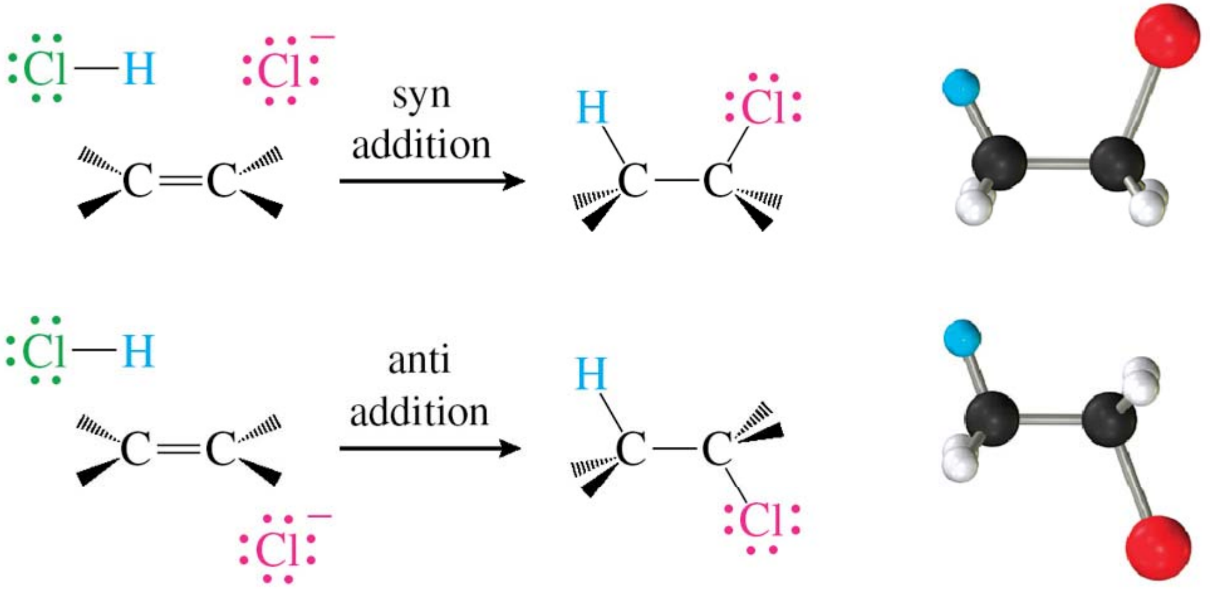


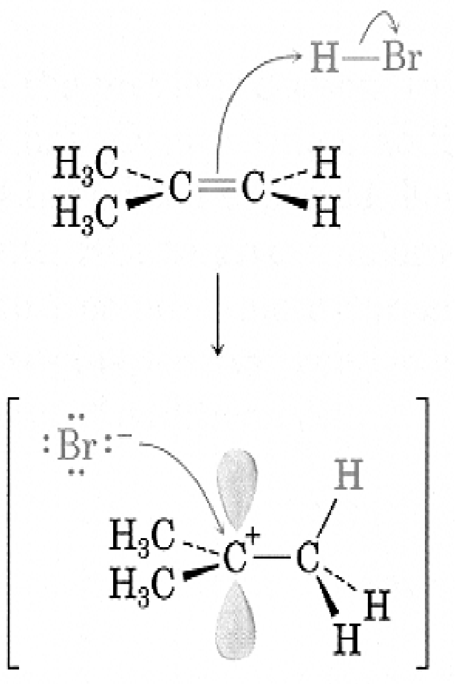
More stable

Only product

Examples in p. 409

Stereochemistry; syn or anti addition



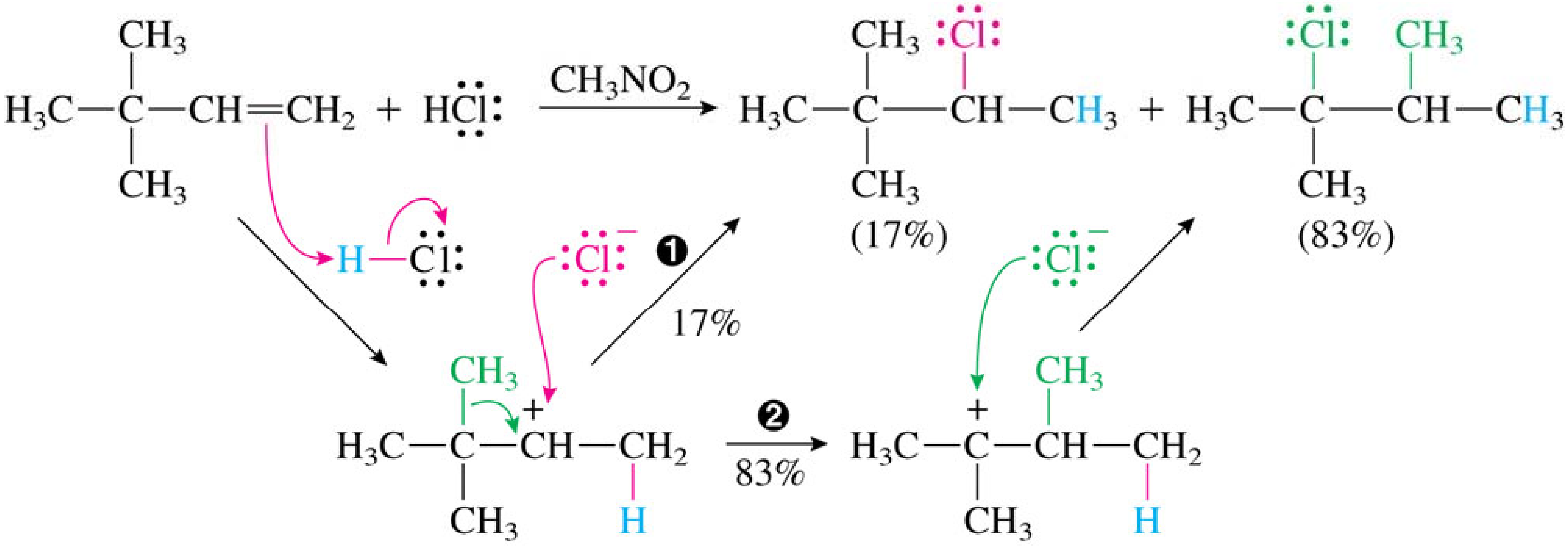


Carbocation intermediate

⇒ **Products are mixtures of syn and anti addition because the intermediate is carbocation.**

⇒ **Under some condition stereochemistry is a issue, while not HX addition case**

Rearrangement



❶ This secondary carbocation reacts with chloride (17%)

❷ and rearranges to the more stable tertiary carbocation (83%).

A tertiary carbocation

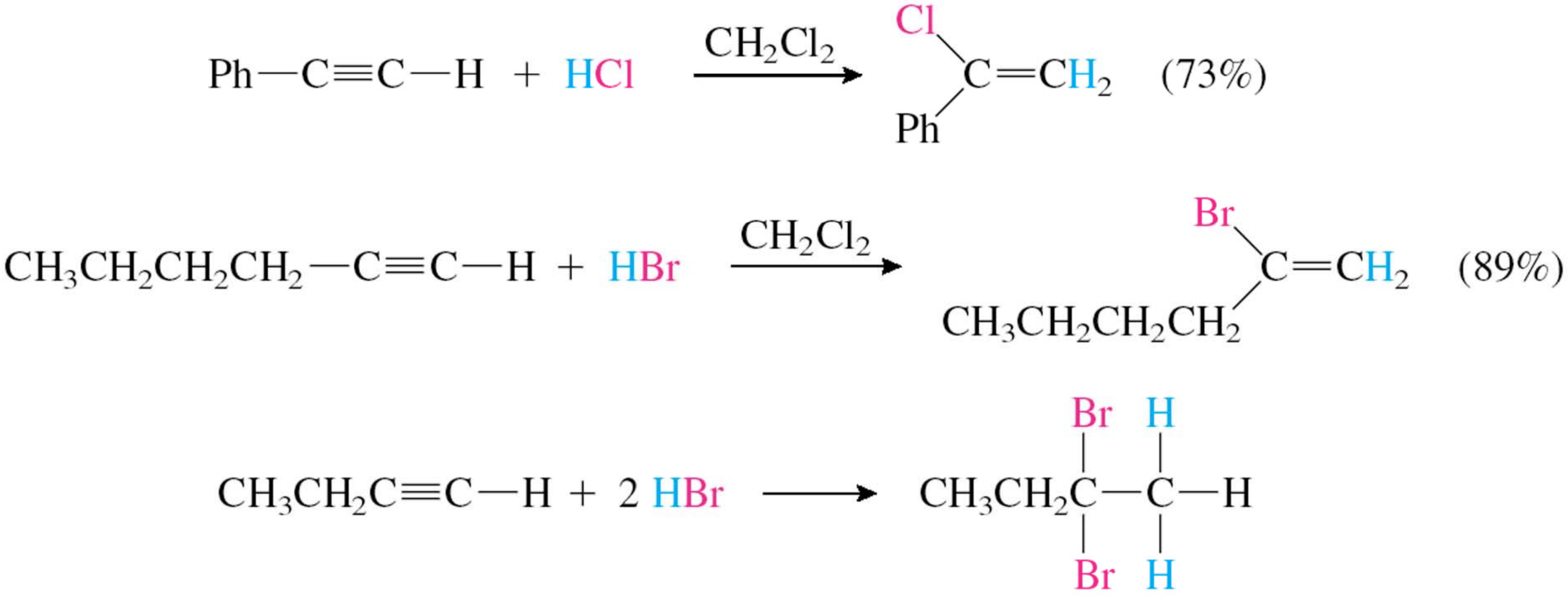
⇒ **mixtures are obtained.**

More stable

addition to the triple bonds

⇒ **Same to the reactions to the double bonds**

examples



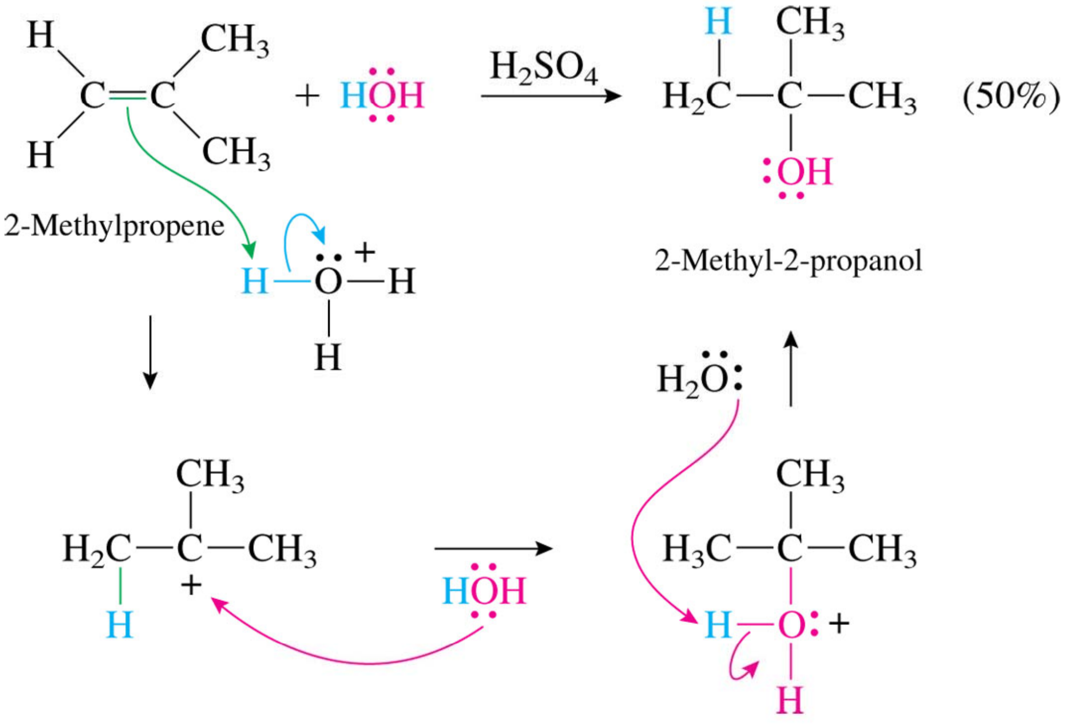
$$CH_3CH_2C{\equiv}C{-}H + 2\,HBr \longrightarrow CH_3CH_2CBr_2{-}CH_2{-}H$$

11.3 Addition of Water (Hydration)

⇒ The rxn of an alkene in water with a strong acid.
⇒ The conjugate base of the strong acid is not nucleophilic (sulfuric acid).
⇒ Then the addition of the elements (H and OH) happens

mechanism

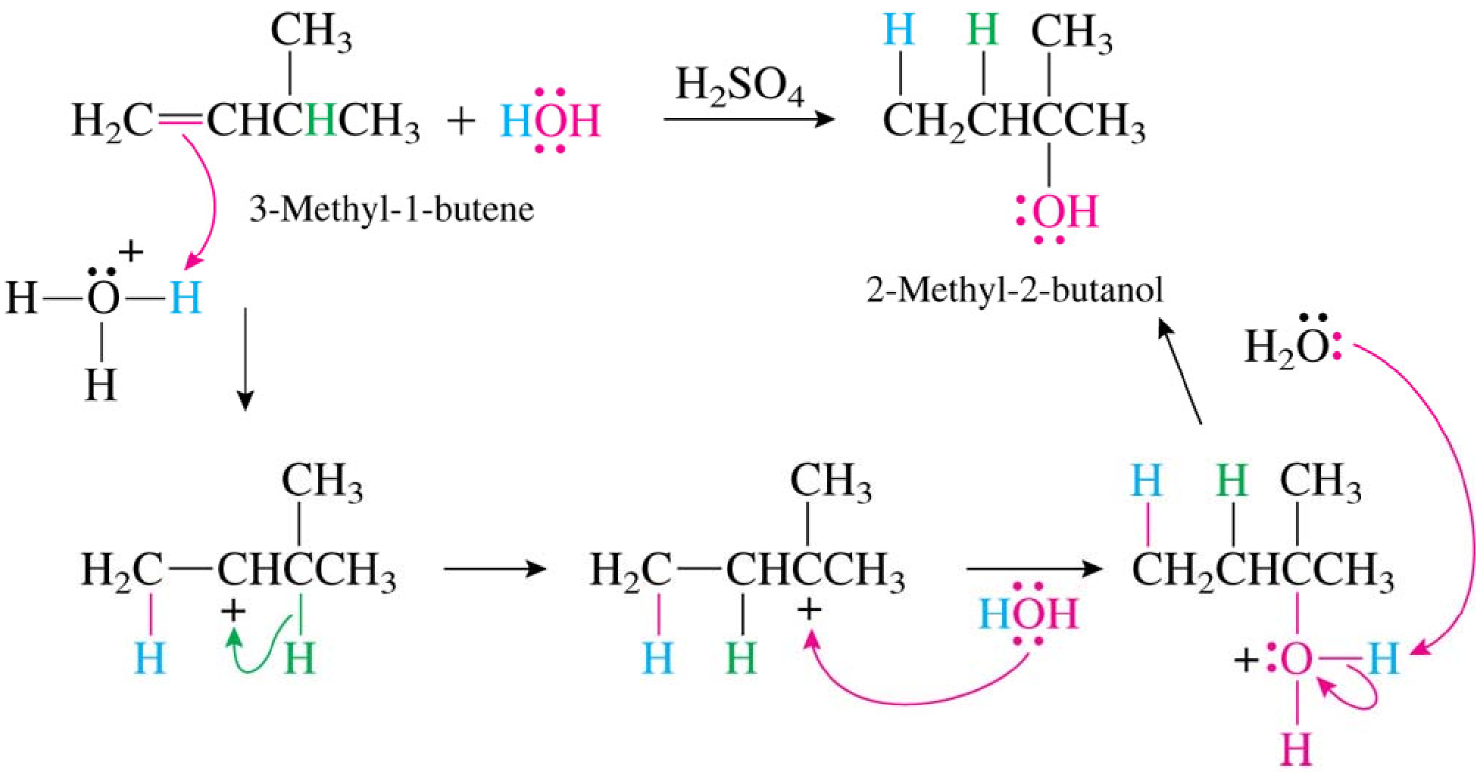
Markovnikov's rule
Loss of stereochemistry



Disadvantages of hydration

⇒ **Low yield because of the strongly acidic condition (nucleophilicity of water, elimination, the reverse rxn)**

⇒ **Carbocation rearrangement is possible**



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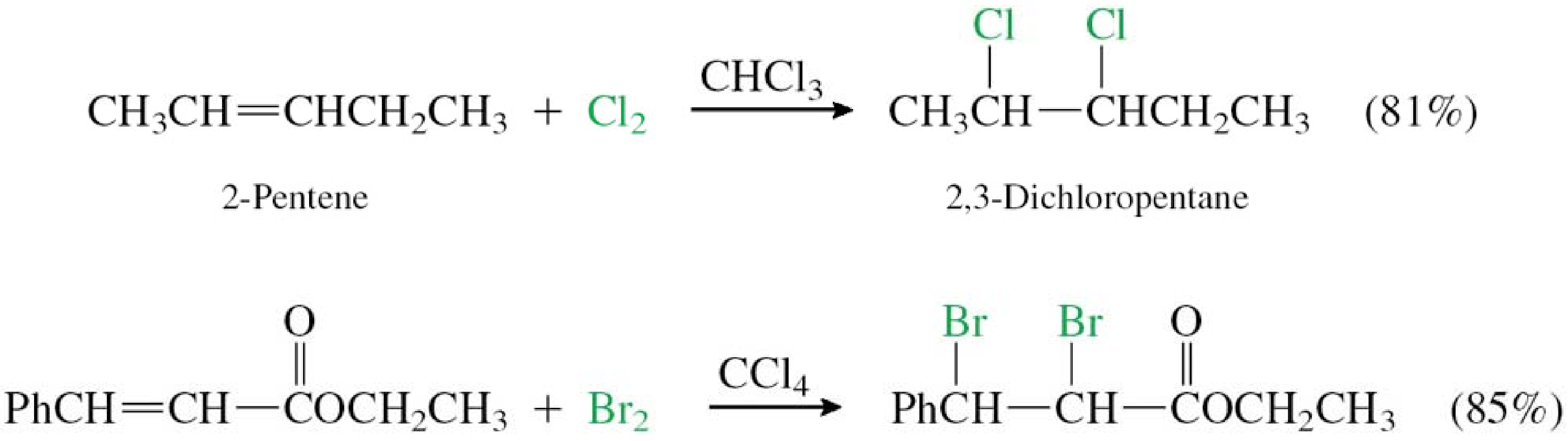
⇒ **Not commonly used for the preparation of alcohols from alkenes ;for higher yield, see 11.6**

