
6

Organic Chemistry

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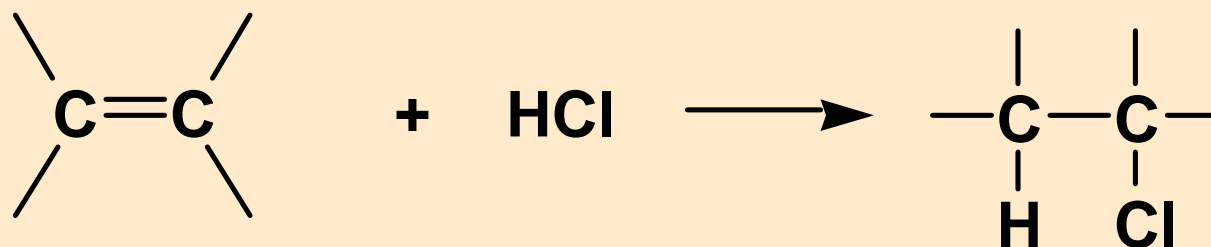
Alkenes II

Chapter 6

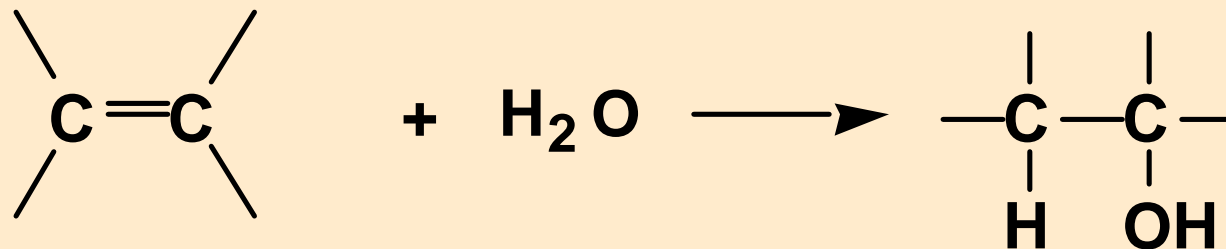
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6 Characteristic Reactions

Hydrochlorination (hydrohalogenation)

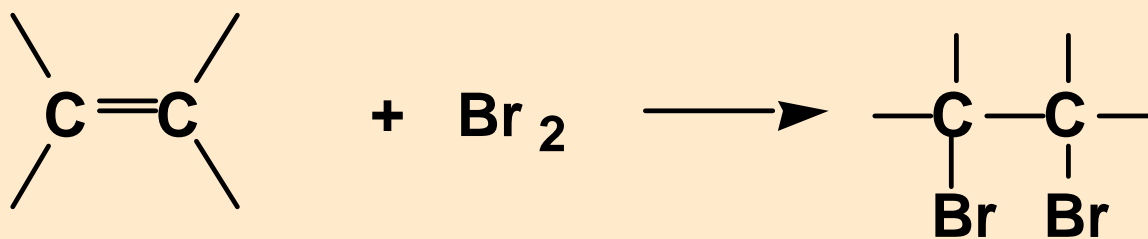


Hydration

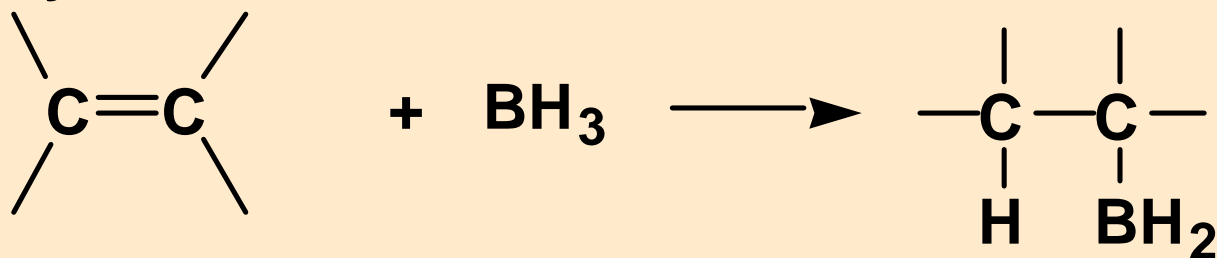


6 Characteristic Reactions

Bromination (halogenation)

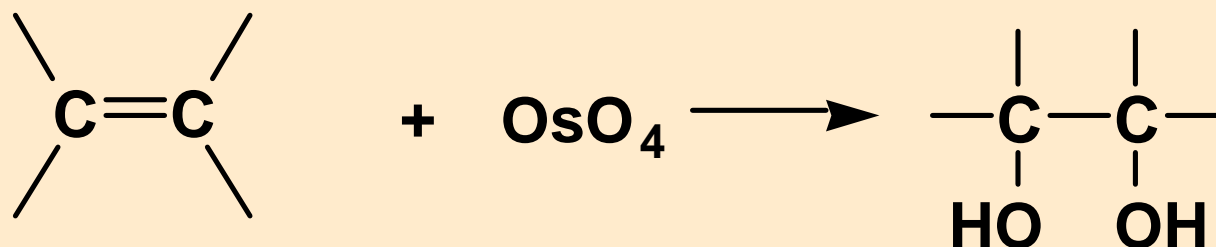


Hydroboration

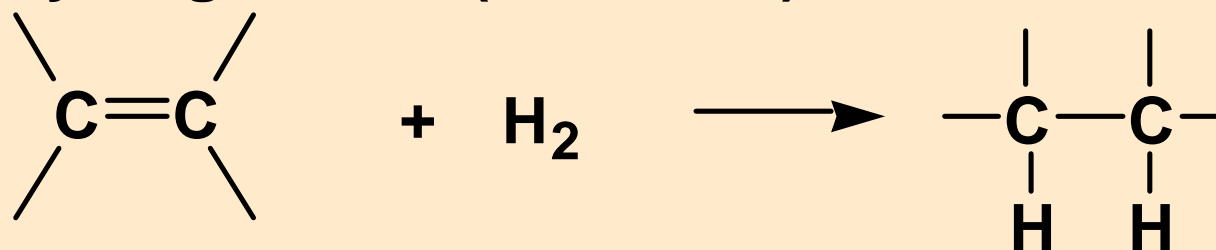


6 Characteristic Reactions

Hydroxylation (oxidation)



Hydrogenation (reduction)

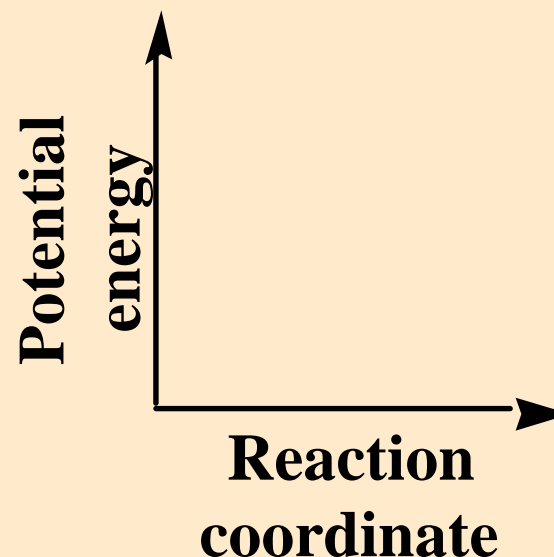


6 Reaction Mechanisms

- u **A reaction mechanism describes details of how a reaction occurs**
 - **which bonds are broken and which new ones are formed**
 - **the order in which bond-breaking and bond-forming steps take place**
 - **the role of the solvent (if any)**
 - **the role of the catalyst (if any)**
 - **the energy of the entire system during the reaction**

6 PE Diagrams

- u **Potential energy (PE) diagram:** a graph showing the changes in energy that occur during a chemical reaction
- u **Reaction coordinate:** a measure of the change in position of atoms during a reaction



6 PE Diagrams

- u **Heat of reaction:** the difference in energy between reactants and products
 - **exothermic:** products are lower in energy than reactants; heat is released
 - **endothermic:** products are higher in energy than reactants; heat is absorbed
- u **Transition state:** an energy maximum on a PE diagram
 - represents an unstable species of maximum PE formed during the course of a reaction

6 Activation Energy

- u **Activation Energy (E_a):** the difference in potential energy between reactants and the transition state
 - determines rate of reaction
 - if activation energy is large, only a few molecular collisions occur with sufficient energy to reach the transition state, and the reaction is slow
 - if activation energy is small, many collisions generate sufficient energy to reach the transition state, and the reaction is fast

6 Activation Energy & Rate

- u Activation energy, E_a , is related to the reaction rate constant, k , by the Arrhenius equation

$$k = Ae^{-E_a/RT}$$

A = frequency of collisions with correct geometry for reaction (sec^{-1})

R = gas constant, $1.987 \times 10^{-3} \text{ kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

T = temperature in degrees Kelvin

6 Activation Energy & Rate

u **Example:** What is the activation energy for a reaction whose rate at 35°C is twice that at 25°C?

u **Solution:**

- the ratio of rate constants k_2 and k_1 for the reaction at temperatures T_2 and T_1 is

$$\frac{k_2}{k_1} = \frac{Ae^{-E_a/RT_2}}{Ae^{-E_a/RT_1}}$$

- taking the ln of both sides and rearranging gives

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

6 Activation Energy & Rate

- Substituting values and solving gives

$$\ln \frac{2}{1} = \frac{E_a \text{ (kcal/mol)}}{1.987 \times 10^{-3} \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} \left(\frac{1}{298\text{K}} - \frac{1}{308\text{K}} \right)$$

$$E_a = 12.6 \text{ kcal/mol (52.7 kJ/mol)}$$

6 Developing a Mechanism

- u Design experiments to reveal details of a particular chemical reaction
- u Propose a set or sets of steps that might account for the overall transformation
- u A mechanism becomes established when it is shown to be consistent with every test that can be devised
- u This does mean that the mechanism is correct, only that it is the best explanation we are able to devise

6 Why Mechanisms?

- u **Framework within which to organize descriptive chemistry**
- u **Intellectual satisfaction derived from constructing models that accurately reflect the behavior of chemical systems**
- u **A tool with which to search for new information and new understanding**

6 Electrophilic Additions

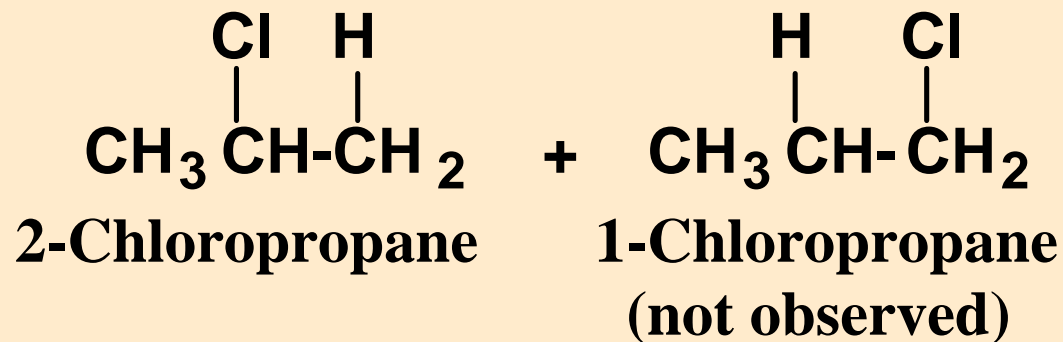
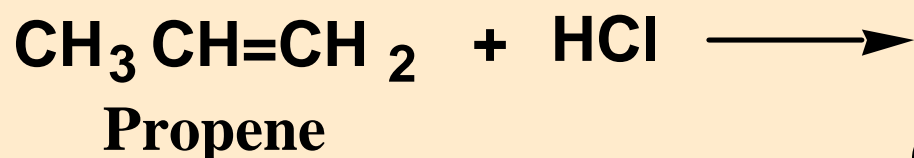
- u Hydrohalogenation using HCl, HBr, HI
- u Hydration using H₂O, H₂SO₄
- u Halogenation using Cl₂, Br₂
- u Halohydrination using HOCl, HOBr
- u Oxymercuration using Hg(OAc)₂, H₂O

6 Addition of HX

- u Carried out with pure reagents or in a polar solvent such as acetic acid
- u Addition is regioselective
- u **Regioselective reaction:** a reaction in which one direction of bond-forming or bond-breaking occurs in preference to all other directions

6 Addition of HX

- u H adds to the less substituted carbon



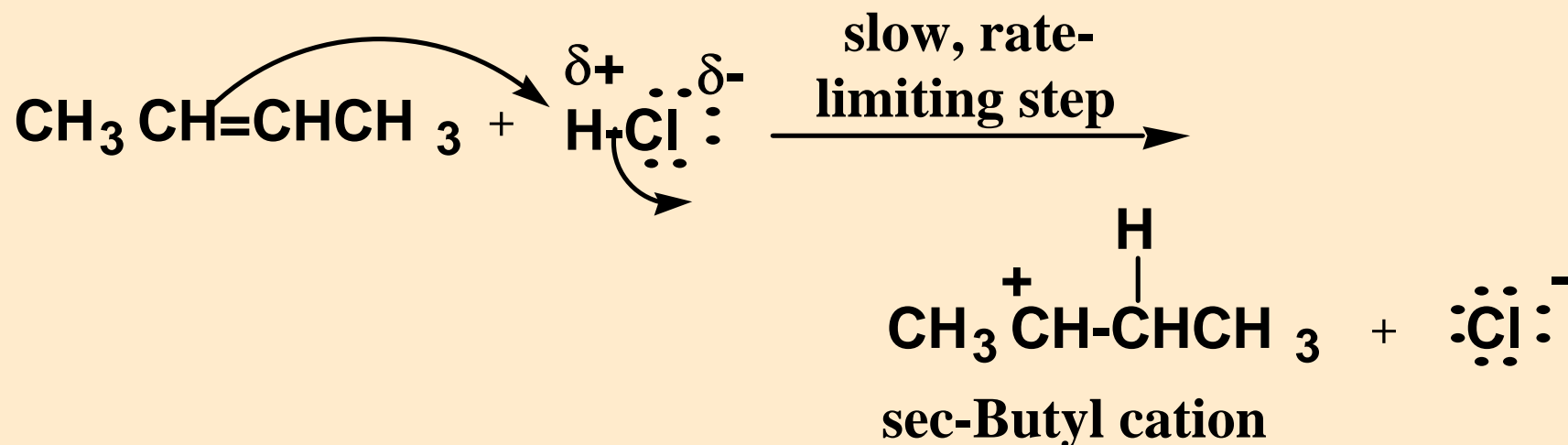
- u **Markovnikov's rule:** in the addition of HX or H₂O to an alkene, H adds to the carbon of the double bond having the greater number of hydrogens

