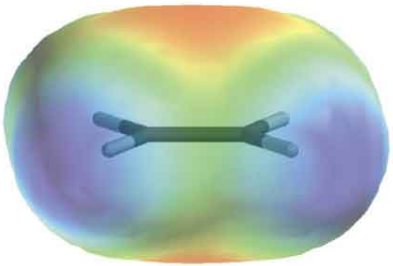
DAMIETTA UNIVERSITY

CHEM-103:

BASIC ORGANIC CHEMISTRY

LECTURE 5

Dr Ali El-Agamey

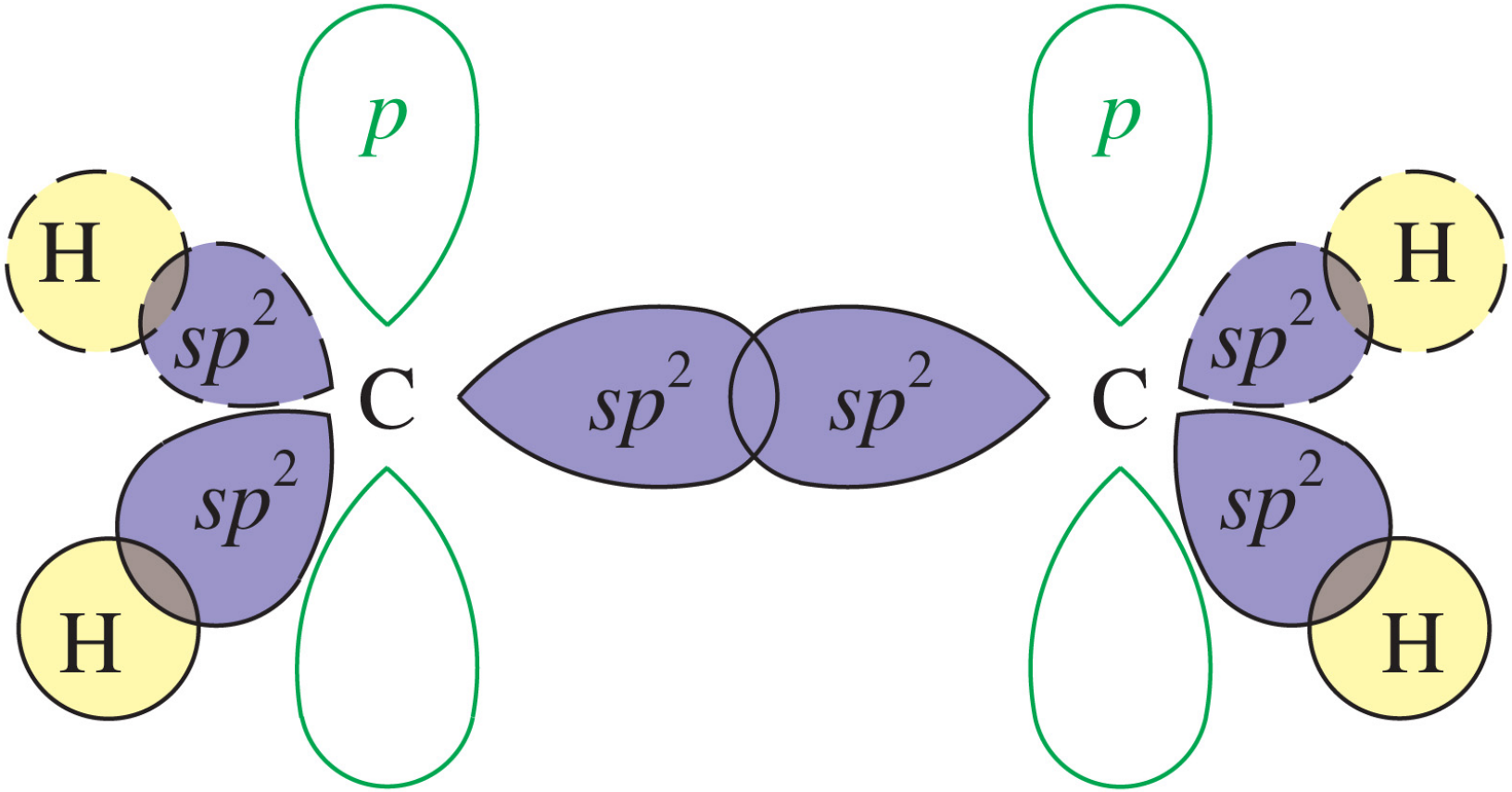


Structure and Synthesis of Alkenes

Introduction

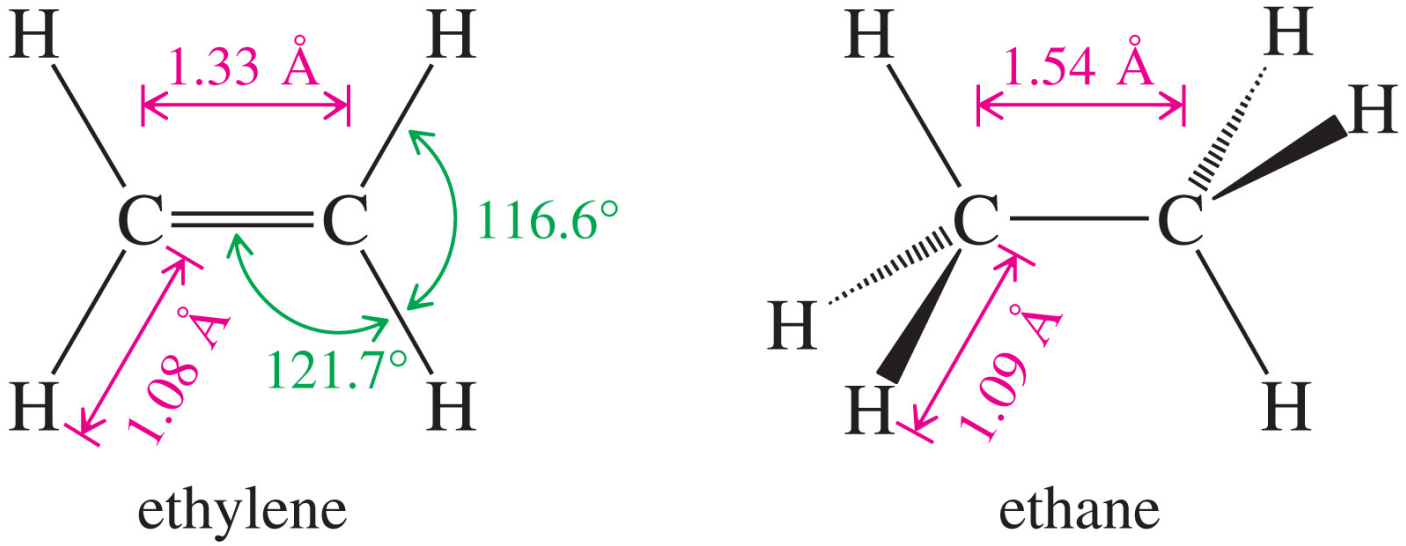
- Alkenes are hydrocarbon with carbon-carbon double bonds.
- Alkenes are also called **olefins**, meaning “oil-forming gas”.
