Organic Chemistry

Oxidation and Reduction

by

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Learning Outcomes

In the end of this chapter, student will have the ability to:

- Define oxidation and reduction
- Describe oxidation and reduction reaction of alkenes, alkynes, alkyl halides and epoxides

Contents

- Oxidizing and reducing agents
- Oxidation and reduction reaction of alkenes, alkynes, alkyl halides and epoxides

Oxidation of Reduction selective reactions

- Alkenes
    - Reduction to alkanes
    - Oxidation
        - to epoxides with peroxyacids
        - to diols with OsO_4 or $KMnO_4^-$
        - Oxidative cleavage to aldehydes/ketones via ozonolysis

- Alkynes
    - Reduction to alkenes and alkynes
    - Oxidative Cleavage

- Alcohol Oxidation with Cr(VI)

- Epoxides and Alkyl Halides with $LiAlH_4$

Oxidation and reduction in terms of electron transfer

Oxidation is the **loss of an electron**

Reduction is the **gain of an electron**

Oxidation occurs when a reactant loses electrons during the reaction.

Reduction occurs when a reactant gains electrons during the reaction.

OIL RIG:

Oxidation **I**s **L**oss of electrons or **O**xidation **I**nvolves **L**oss of electrons

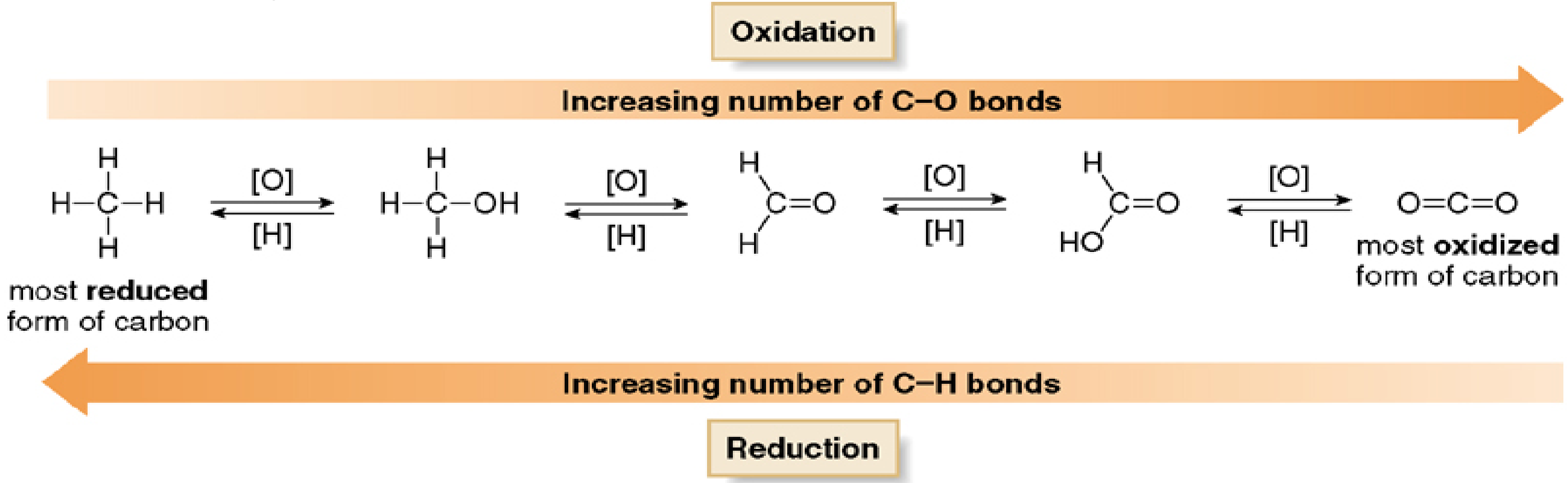
Reduction **I**s **G**ain of electrons or **R**eduction **I**nvolves **G**ain of electrons

Oxidation and Reduction

Introduction

- **Oxidation** results in an increase in the number of C—Z bonds (usually **C—O** bonds) or a decrease in the number of **C—H** bonds.
- **Reduction** results in a decrease in the number of C—Z bonds (usually **C—O** bonds) or an increase in the number of **C—H** bonds.

A general scheme for the oxidation and reduction of a carbon compound



Oxidation

- A reaction that results in a loss of electron density by carbon

Oxidation

- Decreases electron density on carbon by
  - Breaking C-H bond
  - Forming C-O, C-N, or C-X bond

Note: oxidation often adds oxygen; reduction often adds hydrogen

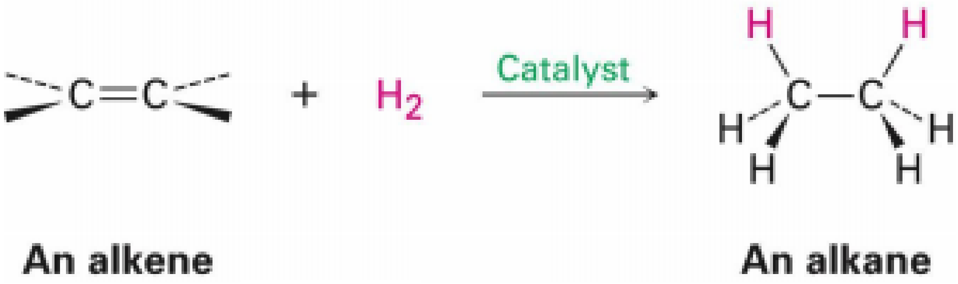
Hydrogenation

- Addition reaction process by which alkenes are reduced to alkanes

Reduction

- Increases electron density on carbon by
  - Forming C-H
  - Breaking C-O, C-N, or C-X bond

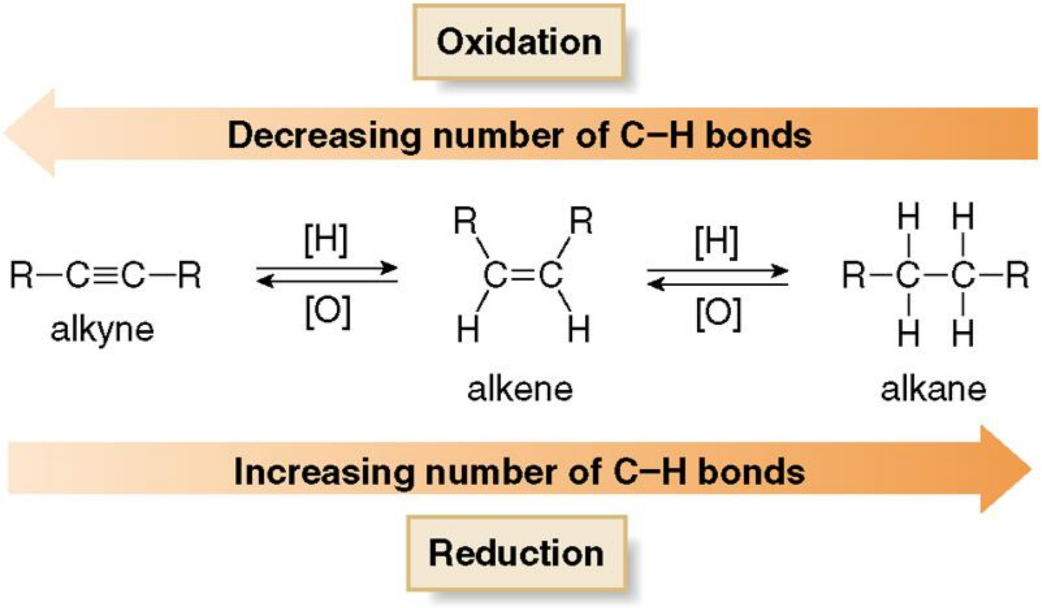
A reduction:



- Sometimes two carbon atoms are involved in a single oxidation or reduction reaction, and the net change in the number of C—H or C—Z bonds at both atoms must be taken into account.

  The conversion of an alkyne to an alkene, or an alkene to an alkane are examples of reduction because each process adds two new C—H bonds to the starting material.