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6 HCl + 2-Butene

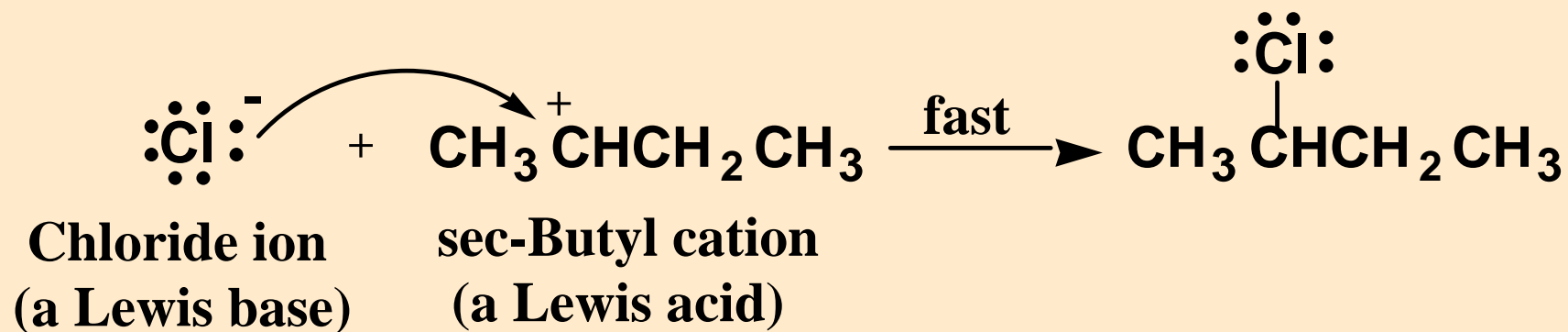
u A two-step mechanism

Step 1: formation of sec-butyl cation, a 2° carbocation intermediate



6 HCl + 2-Butene

Step 2: reaction of the *sec*-butyl cation (a Lewis acid) with chloride ion (a Lewis base)



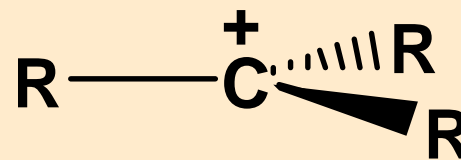
6 Carbocations

- u **Carbocation:** a species containing a positively charged carbon

- u **Carbocations are**
 - classified as 1°, 2°, or 3° depending on the number of carbons bonded to the carbon bearing the positive charge
 - electrophiles, that is, they are “electron-lovers”
 - Lewis acids

6 Carbocation Structure

- u Bond angles about the positively charged carbon are 120°
- u Carbon uses sp^2 hybrid orbitals to form sigma bonds to the three attached groups
- u The unhybridized 2p orbital lies perpendicular to the sigma bond framework and contains no electrons

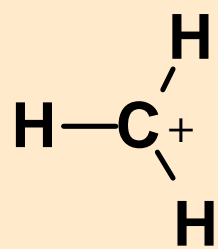


6 Carbocation Stability

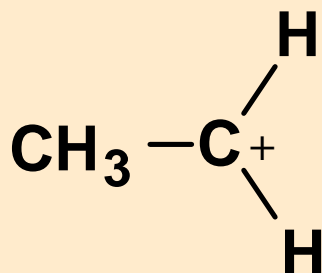
- u A 3° carbocation is more stable than a 2° carbocation, and requires a lower activation energy for its formation
- u A 2° carbocation is, in turn, more stable than a 1° carbocation, and requires a lower activation energy for its formation
- u The methyl cation is so unstable that it is never observed in solution

6 Carbocation Stability

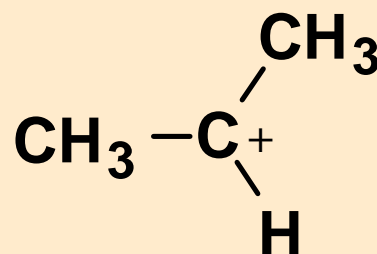
u Relative stability



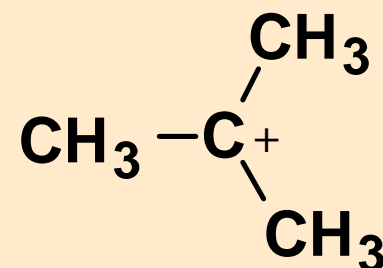
Methyl
cation
(methyl)



Ethyl
cation
(1°)



Isopropyl
cation
(2°)



tert-Butyl
cation
(3°)

Increasing carbocation stability



6 Carbocation Stability

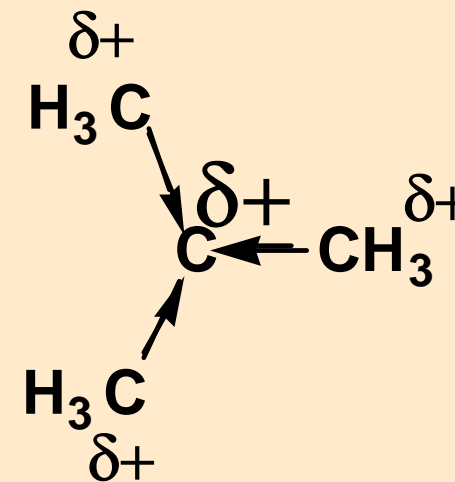
- u We can account for the relative stability of carbocations if we assume that alkyl groups attached to the positively charged carbon are electron-releasing and thereby help delocalize the positive charge of the cation**

- u We account for this electron-releasing ability of alkyl groups by (1) the inductive effect, and (2) hyperconjugation**

6 Carbocation Stability

u The inductive effect

- the electron-deficient carbon bearing the positive charge polarizes electrons of the adjacent sigma bonds toward it
- the positive charge on the cation is not localized on the trivalent carbon, but delocalized over nearby atoms
- the larger the volume over which the positive charge is delocalized, the greater the stability of the cation



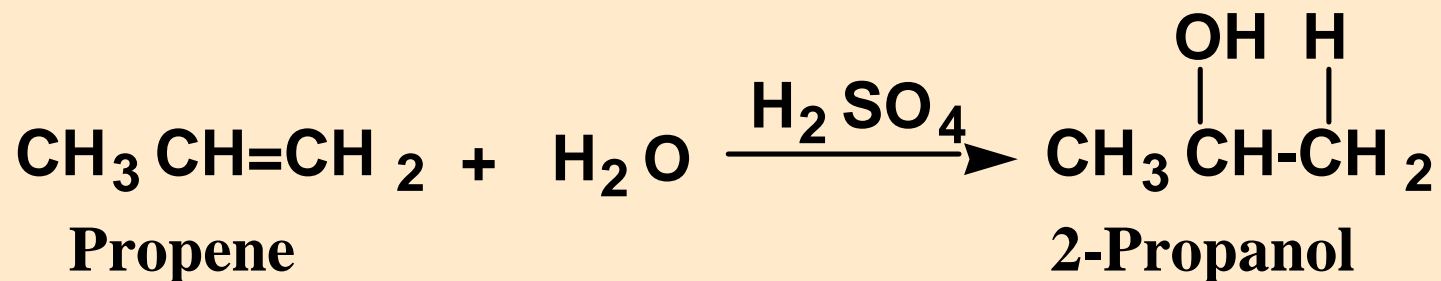
6 Carbocation Stability

u Hyperconjugation

- partial overlap of the σ bonding orbital of an adjacent C-H bond with the vacant 2p orbital of the cationic carbon delocalizes the positive charge and also the electrons of the adjacent σ bond
- replacing a C-H bond with a C-C bond increases the possibility for hyperconjugation

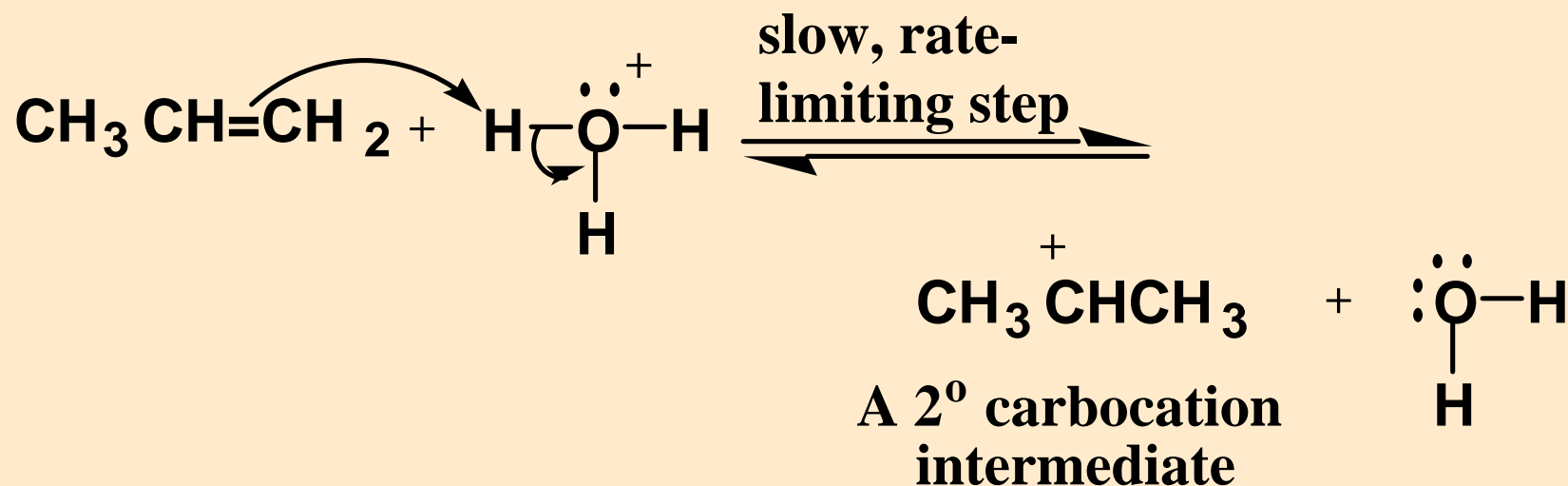
6 Addition of H₂O

- u Addition of water is called hydration
- u Acid-catalyzed hydration of an alkene is regioselective - hydrogen adds to the less substituted carbon of the double bond



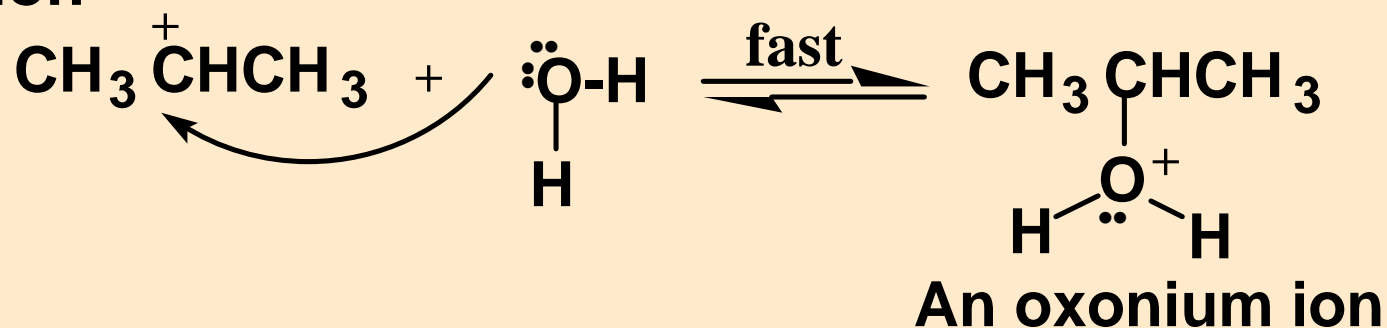
6 Addition of H₂O

Step 1: proton transfer from solvent to the alkene

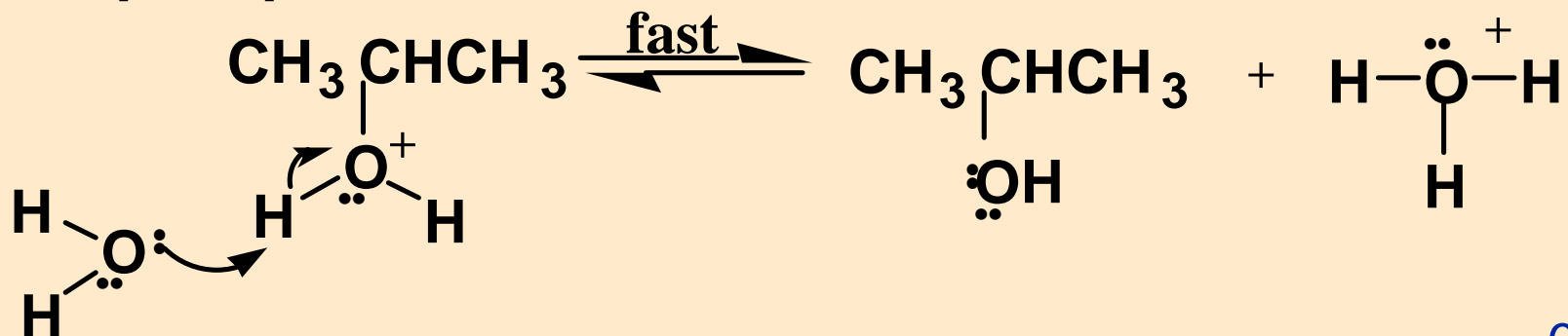


6 Addition of H₂O

Step 2: a Lewis acid/base reaction forms an oxonium ion



Step 3: proton transfer to solvent



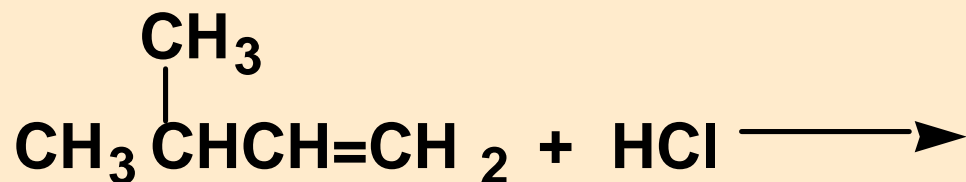
6 C⁺ Rearrangements

- u In electrophilic addition to alkenes, there is the possibility for rearrangement

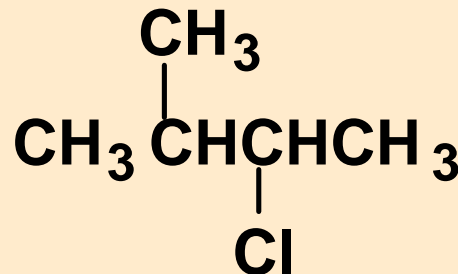
- u **Rearrangement:** any change in connectivity of the atoms in a product compared with the connectivity of the same atoms in the starting material

6 C⁺ Rearrangements

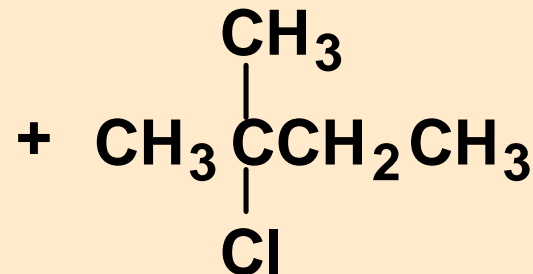
u In addition of HCl to an alkene



3-Methyl-1-butene



2-Chloro-3-methylbutane
(expected)
(40%)

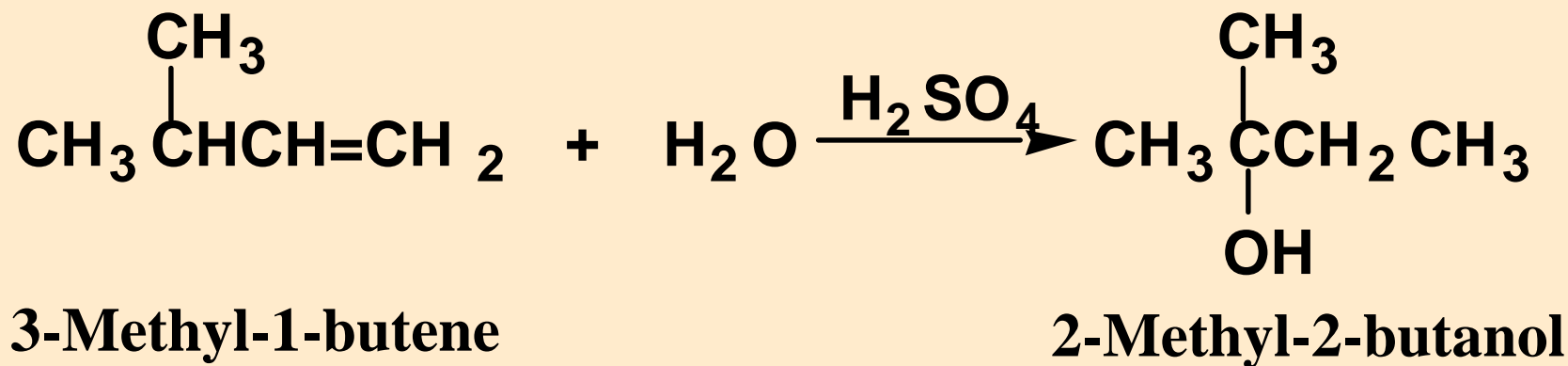


2-Chloro-2-methylbutane
(rearrangement)
(60%)