- The **functional group** of alkenes is the **carbon-carbon double bond**, which is reactive.

Sigma Bonds of Ethylene



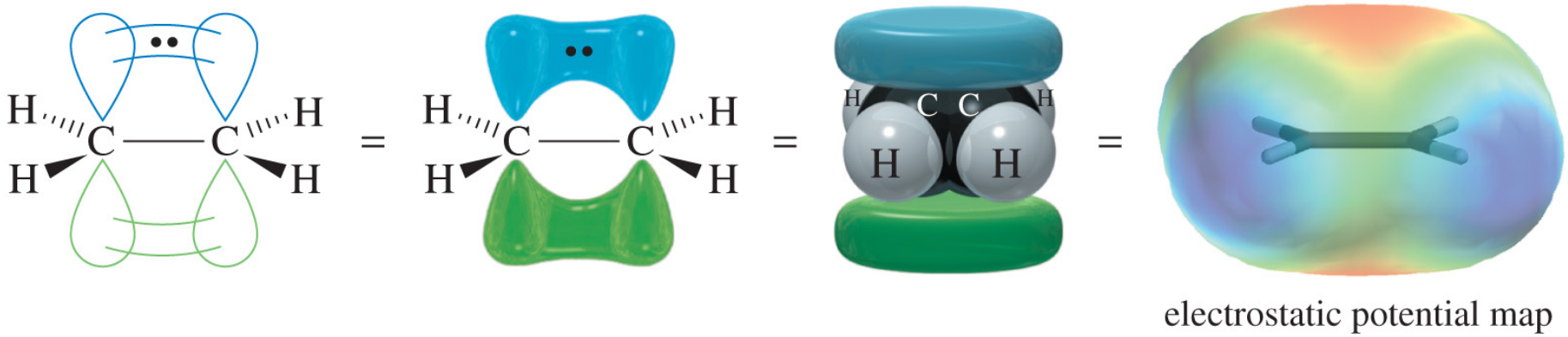
sigma bonding orbitals of ethylene

Bond Lengths and Angles



- sp^2 hybrid orbitals have **more *s* character** than the sp^3 hybrid orbitals.
- **Pi overlap brings carbon atoms closer** shortening the C—C bond from 1.54 Å in alkanes down to 1.33 Å in alkenes.