Oxidation and reduction of hydrocarbons

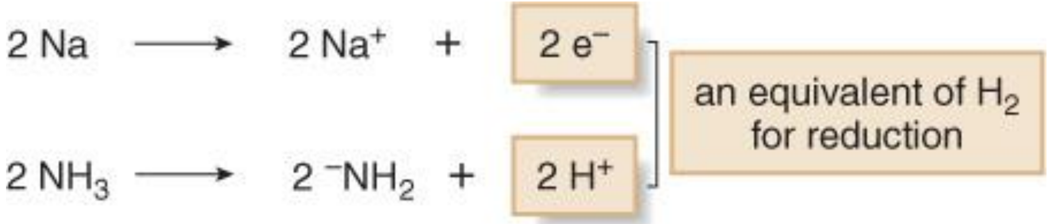


Reducing Agents

Remove oxygen from another substance or give hydrogen to it.

The reactant that contains the element that is oxidized is the reducing agent.

- There are **three types** of reductions differing in how H_2 is added.
- **The simplest** reducing agent is **H_2**. Reductions using H_2 are carried out with a **metal catalyst**.
- **A second way** is to add two protons and two electrons to a substrate—that is, **H_2** = **$2H^+ + 2e^-$**.
  - Reductions of this sort use **alkali metals** as a source of electrons, and **liquid ammonia** as a source of protons.
  - These are called **dissolving metal reductions**.



$$2\,Na \longrightarrow 2\,Na^+ + \boxed{2\,e^-}$$

$$2\,NH_3 \longrightarrow 2\,{}^-NH_2 + \boxed{2\,H^+}$$

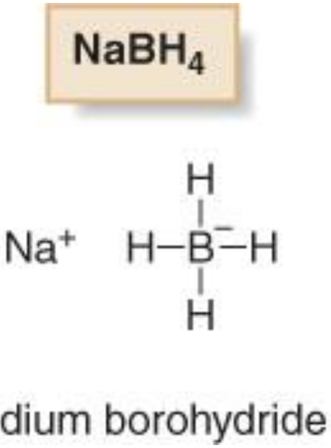
an equivalent of H_2 for reduction

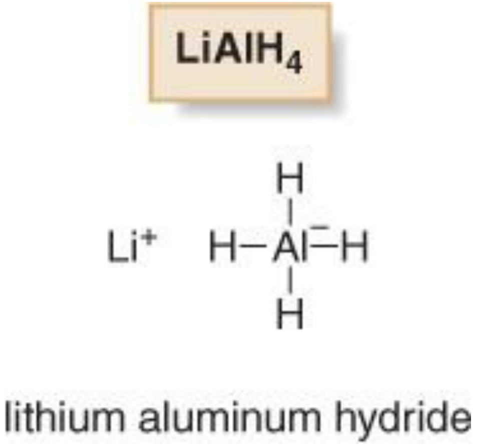
The oxidized substance is always the reducing agent

- **The third way** to add H_2 is to add hydride (H^-) and a proton (H^+).

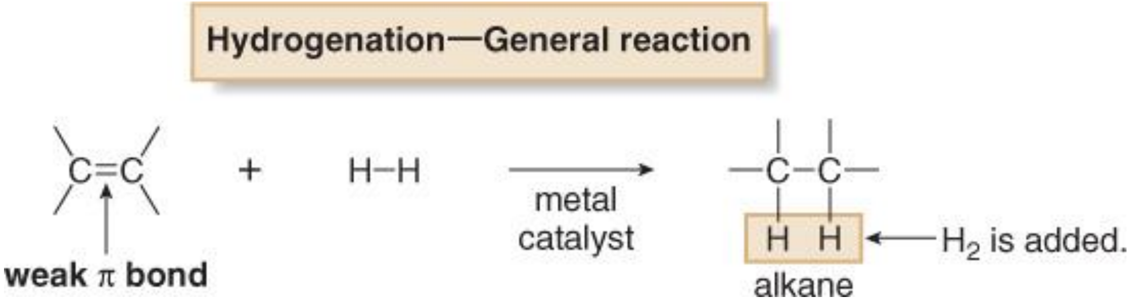
The most common hydride reducing agents contain a hydrogen atom bonded to **boron** (B) or **aluminum** (Al). Simple examples include sodium borohydride (**$NaBH_4$**) and lithium aluminum hydride (**$LiAlH_4$**).

- $NaBH_4$ and $LiAlH_4$ deliver H^- to the substrate, and then a proton is added from H_2O or an alcohol.