11.4 Addition of Halogens

⇒ **Addition of Cl_2 and Br_2 to give dihalides**

⇒ **The other halogens are not commonly used because F_2 is too reactive and I_2 is not reactive enough**

⇒ **Inert solvents, such as CCl_4, $CHCl_3$, or CH_2Cl_2 are used.**



$$CH_3CH{=}CHCH_2CH_3 + Cl_2 \xrightarrow{CHCl_3} CH_3\overset{\overset{Cl}{|}}{C}H-\overset{\overset{Cl}{|}}{C}HCH_2CH_3 \quad (81\%)$$

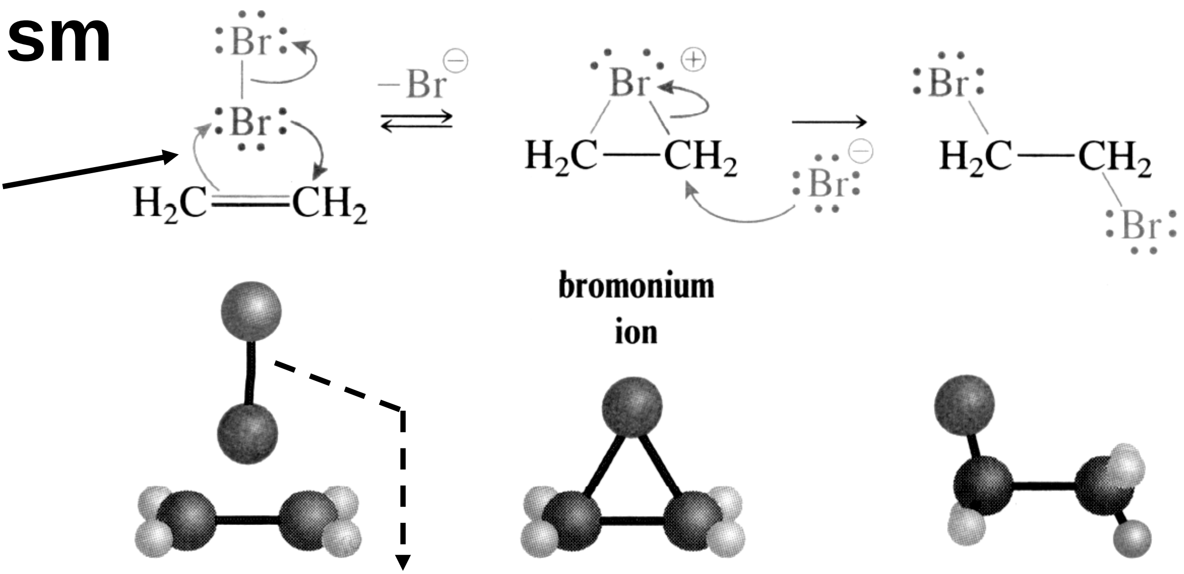
2-Pentene

2,3-Dichloropentane

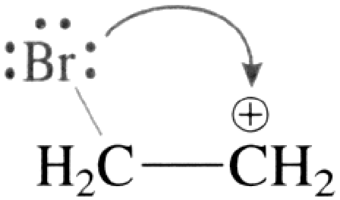
$$PhCH{=}CH-\overset{\overset{O}{\|}}{C}OCH_2CH_3 + Br_2 \xrightarrow{CCl_4} PhCH-\overset{\overset{Br}{|}}{C}H-\overset{\overset{O}{\|}}{C}OCH_2CH_3 \quad (85\%)$$

⇒ **Bromination; test for the double (or triple) bonds because Br_2 in carbon tetra chloride has red-brown color, after rxn (a few drops of alkene) it becomes colorless**

mechanism



Electrophile; attract electrons of the pi bond



As bromonium ion is much stable than carbocation, this step is instaneous; stability, octet rule

Resembles a protonated epoxide in both structures and rxns

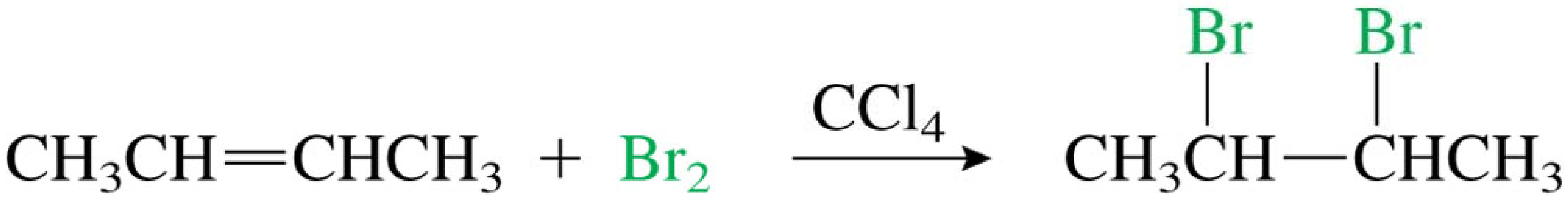
Stereochemistry; S_N2 (related to chirality)

⇒ The nucleophilic bromide approaches from the side opposite the leaving bromine.

Regiochemistry; S_N1 (to which carbon ?)

⇒ The nucleophile bonds to the carbon that would be more stable as a carbocarbon.

the stereochemistry of the reaction of bromine with 2-butene

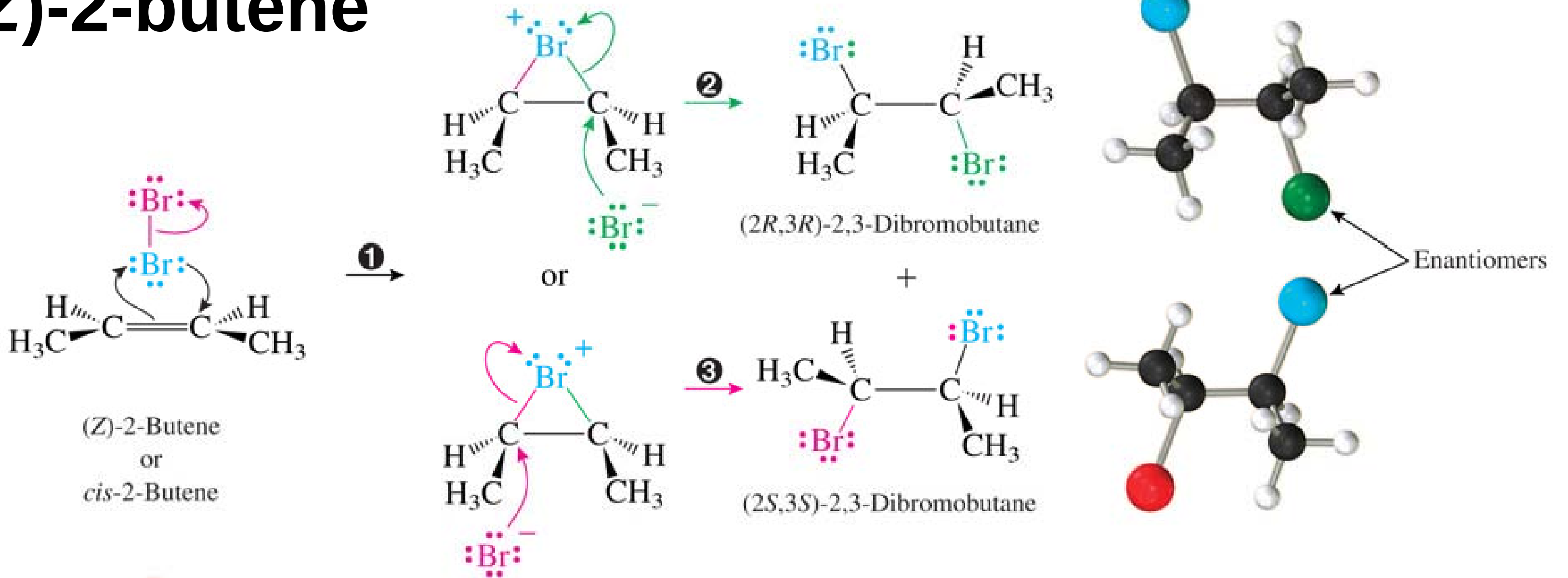


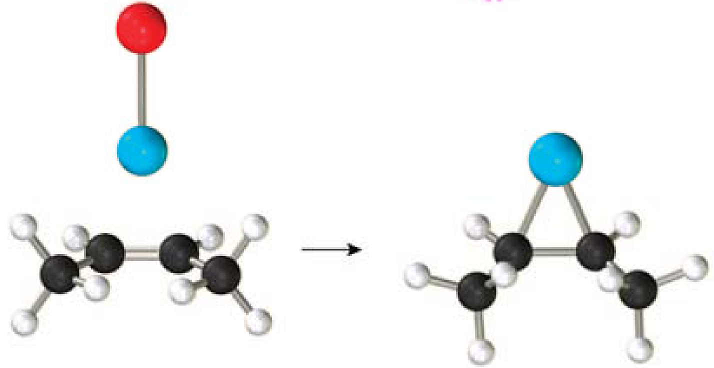
$$CH_3CH{=}CHCH_3 + Br_2 \xrightarrow{CCl_4} CH_3\overset{\overset{\displaystyle Br}{|}}{C}H-\overset{\overset{\displaystyle Br}{|}}{C}HCH_3$$

2-Butene

2,3-Dibromobutane

(*Z*)-2-butene





❶ Because both of the new C—Br bonds are to the same Br, they must be formed on the same side of the plane of the double bond, the top side in this drawing. Therefore, the bromonium ion results from syn addition. Because the bromine has added in a syn manner, the methyl groups, which were cis in the starting alkene, are cis in the bromonium ion.

The bromide nucleophile approaches from the bottom side, opposite the leaving positive bromine. The two carbons are identical so the bromide attacks them in equal amounts.

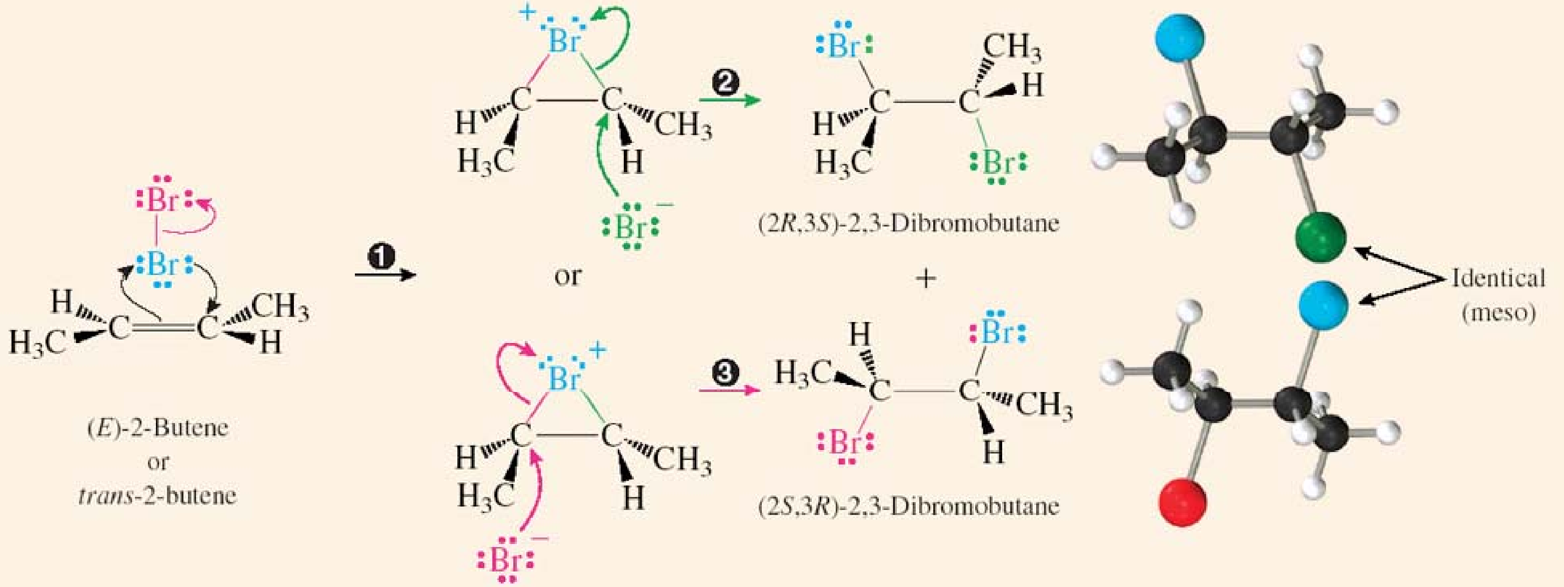
❷ (2*R*,3*R*)-2,3-Dibromobutane results from the bromide approaching according to the green arrow. Note that the two bromines have added anti to the double bond.

❸ (2*S*,3*S*)-2,3-Dibromobutane results from the bromide approaching according to the red arrow. It is the mirror image, the enantiomer, of the compound above it. The two dibromides are formed in equal amounts. The product is racemic, as it must be because the starting materials are not chiral.

⇒ A racemic mixture

(*E*)-2-butene

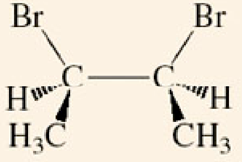
⇒ **Only one product, a meso diastereomer**



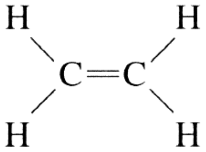
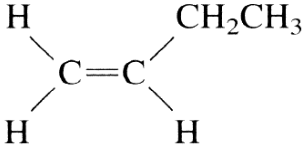
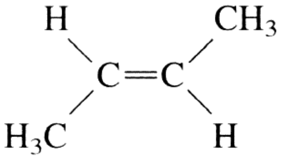
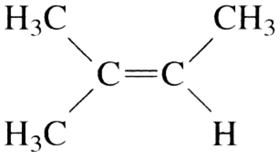
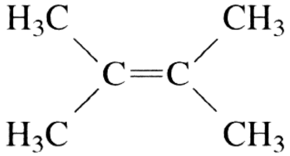
❶ The bromine has added in a syn manner, the methyl groups, which were trans in the starting alkene, are trans in the bromonium ion. The bromide nucleophile then approaches from the bottom side, opposite the leaving positive bromine. The two carbons are identical so the bromide attacks them in equal amounts.

❷ (2*R*,3*S*)-2,3-Dibromobutane results from the bromide approaching according to the green arrow. Note that the two bromines have added anti to the double bond.

❸ (2*S*,3*R*)-2,3-Dibromobutane results from the bromide approaching according to the red arrow. It is a superimposable mirror image of the compound above it. The two dibromides are identical—the product is *meso*-2,3-dibromobutane. If the compound is shown in its most symmetrical conformation, the internal plane of symmetry is apparent.

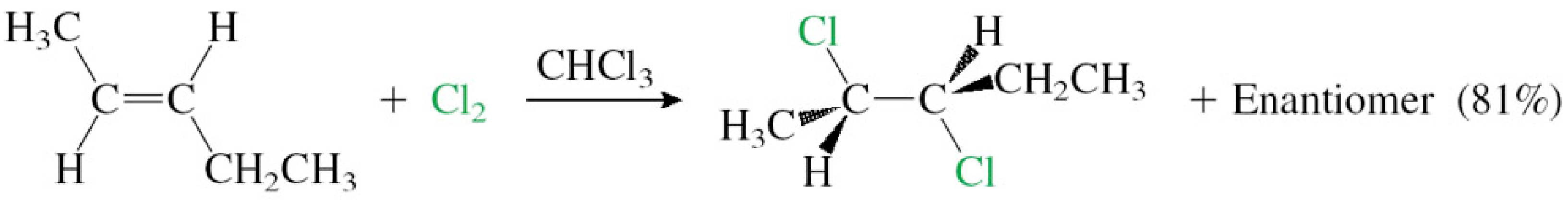


Relative Rates of Reaction of Alkenes with Bromine. (The reaction is the alkene plus Br_2 in methanol as solvent.)