Pi Bonding in Ethylene



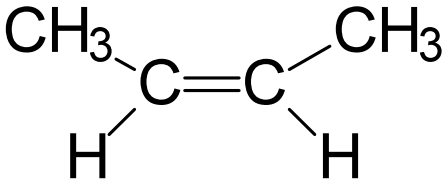
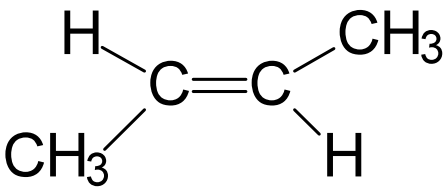
- The pi bond in ethylene is formed by overlap of the unhybridized *p* orbitals of the sp^2 hybrid carbon atoms.
- Each carbon has one unpaired electron in the *p* orbital.
- This **overlap** requires the two ends of the molecule to be **coplanar**.

Physical Properties of Alkenes

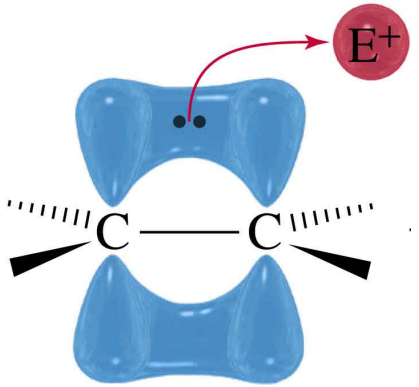
- Low boiling points, increasing with mass.
- Branched alkenes have lower boiling points.
- Less dense than water.
- Slightly polar:
  - Pi bond is polarizable, so instantaneous dipole–dipole interactions occur.
  - **Alkyl groups are electron-donating** toward the pi bond, so may have a small dipole moment.

Disubstituted Isomers

- Stability: **cis < geminal < trans isomer**
- The **less stable** isomer has a **higher exothermic heat of hydrogenation**.

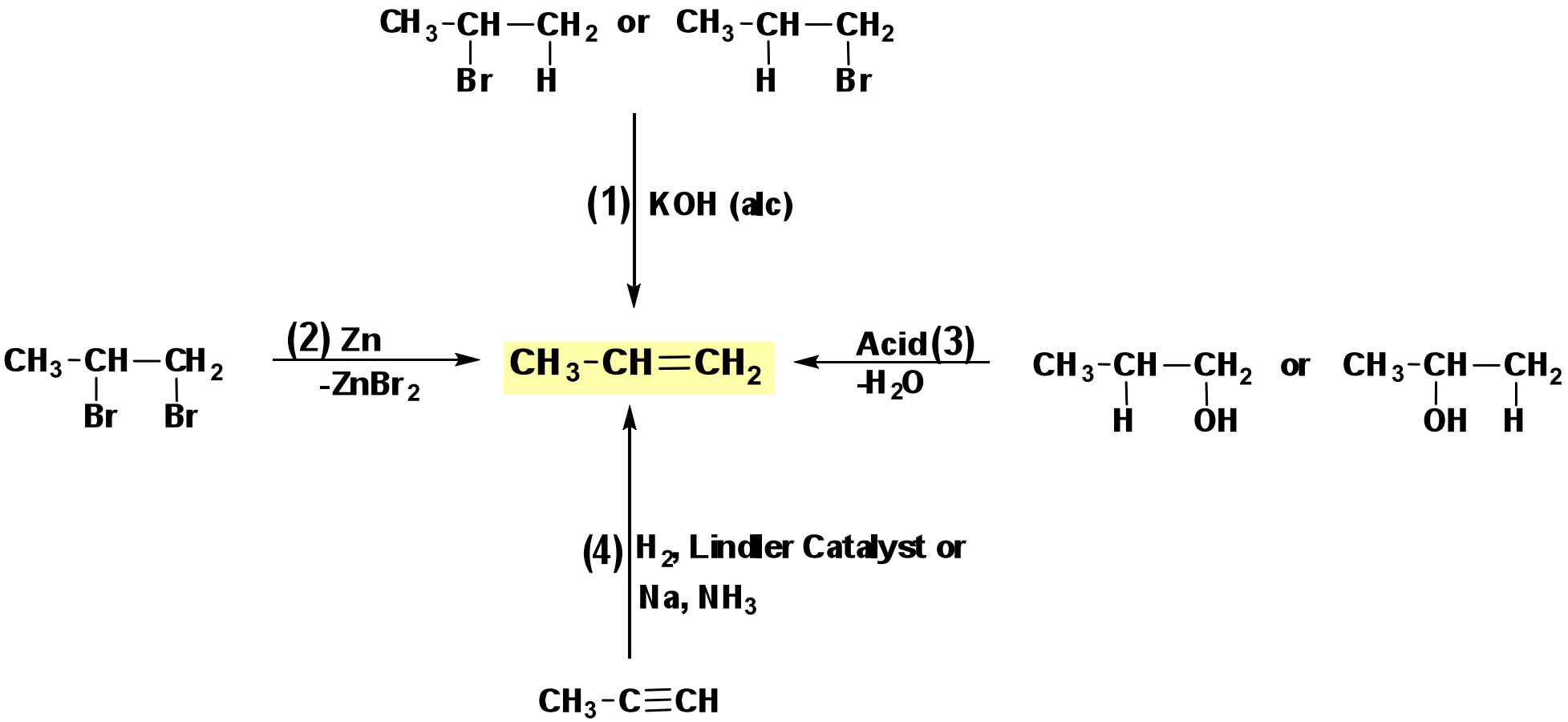
cis-2-butene		-120 kJ
iso-butene	$(CH_3)_2C{=}CH_2$	-117 kJ
trans-2-butene		-116 kJ