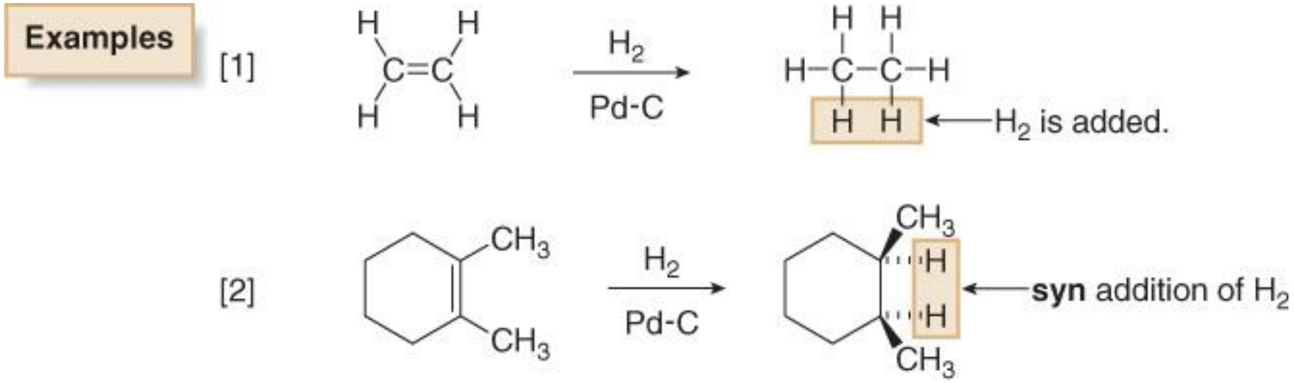


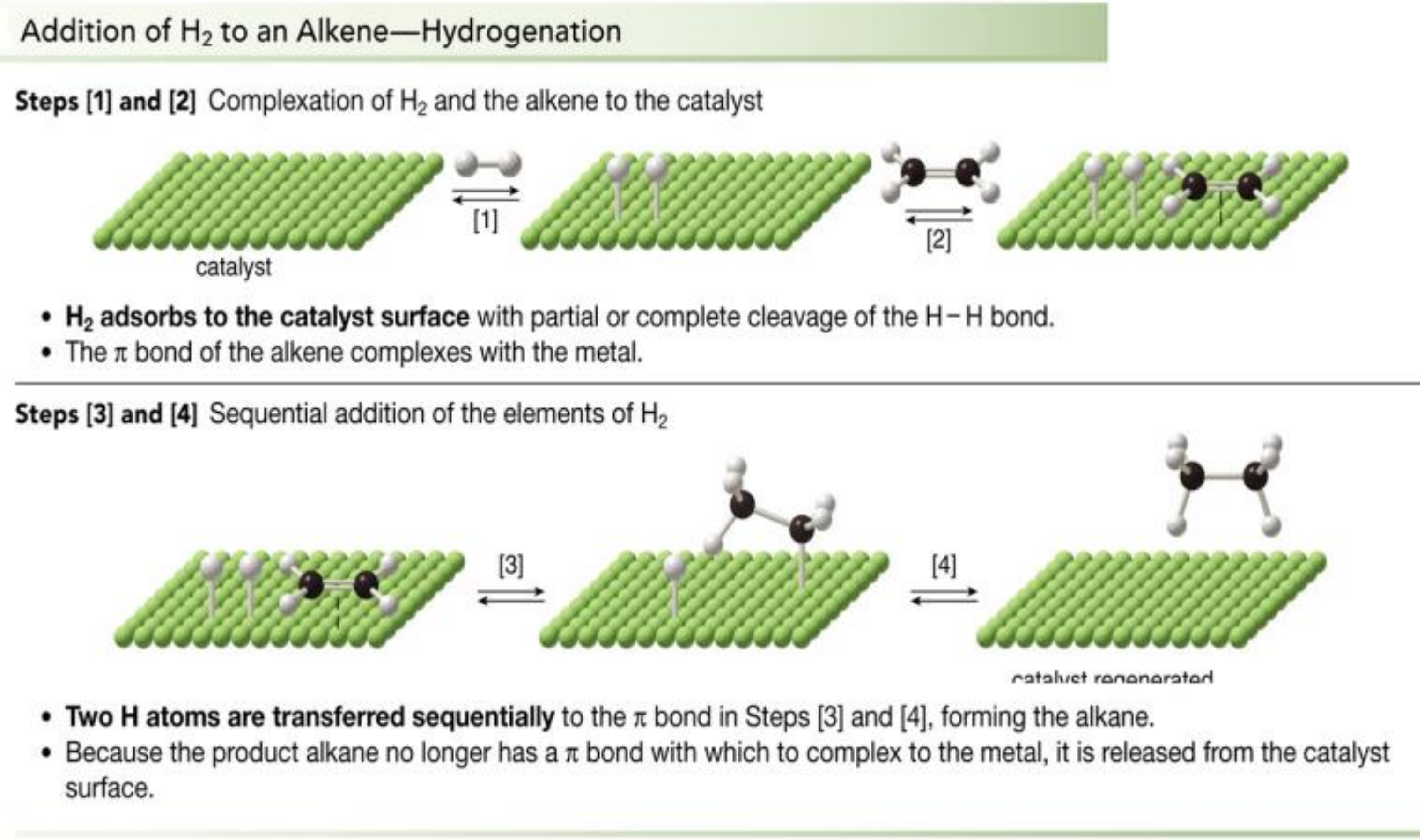


Reduction of Alkenes—Catalytic Hydrogenation



- The addition of H_2 occurs only in the presence of a metal catalyst, and thus it is called **catalytic hydrogenation**.
- The catalyst consists of a metal—usually **Pd**, **Pt**, or **Ni**, **adsorbed** onto a finely divided inert solid, such as charcoal.
- H_2 adds in a **syn** fashion.





Addition of H_2 to an Alkene—Hydrogenation

Steps [1] and [2] Complexation of H_2 and the alkene to the catalyst

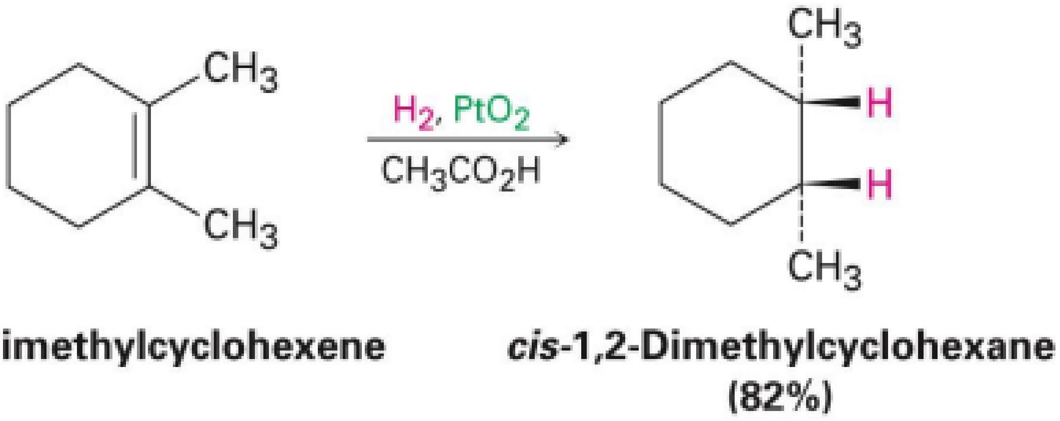
- **H_2 adsorbs to the catalyst surface** with partial or complete cleavage of the H − H bond.
- The π bond of the alkene complexes with the metal.

Steps [3] and [4] Sequential addition of the elements of H_2

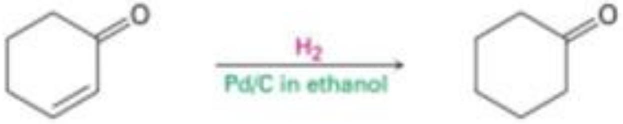
- **Two H atoms are transferred sequentially** to the π bond in Steps [3] and [4], forming the alkane.
- Because the product alkane no longer has a π bond with which to complex to the metal, it is released from the catalyst surface.

Catalytic hydrogenation

- A heterogeneous process that takes place on the surface of insoluble catalyst particles
- Common catalysts for alkene hydrogenation:
  - Platinum – PtO_2 (*Adams' Catalyst*)
  - Palladium – very fine powder supported on inert material such as charcoal (Pd/C)
- Occurs with *syn* stereochemistry
  - Both hydrogens add to the double bond from the same side

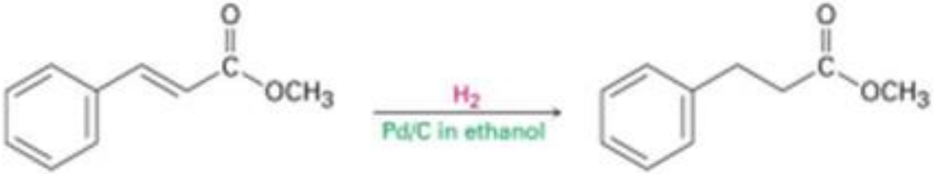


Other unsaturated functional groups are much less reactive toward catalytic hydrogenation under normal reaction conditions.



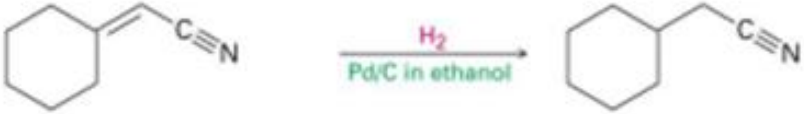
Cyclohex-2-enone

Cyclohexanone
(ketone *NOT* reduced)



Methyl 3-phenylpropenoate

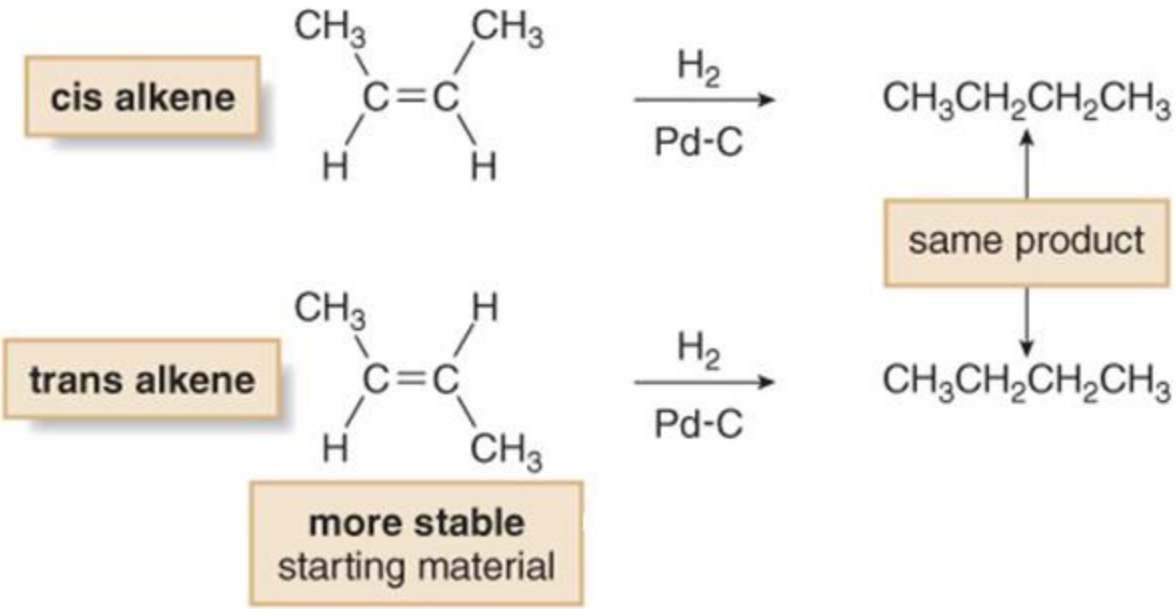
Methyl 3-phenylpropanoate
(aromatic ring *NOT* reduced)