Alkene	**Relative Rate**
	1
	1×10^2
	2×10^3
	1×10^5
	2×10^6

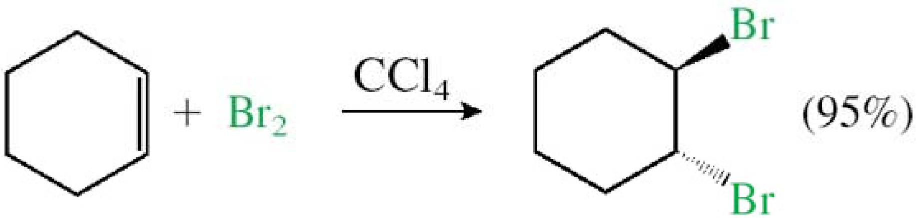
e- donating alkyl enhances the nucleophilicity of double bond

examples



(*E*)-2-Pentene

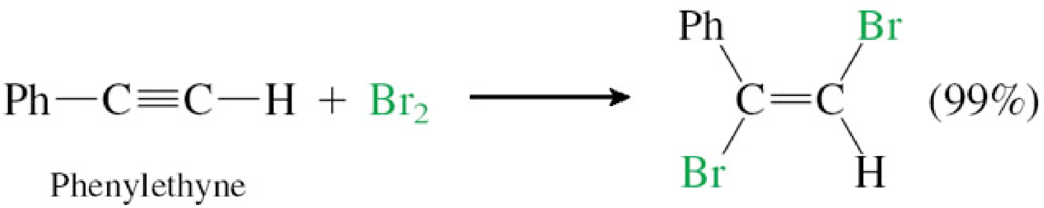
(2*S*,3*R*)-2,3-Dichloropentane



Cyclohexene

trans-1,2-Dibromocyclohexane

Racemic



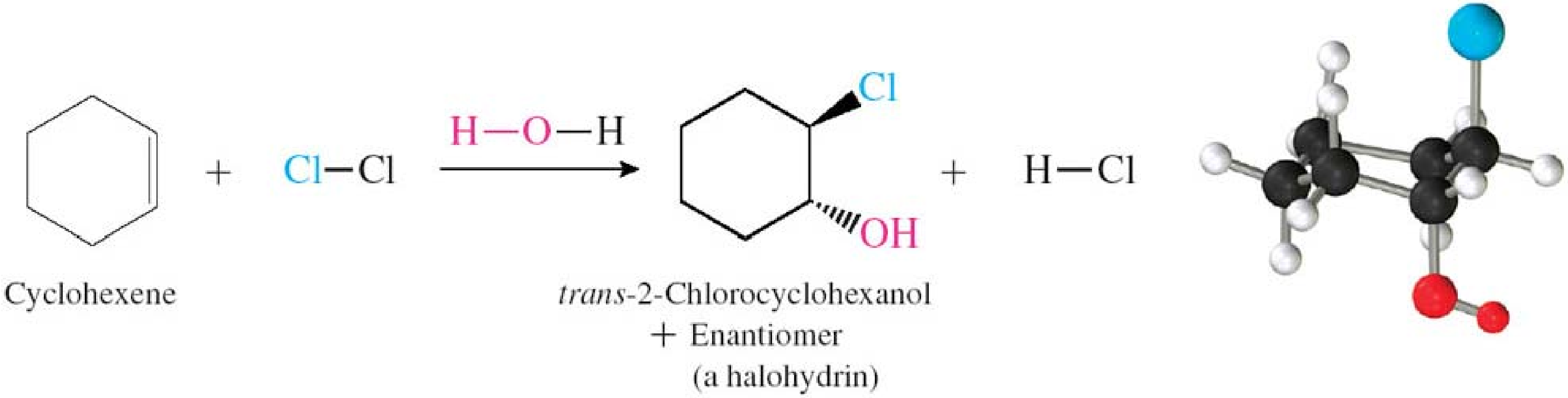
Phenylethyne

(*E*)-1,2-Dibromo-1-phenylethene

11.5 Halohydrin Formation

⇒ **The rxn of chlorine and bromine with alkenes in a nucleophilic solvent, such as water.**

⇒ **Then the addition of a halogen and a hydroxy group to the double bond happens.**

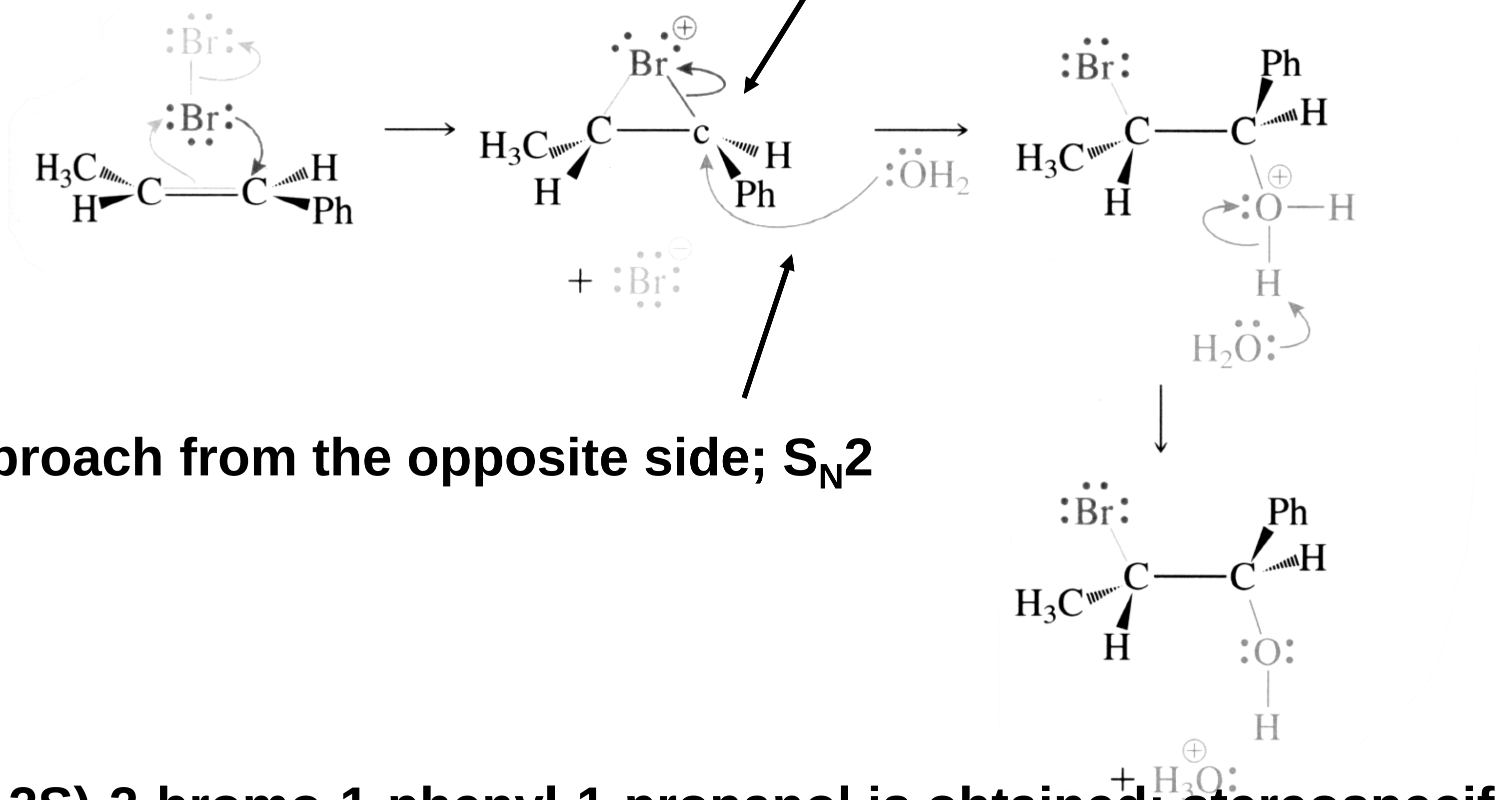


⇒ **Water acts as a Nü rather than the halide anion because water is the solvent (very high conc. of water).**

mechanism

⇒ S_N2; stereochemistry
S_N1; regiochemistry

⇒ Similar to that of halogen addition



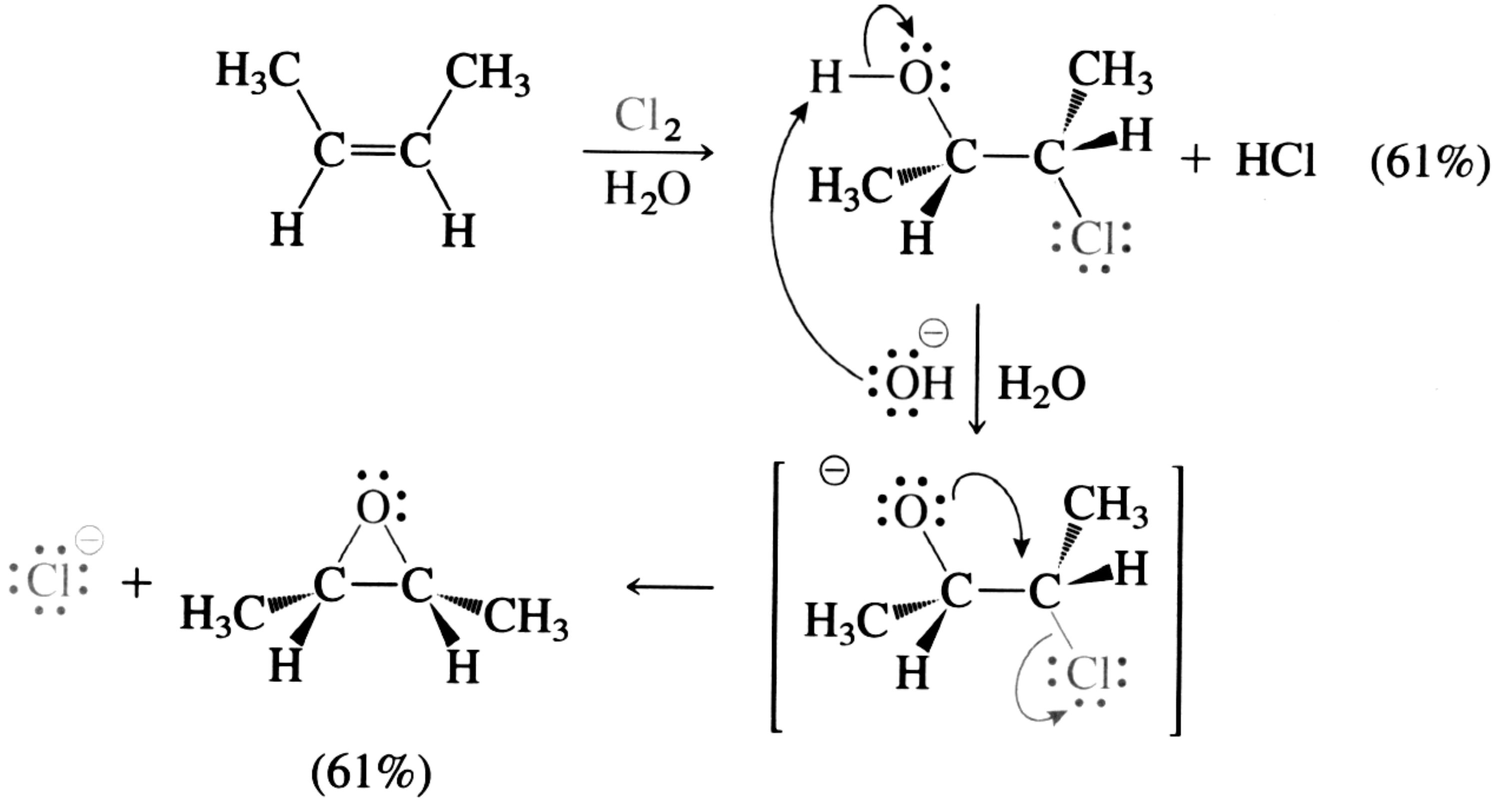
More stable as a carbocation; S_N1

Approach from the opposite side; S_N2

⇒ Only (1R,2S)-2-bromo-1-phenyl-1-propanol is obtained; stereospecific (S_N2)

Application of halohydrin

⇒ The preparation of epoxide



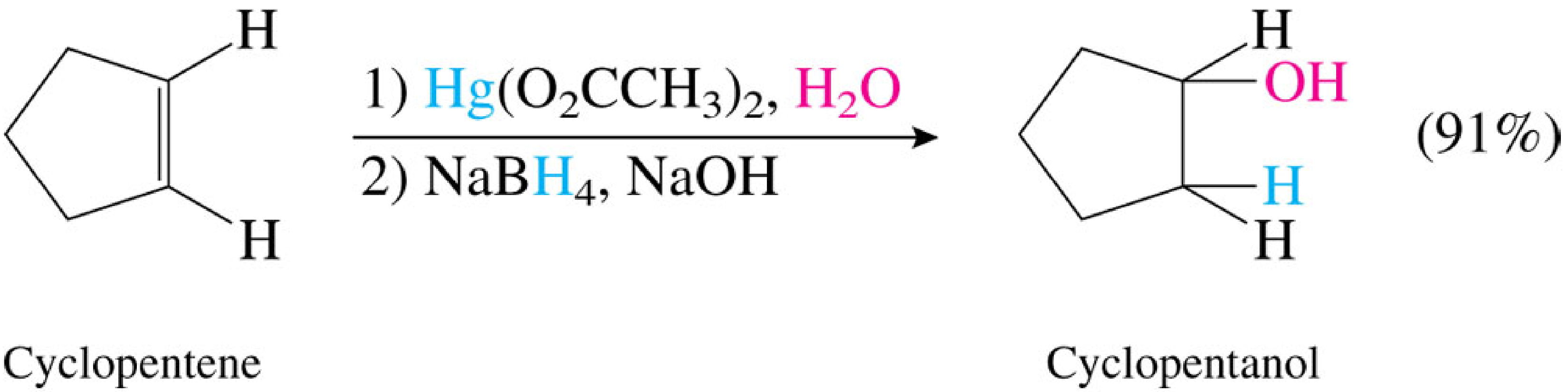
11.6 Oxymercuration-Reduction

⇒ **Another approach to prepare alcohols by adding water to alkenes.**

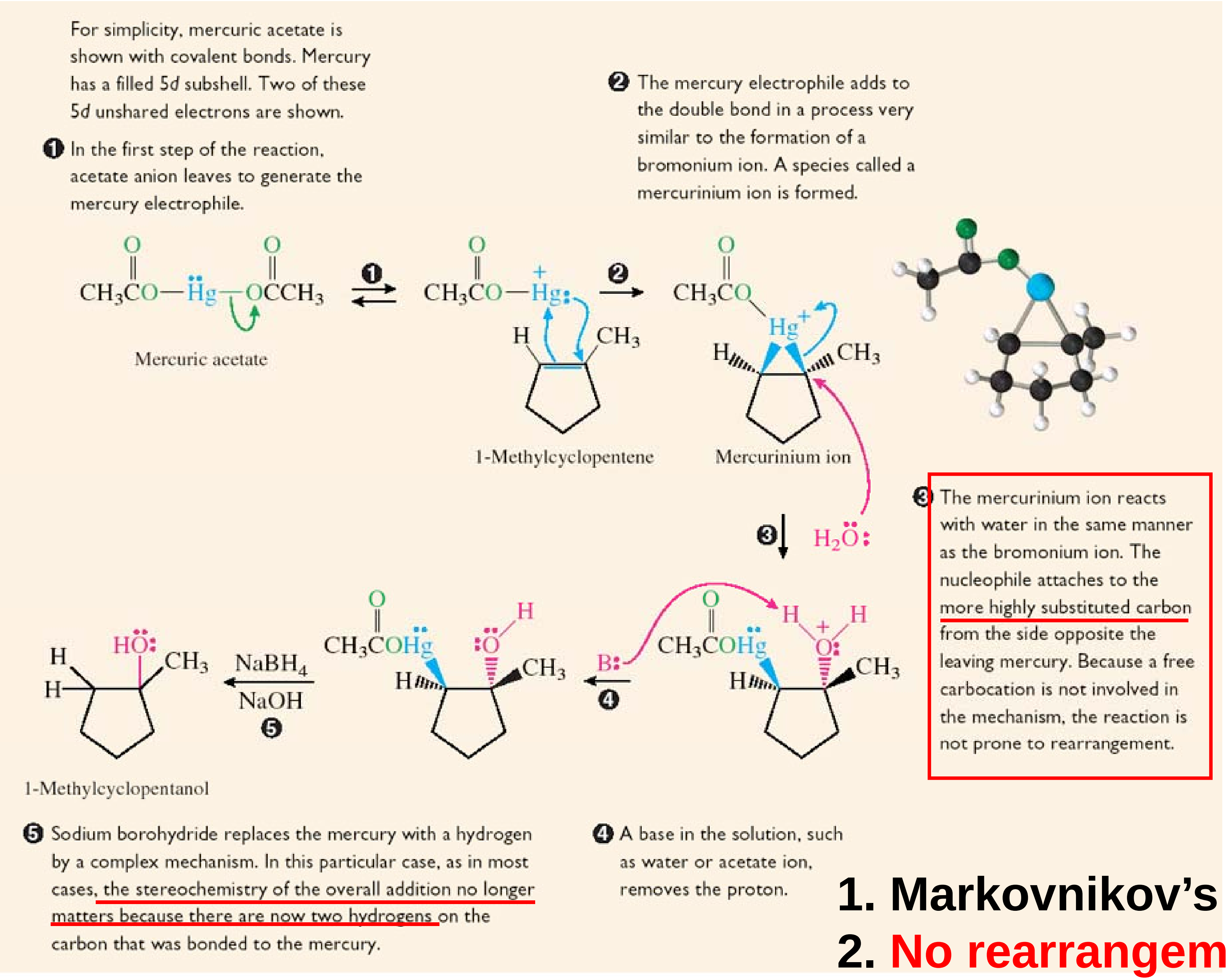
⇒ **Two step rxn.**

1. The alkene is reacted with mercuric acetate in water

2. Treatment with sodium borohydride in NaOH sol'n



mechanism



For simplicity, mercuric acetate is shown with covalent bonds. Mercury has a filled 5*d* subshell. Two of these 5*d* unshared electrons are shown.

❶ In the first step of the reaction, acetate anion leaves to generate the mercury electrophile.

❷ The mercury electrophile adds to the double bond in a process very similar to the formation of a bromonium ion. A species called a mercurinium ion is formed.