Organic Chemistry, 7th Edition
L. G. Wade, Jr.



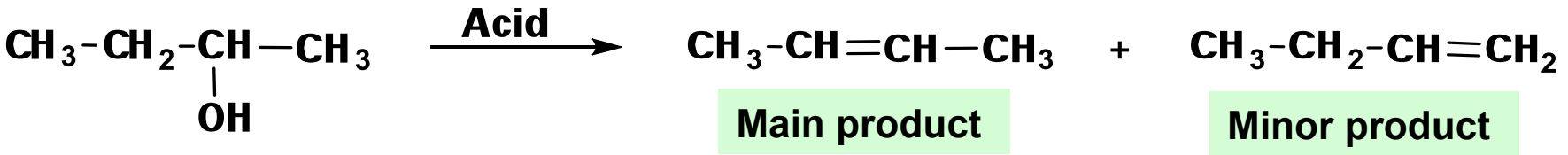
Syntheses and Reactions of Alkenes

Preparation of Alkenes



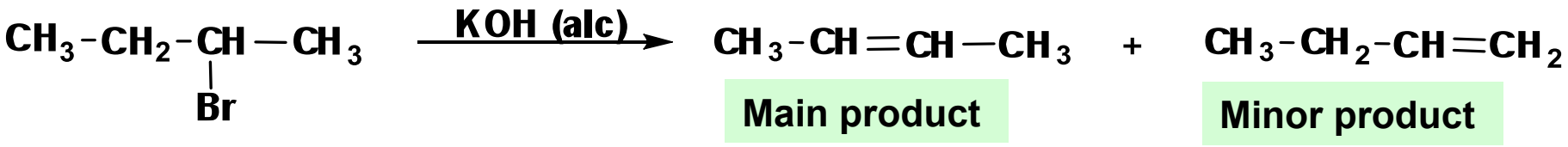
(1) Dehydrohalogenation of alkyl halide; (2) Dehalogenation of vicinal dihalides; (3) Dehydration of alcohols; (4) Reduction of Alkynes