Cyclohexylideneacetonitrile

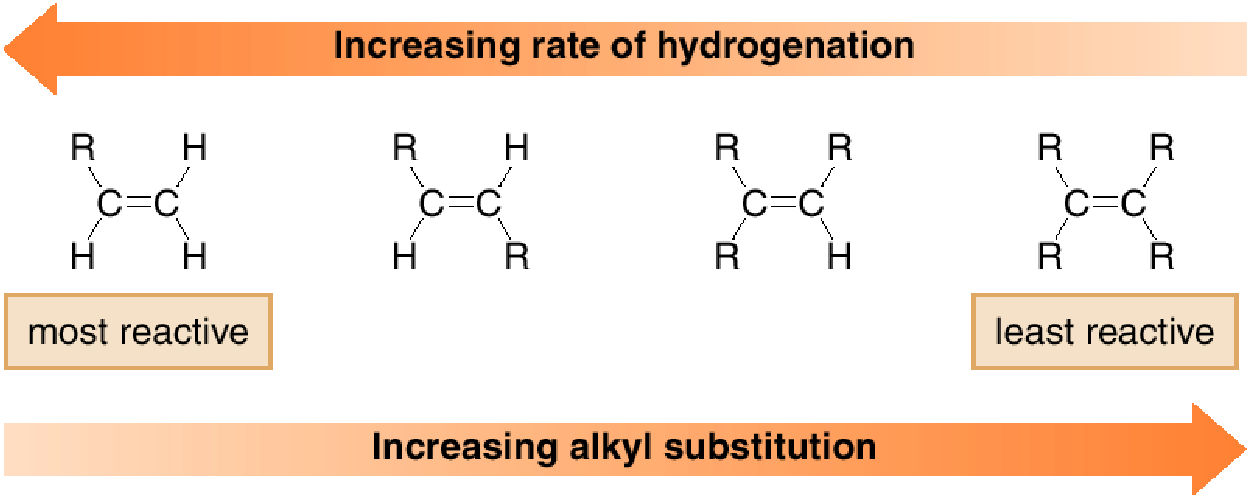
Cyclohexylacetonitrile
(nitrile *NOT* reduced)

- **Two different alkenes** that are **hydrogenated** to form the
- **same alkane**.



- The **mechanism explains two facts** about **hydrogenation**:

- Rapid, sequential addition of H_2 occurs from the side of the alkene complexed to the metal surface, resulting in syn addition.
- Less crowded double bonds complex more readily to the catalyst surface, resulting in faster reaction.



Increasing rate of hydrogenation

most reactive

least reactive

Increasing alkyl substitution

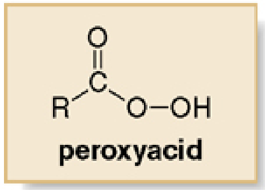
Oxidizing Agents

Give oxygen to another substance or remove hydrogen from it.

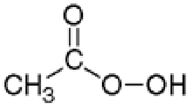
The reactant that contains the element that is reduced is the oxidizing agent.

- There are **two** main categories of oxidizing agents:
  1. Reagents that contain an **oxygen-oxygen** bond
  2. Reagents that contain **metal-oxygen** bonds
- Oxidizing agents containing an **O—O** bond include **O_2**, **O_3** (**ozone**), **H_2O_2** (**hydrogen peroxide**), **$(CH_3)_3COOOH$** (***tert*-butyl hydroperoxide**), and peroxyacids.
- **Peroxyacids** (or peracids) have the general formula **RCO_3H**.

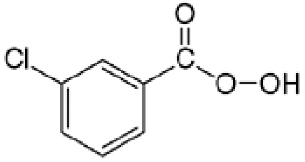
Common peroxyacids



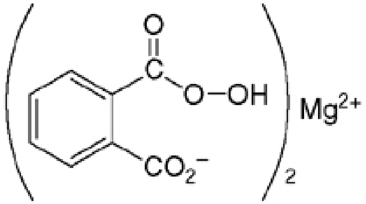
peroxyacid



peroxyacetic acid



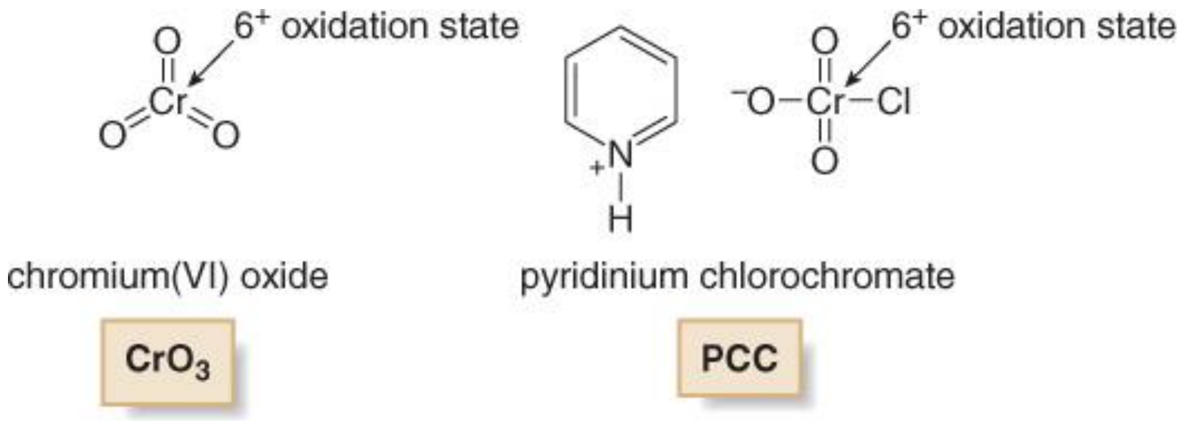
meta-chloroperoxybenzoic acid
mCPBA



magnesium monoperoxyphthalate
MMPP

The reduced substance is always the oxidizing agent

- The most common oxidizing agents with **metal-oxygen** bonds contain either chromium +6 (six Cr—O bonds) or manganese +7 (seven Mn—O bonds).
- Common Cr^{6+} reagents include **CrO_3** and sodium or potassium dichromate (**$Na_2Cr_2O_7$ and $K_2Cr_2O_7$**). **Pyridinium chlorochromate** (**PCC**) is a more selective Cr^{6+} oxidant.

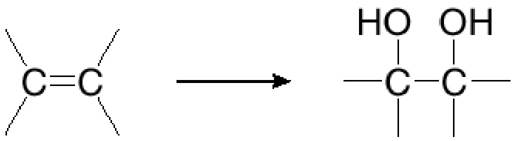


- The most common Mn^{7+} reagent is **$KMnO_4$** (**potassium permanganate**).
- Other oxidizing agents that contain metals include **OsO_4** (**osmium tetroxide**) and **Ag_2O** [**silver(I) oxide**].

Dihydroxylation of alkenes

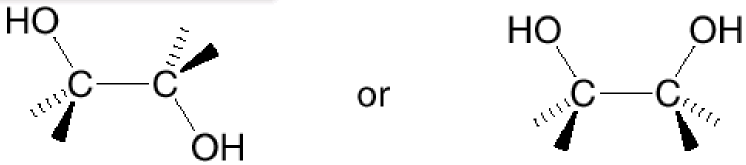
- Dihydroxylation is the addition of **two hydroxy groups** to a double bond, forming a **1,2-diol** **or** **glycol.**
- Depending on the **reagent**, the two new OH groups can be added to the opposite sides (**anti addition**) or the same side (**syn addition**) of the double bond.