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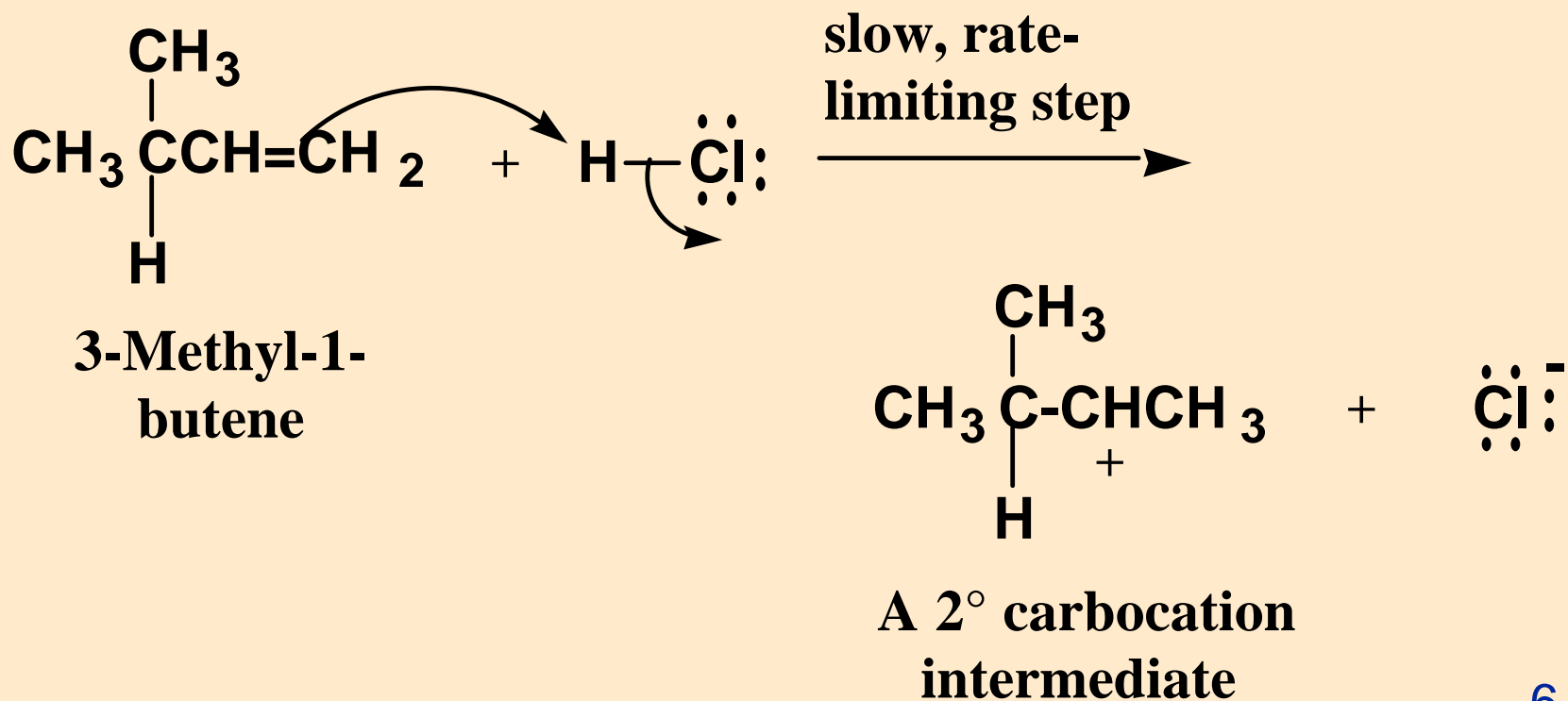
6 C⁺ Rearrangements

u In acid-catalyzed hydration of an alkene



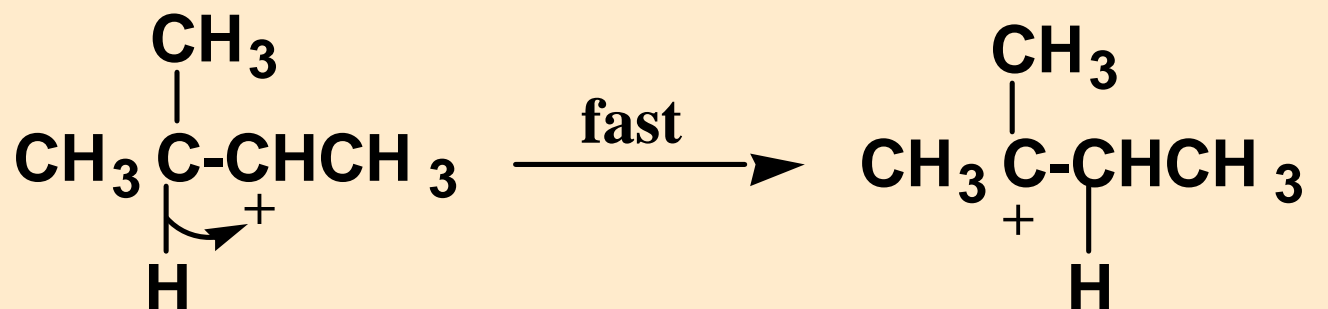
6 C⁺ Rearrangements

- u Driving force is rearrangement of a less stable carbocation to a more stable one



6 C⁺ Rearrangements

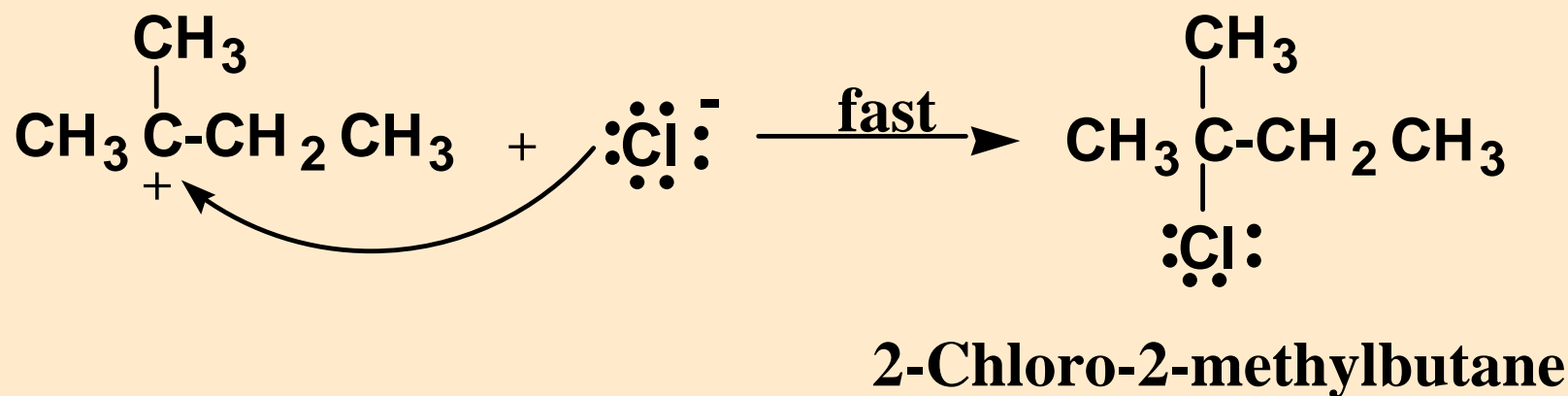
- u The less stable 2° carbocation rearranges to a more stable 3° one by shift of a hydrogen atom with its bonding electrons



A 3° carbocation
intermediate

6 C⁺ Rearrangements

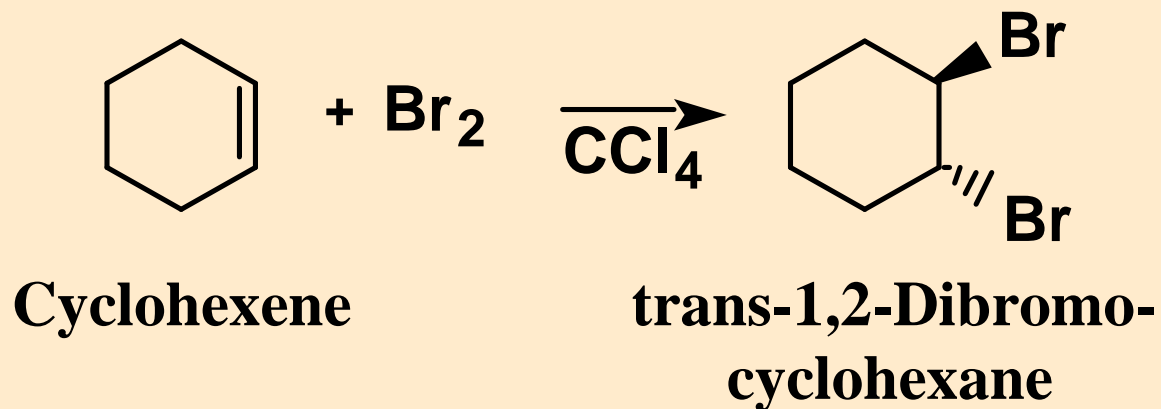
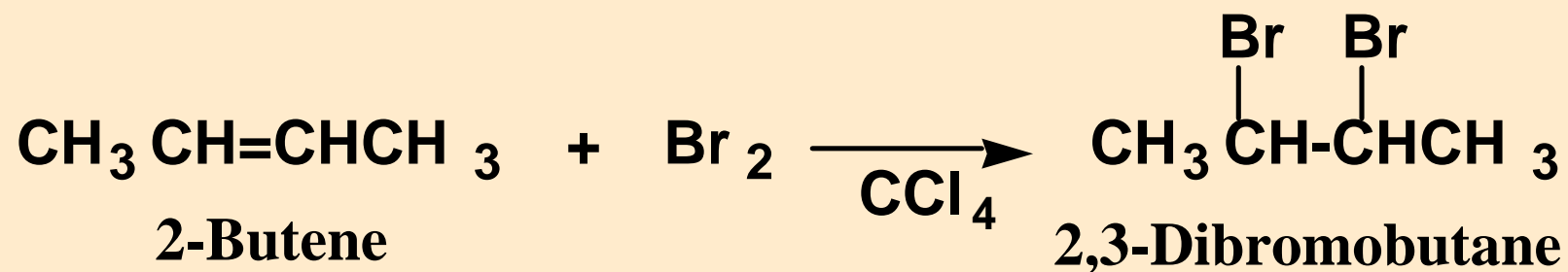
- u Reaction of the more stable carbocation (a Lewis acid) with chloride ion (a Lewis base) completes the reaction



6 Addition of Cl_2 and Br_2

- u Carried out with either the pure reagents or in an inert solvent such as CCl_4 or CH_2Cl_2
- u Addition is stereoselective
- u **Stereoselective reaction:** a reaction in which one stereoisomer is formed or destroyed in preference to all others than might be formed or destroyed.

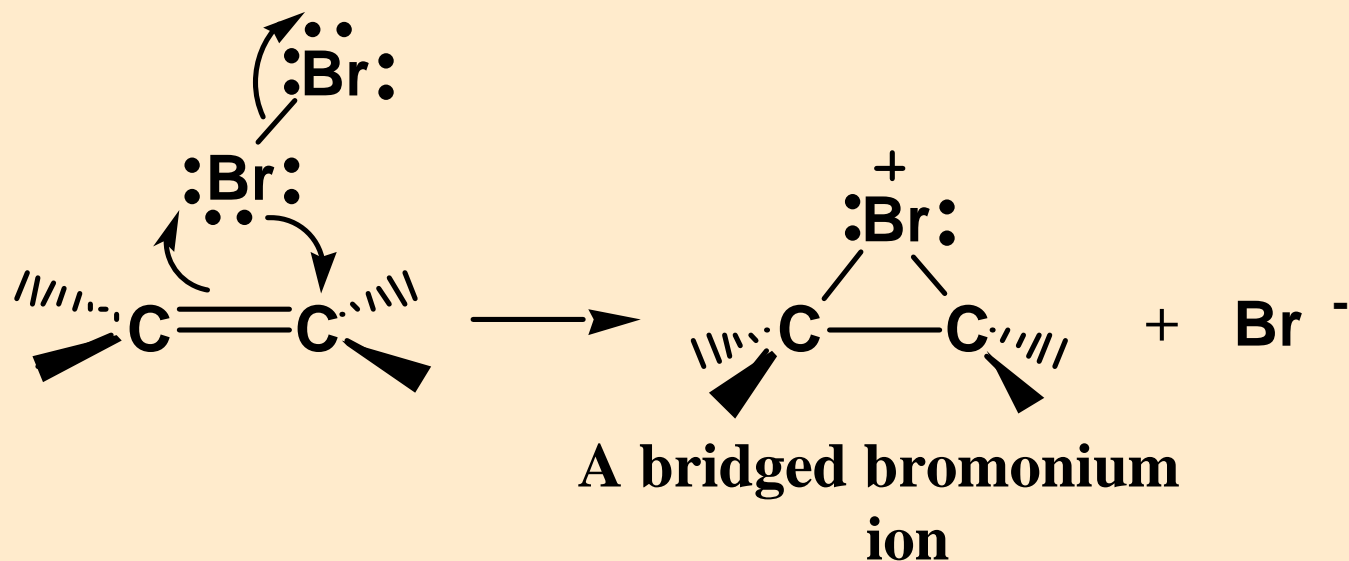
6 Addition of Cl₂ and Br₂



6 Addition of Cl_2 and Br_2

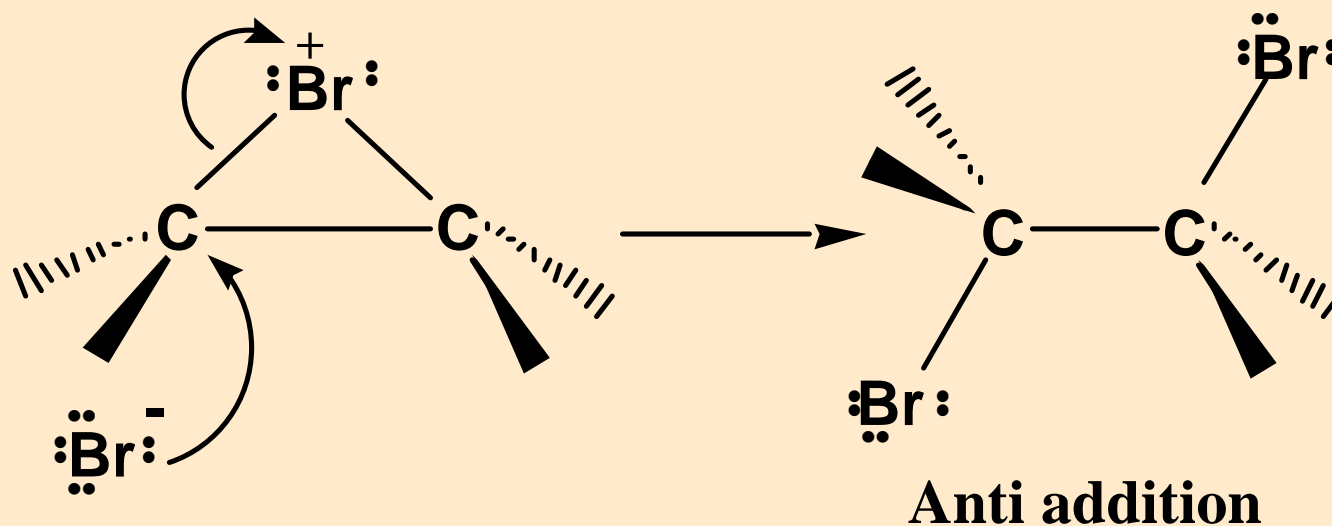
u Addition involves a two-step mechanism