Preparation of Alkenes



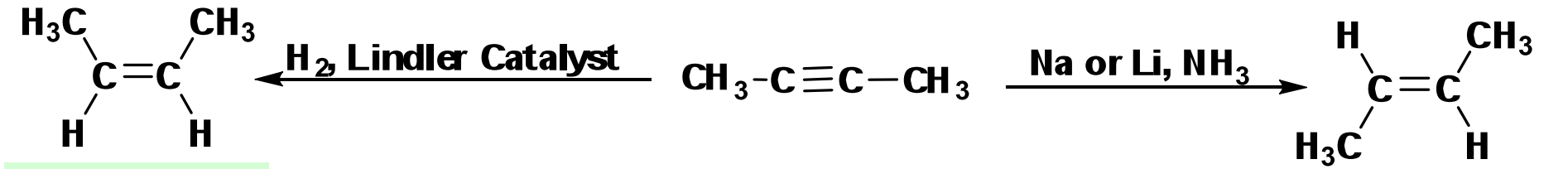
Main product

Minor product



Main product

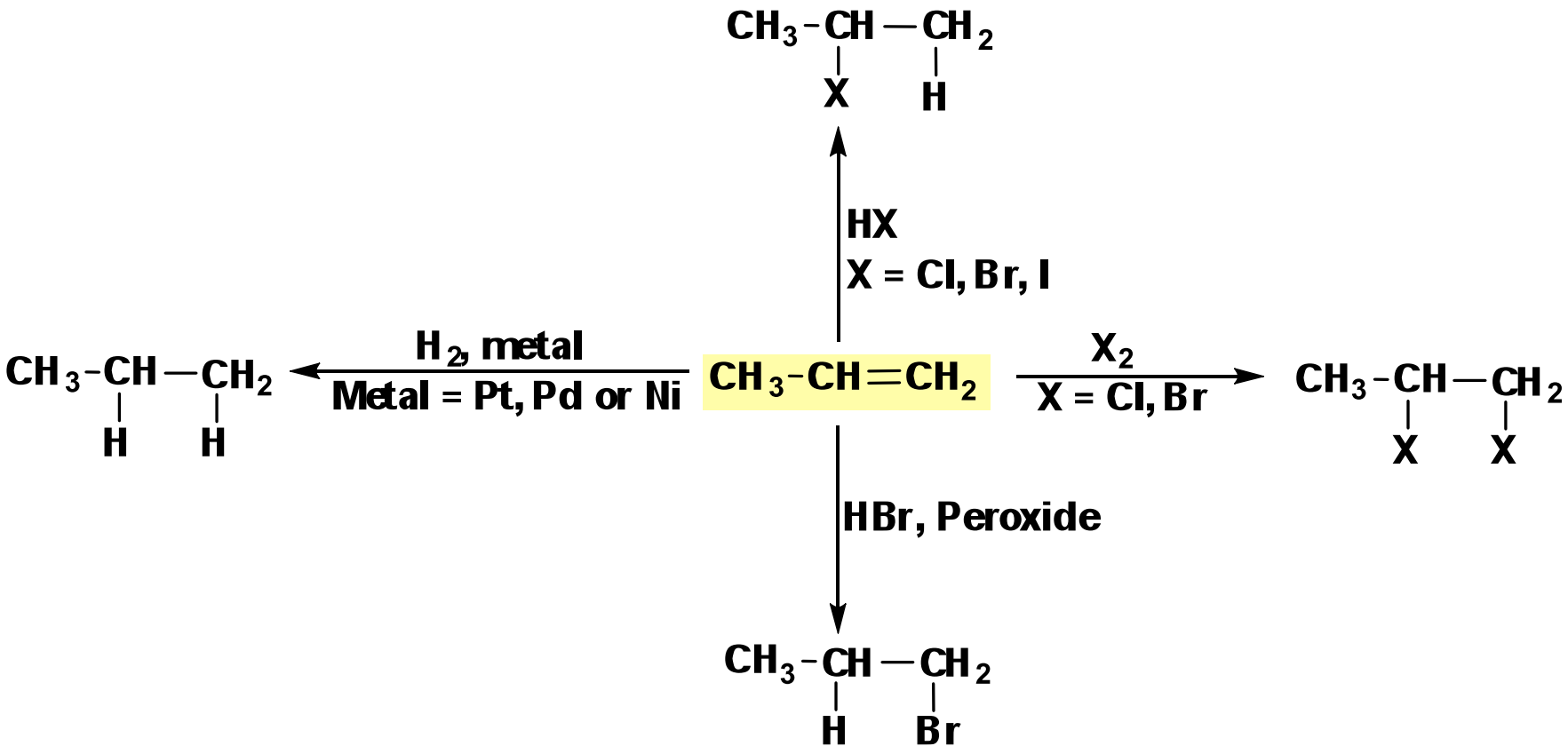
Minor product



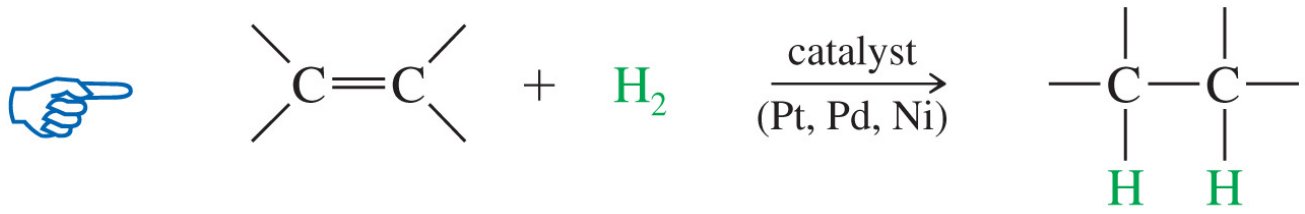
cis-But-2-ene

trans-But-2-ene

(1) Reactions of Alkenes



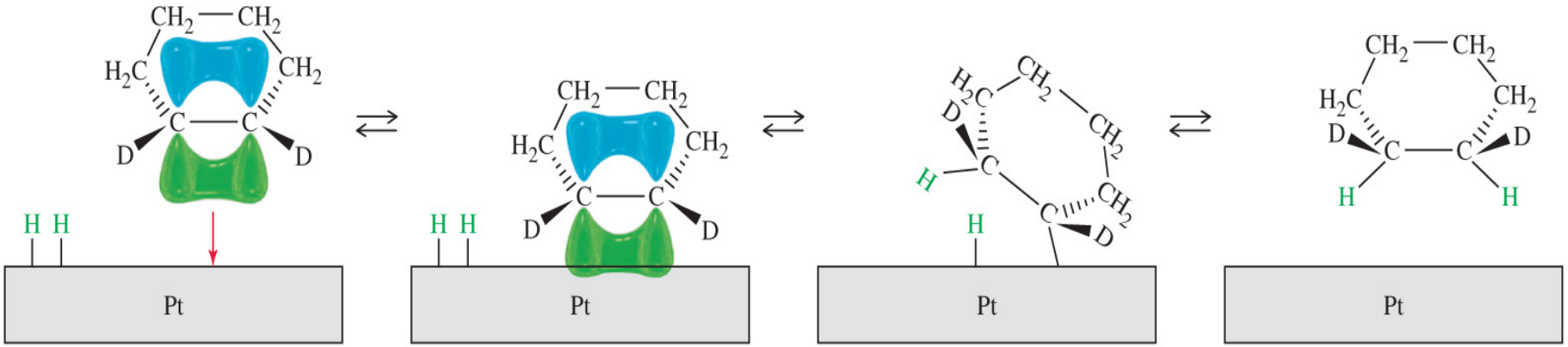
Hydrogenation of Alkenes



Example

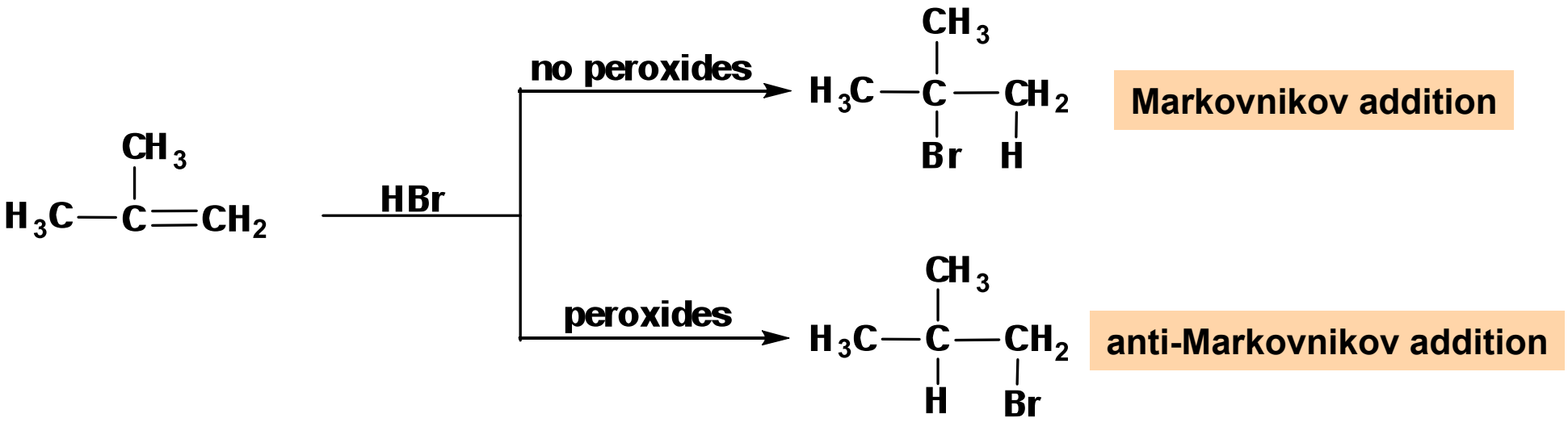
- Hydrogen (H_2) can be added across the double bond in a process known as ***catalytic hydrogenation***.
- The reaction **only** takes place if a catalyst is used. The most commonly used catalysts are palladium (Pd), platinum (Pt), and nickel (Ni), but there are other metals that work just as well.
- **Syn addition** of hydrogen.

Mechanism of Catalytic Hydrogenation



- The hydrogen and the alkene are **adsorbed** on the metal surface.
- Once adsorbed, the hydrogens insert across **the same face of the double bond** and the reduced product is released from the metal.
- The reaction has a **syn stereochemistry** since both hydrogens will add to the **same side** of the double bond.