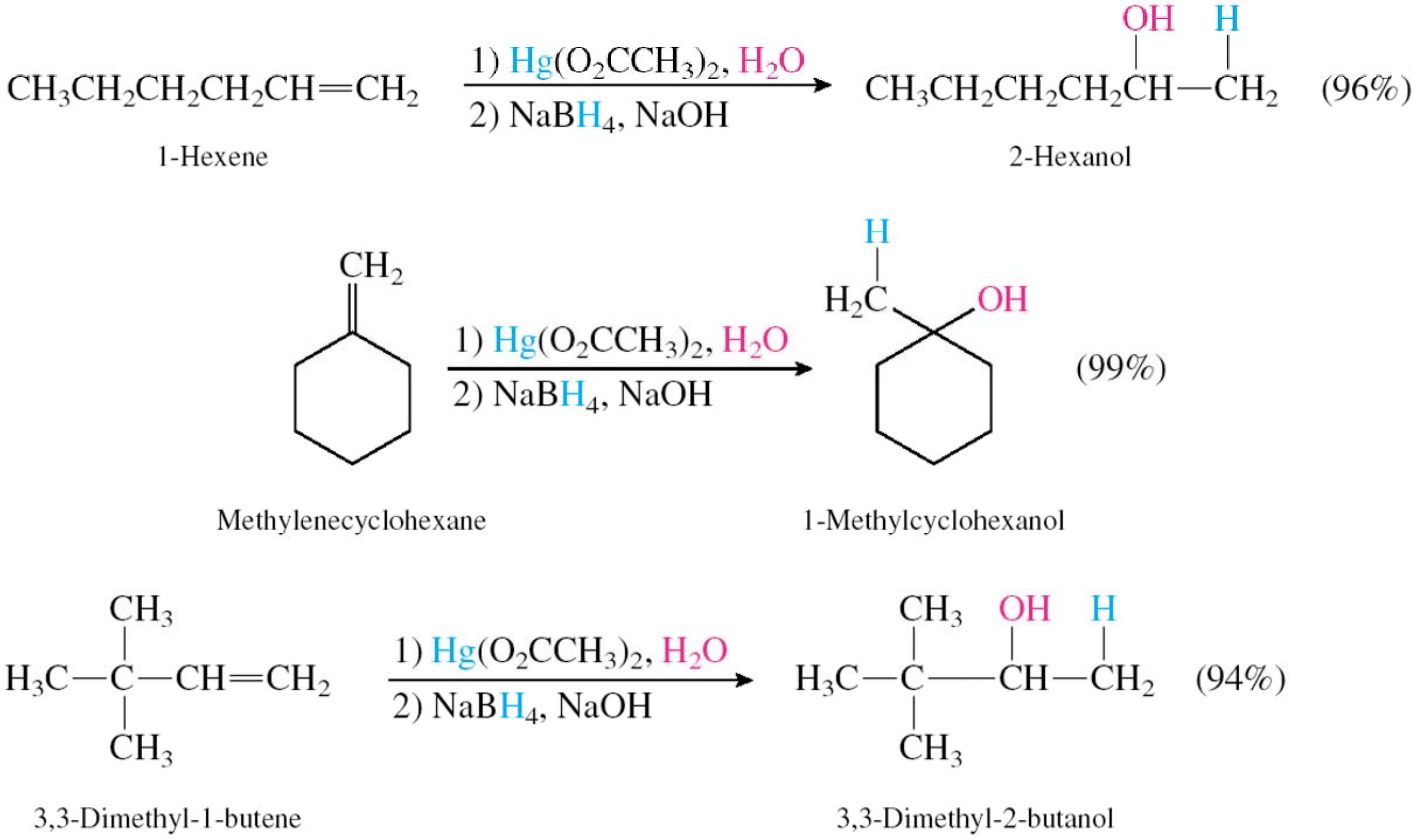
❸ The mercurinium ion reacts with water in the same manner as the bromonium ion. The nucleophile attaches to the more highly substituted carbon from the side opposite the leaving mercury. Because a free carbocation is not involved in the mechanism, the reaction is not prone to rearrangement.

❹ A base in the solution, such as water or acetate ion, removes the proton.

❺ Sodium borohydride replaces the mercury with a hydrogen by a complex mechanism. In this particular case, as in most cases, the stereochemistry of the overall addition no longer matters because there are now two hydrogens on the carbon that was bonded to the mercury.

1. **Markovnikov’s rule**
2. **No rearrangement**

examples



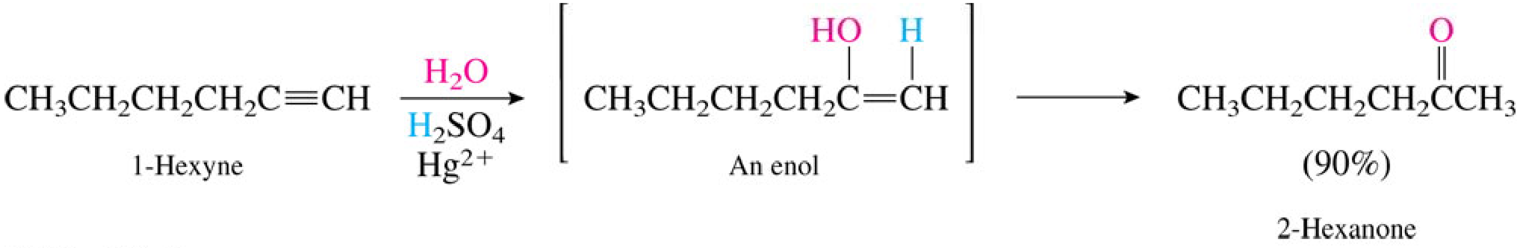
⇒ **High yields**

⇒ **Markovnikov orientation**
and no rearrangement

The addition of water to alkynes

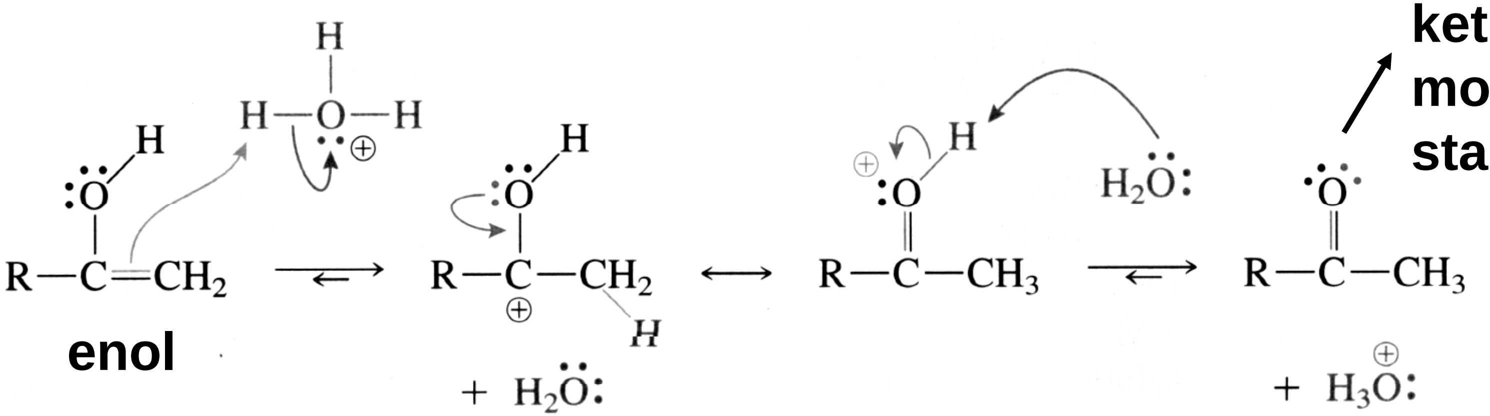
⇒ The rxn of mercury (II) salts with a strong acid (H_2SO_4) in water.

⇒ Mercury replaced by hydrogen spontaneously; one step rxn.



$$CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[H_2SO_4,\ Hg^{2+}]{H_2O} \left[CH_3CH_2CH_2CH_2\overset{HO}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}H \right] \longrightarrow CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$$

keto-enol tautomerization in the presence of acid

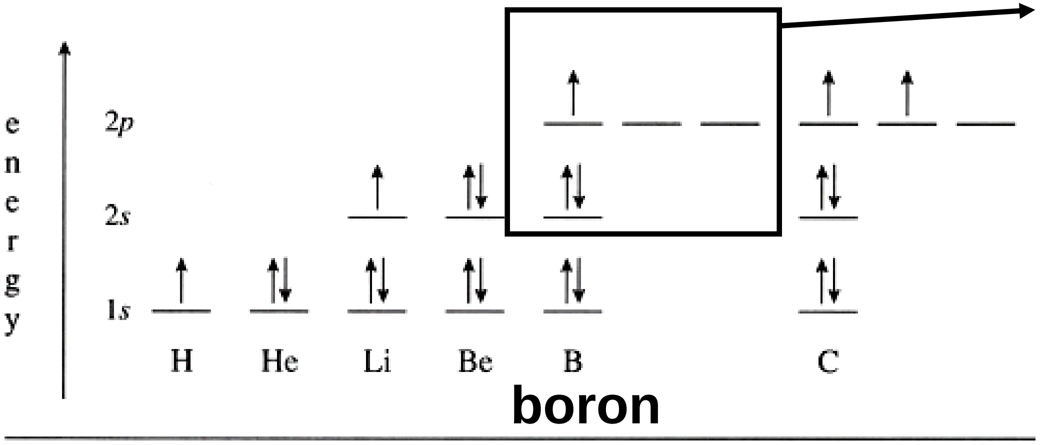


ketone; more stable

enol

⇒ A good method for the preparation of ketones

Borane



Valence shell

Changed to three sp^2 AO's with one electron each and one empty p AO

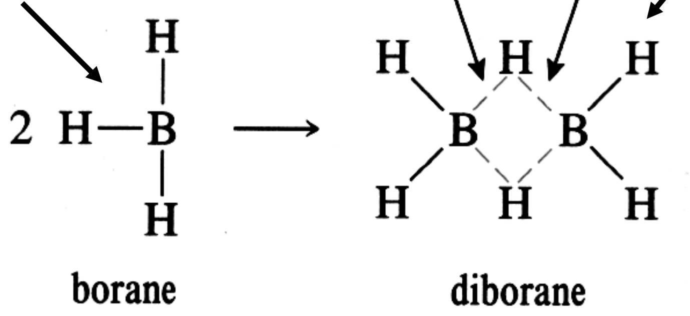
Three sp^2; trigonal planar

Similar to carbocation

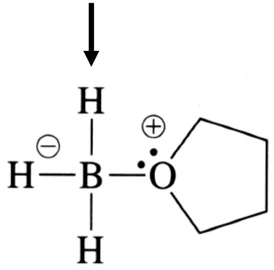
Lewis acid; e⁻ deficient

three-center,
two-electron bond

Octet rule is satisfied; stable



Borane (Lewis acid) + THF (L. base)



complex

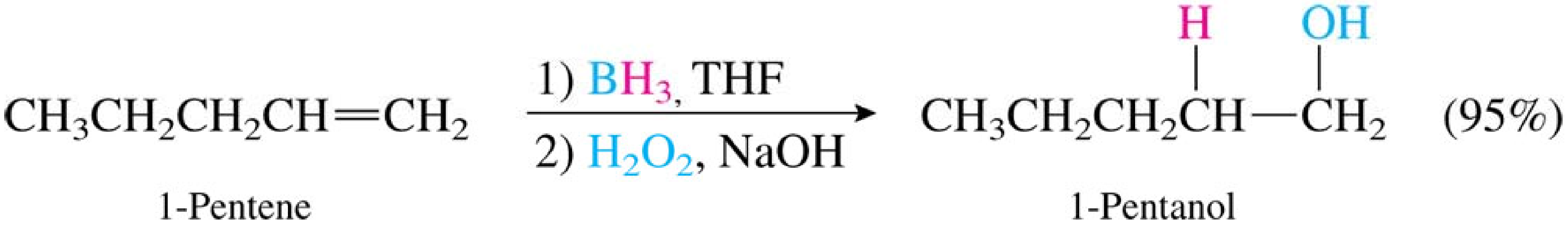
⇒ Borane can be used as a electophile

11.7 Hydroboration-Oxidation

⇒ **Addition of H and OH (elements of H_2O) to alkenes.**

⇒ **Two step rxn.**

1. **The alkene is reacted with a complex of BH_3 and THF**
2. **Treatment with hydrogen peroxide in basic sol’n**



$$CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[\text{2) } H_2O_2\text{, NaOH}]{\text{1) } BH_3\text{, THF}} CH_3CH_2CH_2\overset{H}{\overset{|}{C}}H-\overset{OH}{\overset{|}{C}}H_2 \quad (95\%)$$

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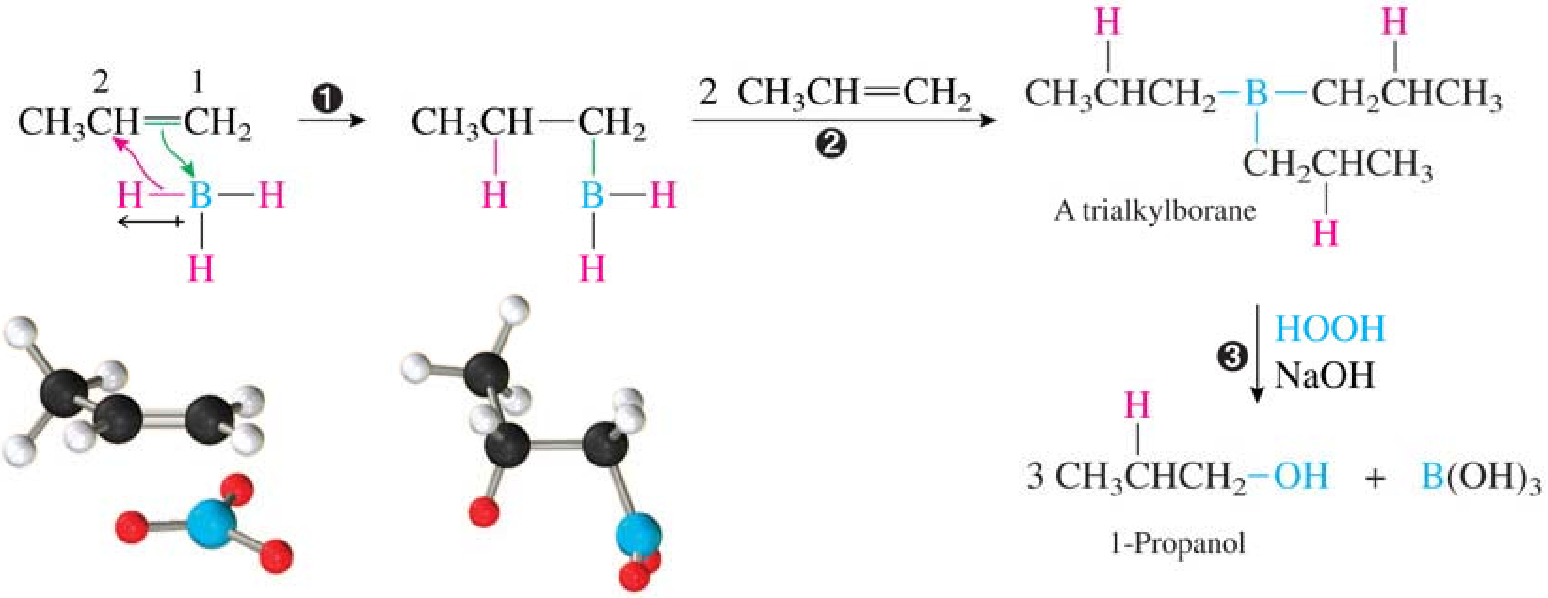
mechanism



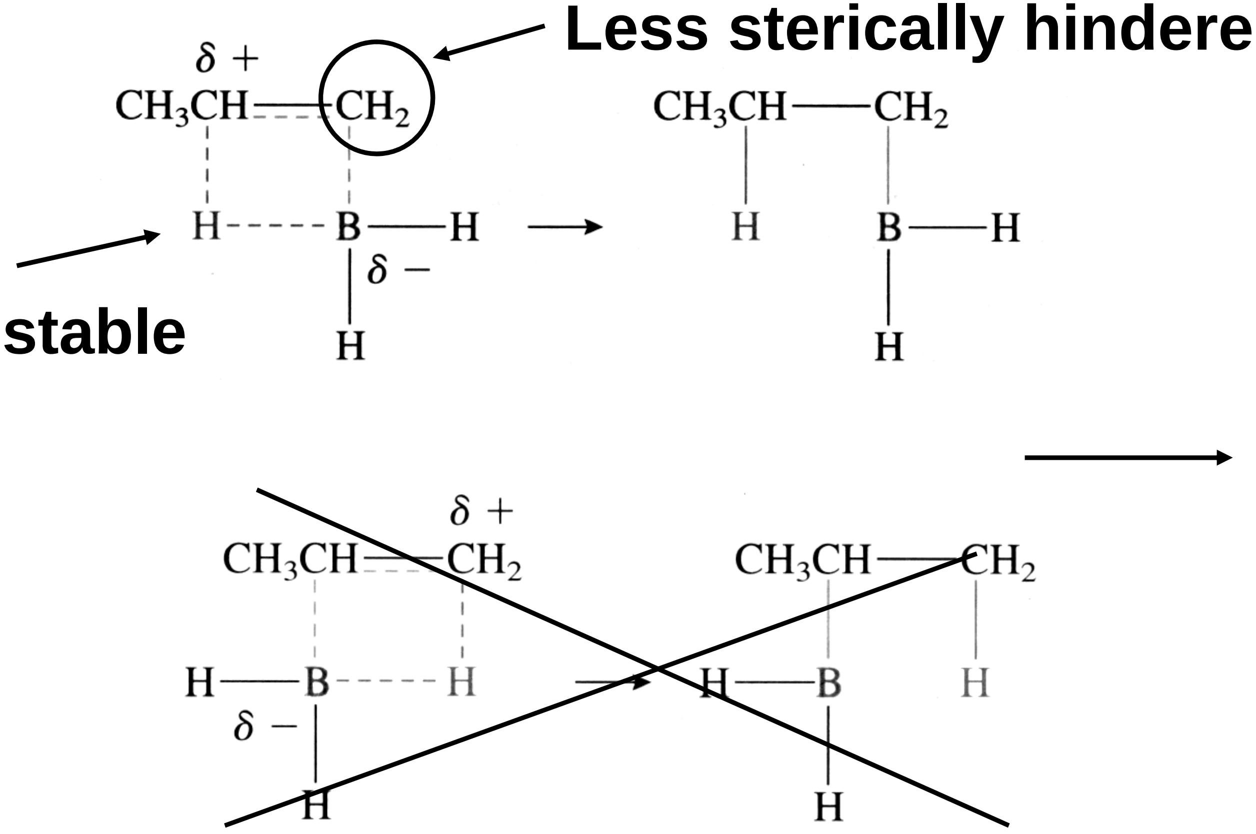
❶ Boron, with its empty *p* orbital, that acts as the electrophile. As positive charge begins to build up on C-2, the hydrogen, which has a partial negative charge because it is more electronegative than the boron, acts as a nucleophile. The C—H and C—B bonds are formed and the B—H and C—C pi bonds are broken in a single step. In accord with the mechanistic version of Markovnikov's rule, the electrophile, the boron, adds to the carbon bonded to more hydrogens.

❷ Both of the other two B—H bonds also add to alkene molecules. The overall result is that one borane molecule reacts with three alkene molecules to produce a boron attached to three alkyl groups, a trialkylborane.

❸ In the next step of the reaction, hydrogen peroxide breaks each C—B bond, replacing them with C—OH and B—OH bonds. (An understanding of the mechanism of this step is not important.)

⇒ Regioselective (syn add.) and Anti-Markovnikov addition !

Why anti-Markovnikov?