Step 1: formation of a bridged bromonium ion intermediate



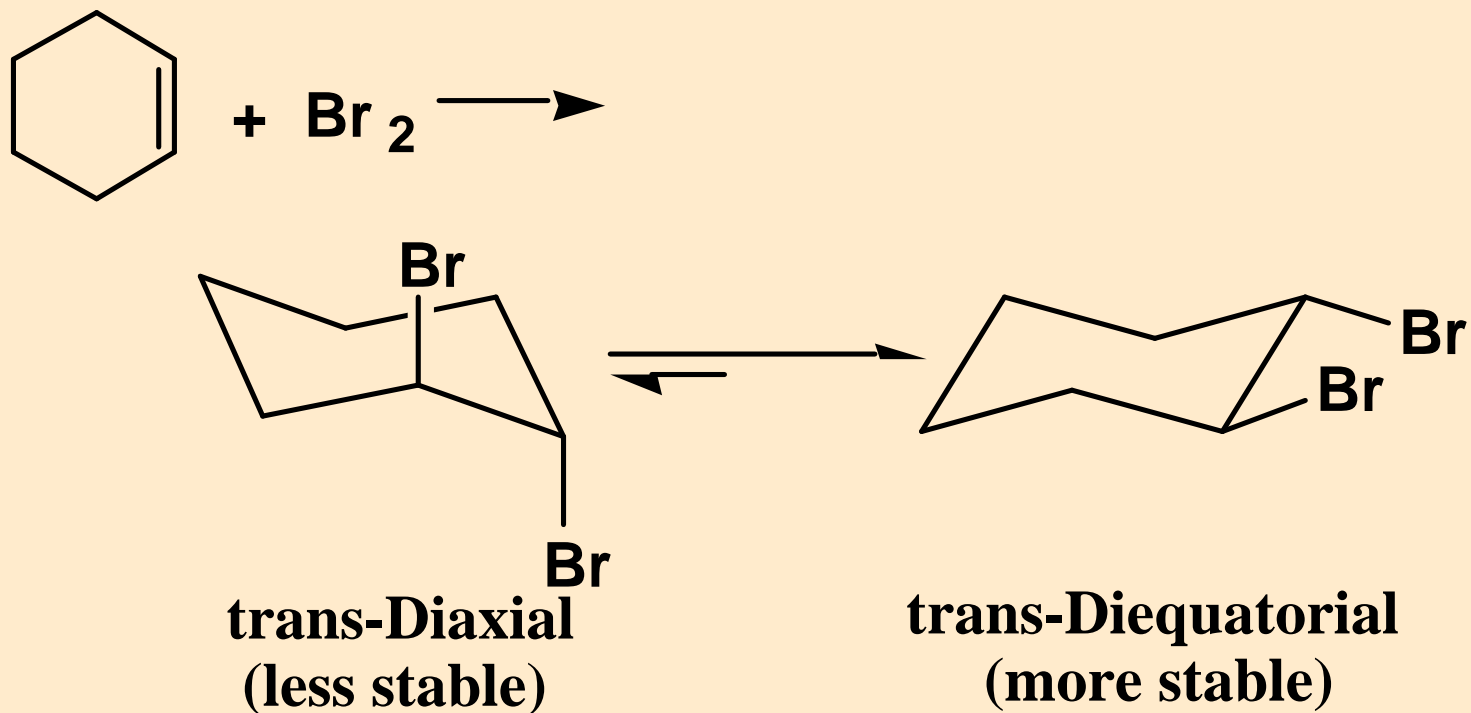
6 Addition of Cl_2 and Br_2

Step 2: Attack of halide ion from the opposite side of the three-membered ring



6 Addition of Cl_2 and Br_2

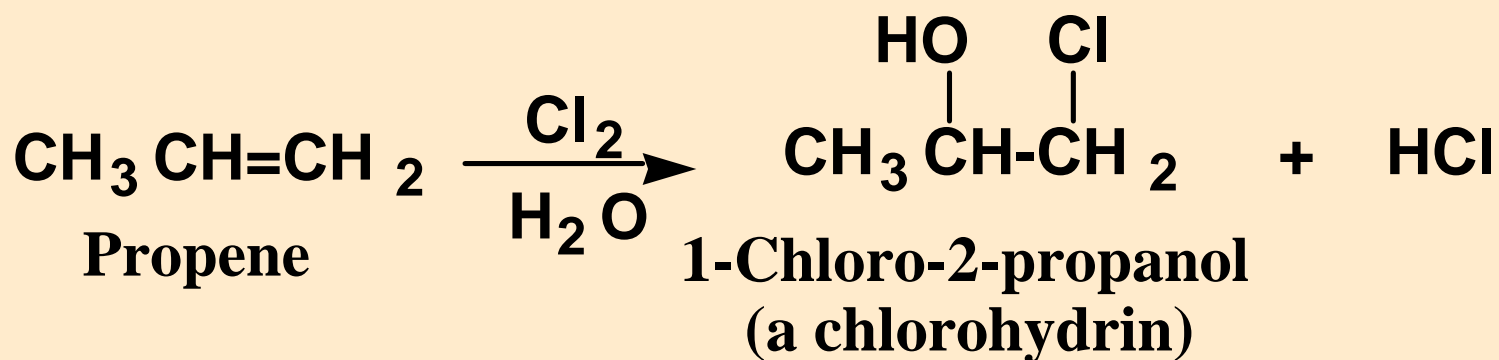
- u For a cyclohexene, anti coplanar addition corresponds to *trans*-diaxial addition



6-40

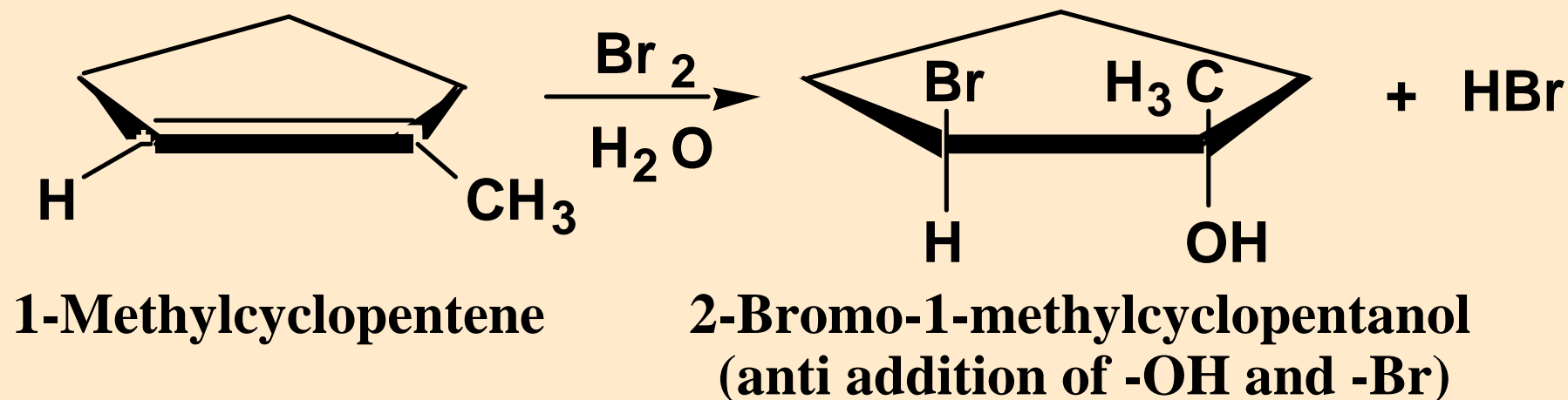
6 Addition of HOCl and HOBr

- u Treatment of an alkene with Br_2 or Cl_2 in water forms a halohydrin
- u **Halohydrin:** a compound containing $-\text{OH}$ and $-\text{X}$ on adjacent carbons



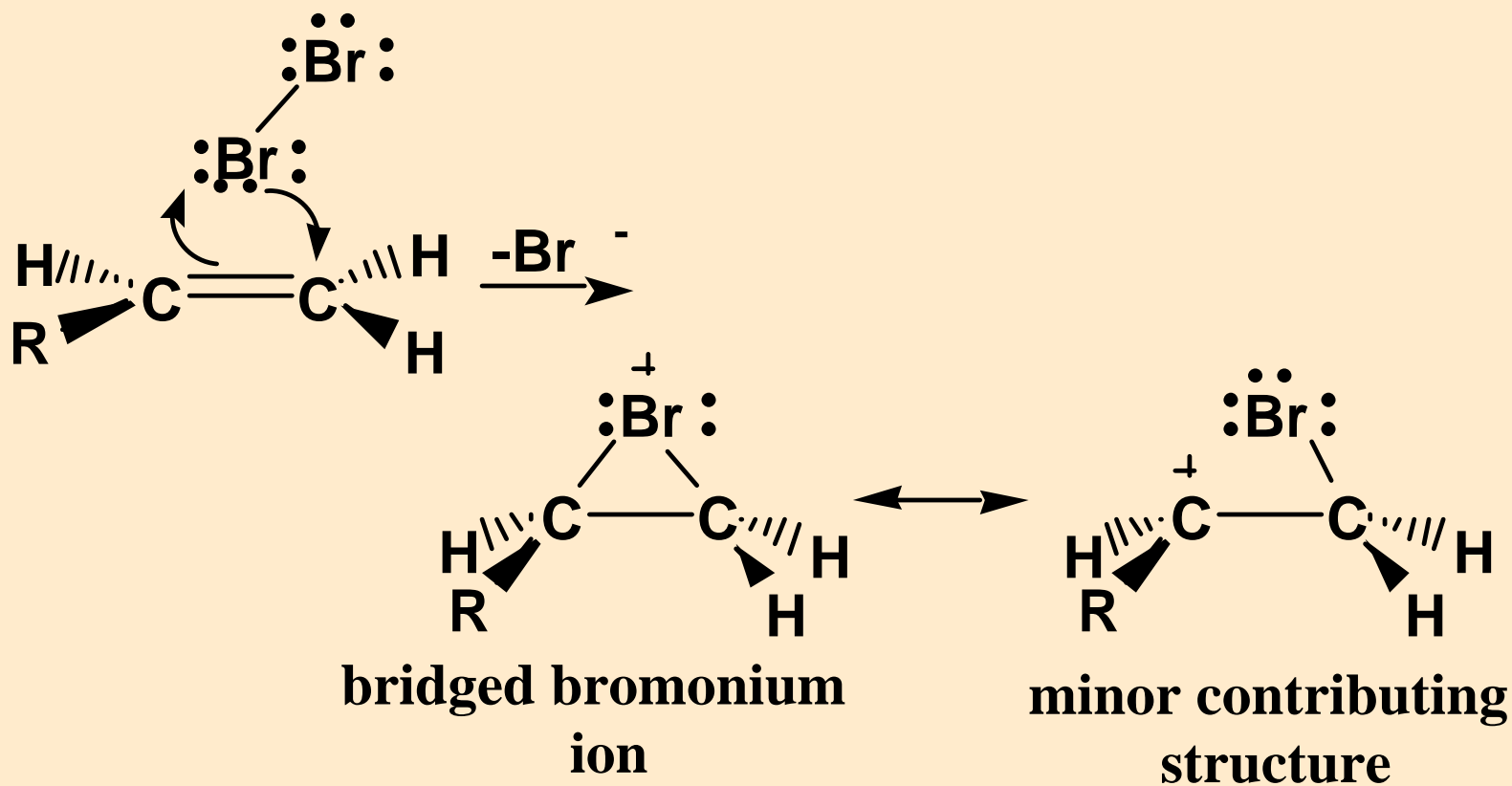
6 Addition of HOCl and HOBr

- u Reaction is both regioselective (anti addition) and stereoselective (OH to the more substituted carbon)



6 Addition of HOCl and HOBr

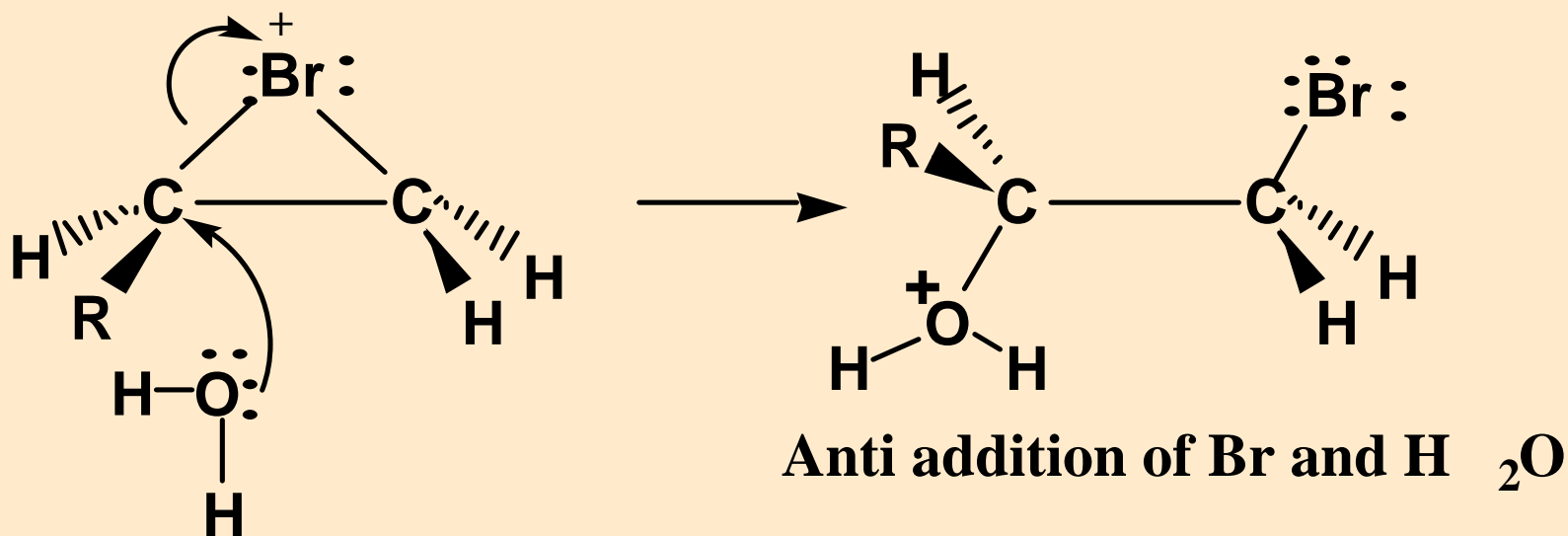
Step 1: formation of a bridged-halonium ion intermediate