Influence of peroxides



Problems

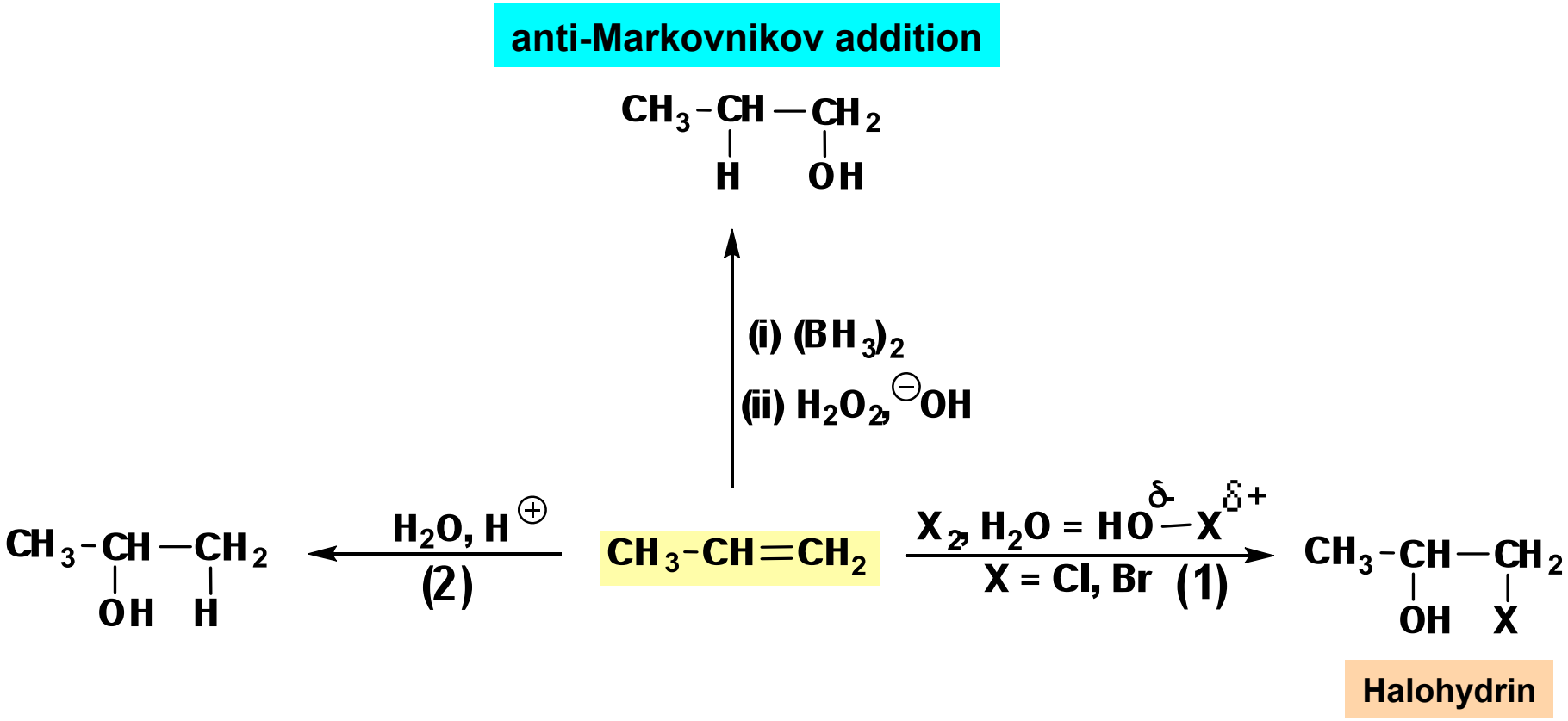
Show how you would accomplish the following synthetic conversions:

(a) Convert 1-methylcyclohexene to 1-bromo-1-methylcyclohexane.

(b) Convert 1-methylcyclohexene to 1-bromo-2-methylcyclohexane.

(c) Convert 1-methylcyclohexanol to 1-bromo-2-methylcyclohexane.