Less sterically hindered

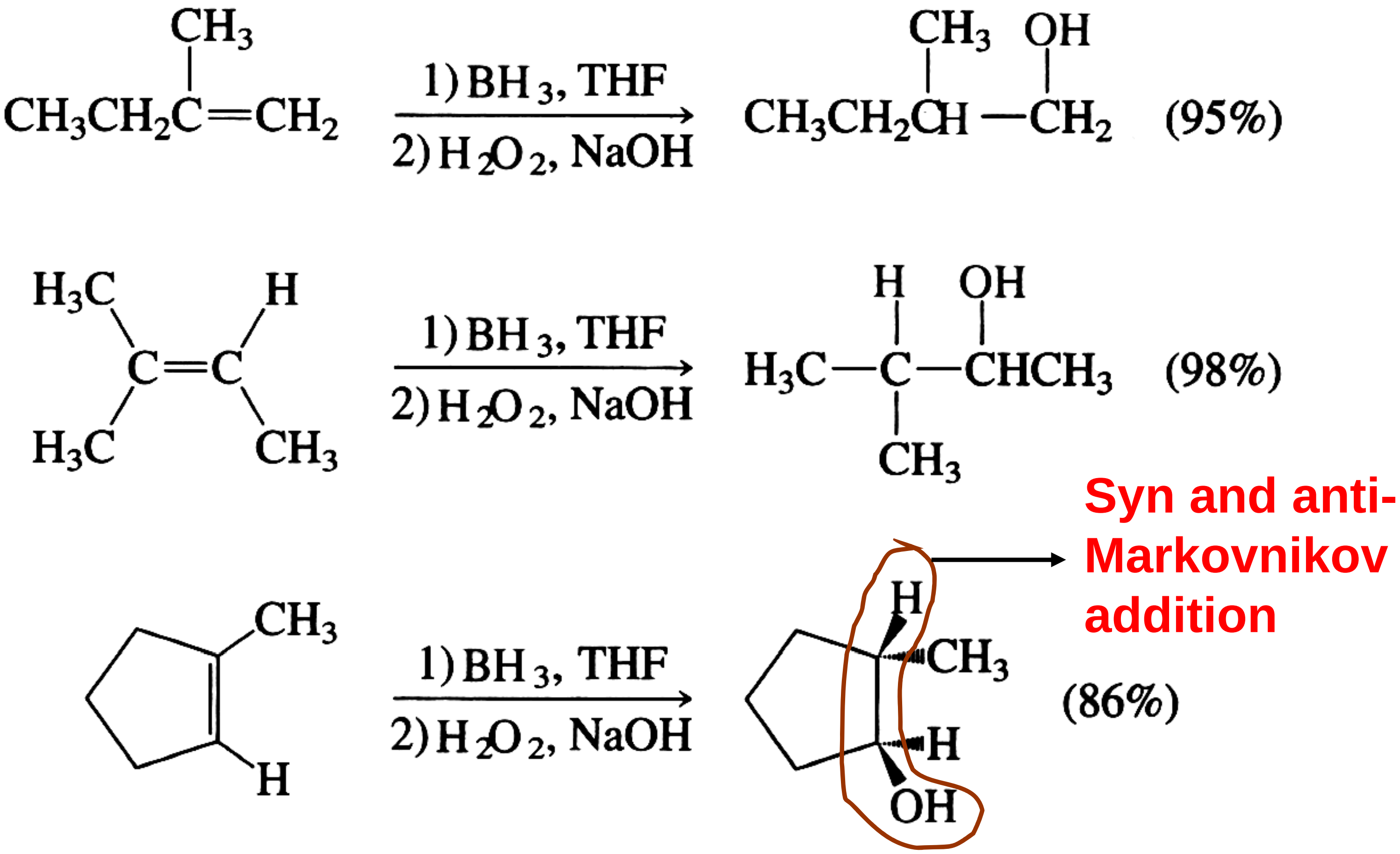
more stable

possible transition state

⇒ **The hydroxy group replace the boron with complete retention of configuration**

⇒ **Anti-Markovnikov orientation and syn stereochemistry**

examples

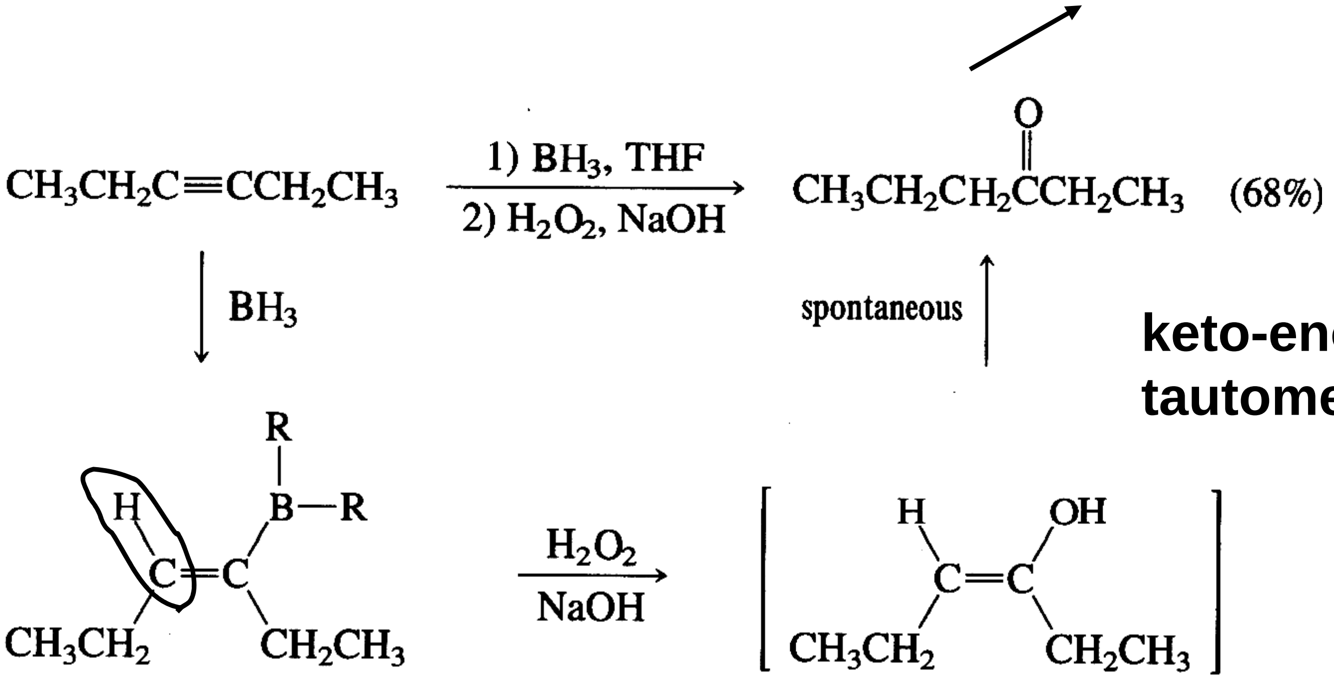


Syn and anti-Markovnikov addition

Hydroboration of alkynes

1. internal alkynes; one borane can react with one 1-alkyne

more stable



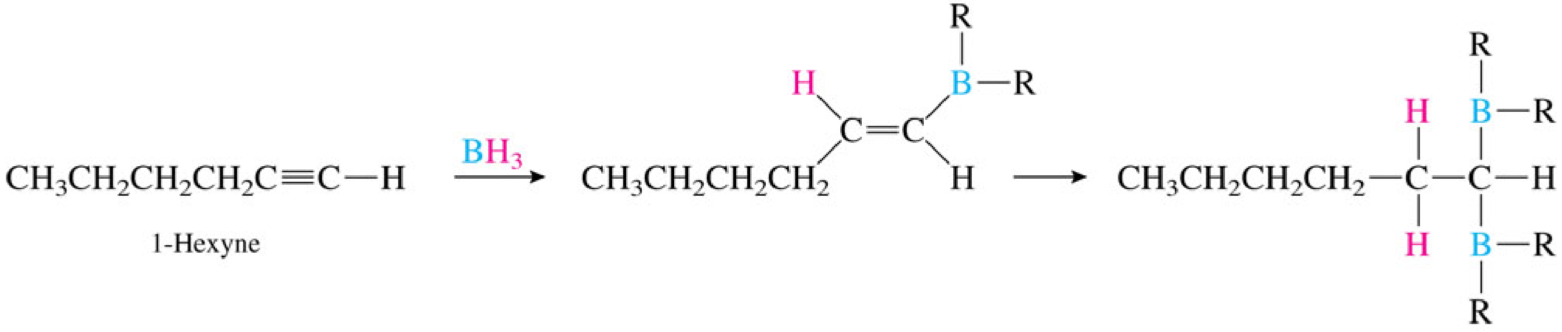
keto-enol tautomerization

a vinylborane

⇒ **Due to the steric hindrance no further addition of borane to a vinylborane**

2. 1-alkynes

⇒ **Two boranes can react with one 1-alkyne because the are less steric hindrance**



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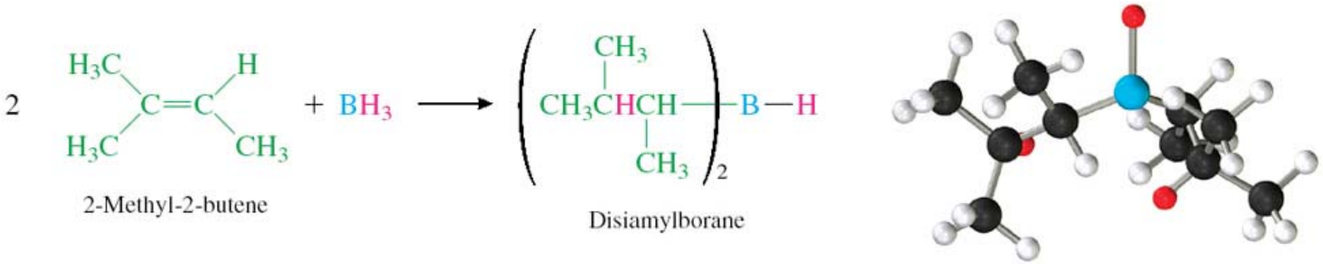
Then how can we make aldehyde form 1-alkyne?

⇒ **Use diisoamylborane**



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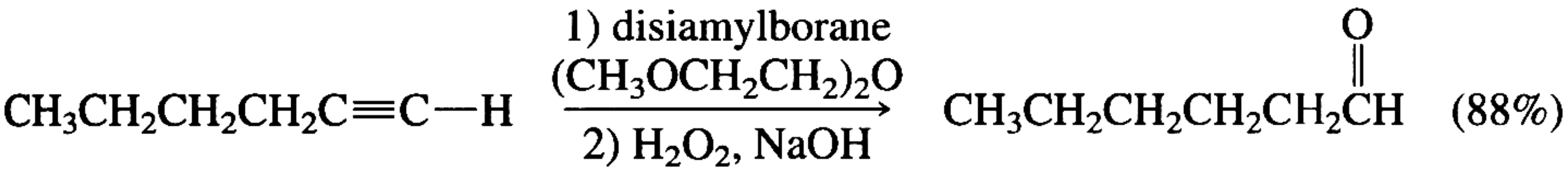
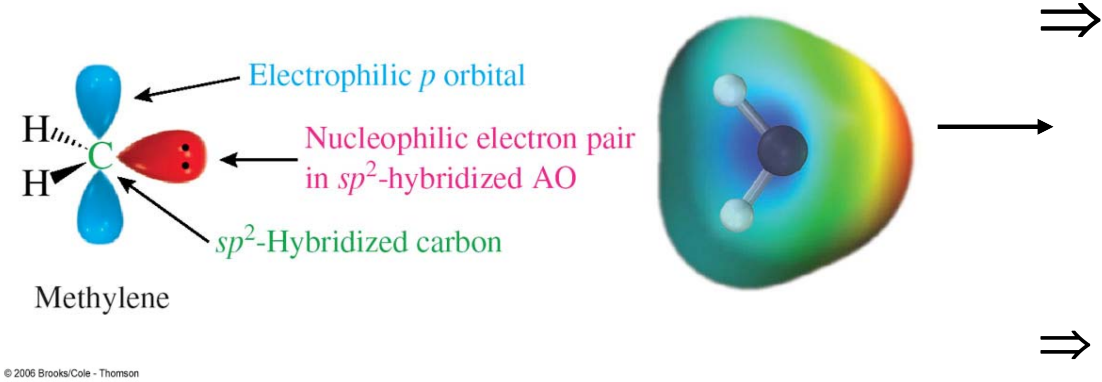


$$CH_3CH_2CH_2CH_2C{\equiv}C{-}H \xrightarrow[\text{2) } H_2O_2\text{, NaOH}]{\text{1) disiamylborane, } (CH_3OCH_2CH_2)_2O} CH_3CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}H \quad (88\%)$$

11.8 Addition of Carbenes

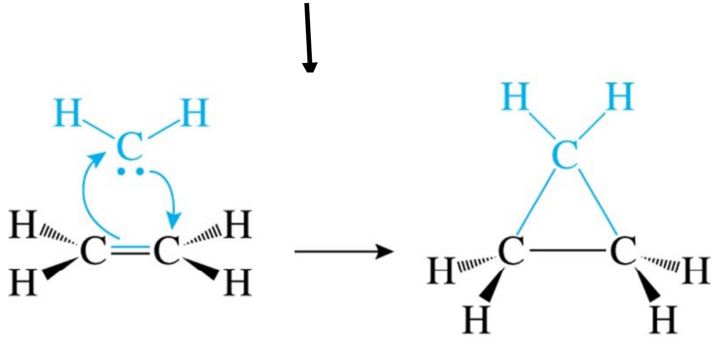
Carbene; a carbon with only two bonds and as unshared pair of electrons, therefore very reactive.



Methylene

⇒Similar to the rxns of Br_2 and mercury species (both nucleophilic and electrophilic); forming three membered ring

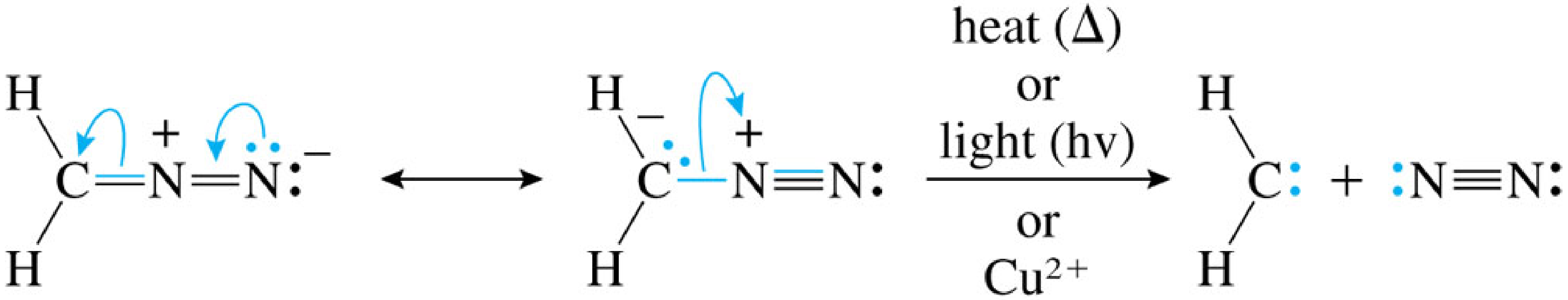
⇒ difference; rxn stops after forming three membered ring



Cyclopropane

Preparation of a carbene or carbenoid

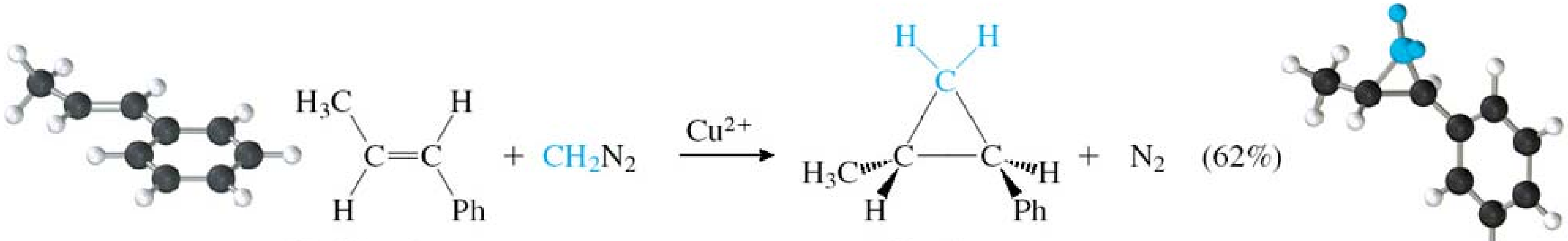
1. Elimination of N_2 from diazocompound