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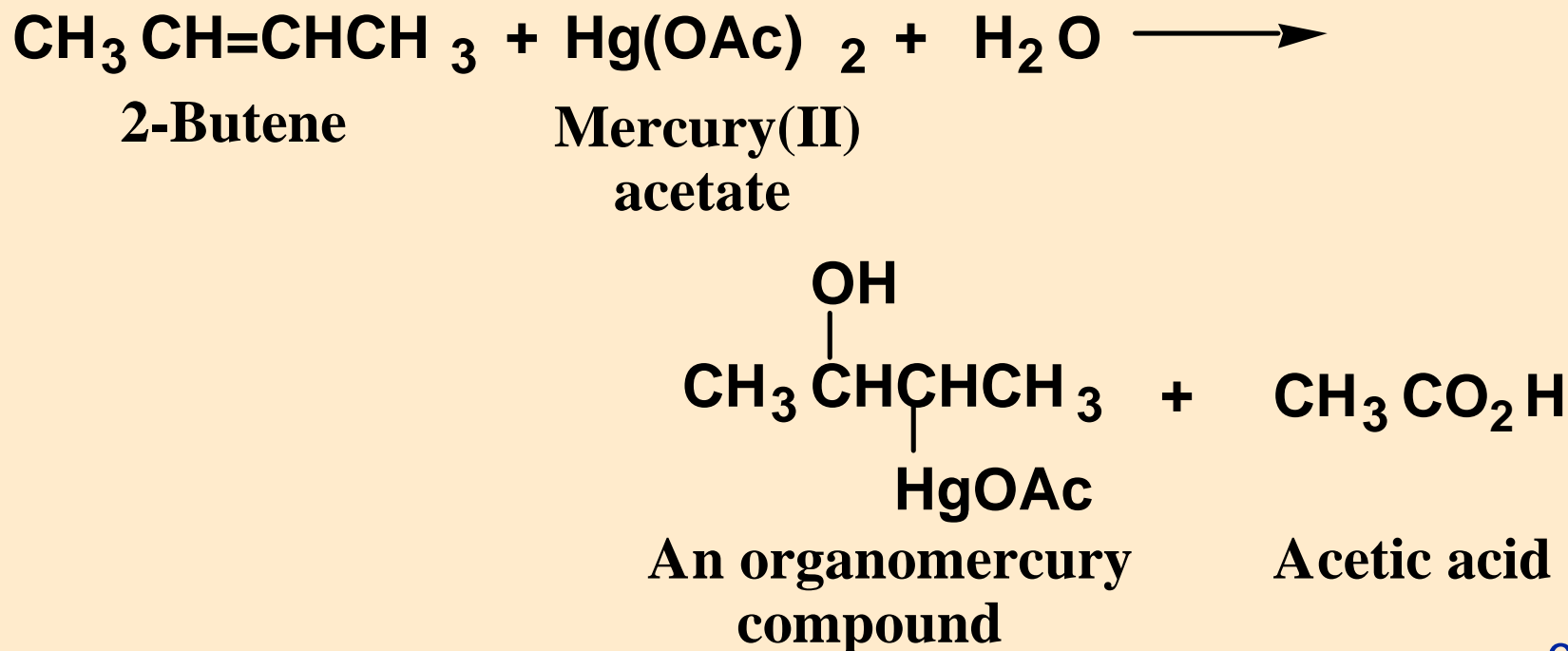
6 Addition of HOCl and HOBr

Step 2: attack of H₂O on the more substituted carbon and opening of the three-membered ring



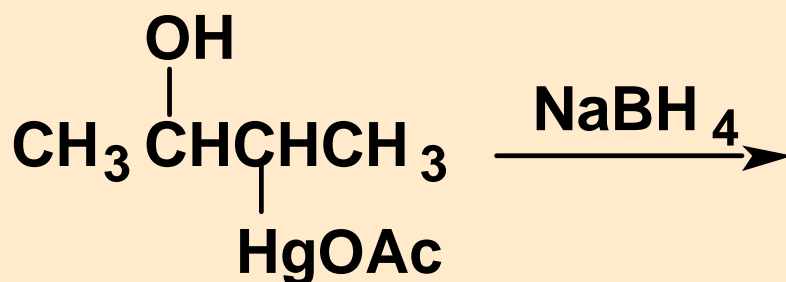
6 Oxymercuration/Reduction

- Oxymercuration:** the addition of Hg(II) to one carbon of a double bond and oxygen to the other

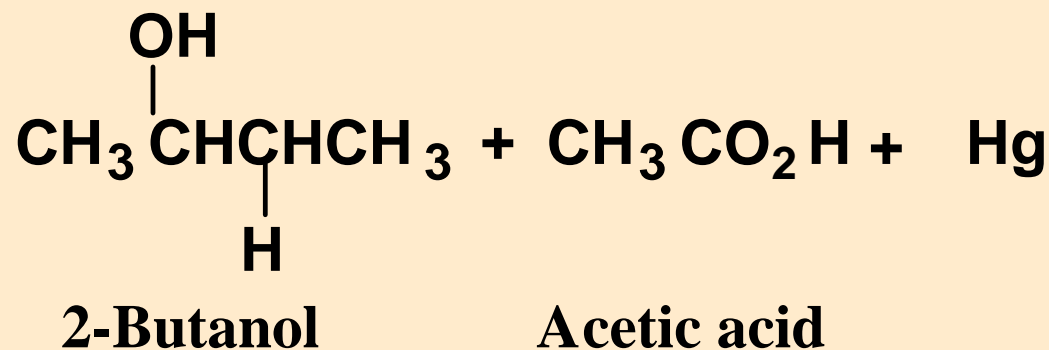


6 Oxymercuration/Reduction

u Reduction with NaBH_4 replaces Hg by H

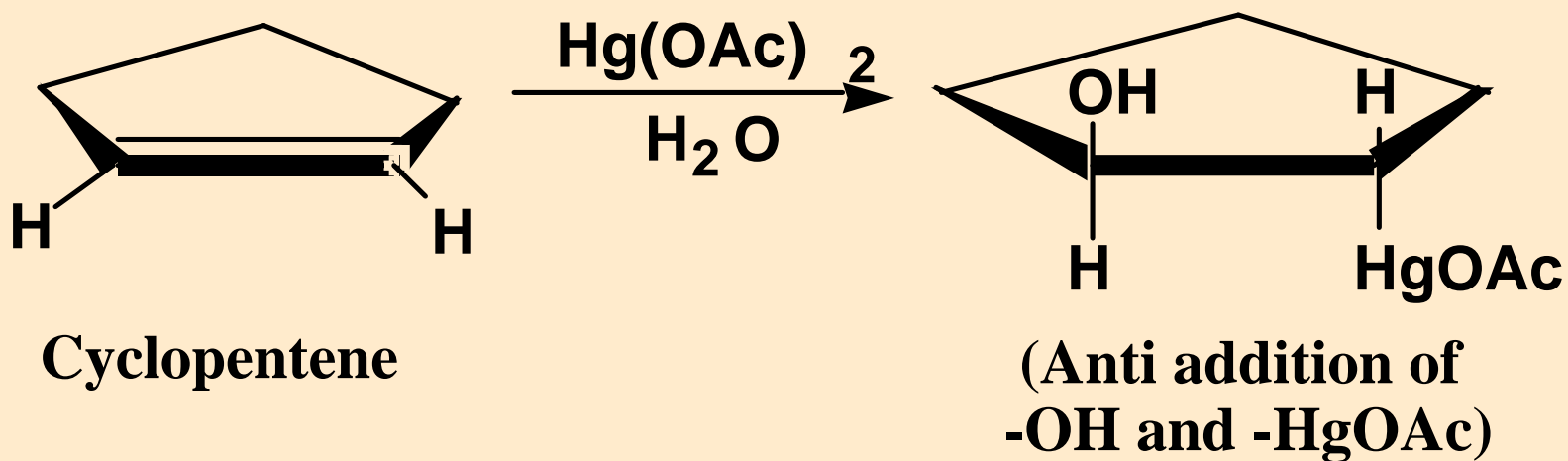


An organomercury
compound



6 Oxymercuration/Reduction

- u Addition of Hg(II) and oxygen is anti coplanar stereoselective



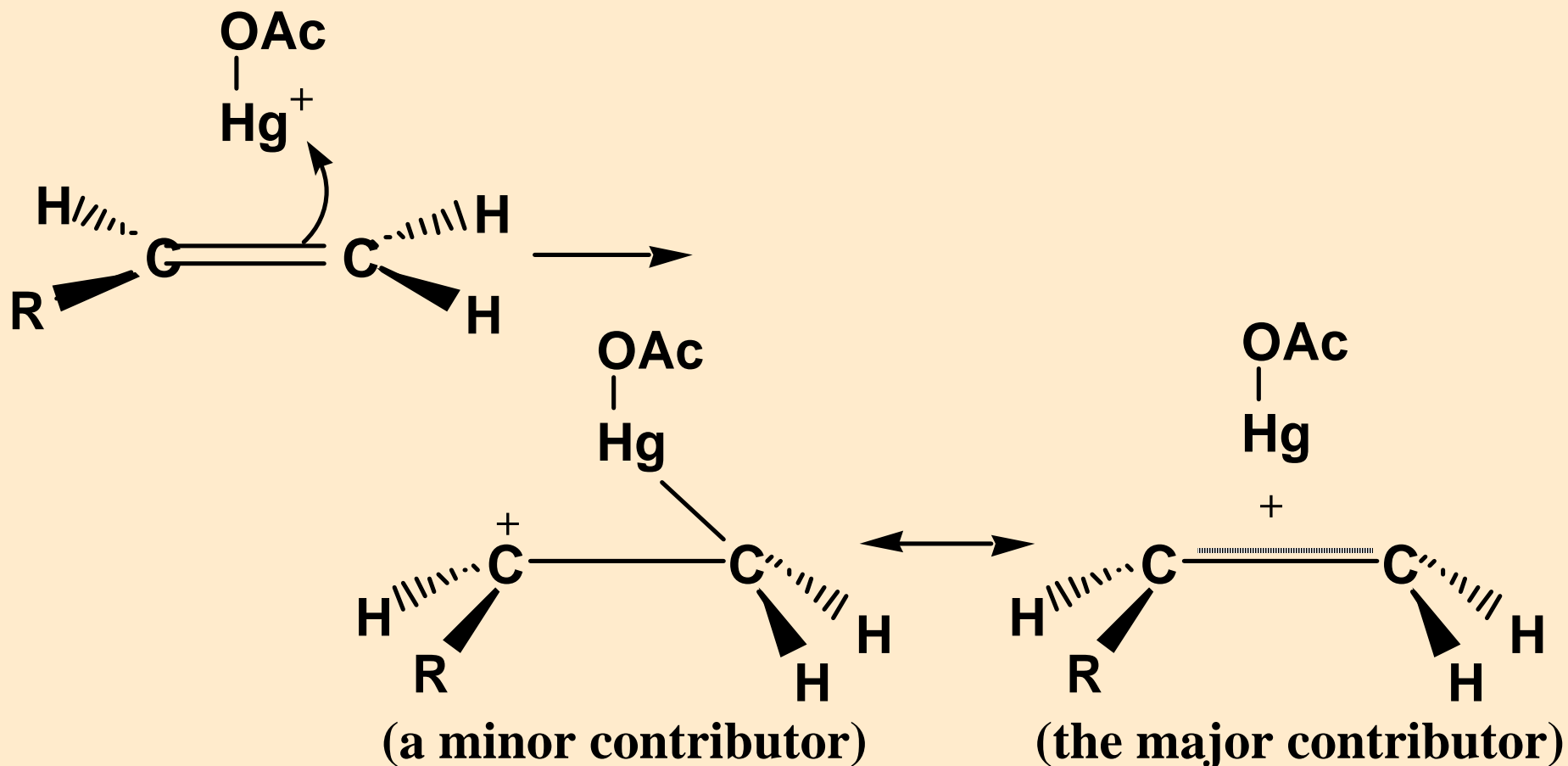
6 Oxymercuration/Reduction

Step 1: dissociation of mercury (II) acetate to give AcOHg^+ , a Lewis acid



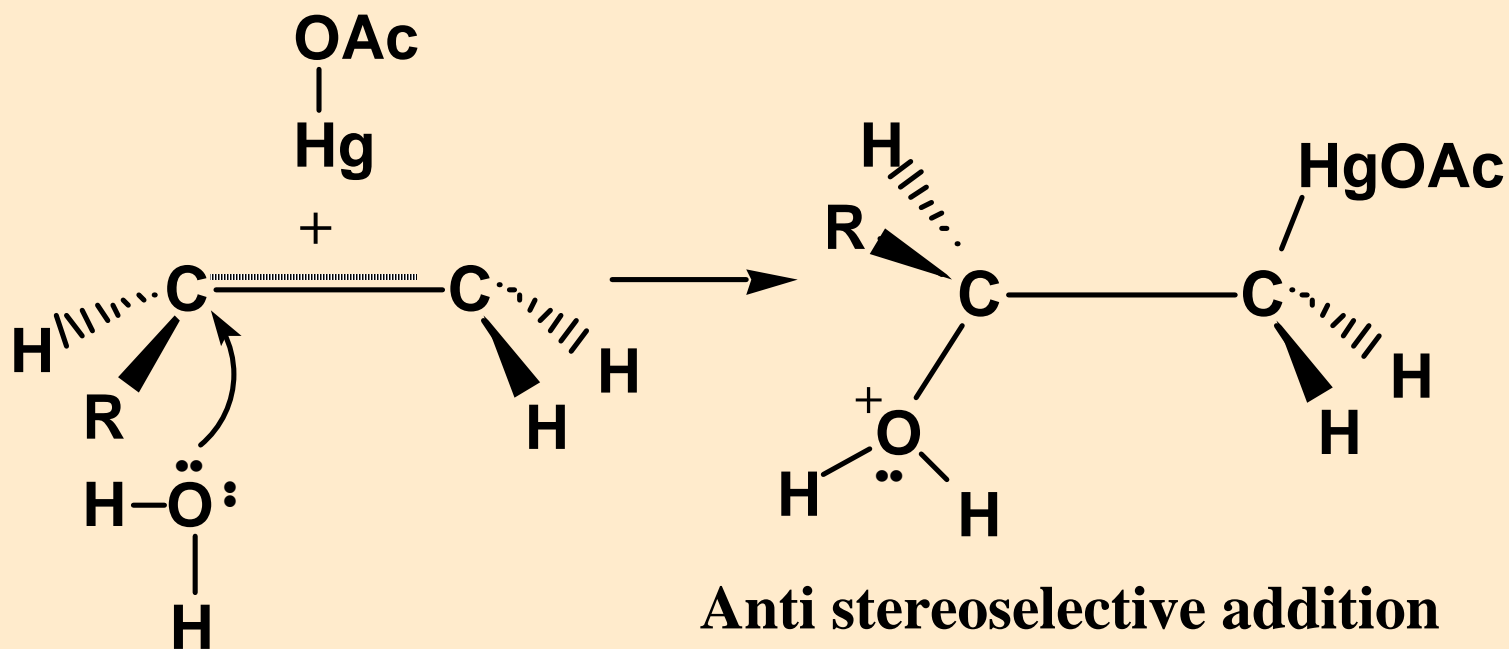
Step 2: attack of AcOHg^+ on the double bond to give a bridged mercurinium ion intermediate in which the two electrons of the pi bond form a two-atom three-center bond

6 Oxymercuration/Reduction



6 Oxymercuration/Reduction

Step 3: stereoselective and regioselective attack of H₂O on the bridged intermediate