Dihydroxylation—General reaction



1,2-diol or glycol

Stereochemistry



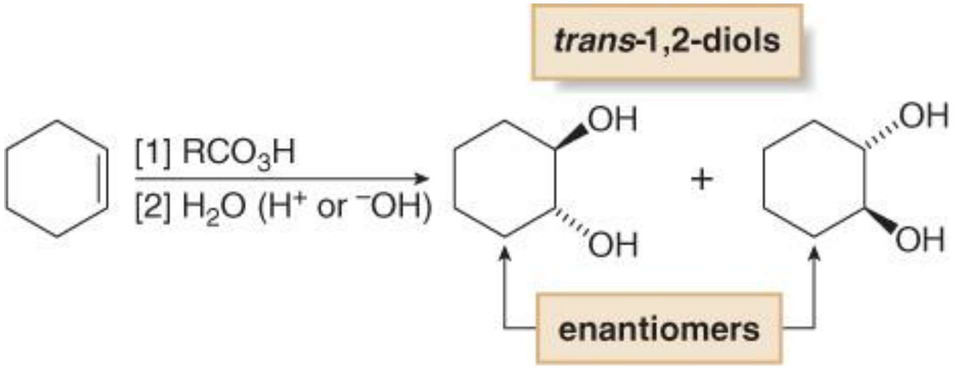
anti addition product

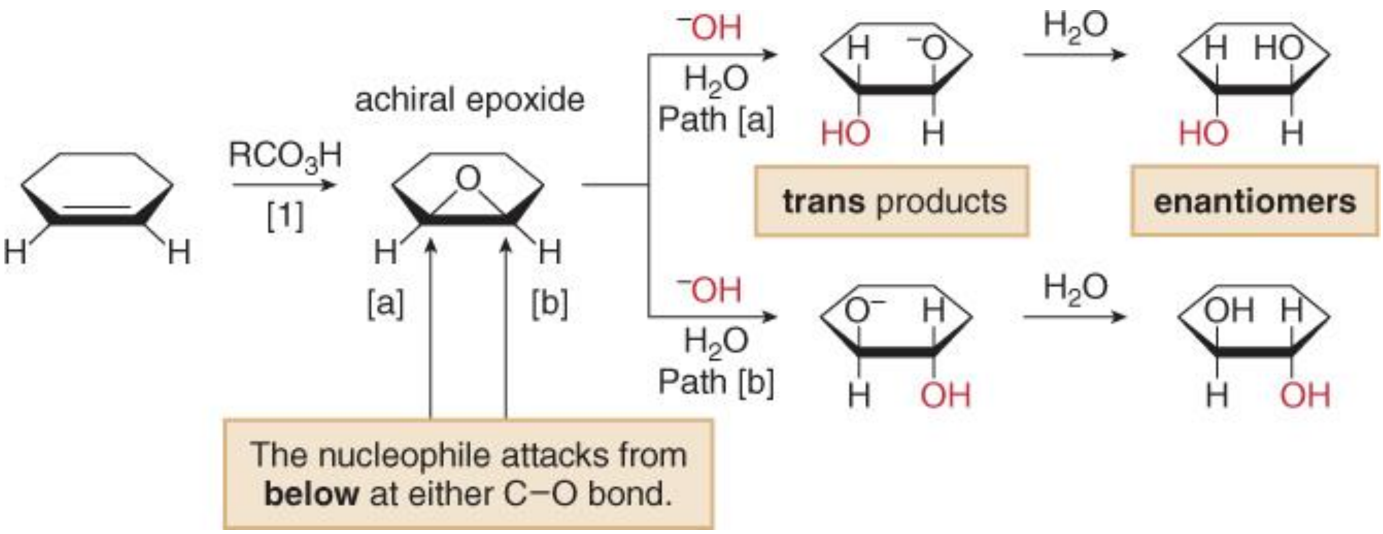
2 OH's added on **opposite** sides of the C=C

syn addition product

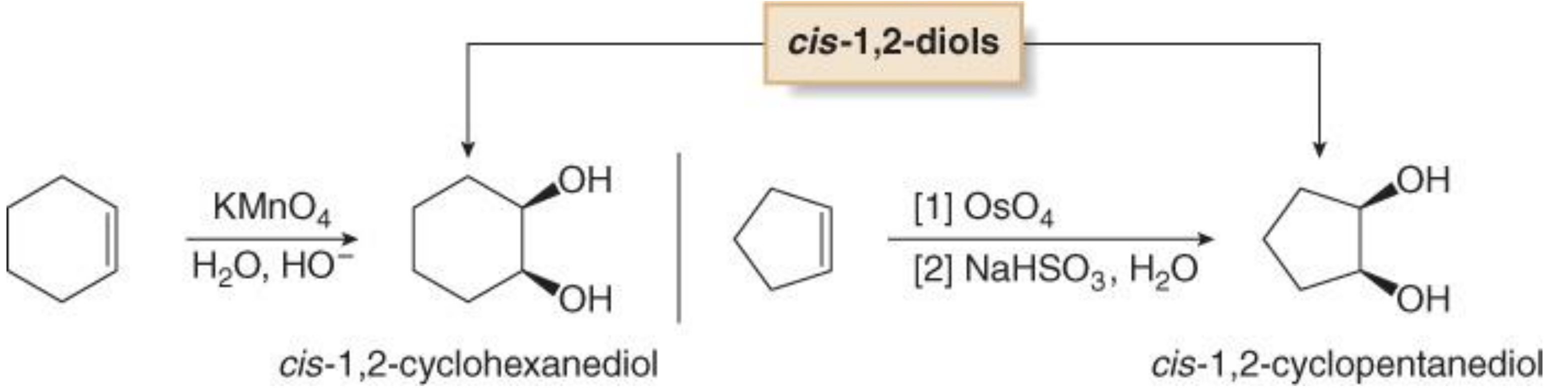
2 OH's added on the **same** side of the C=C

- **Anti dihydroxylation** is achieved in **two steps**—epoxidation, followed by ring opening with ^{-}OH or H_3O^+.