Diazomethane

⇒ **Heating or irradiation with metal cations such as Cu^{2+}**

example

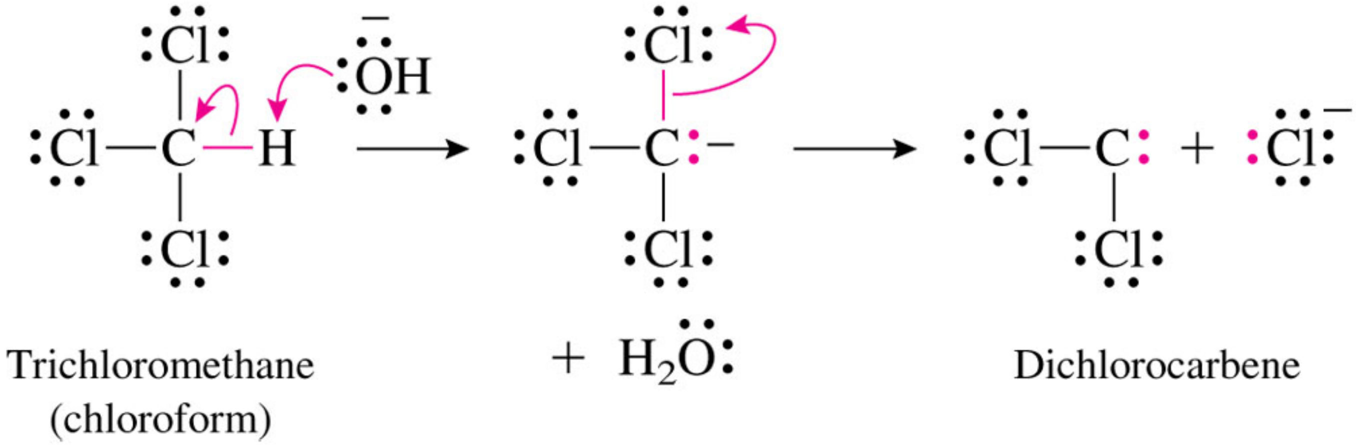


(*E*)-1-Phenylpropene

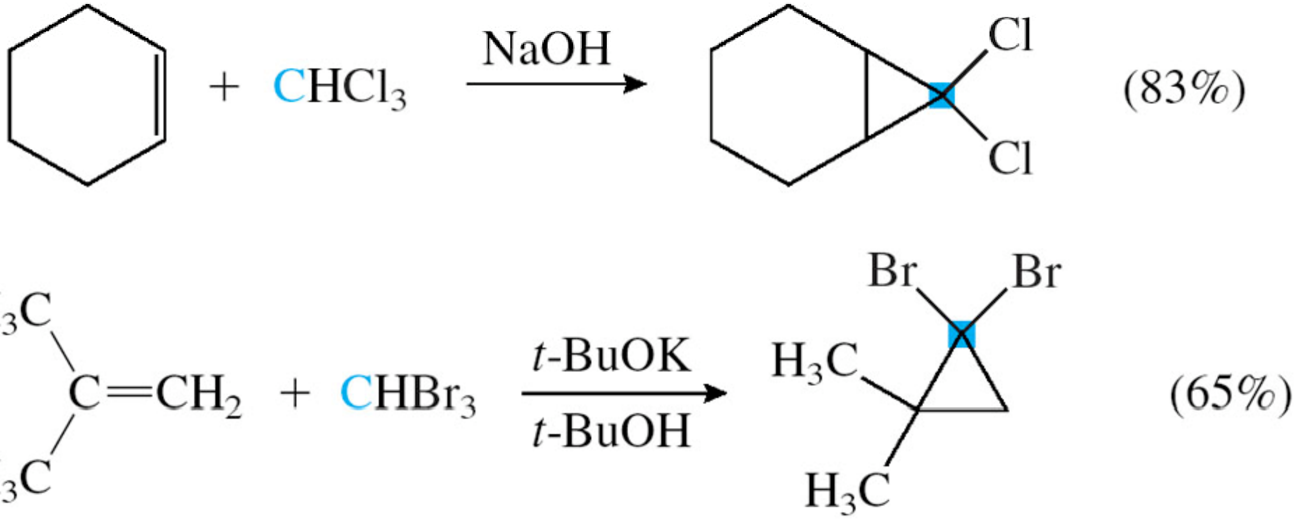
+ Enantiomer

trans-1-Methyl-2-phenylcyclopropane

2. Elimination of a proton and a leaving group (chloride or bromide) from $CHCl_3$ or $CHBr_3$; 1,1-elimination or α-elimination



examples



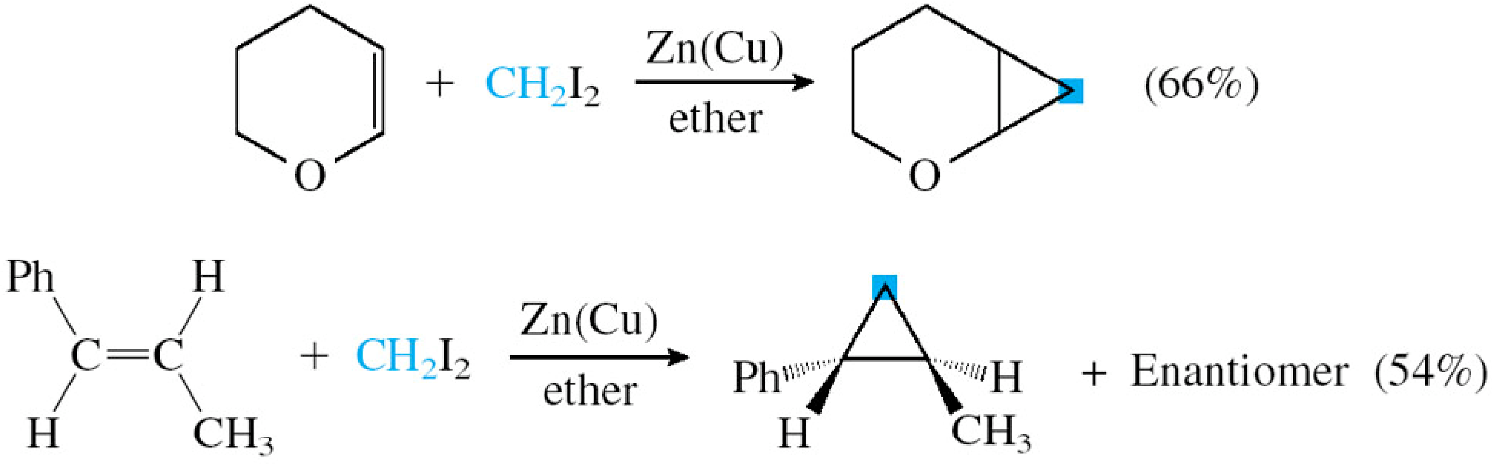
3. Formation of carbenoid by rxn of diiodomethane with zinc metal from Zn/Cu alloy

⇒ Then Simmons-Smith reaction is employed to produce a cyclopropane ring.

$$\underset{\text{Diiodomethane}}{CH_2I_2} + :Zn(Cu) \longrightarrow \underset{\text{A carbenoid}}{I{-}CH_2{-}Zn{-}I}$$

Reacts like $\ddot{C}H_2$

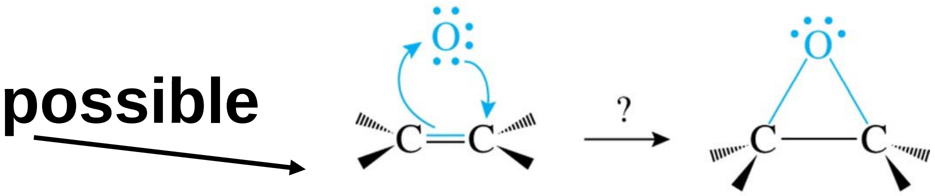
examples



11.9 Epoxidation

⇒ An oxygen atom is analogous to carbene; 6 valennce electrons

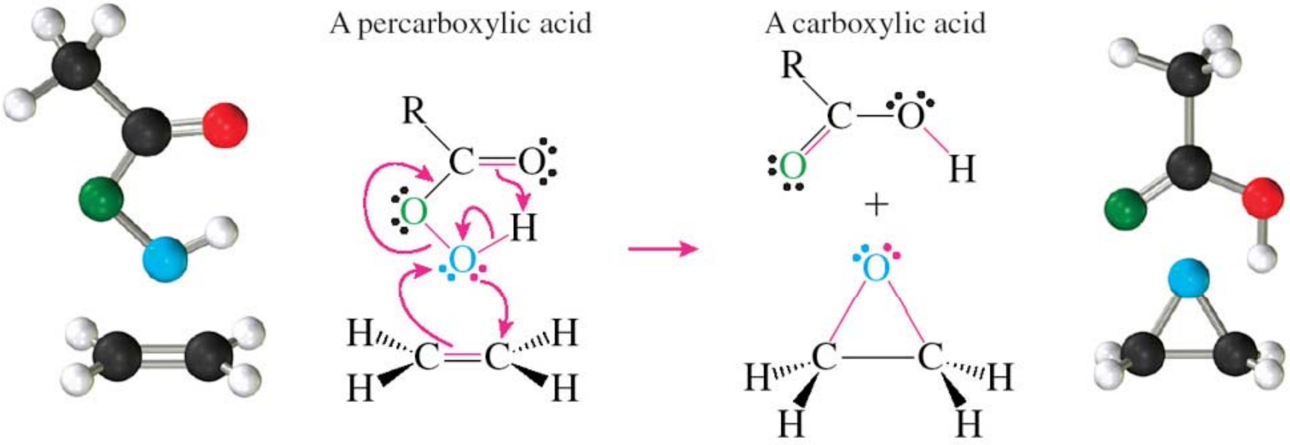
⇒ Then similar rxn might be possible



An epoxide

⇒ The problem is oxygen atoms are not available

⇒ Therefore we are using peroxycarboxylic acids



Ethene

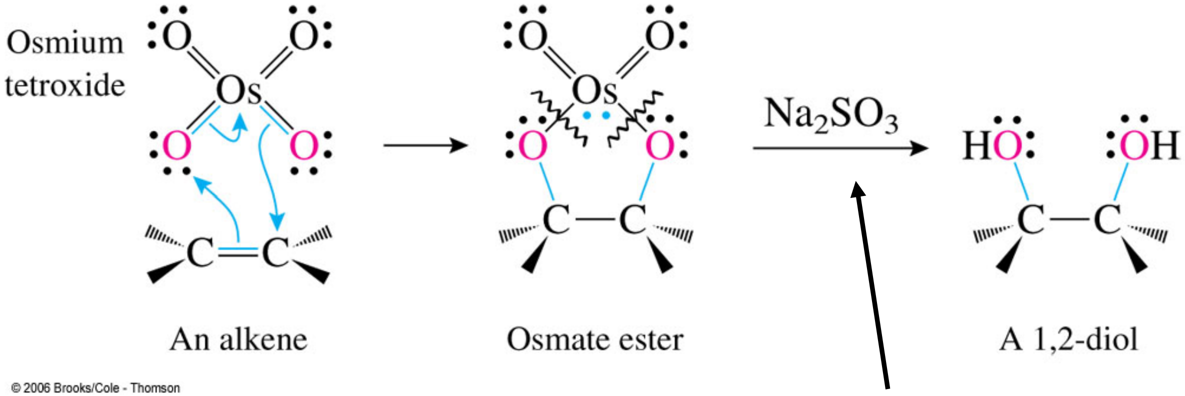
Oxirane
(ethylene oxide)

⇒ Syn stereochemistry

⇒ See examples in p439.

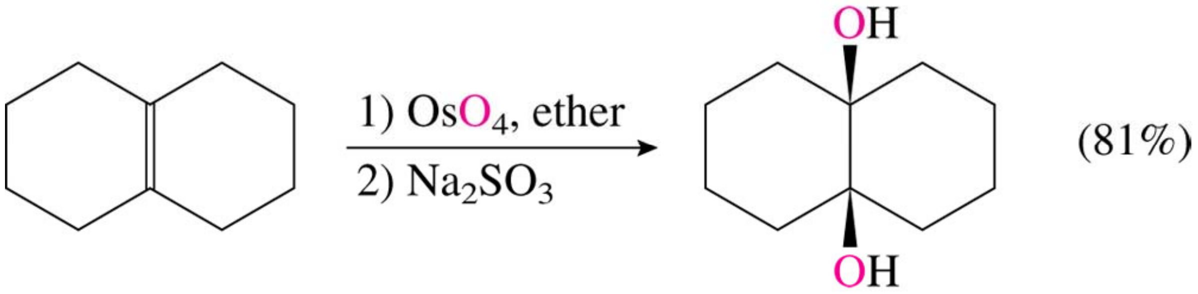
11.10 Hydroxylation

- ⇒ Osmium tetroxide (OsO_4) and potassium permanganate ($KMnO_4$) can add hydroxy groups to both carbons of a carbon-carbon double bond
- ⇒ *syn* addition to form cyclic and then give 1,2-diol



Sodium sulfite is used for the cleavage the Os-O bonds

example

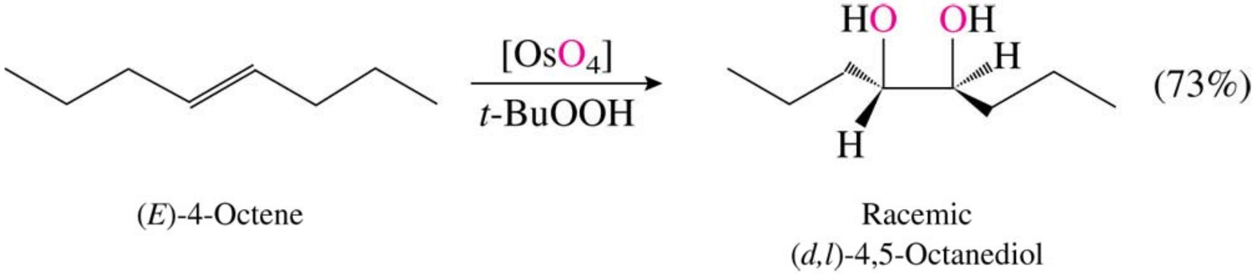


Advantages and disadvantages using OsO_4 and $KMnO_4$

- ⇒ OsO_4; high yields while toxic and very expensive
- ⇒ $KMnO_4$; cheaper while yield is low

using OsO_4 with some additional oxidizing agent, such as *tert*-butyl peroxide

- ⇒ high yields
- ⇒ Peroxide cleave the ester to the diols and oxidize the osonium back to the tetroxide; only small amout of osonium tetroxide is needed.

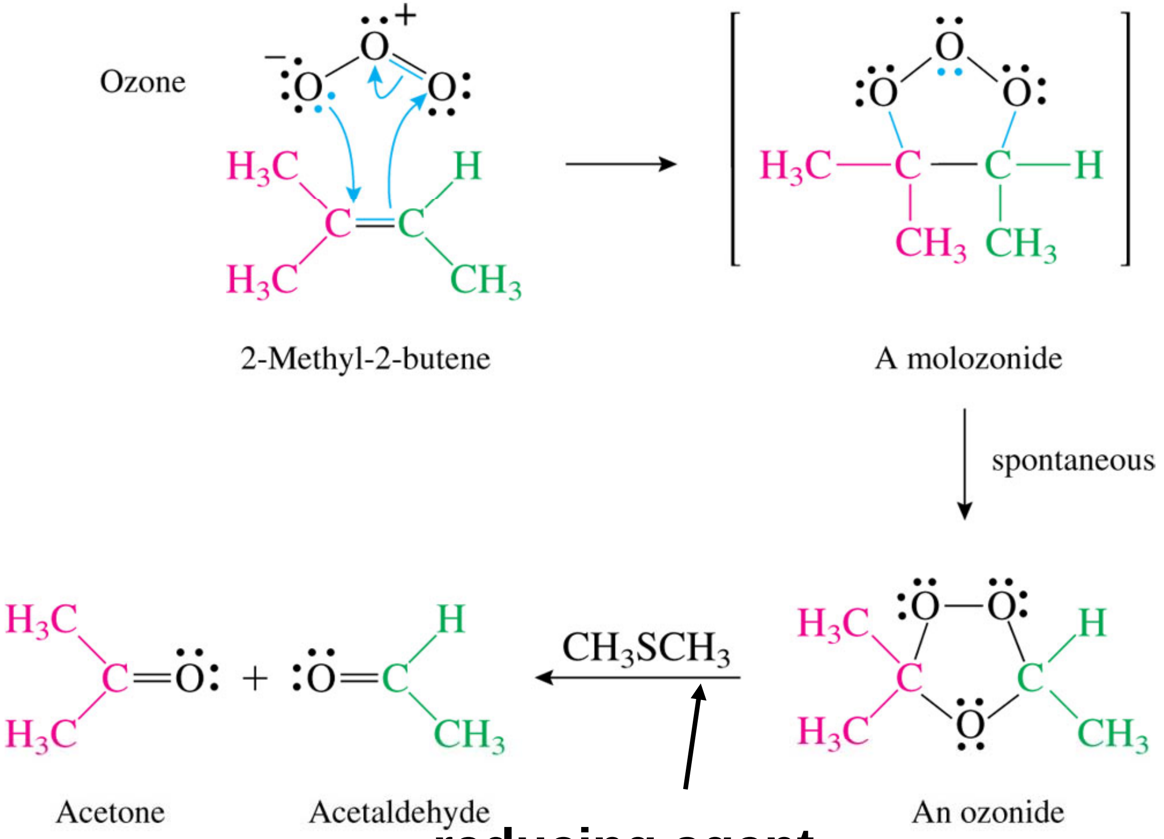


11.11 Ozonolysis

⇒ Rxn of ozone(O_3) with alkenes to produce aldehydes or ketones

⇒ O_3; nucleophilic and electrophilic

⇒ Structure determination of alkene (see p443)



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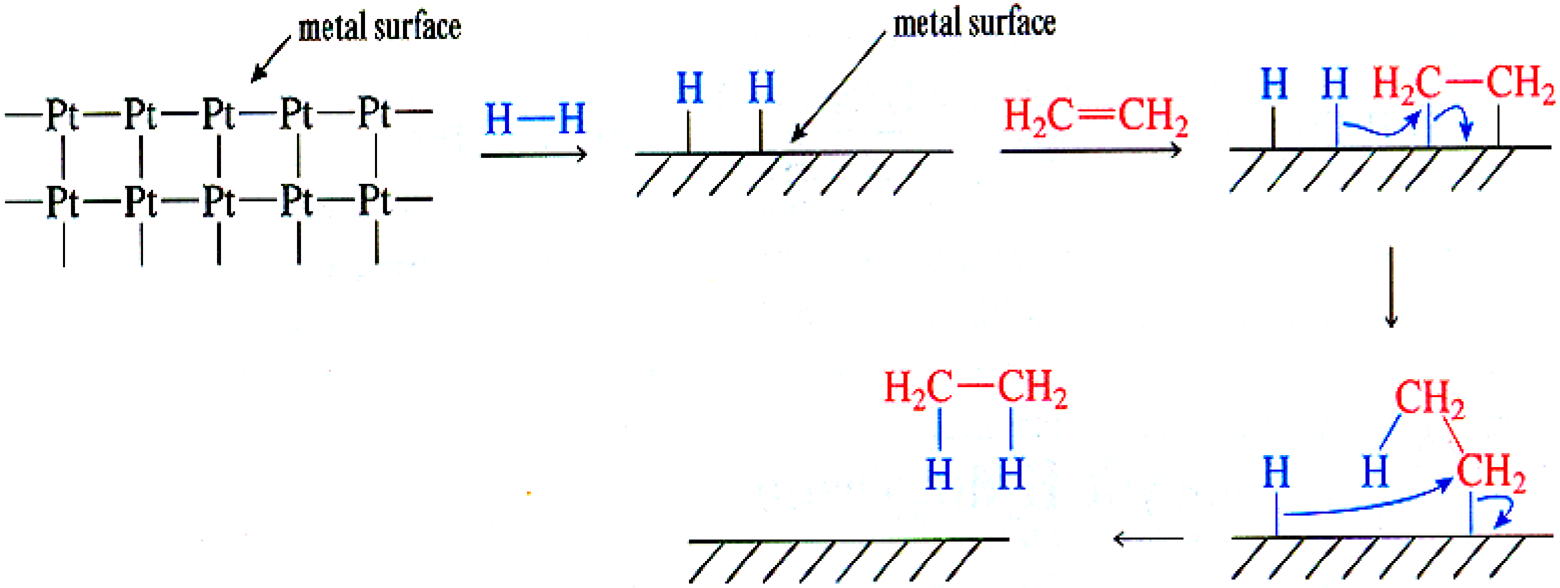
reducing agent

