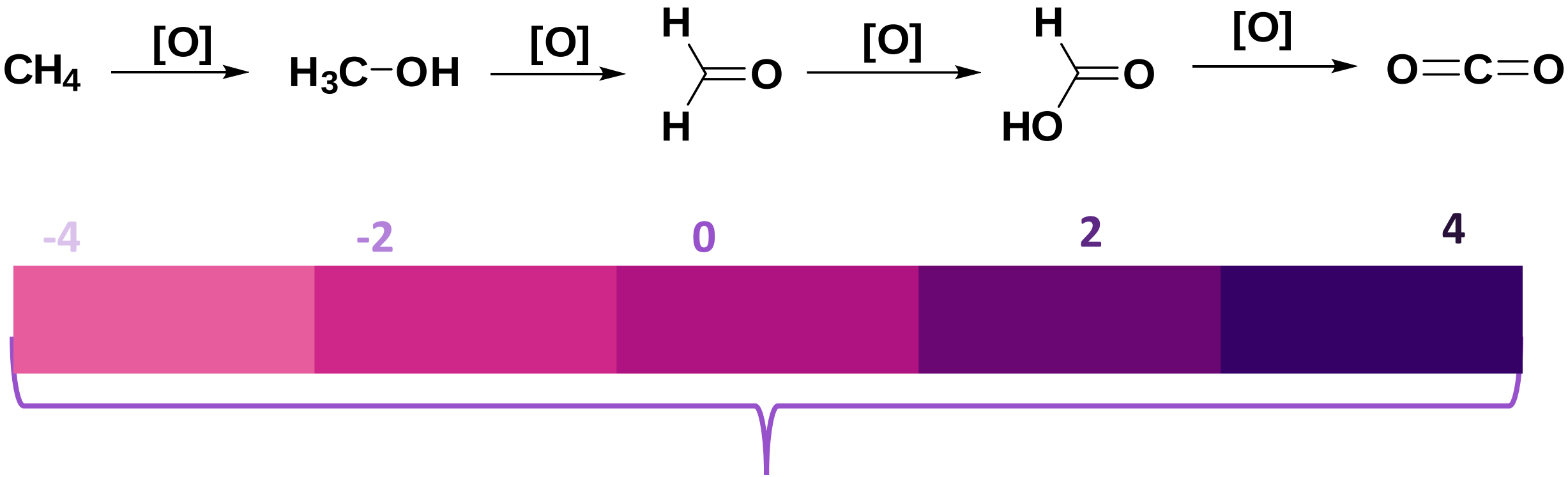
# Oxidation reaction



# $KMnO_4$ oxidation

Mn(VII) is reduced under acidic conditions to Mn(IV) or Mn(II) according to the half-reactions shown below, with the indicated cell potentials.

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad E^o = 1.68\,V$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad E^o = 1.5\,V$$

$$MnO_4^- + 2H_2O + 3e^- \rightarrow Mn^{2+} + 4OH^- \quad E^o = 0.6\,V$$

## General Reactivity with Organic Molecules

$KMnO_4$ is able to oxidize carbon atoms if they contain sufficiently weak bonds, including

1. Carbon atoms with ππ bonds, as in alkenes and alkynes
2. Carbon atoms with weak C-H bonds, such as
- C-H bonds in the alpha-positions of substituted aromatic rings
- C-H bonds in carbon atoms containing C-O bonds, including alcohols and aldehydes

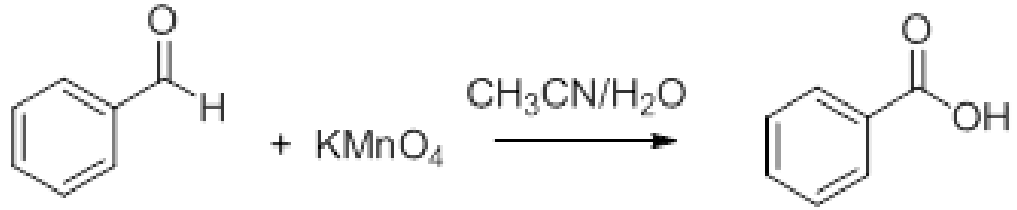
3. Carbons with exceptionally weak C-C bonds such as
- C-C bonds in a glycol
- C-C bonds next to an aromatic ring and an oxygen

$KMnO_4$ also oxidizes phenol to para-benzoquinone.