6 Oxymercuration/Reduction

Step 4: proton transfer to solvent completes oxymercuration

- u The fact that oxymercuration occurs without rearrangement indicates that the intermediate is not a true carbocation, but rather a resonance hybrid closely resembling a bridged mercurinium ion intermediate.**

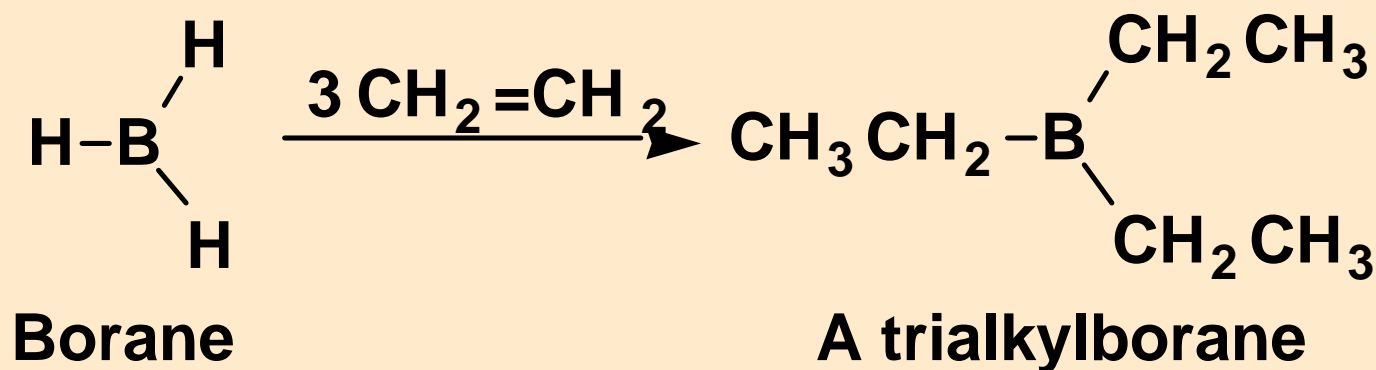
6 Oxymercuration/Reduction

- u Regioselectivity is accounted for by at least some carbocation character in the bridged intermediate

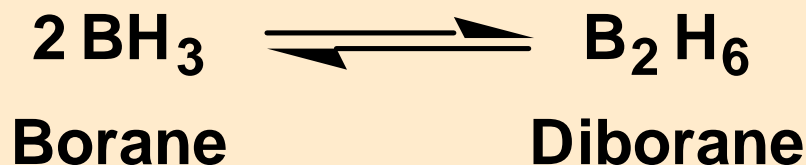
- u Stereoselectivity is accounted for by anti attack on the bridged intermediate

6 Hydroboration/Oxidation

- u **Hydroboration:** the addition of borane, BH_3 , to an alkene to form a trialkylborane

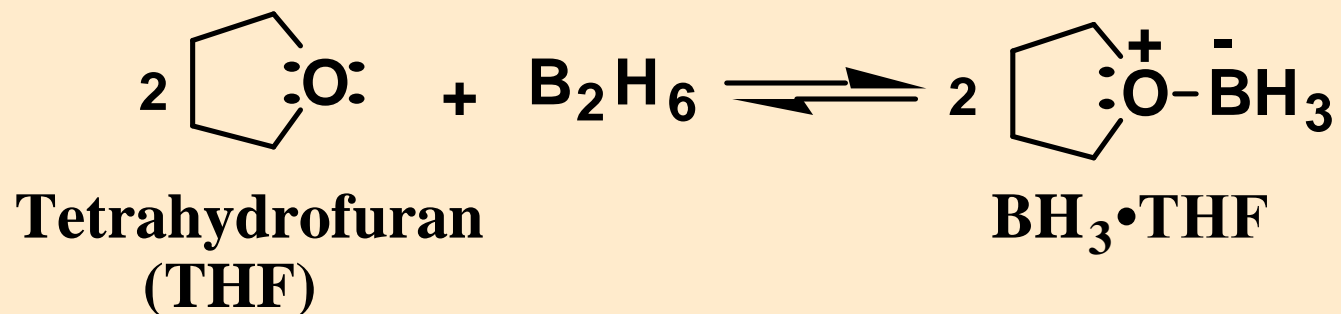


- u Borane dimerizes to diborane, B_2H_6



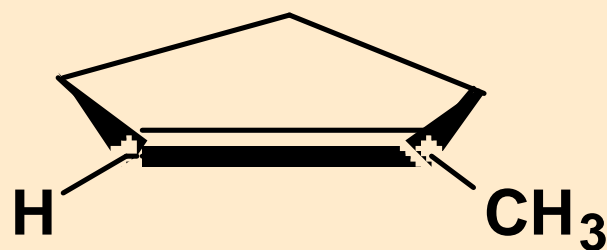
6 Hydroboration/Oxidation

- u Borane forms a stable complex with ethers such as THF. The reagent is used most often as a commercially available solution of BH_3 in THF

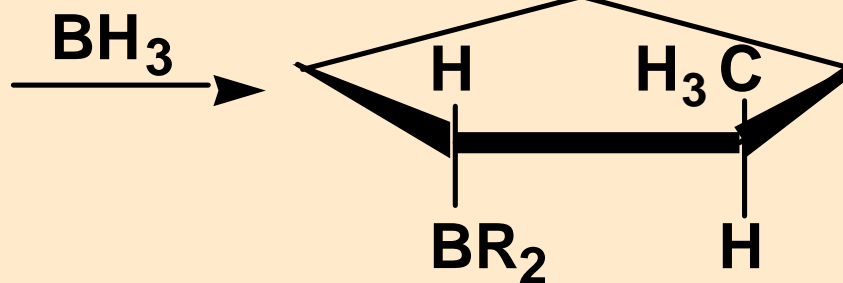


6 Hydroboration/Oxidation

- u Hydroboration is both regioselective (boron to the less hindered carbon) and stereoselective (syn addition)



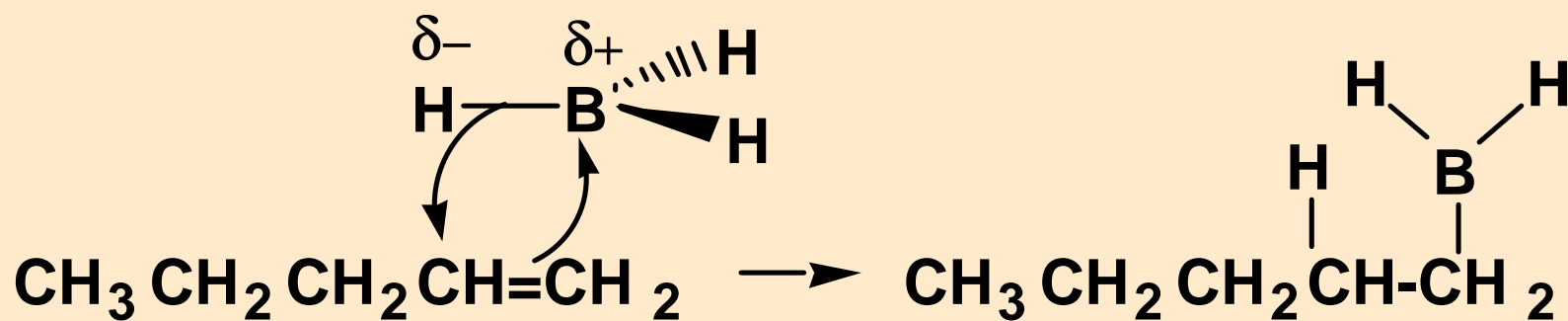
1-Methylcyclopentene



(Syn addition of BH_3)
(R = 2-methylcyclopentyl)

6 Hydroboration/Oxidation

- u Mechanism involves concerted regioselective and stereoselective addition of B and H to the carbon-carbon double bond

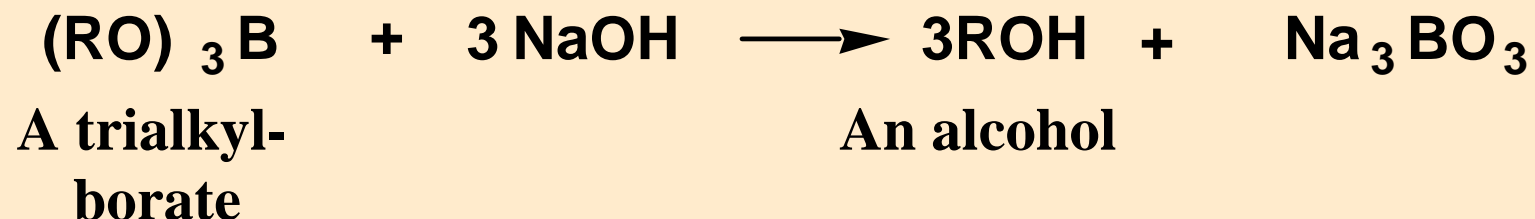


Bond breaking and bond forming occur simultaneously

Boron adds to the less substituted carbon of the double bond

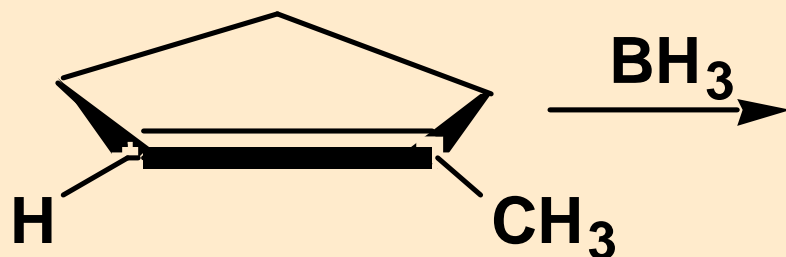
6 Hydroboration/Oxidation

- u **Trialkylboranes are rarely isolated. Oxidation with alkaline hydrogen peroxide gives an alcohol and sodium borate**

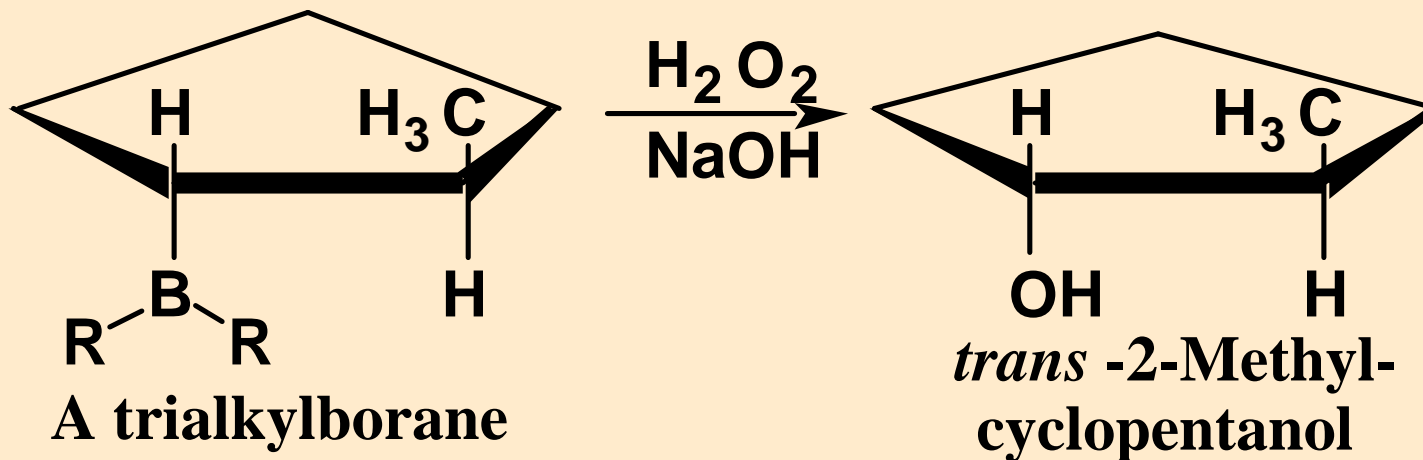


- u **The result of hydroboration/oxidation is regioselective and stereoselective hydration of a carbon-carbon double bond**

6 Hydroboration/Oxidation



1-Methylcyclopentene



A trialkylborane
(R = 2-methylcyclopentyl)

trans -2-Methyl-
cyclopentanol

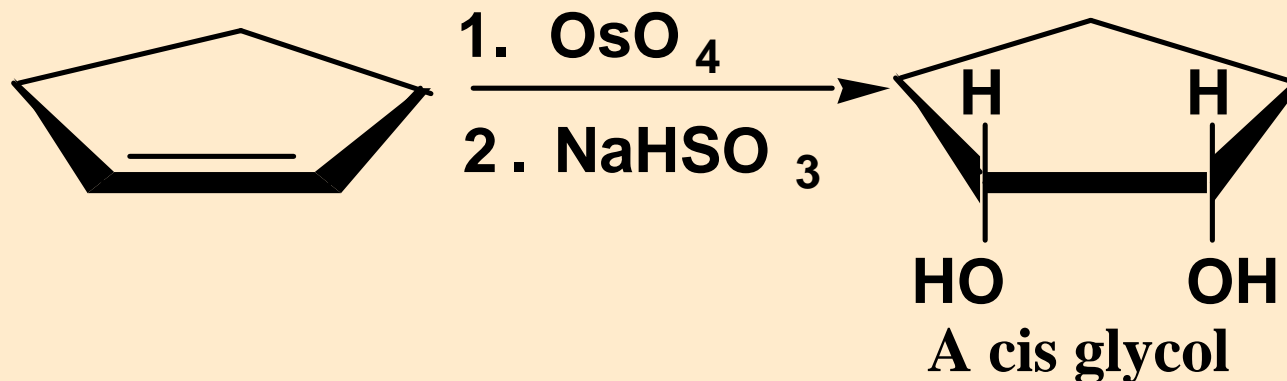
6 Oxidation/Reduction

- u **Oxidation:** the loss of electrons
- u **Reduction:** the gain of electrons

- u **Recognize using a balanced half-reaction**
 1. write a half-reaction showing one reactant and its product(s)
 2. complete a material balance. Use H_2O and H^+ in acid solution; use H_2O and OH^- in basic solution
 3. complete a charge balance using electrons, e^-

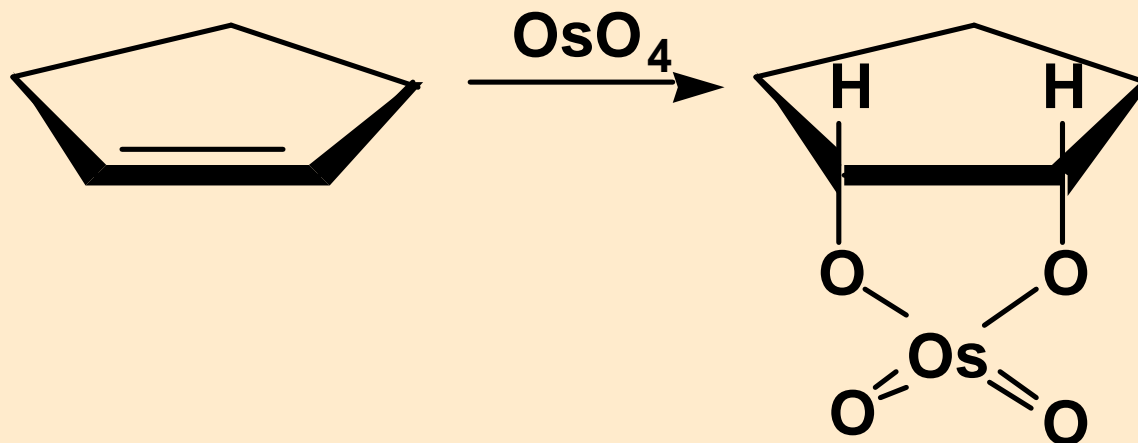
6 Oxidation with OsO_4

- u Oxidation by OsO_4 converts an alkene to a glycol, a compound with $-\text{OH}$ groups on two adjacent carbons
 - oxidation is syn stereoselective