11. 12 Catalytic Hydrogenation

⇒ **Rxn of an alkene with hydrogen in the presence of metal catalysts such as nickel (Ni), palladium (Pd), and platinum (Pt).**

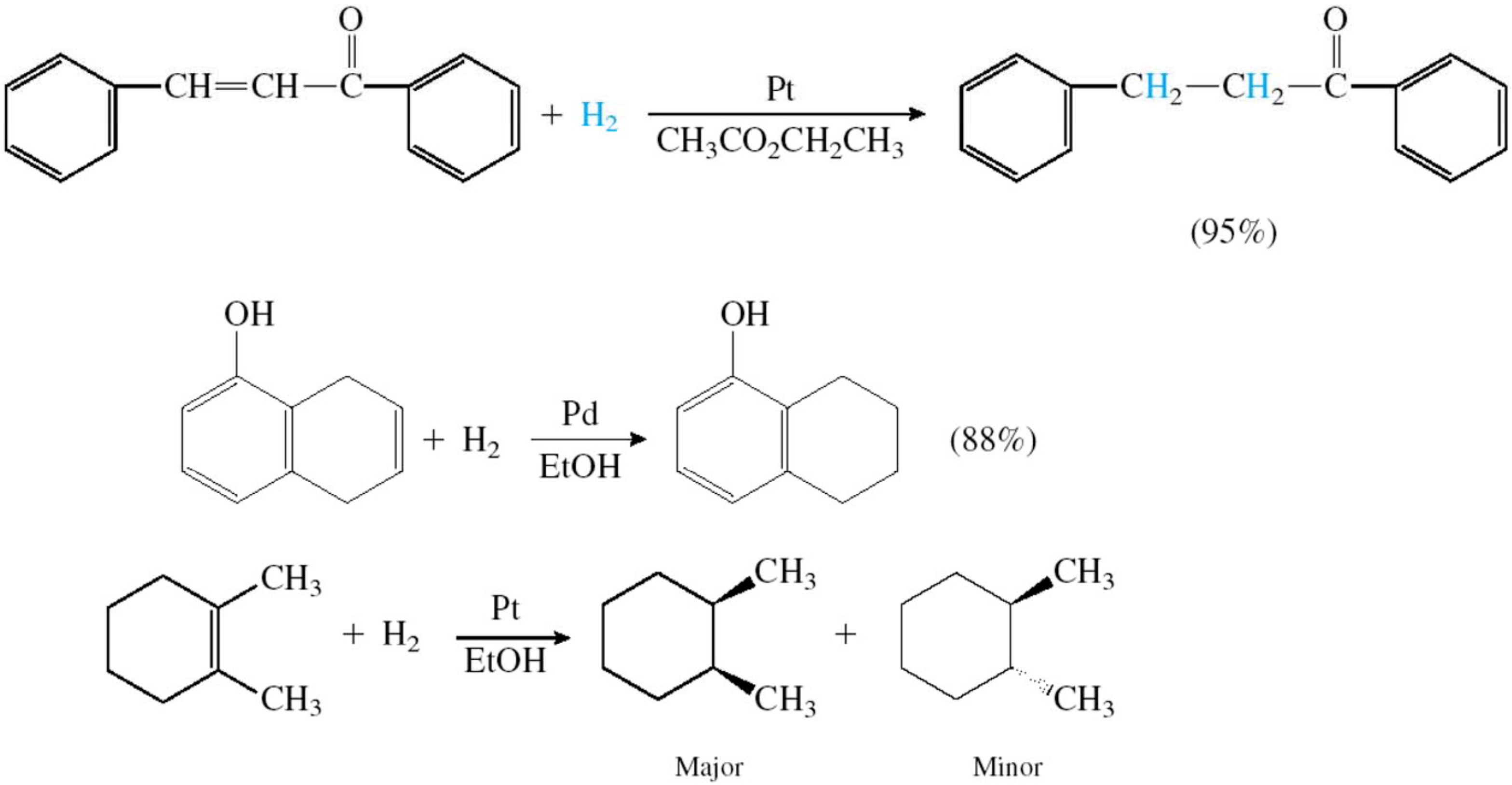
⇒ **not electrophilic but catalytic.**



⇒ **Selective hydrogenation of C-C double and triple bonds are possible in mild condition (RT & a few atm).** **The double bonds in the aromatic rings and C-O double bonds are not hydrogenated.**

⇒ **Syn addition is the major rxn.**

examples

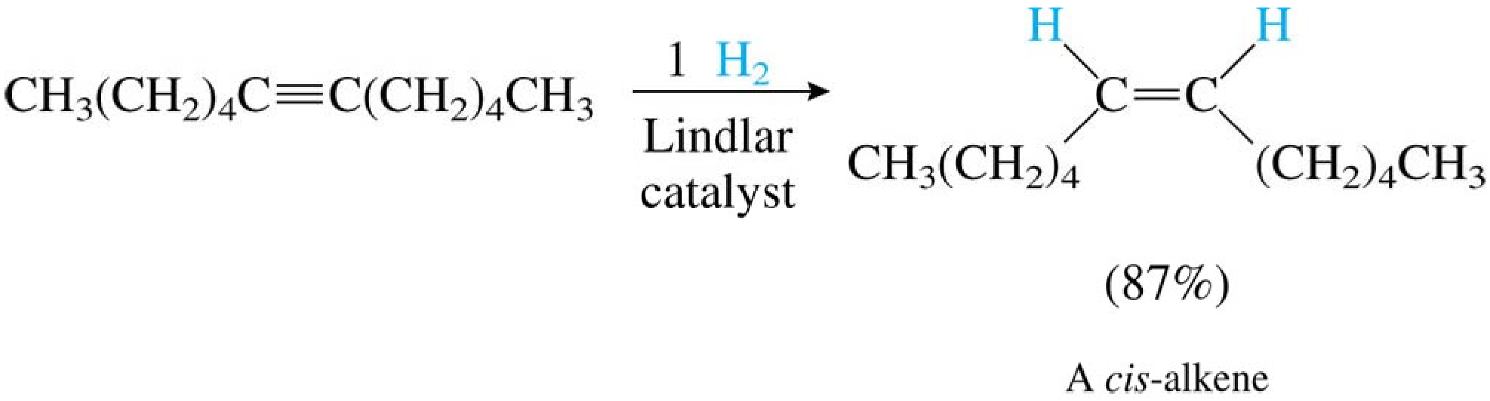


The rxn of alkyne H_2 with metal catalysts yields alkane.

Then how can we obtaine alkene for alkyne?

⇒ Use Lindlar catalyst!

⇒ Lindlar catalyst is a deactivated form of palladium



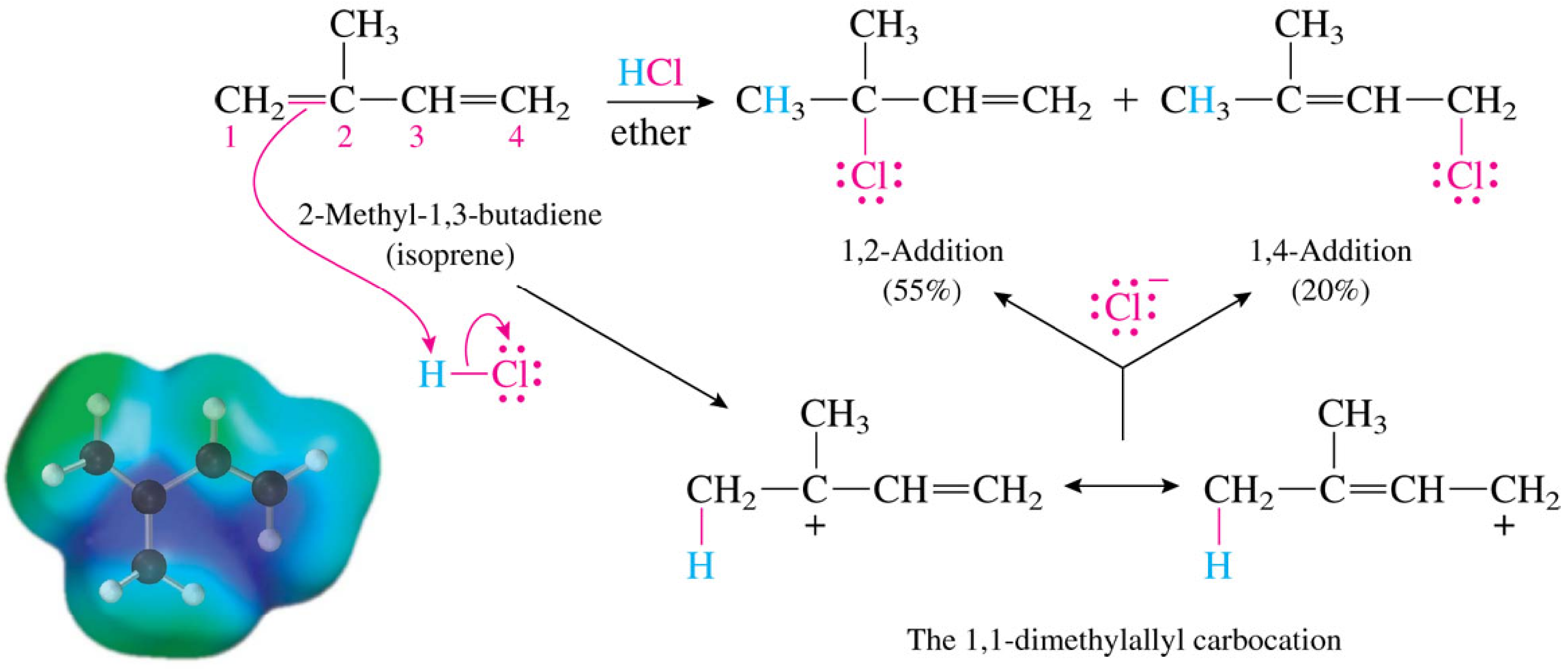
⇒ Syn addition of hydrogen

⇒ Then cis-alkenes are obtained.

11.13 Addition to conjugated dienes

⇒ **Rxn of a conjugated diene with hydrogen halide.**

⇒ **1,2-addition and 1,4-addition are possible.**



$$CH_2{=}\overset{CH_3}{C}{-}CH{=}CH_2 \xrightarrow[\text{ether}]{HCl} CH_3{-}\overset{CH_3}{\underset{:Cl:}{C}}{-}CH{=}CH_2 + CH_3{-}\overset{CH_3}{C}{=}CH{-}\underset{:Cl:}{CH_2}$$

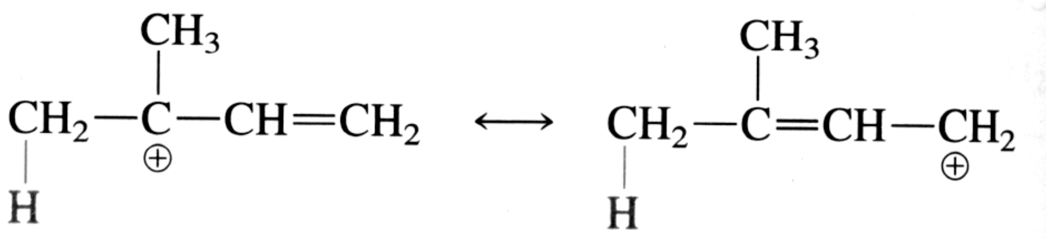
$$\underset{H}{CH_2}{-}\overset{CH_3}{\underset{+}{C}}{-}CH{=}CH_2 \longleftrightarrow \underset{H}{CH_2}{-}\overset{CH_3}{C}{=}CH{-}\underset{+}{CH_2}$$

Electrostatic potential map
of the 1,1-dimethylallyl carbocation

son

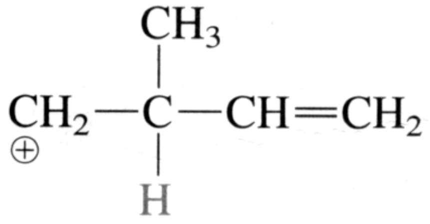
⇒ **1,2-addition is major rxn due to carbocation stability**

⇒ **Proton is added to carbon 1, not 2, 3, or 4. Why?**



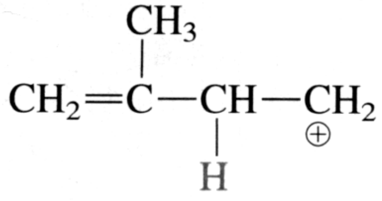
$$\mathrm{\underset{\displaystyle H}{\underset{|}{CH_2}}-\overset{\displaystyle CH_3}{\overset{|}{\underset{\oplus}{C}}}-CH{=}CH_2 \longleftrightarrow \underset{\displaystyle H}{\underset{|}{CH_2}}-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH-\underset{\oplus}{CH_2}}$$

addition to carbon 1



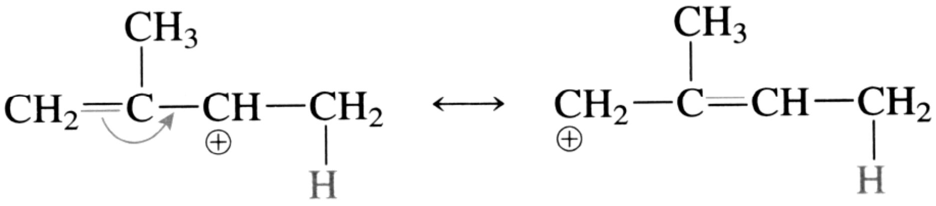
$$\mathrm{\underset{\oplus}{CH_2}-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}}-CH{=}CH_2}$$

addition to carbon 2



$$\mathrm{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle H}{|}}{CH}-\underset{\oplus}{CH_2}}$$

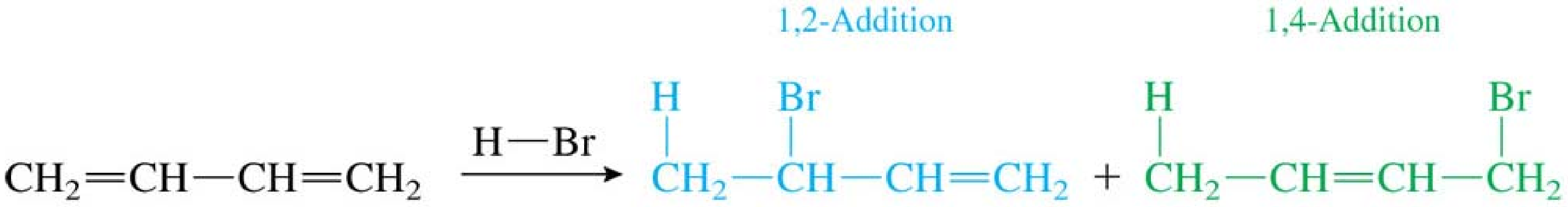
addition to carbon 3



$$\mathrm{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\oplus}{CH}-\underset{\underset{\displaystyle H}{|}}{CH_2} \longleftrightarrow \underset{\oplus}{CH_2}-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH-\underset{\underset{\displaystyle H}{|}}{CH_2}}$$

addition to carbon 4

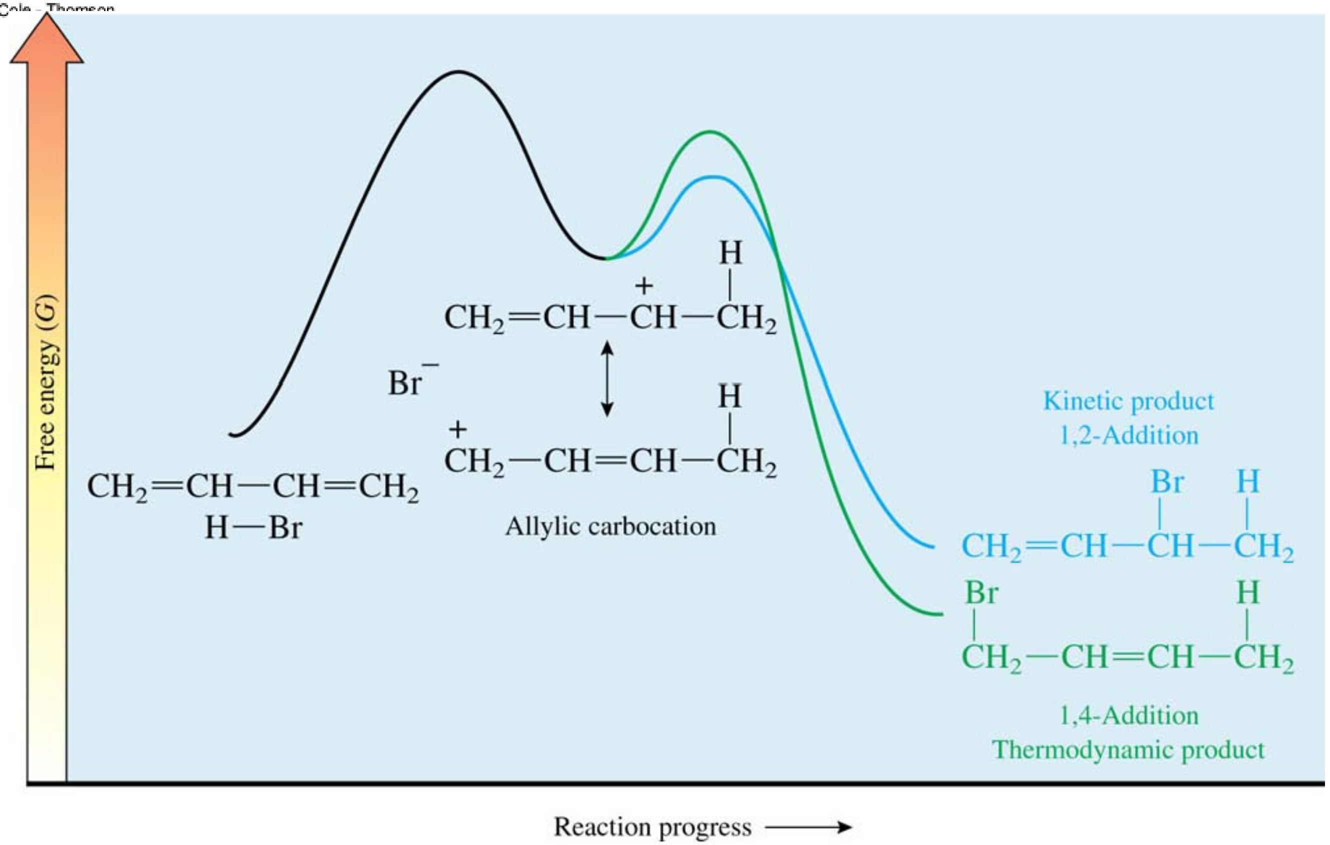
⇒ **The proton should add so as to produce the most stable carbocation**