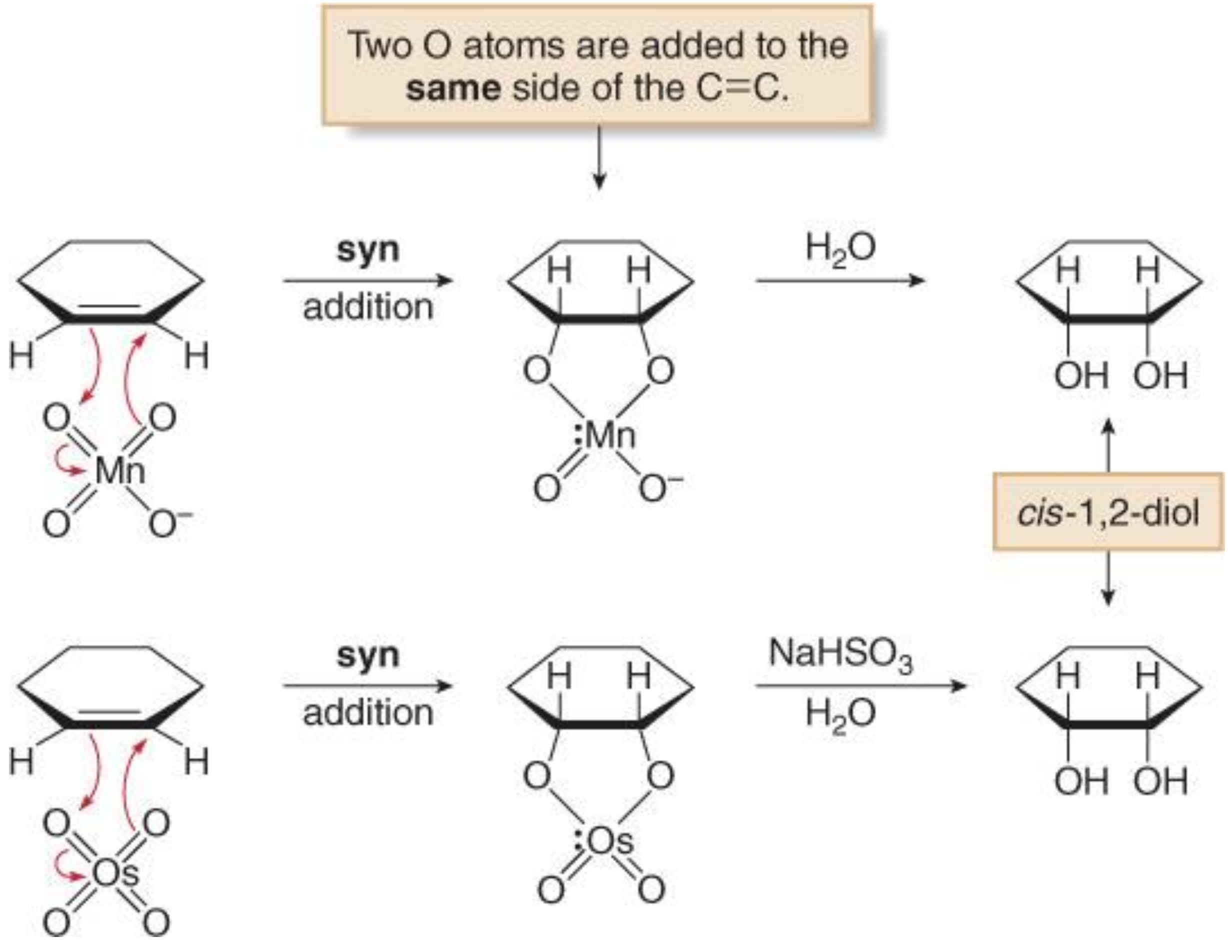




- **Syn hydroxylation** results when an alkene is treated with either **$KMnO_4$ or OsO_4**. With OsO_4 sodium bisulfite is added in the hydrolysis step.



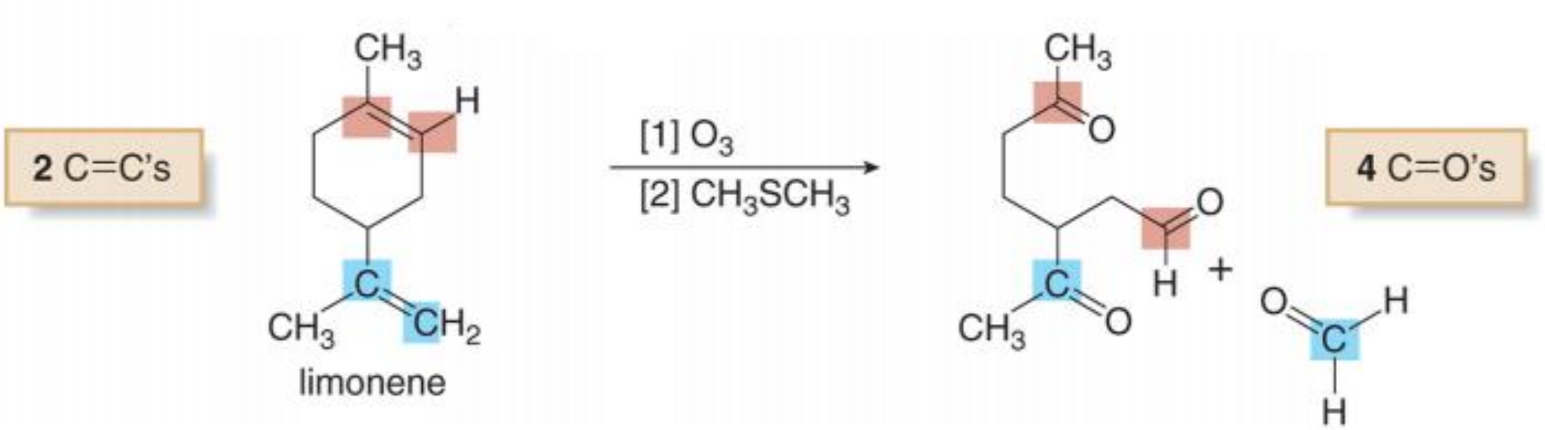
- Each reagent adds two oxygen atoms in a syn fashion.
- Hydrolysis of the cyclic intermediate cleaves the metal oxygen bonds, forming a *cis*-1,2-diol.



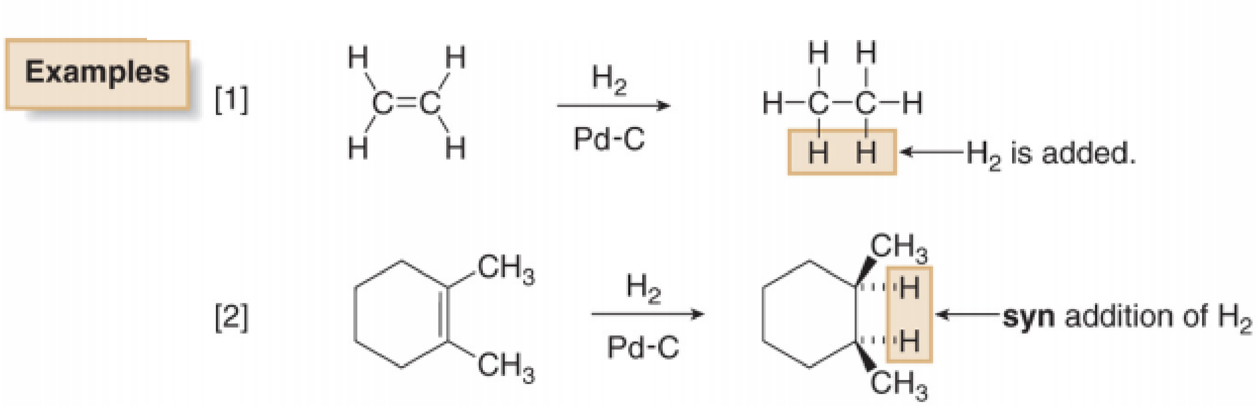
Two O atoms are added to the **same** side of the C=C.

cis-1,2-diol

Ozonolysis


2 C=C's
CH_3
H
CH_3
C
CH_2
limonene
[1] O_3
[2] CH_3SCH_3
CH_3
O
O
H
C
CH_3
O
+
O
H
C
H
4 C=O's

Hydrogenation: Reduction to Alkanes

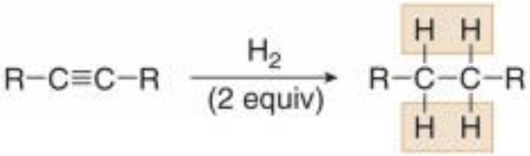


H_2 is added.

syn addition of H_2

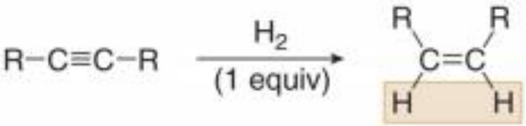
Hydrogenation of Alkynes

- Adding two equivalents of H_2 forms an alkane.



alkane

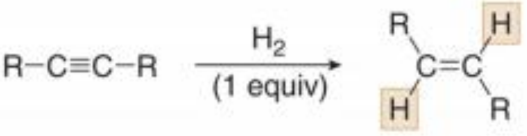
- Adding one equivalent of H_2 in a syn fashion forms a cis alkene.



syn addition

cis alkene

- Adding one equivalent of H_2 in an anti fashion forms a trans alkene.