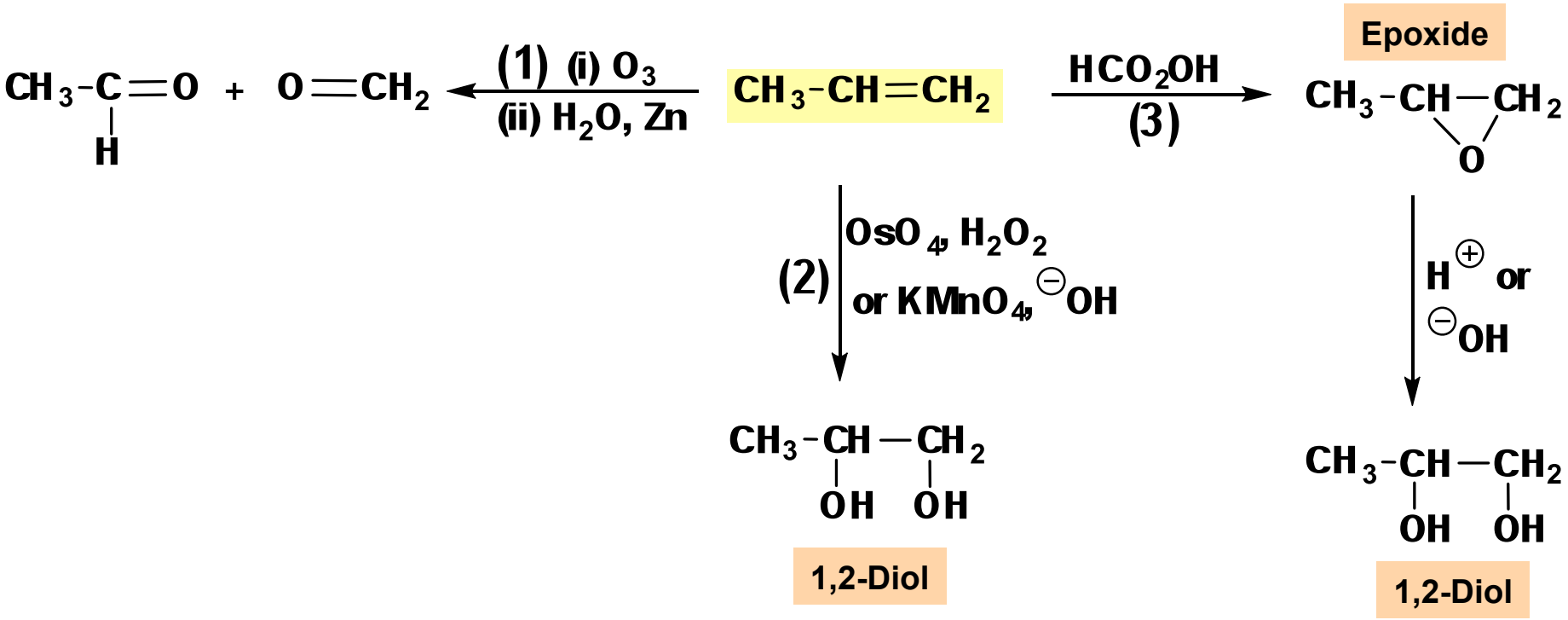
(2) Reactions of Alkenes



$(BH_3)_2$ is called diborane

(1) Halohydrin formation; (2) Hydration (addition of water)

(3) Reactions of Alkenes

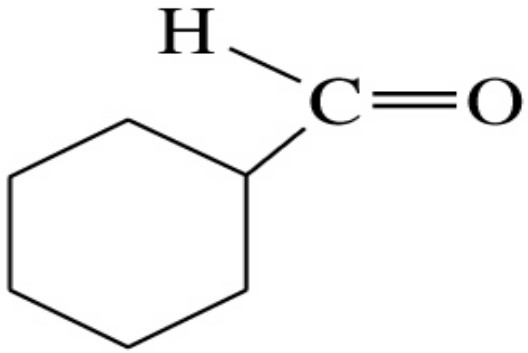


(1) Ozonolysis; (2) Hydroxylation; (3) Epoxidation

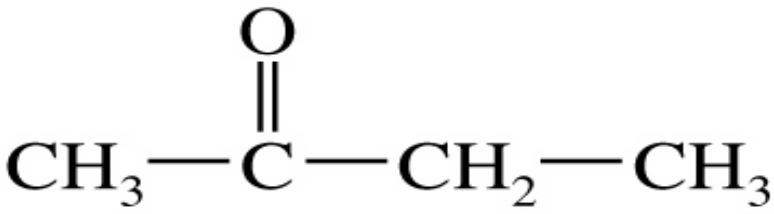
HCO_2OH is called peroxyacid

Solved Problem

Ozonolysis of an unknown alkene gives an equimolar mixture of cyclohexanecarbaldehyde and 2-butanone. **Determine the structure of the original alkene.**



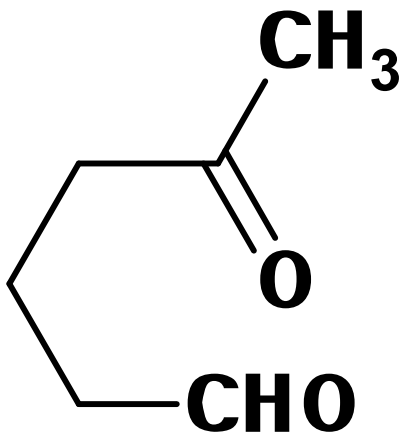
cyclohexanecarbaldehyde



2-butanone

Problem

Ozonolysis of an unknown alkene gives compound A.
Determine the structure of the original alkene.



A

Homework

(1) What are the products of the ozonolysis of (a) 2-hexene (b) 3-hexene.

(2) Ozonolysis of an unknown alkene gives acetone and formaldehyde. **Determine** the structure of the original alkene.

Problems

(1) Show how you would convert 1-methylcyclopentanol to 2-methylcyclopentanol.

(2) Show how you would prepare 1-bromopropane from 2-bromopropane.

(3) Show how you would prepare 1,2-epoxypropane from 2-propanol.