6 Oxidation with OsO_4

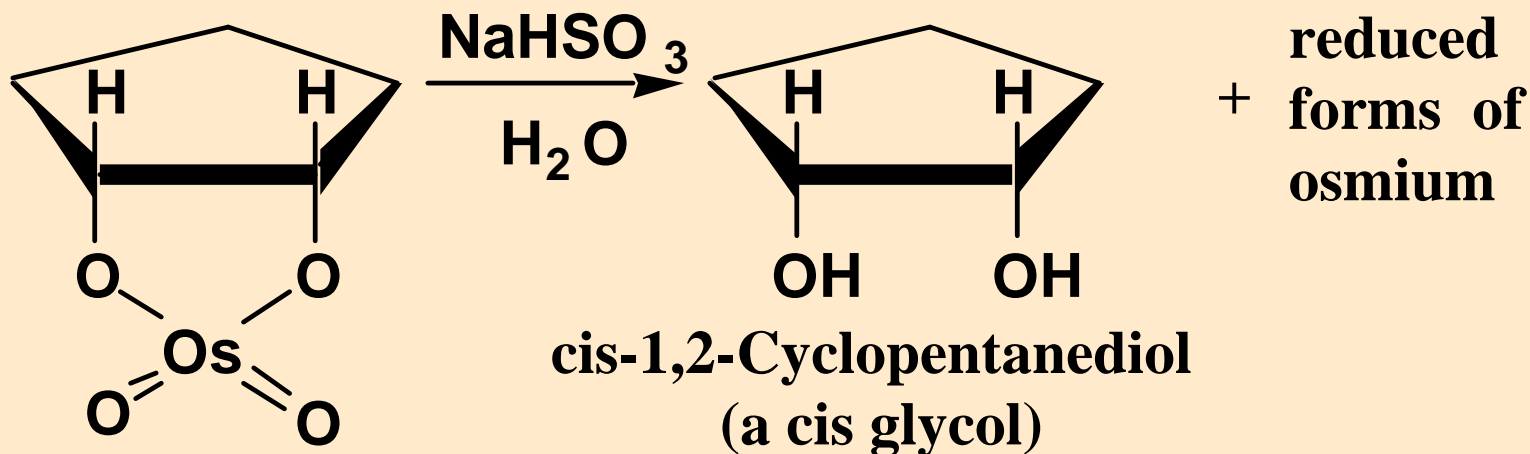
- u Intermediate is a cyclic osmic ester containing a five-membered ring



(A cyclic osmate ester)

6 Oxidation with OsO_4

- u Reduction of the osmic ester with NaHSO_3 gives the glycol and a reduced form of osmium

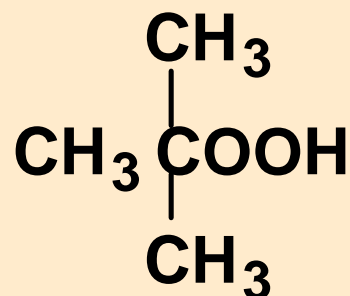


6 Oxidation with OsO_4

- u OsO_4 is both expensive and highly toxic
- u It is used in catalytic amounts with another oxidizing agent to reoxidize its reduced forms and, thus, recycle OsO_4



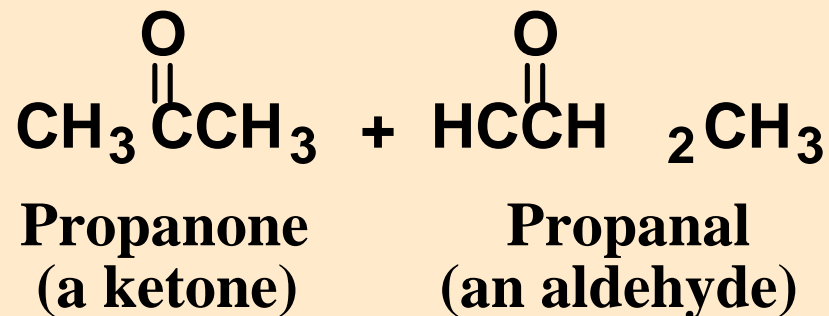
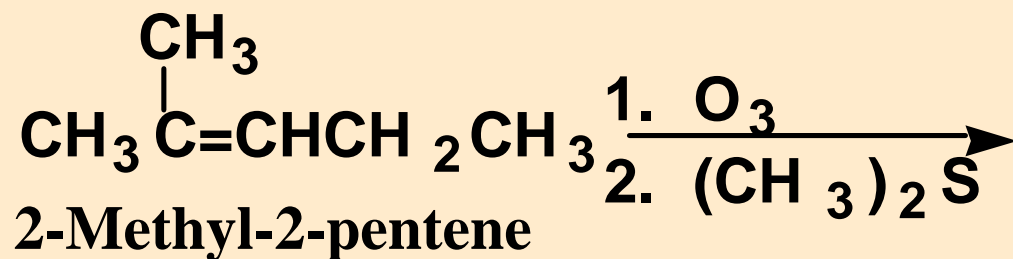
Hydrogen
peroxide



tert -Butyl hydroperoxide
(t-BuOOH)

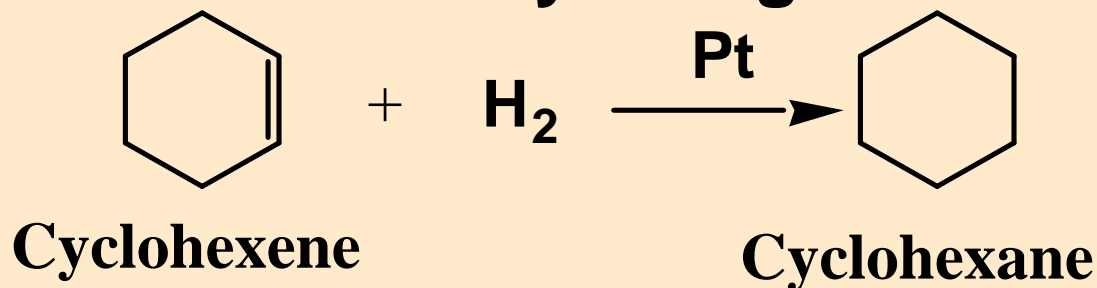
6 Oxidation with O₃

- u Treatment of an alkene with ozone followed by a weak reducing agent cleaves the C=C and forms two carbonyl groups in its place



6 Reduction of Alkenes

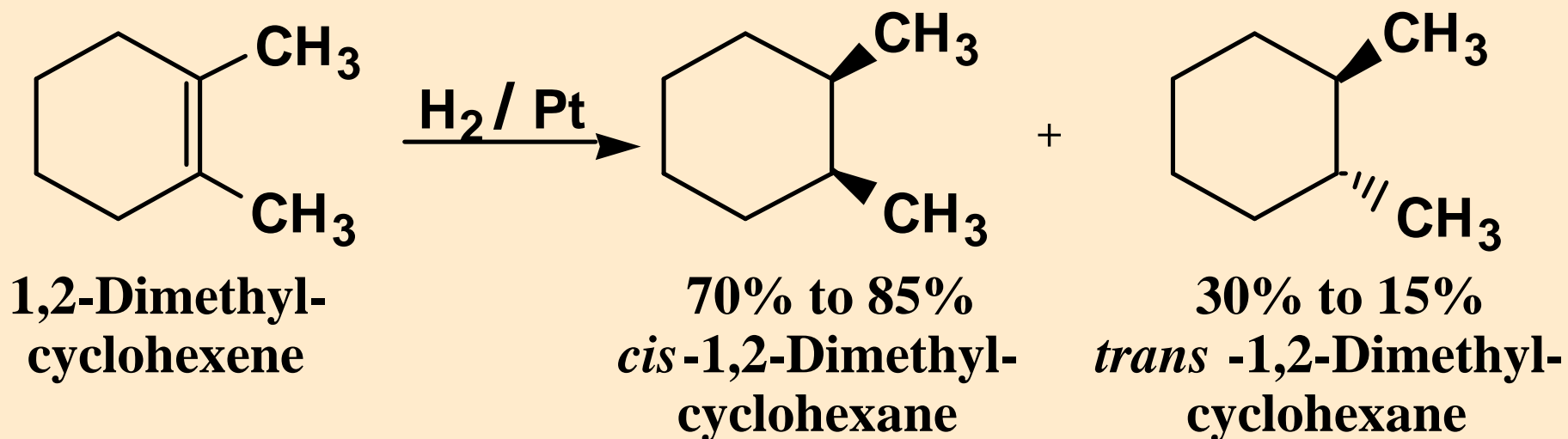
- u Most alkenes react with H_2 in the presence of a transition metal catalyst to give alkanes



- commonly used catalysts are Pt, Pd, Ru, and Ni
- u The process is called catalytic reduction or, alternatively, catalytic hydrogenation

6 Reduction of Alkenes

u Most common pattern is syn stereoselectivity



6 Reduction of Alkenes

u Mechanism of catalytic hydrogenation

- H_2 is absorbed on the metal surface with formation of metal-hydrogen bonds
- the alkene is also absorbed with formation of metal-carbon bonds
- a hydrogen atom is transferred to the alkene forming one new C-H bond
- a second hydrogen atom is transferred forming the second C-H bond

6 ΔH° of Hydrogenation

- u In catalytic hydrogenation, there is net conversion of one pi bond to one sigma bond
- u Catalytic hydrogenation of an alkene is exothermic
- u Heats of hydrogenation depend on the degree of substitution of the carbon-carbon double bond

6 ΔH° of Hydrogenation

Name	Structural Formula	ΔH° (kcal/mol)
ethylene	$\text{CH}_2 = \text{CH}_2$	-32.8
propene	$\text{CH}_3 \text{CH} = \text{CH}_2$	-30.1
1-butene	$\text{CH}_3 \text{CH}_2 \text{CH} = \text{CH}_2$	-30.3
cis-2-butene	$\text{CH}_3 \text{CH} = \text{CHCH}_3$	-28.6
trans-2-butene	$\text{CH}_3 \text{CH} = \text{CHCH}_3$	-27.6
2-methyl-2-butene	$(\text{CH}_3)_2 \text{C} = \text{CHCH}_3$	-26.9
2,3-dimethyl-2-butene	$(\text{CH}_3)_2 \text{C} = \text{C}(\text{CH}_3)_2$	-26.6

6 ΔH° of Hydrogenation

- u The greater the degree of substitution of a double bond, the lower its heat of hydrogenation
 - the greater the degree of substitution, the more stable the double bond

- u The heat of hydrogenation of a *trans* alkene is lower than that of the isomeric *cis* alkene
 - a *trans* alkene is more stable than its isomeric *cis* alkene. The difference is due to nonbonded interaction strain in the *cis* alkene

6 ΔH° of Hydrogenation

cis -2-Butene
(less stable)

trans-2-Butene
(more stable)

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6 Conjugated Dienes

- u **Conjugated diene:** the double bonds are separated by one single bond



1,3-Pentadiene
(a conjugated diene)



1,4-Pentadiene
(an unconjugated diene)



1,2-Pentadiene
(a cumulated diene)

6 Conjugated Dienes

- u From heats of hydrogenation, we determine that conjugated dienes are more stable than isomeric unconjugated dienes by approximately 3.5 to 4.0 kcal/mol

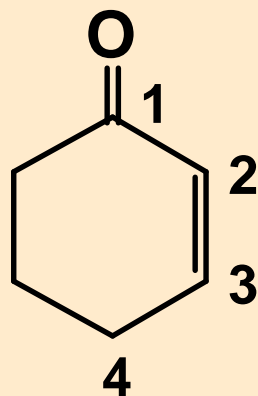
Name	Structural Formula	ΔH° (kcal/mol)
1-butene	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	-30.3
1,3-butadiene	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	-56.5

6 Conjugated Dienes

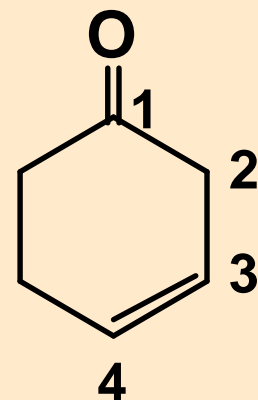
- u the extra stability of conjugated dienes arises because of the additional delocalization of electron density over the four parallel 2p atomic orbitals

6 Conjugated Dienes

- u Compounds containing conjugated carbon-carbon and carbon-oxygen double bonds are also more stable than their unconjugated isomers



2-Cyclohexenone
(more stable)



3-Cyclohexenone
(less stable)

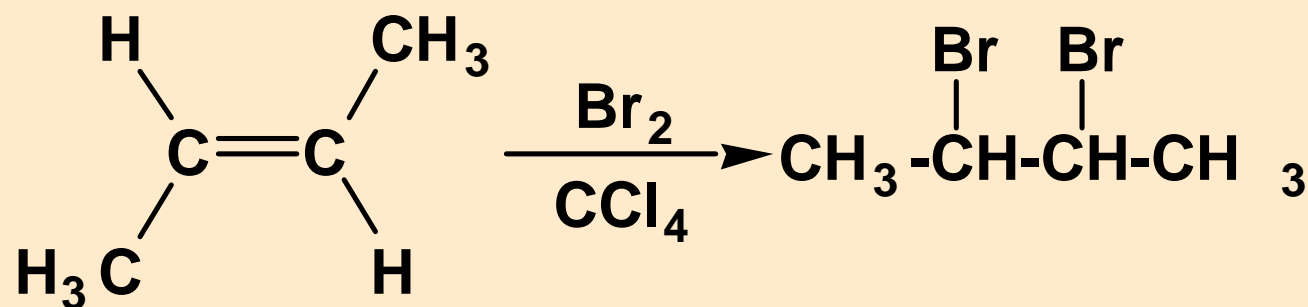
6 Reaction Stereochemistry

- u In several of the reactions presented in this chapter, stereocenters are created

- u Where one or more stereocenters are created, is the product
 - one enantiomer and, if so, which one?
 - a pair of enantiomers?
 - a meso compound?
 - a mixture of stereoisomers?
 - or what?

6 Reaction Stereochemistry

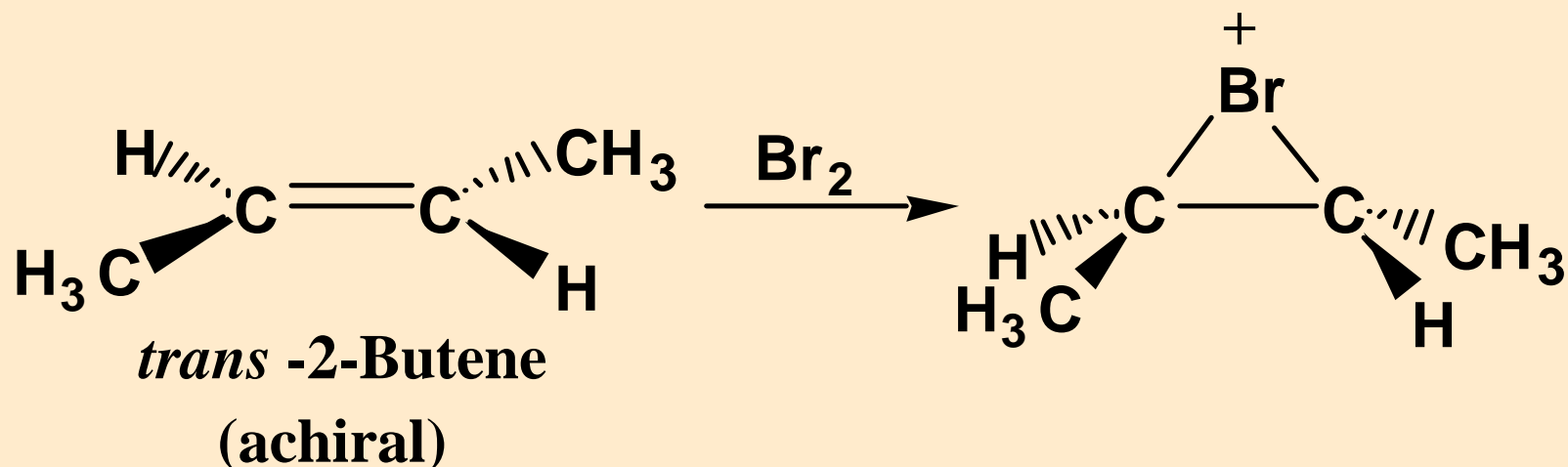
- u Which of the three possible stereoisomers of 2,3-dibromobutane are formed in the addition of bromine to trans-2-butene?