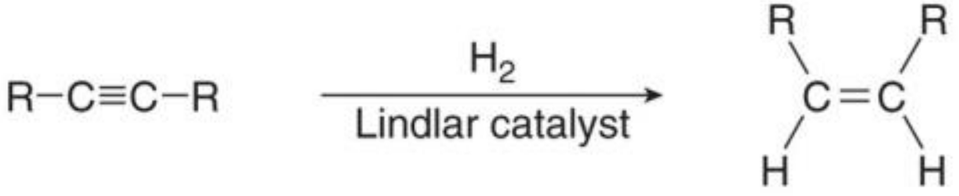


anti addition

trans alkene

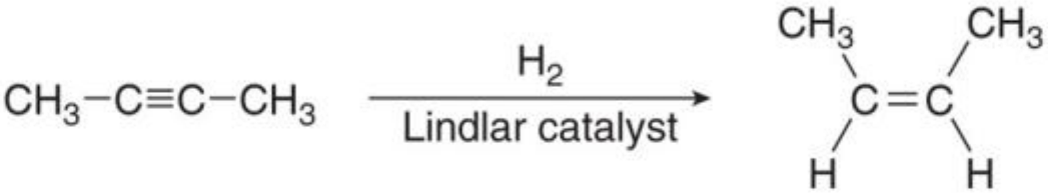
Reducing Alkyne to cis-Alkene:

General reaction



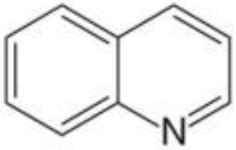
cis alkene

Example



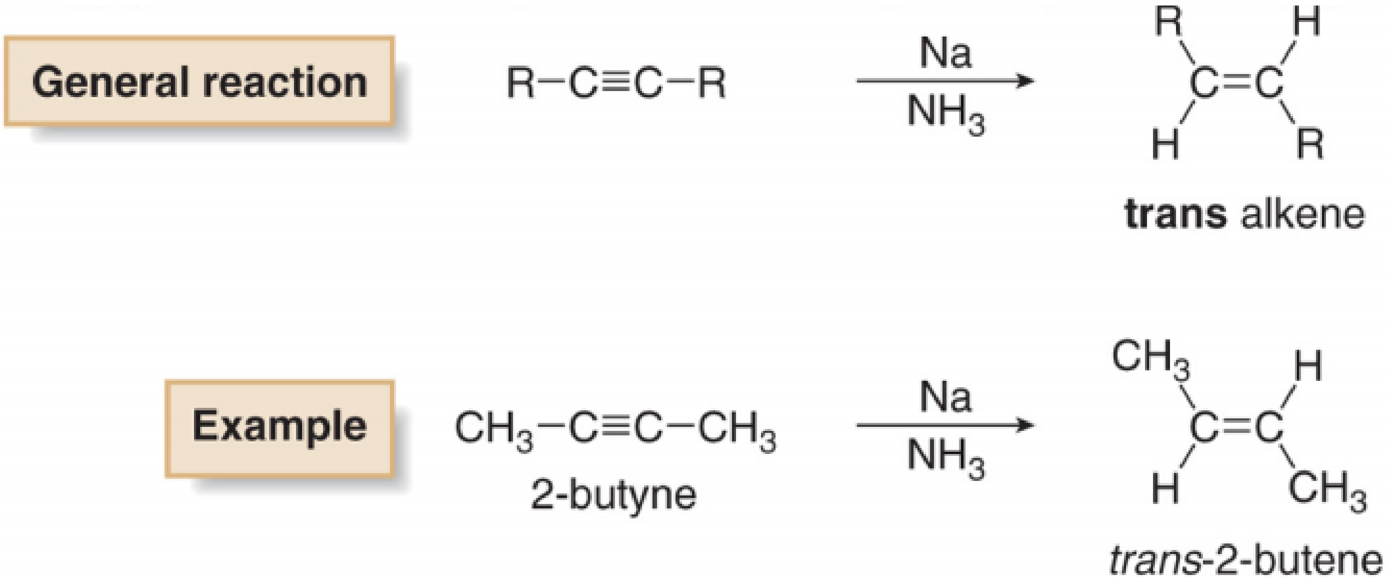
Pd on $CaCO_3$
+ $Pb(OCOCH_3)_2$ + quinoline

Lindlar catalyst



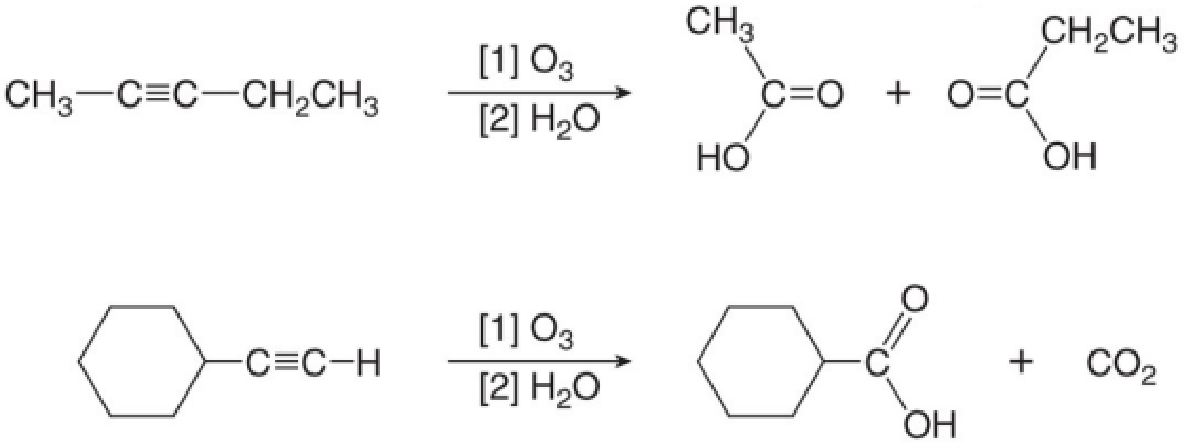
quinoline

Reducing Alkyne to trans-alkene

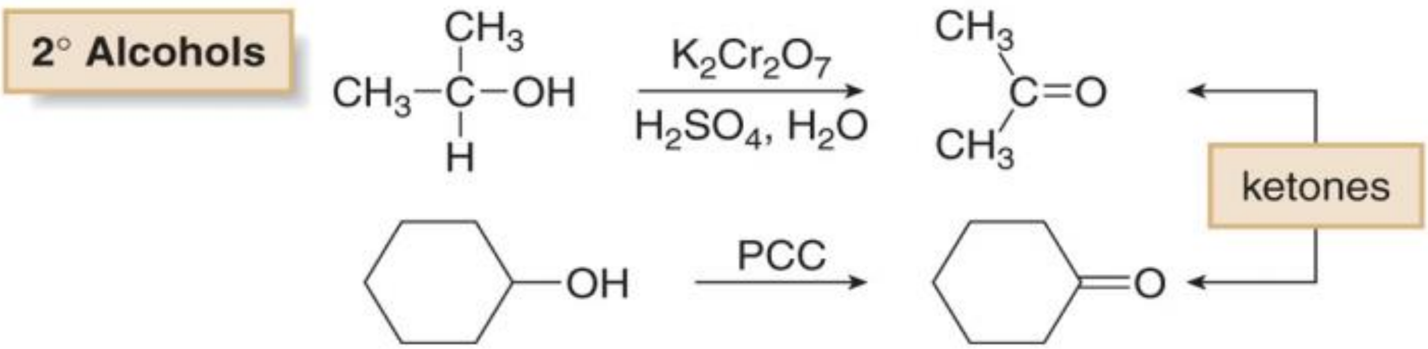


Oxidative Cleavage of Alkynes

Examples

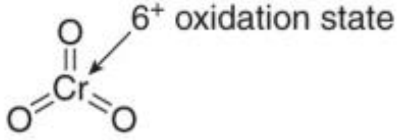


Oxidation of Alcohols with Cr(VI)