$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{H{-}Br} \overset{H}{CH_2}{-}\overset{Br}{CH}{-}CH{=}CH_2 + \overset{H}{CH_2}{-}CH{=}CH{-}\overset{Br}{CH_2}$$

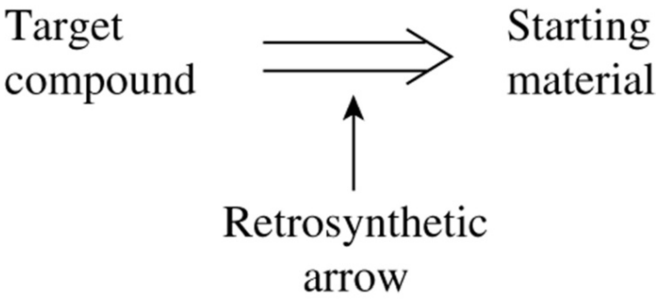
1,3-Butadiene

	3-Bromo-1-butene	1-Bromo-2-butene
At –80°C	80%	20%
At 45°C	15%	85%

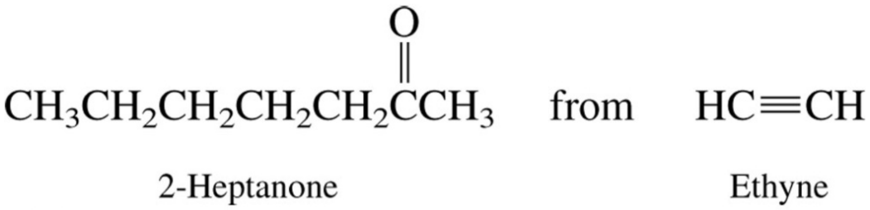


11.4 Synthesis

Retrosynthetic arrow

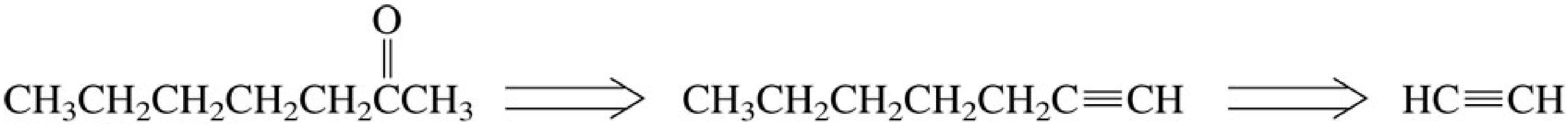


Example

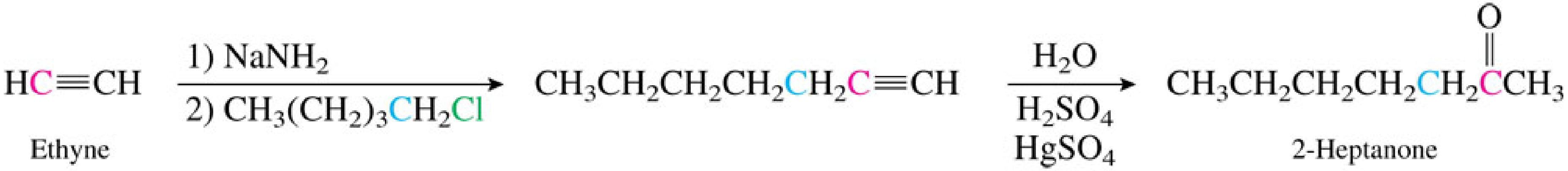


$CH_3CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$ from $HC{\equiv}CH$

2-Heptanone Ethyne



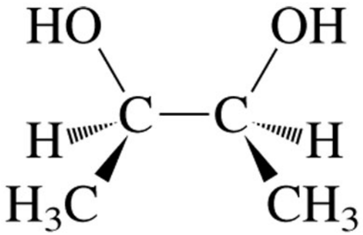
$$CH_3CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 \Longrightarrow CH_3CH_2CH_2CH_2CH_2C{\equiv}CH \Longrightarrow HC{\equiv}CH$$



$$HC{\equiv}CH \xrightarrow[\text{2) } CH_3(CH_2)_3CH_2Cl]{\text{1) } NaNH_2} CH_3CH_2CH_2CH_2CH_2C{\equiv}CH \xrightarrow[H_2SO_4 \atop HgSO_4]{H_2O} CH_3CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$$

Ethyne 2-Heptanone

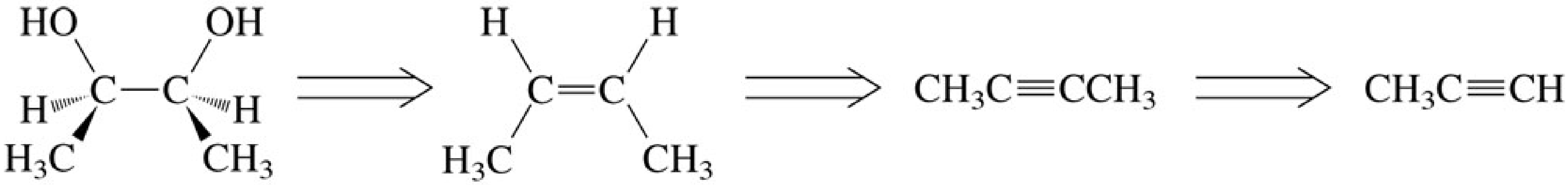
Example



meso-2,3-Butanediol

from $CH_3C{\equiv}C{-}H$

Propyne



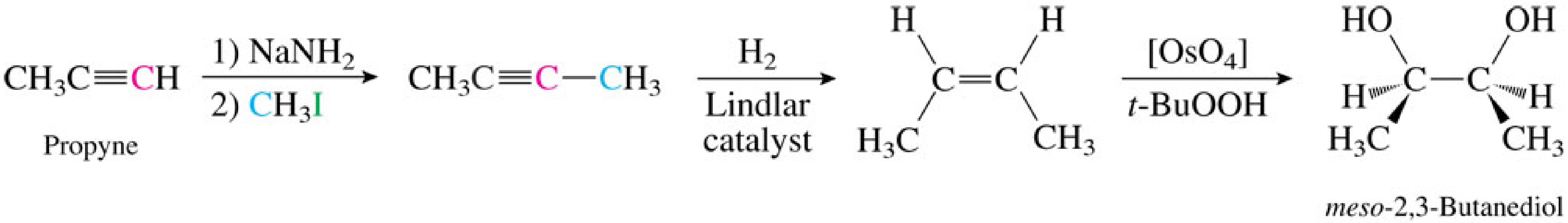
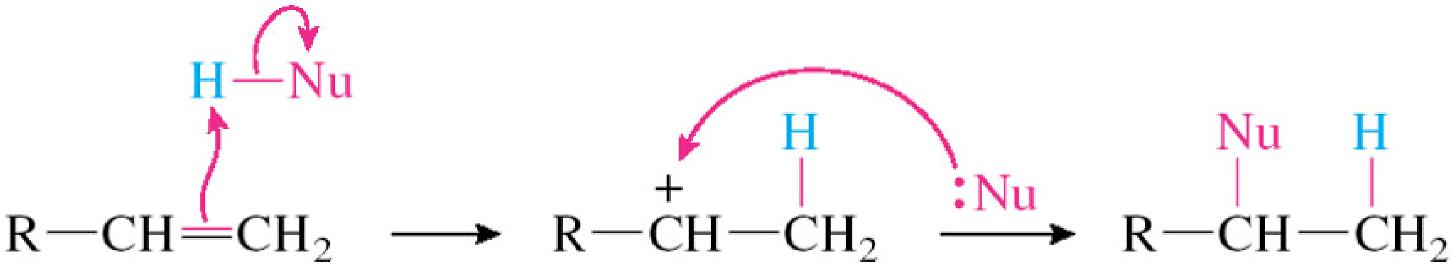


Table 11.2 Addition Reactions Following a Carbocation Mechanism

These reactions proceed by initial addition of a proton to the alkene to give a carbocation intermediate. The nucleophile adds in the second step.



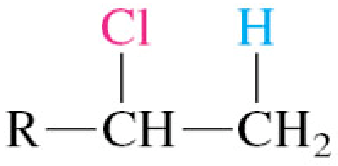
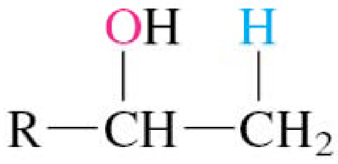
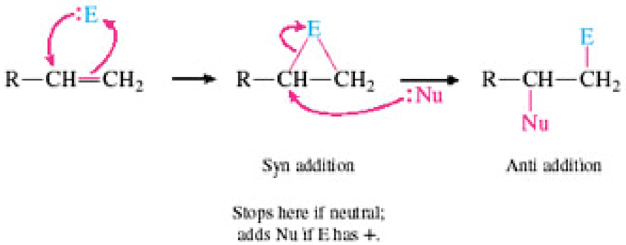
Reagent	Product	Comments
H—Cl (HF, HBr, HI) (Section 11.2)	 $R-\overset{Cl}{CH}-\overset{H}{CH_2}$	All of these reactions proceed with Markovnikov orientation and random stereochemistry. Watch for carbocation rearrangements.
H_3O^+ (Section 11.3)	 $R-\overset{OH}{CH}-\overset{H}{CH_2}$	

Table 11.3 Addition Reactions Proceeding through a Three-Membered Cyclic Intermediate

When the electrophile also has an unshared pair of electrons, addition initially produces a three-membered ring. If the ring is uncharged, the reaction stops here. If the ring has a positive charge, a nucleophile attacks and opens the ring.



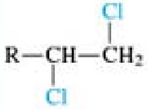
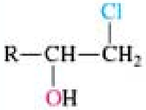
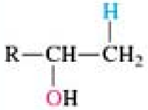
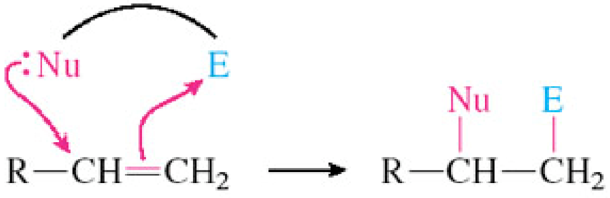
Reagent	Product	Comments
CH_2N_2 (CHX_3/OH^-) $(CH_2I_2, Zn/Cu)$ (Section 11.8)		Carbenes add to give cyclopropane derivatives. These are syn additions. The Simmons-Smith reaction generates a carbenoid that reacts like methylene.
$R'CO_3H$ (Section 11.9)		Percarboxylic acids add to alkenes to give epoxides in a syn addition.
Cl_2 (Br_2)	 $R-\underset{Cl}{CH}-\overset{Cl}{CH_2}$	Chlorine and bromine add with anti stereochemistry.
Cl_2/H_2O (Br_2/H_2O) (Section 11.4)	 $R-\underset{OH}{CH}-\overset{Cl}{CH_2}$	In water as solvent, Cl_2 and Br_2 add to give halohydrins, with the OH on the more substituted carbon and anti stereochemistry.
1) $Hg(O_2CCH_3)_2$, H_2O 2) $NaBH_4$, NaOH (Section 11.6)	 $R-\underset{OH}{CH}-\overset{H}{CH_2}$	The oxymercuration reaction is a method for the Markovnikov addition of water without rearrangement.
Hg^{2+}, H_2O, H_2SO_4 (Section 11.6)	 $R-\overset{O}{\overset{\Vert}{C}}-CH_3$ from $R-C\equiv CH$	The initial product, an enol, tautomerizes to a ketone.

Table 11.4 Addition Reactions Where the Nucleophile and Electrophile Are Linked

When the electrophile and nucleophile are part of the same molecule, concerted additions occur with syn stereochemistry.



Syn addition

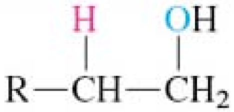
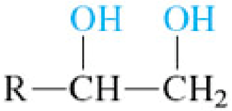
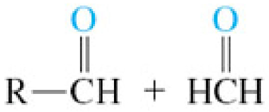
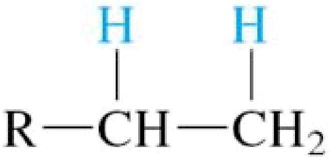
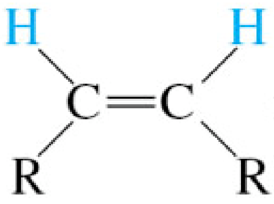
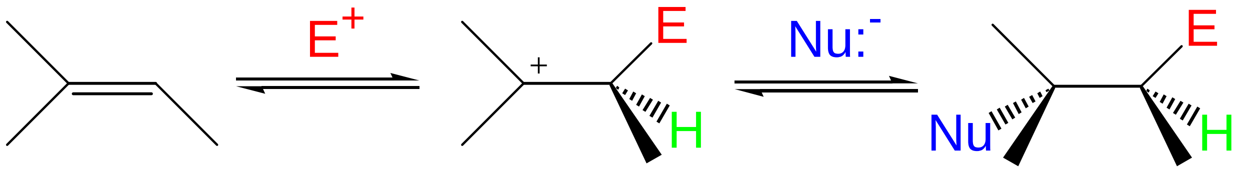
Reagent	Product	Comments
1) BH_3, THF 2) H_2O_2, NaOH (Section 11.7)	 $R-\overset{H}{\overset{\vert}{C}}H-\overset{OH}{\overset{\vert}{C}}H_2$	The hydroboration reaction results in anti-Markovnikov addition of water with syn stereochemistry.
1) Disiamylborane 2) H_2O_2, NaOH (Section 11.7)	 $R-CH_2-\overset{O}{\overset{\Vert}{C}}H$ from $R-C\equiv CH$	The reaction of 1-alkynes with the hindered borane produces aldehydes.
OsO_4, t-BuOOH or $KMnO_4$, H_2O, NaOH (Section 11.10)	 $R-\overset{OH}{\overset{\vert}{C}}H-\overset{OH}{\overset{\vert}{C}}H_2$	Osmium tetroxide and permanganate result in the syn addition of hydroxy groups to the alkene.
1) O_3 2) $(CH_3)_2S$ (Section 11.11)	 $R-\overset{O}{\overset{\Vert}{C}}H + H\overset{O}{\overset{\Vert}{C}}H$	Ozone can be used to cleave the alkene to two carbonyl compounds.

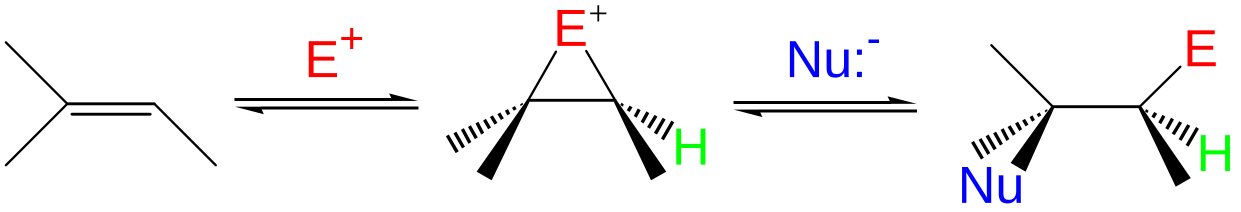
Table 11.5 Catalytic Hydrogenation Reactions

Reagent	Product	Comments
H_2, cat. (Ni, Pd, Pt) (Section 11.12)	 $R-\overset{\overset{H}{\vert}}{C}H-\overset{\overset{H}{\vert}}{C}H_2$	Catalytic hydrogenation results in the addition of hydrogen to the alkene.
H_2 Lindlar catalyst (Section 11.12)	 from $R-C\equiv C-R$	Addition of hydrogen to an alkyne using Lindlar catalyst produces a *cis*-alkene.

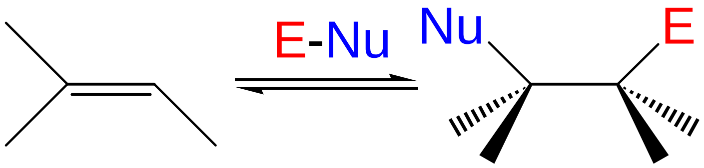
Summary



regioselective
Not stereo-selective



regioselective
anti addition



regioselective
syn addition

공부하는 방법

- 그저 익숙하도록 읽는 것뿐이다. 글을 읽는 사람이 비록 글의 뜻은 알았으나, 만약 익숙하지 못하면 읽자마자 곧 잊어버리게 되어, 마음에 간직할 수 없을 것은 틀림없다. 이미 읽고 난 뒤에, 또 거기에 자세하고 익숙해질 공부를 더한 뒤라야 비로소 마음에 간직할 수 있으며, 또 흐뭇한 맛도 있을 것이다. - 퇴계 이황
- 博約兩至

  진리를 넓게 배우고 그것을 요약할 줄 아는 학문의 두 경지

  - 陶山 李夫子

유기화학에서 원하는 것은 암기가 아니다. 목표는 많은 기본지식을 통하여 설계의 능력을 기르는 것이다.

- 이종찬