- the three possible stereoisomers for this compound are a pair of enantiomers and a meso compound

6 Reaction Stereochemistry

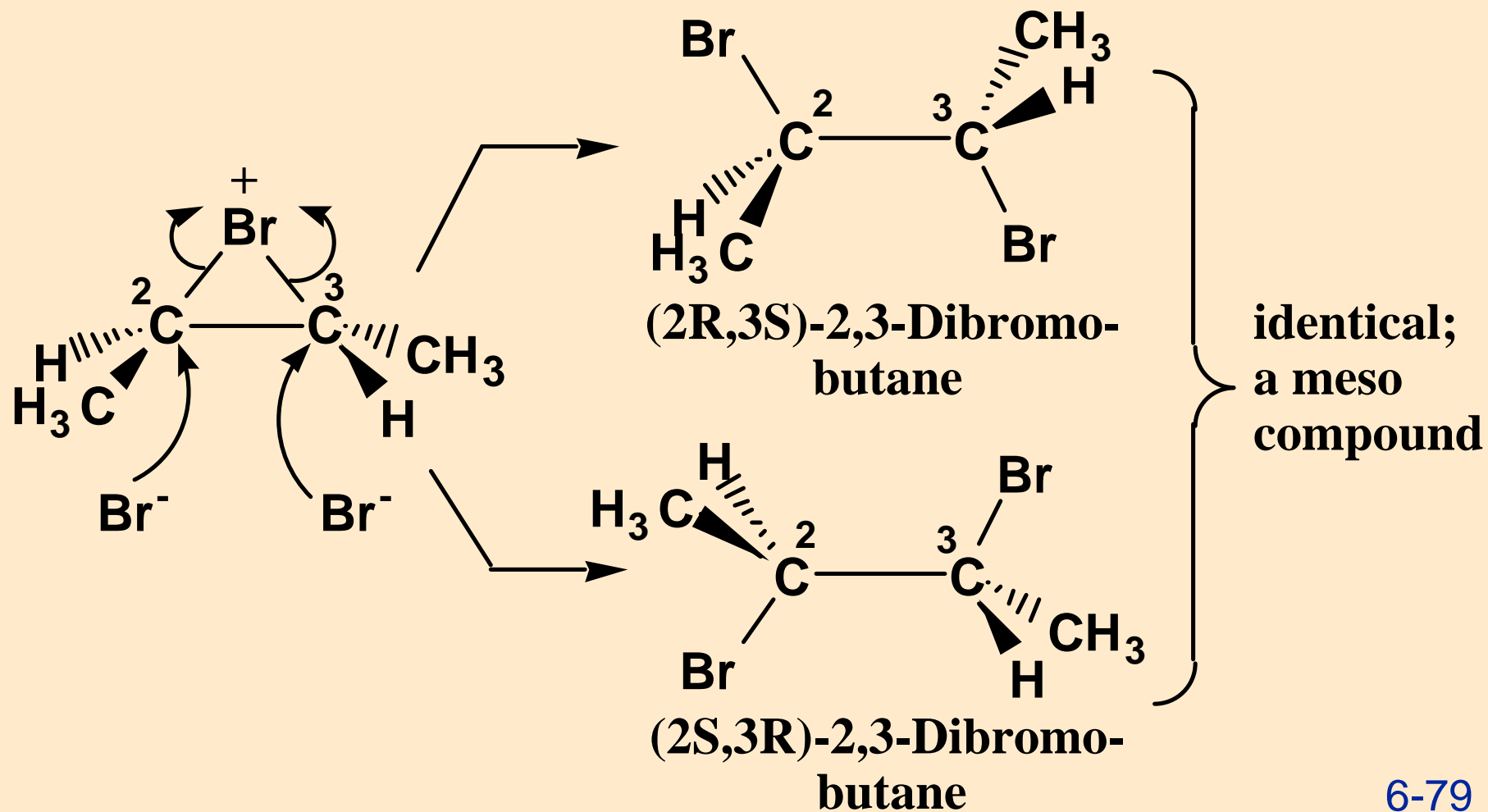
- u Reaction of bromine with the alkene forms a cyclic bromonium ion intermediate



- u which is then opened by attack of bromide ion from the side opposite the bromine bridge

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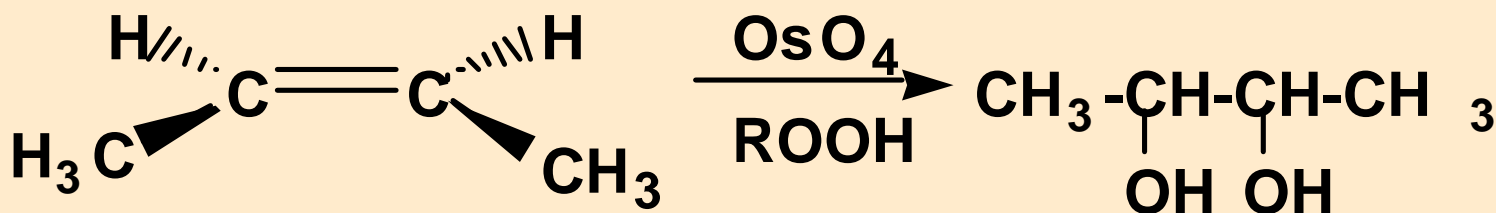
6 Reaction Stereochemistry



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6 Reaction Stereochemistry

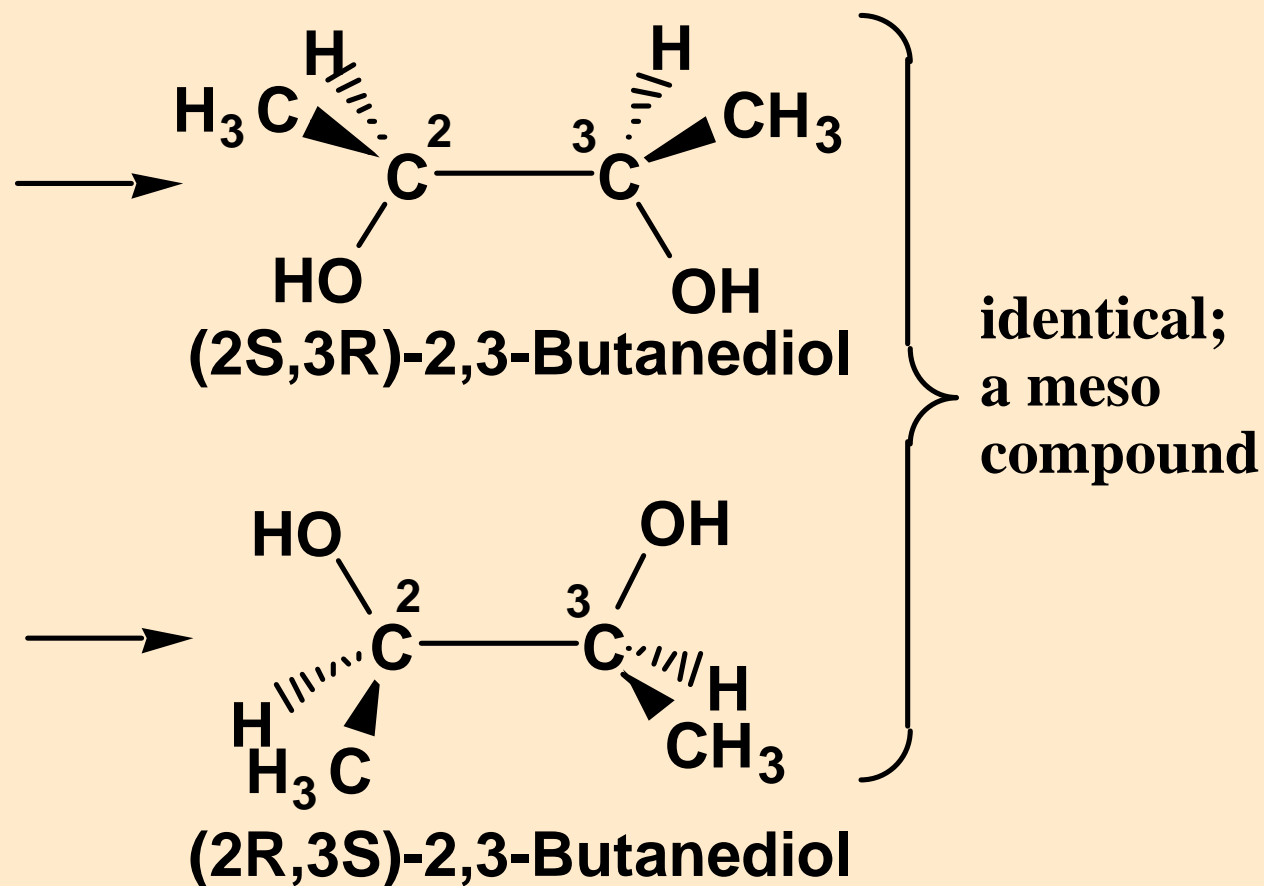
- u How many and what kind of stereoisomers are formed in the oxidation of *cis*-2-butene by OsO_4 ?



cis-2-Butene
(achiral)

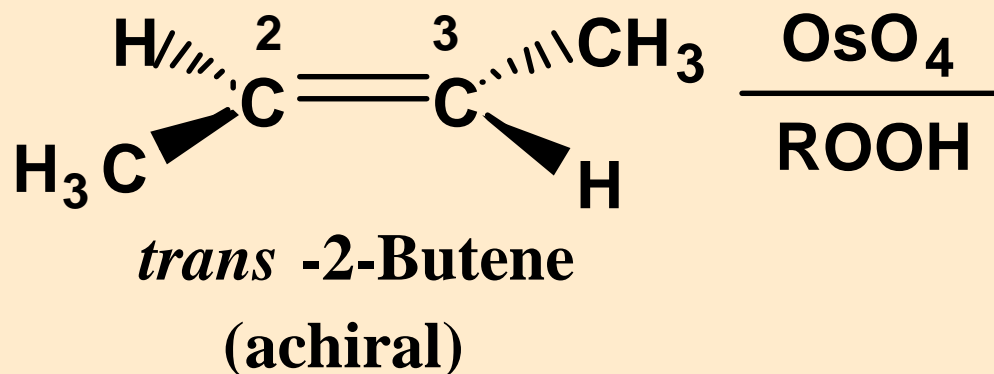
three stereoisomers are possible for 2,3-butanediol; a meso compound and a pair of enantiomers

6 Reaction Stereochemistry

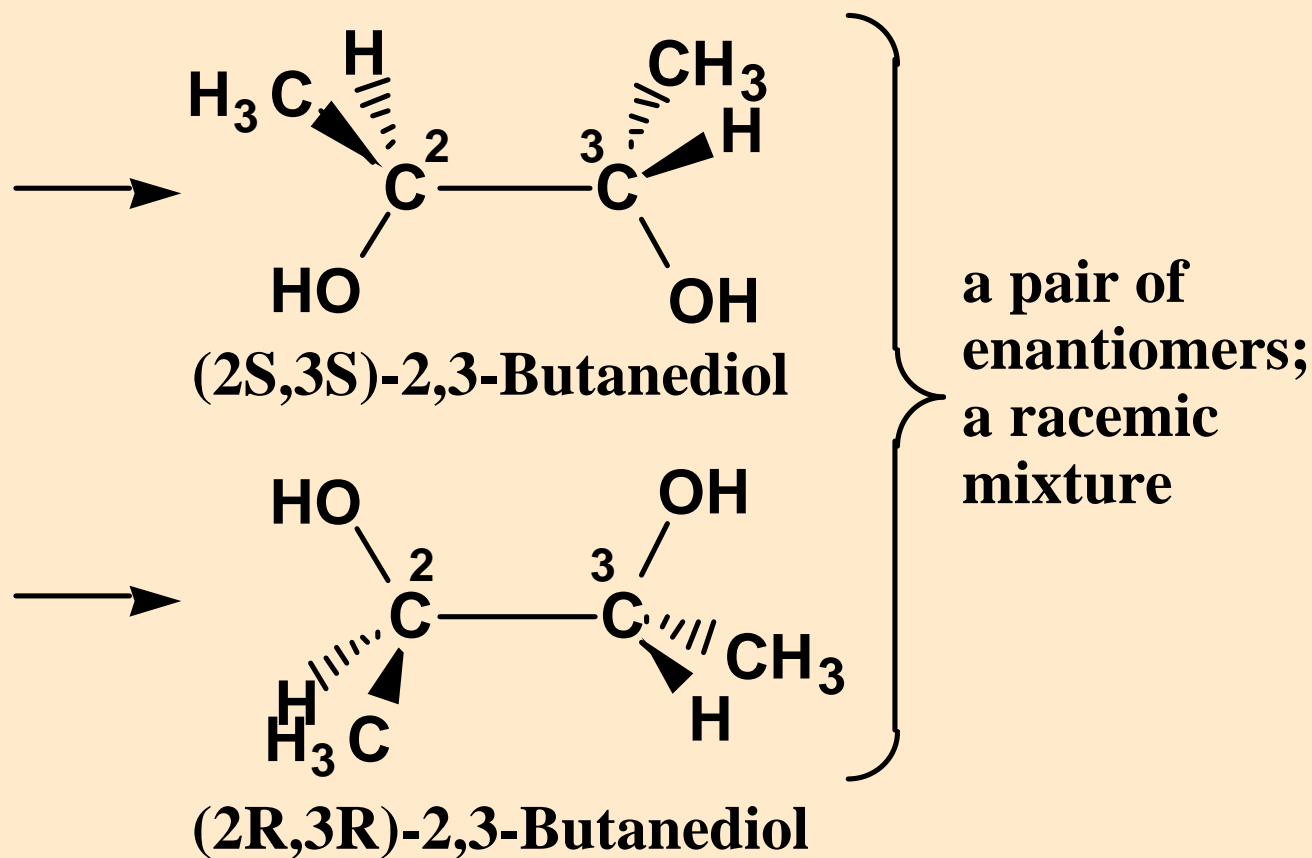


6 Reaction Stereochemistry

- u How many and what kind of stereoisomers are formed in the oxidation of *trans*-2-butene by OsO_4 ?



6 Reaction Stereochemistry



6 Reaction Stereochemistry

- u **Enantiomerically pure products can never be formed from achiral starting materials and reagents**

- u **An enantiomerically pure product can be generated in a reaction if at least one of the reactants is enantiomerically pure, or if the reaction is carried out in an achiral environment**

6

Alkenes II

End Chapter 6

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