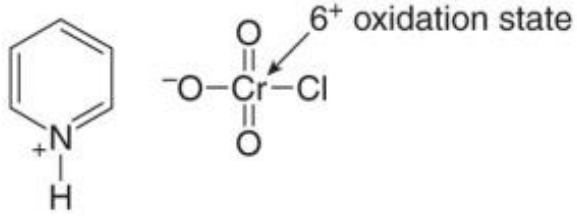
2° Alcohols

ketones



chromium(VI) oxide

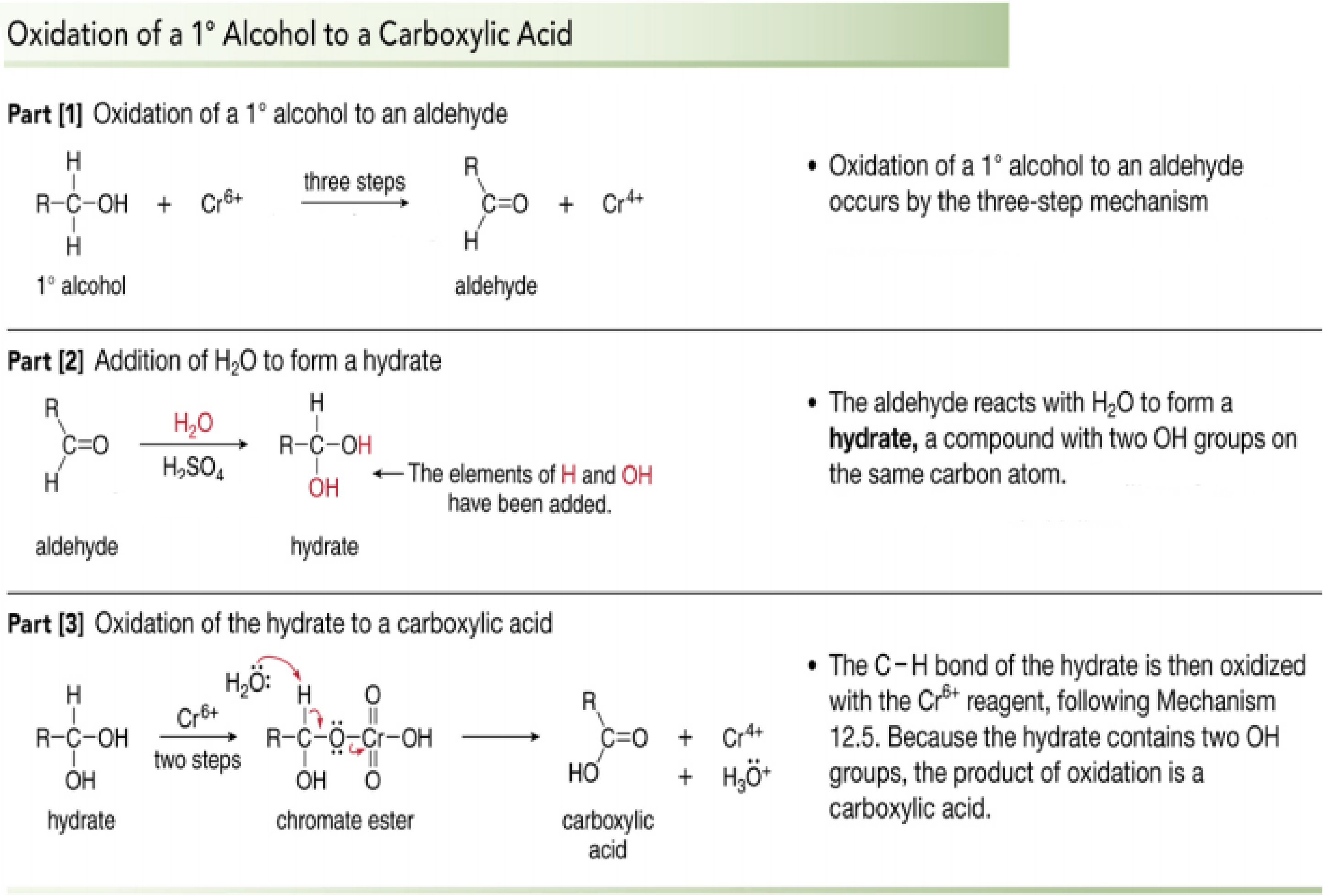
CrO_3



pyridinium chlorochromate

PCC

Oxidation of a 1° Alcohol



Oxidation of a 1° Alcohol to a Carboxylic Acid

Part [1] Oxidation of a 1° alcohol to an aldehyde

- Oxidation of a 1° alcohol to an aldehyde occurs by the three-step mechanism

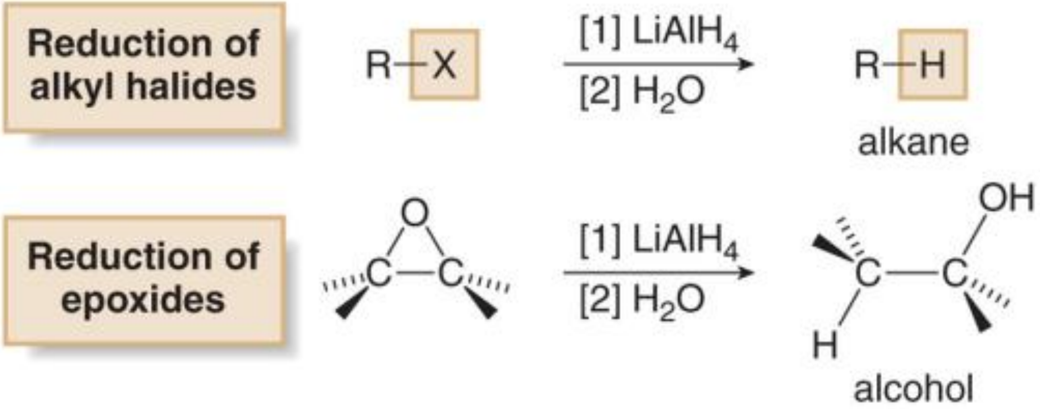
Part [2] Addition of H_2O to form a hydrate

- The aldehyde reacts with H_2O to form a **hydrate,** a compound with two OH groups on the same carbon atom.

Part [3] Oxidation of the hydrate to a carboxylic acid

- The C–H bond of the hydrate is then oxidized with the Cr^{6+} reagent, following Mechanism 12.5. Because the hydrate contains two OH groups, the product of oxidation is a carboxylic acid.

Reduction with $LiAlH_4$



Reduction of alkyl halides

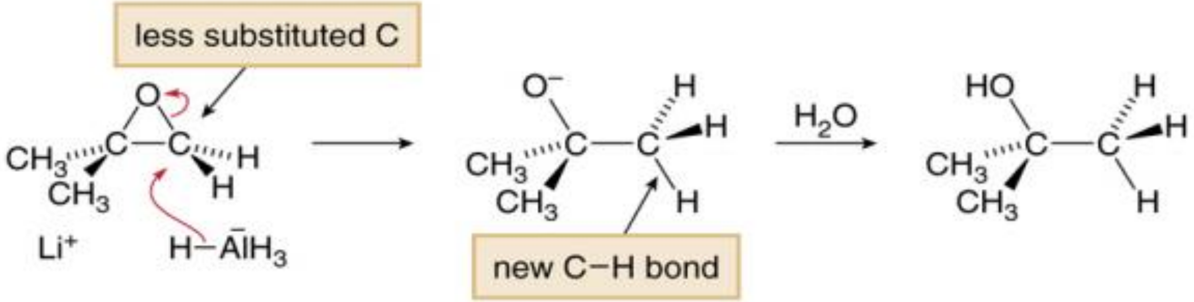
$$R{-}\boxed{X} \xrightarrow[\text{[2] } H_2O]{\text{[1] } LiAlH_4} R{-}\boxed{H}$$

alkane

Reduction of epoxides

alcohol

$$CH_3CH_2CH_2CH_2{-}\boxed{Cl} \xrightarrow[\text{[2] } H_2O]{\text{[1] } LiAlH_4} CH_3CH_2CH_2CH_2{-}\boxed{H}$$



less substituted C

new C−H bond