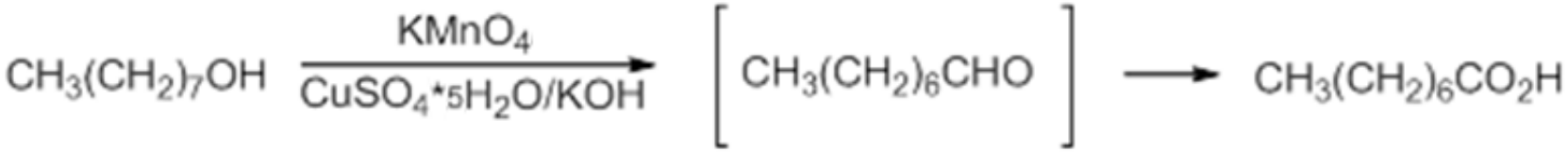
# $KMnO_4$ oxidation

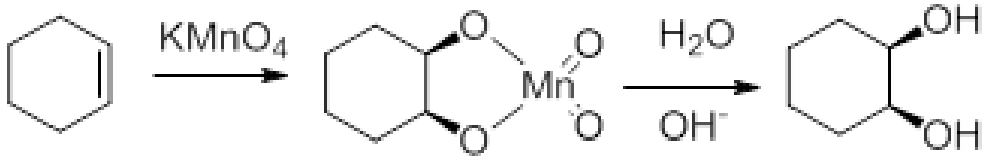
## Aldehydes

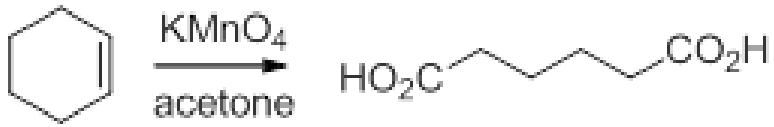
Aldehydes RCHO are readily oxidized to carboxylic acids.

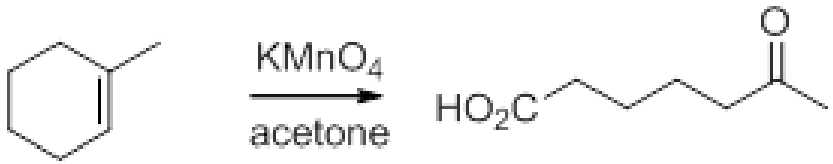



## Alcohols

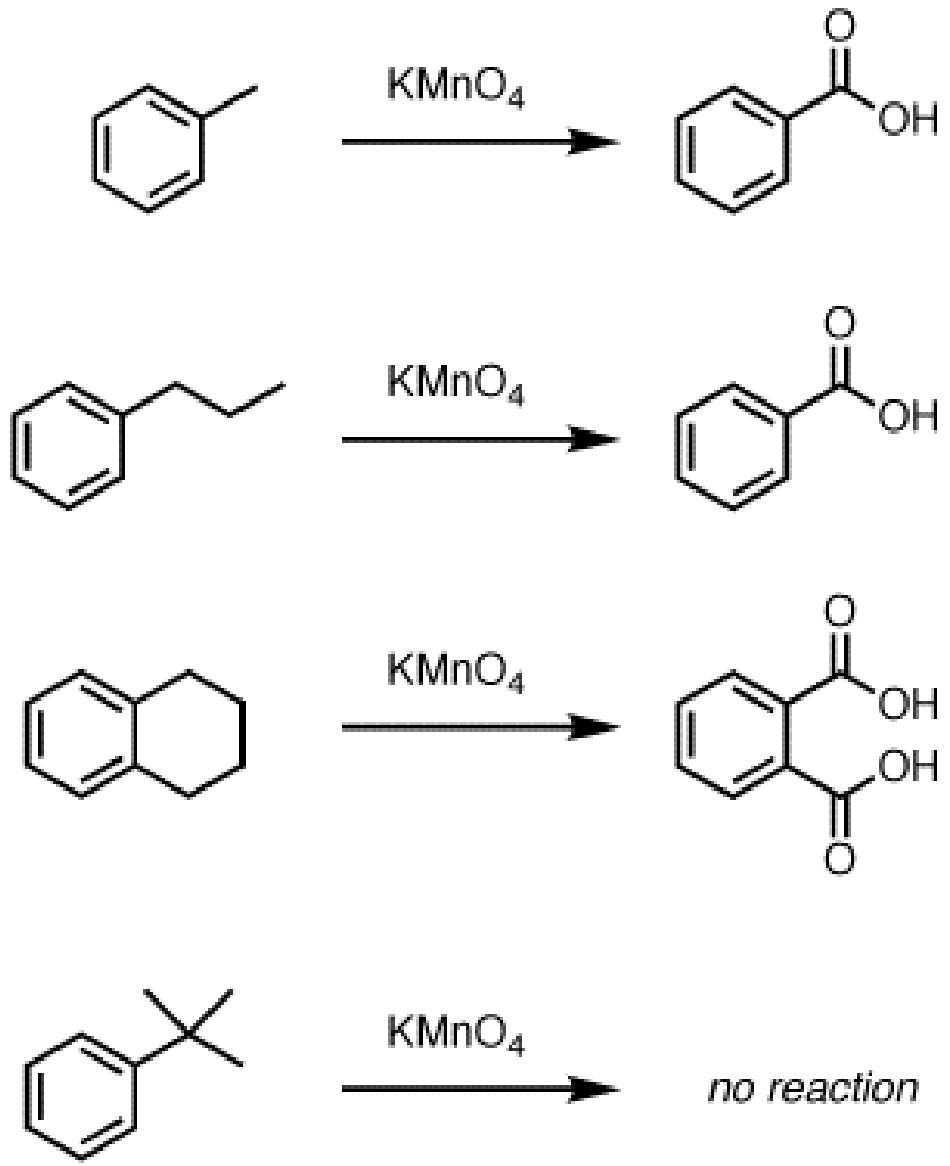


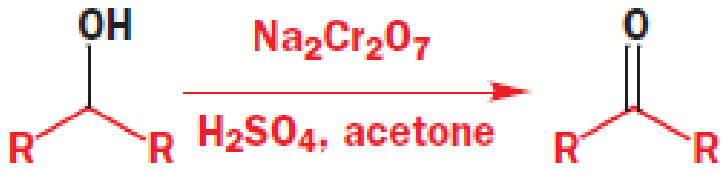
# Oxidation in Aromatic molcules

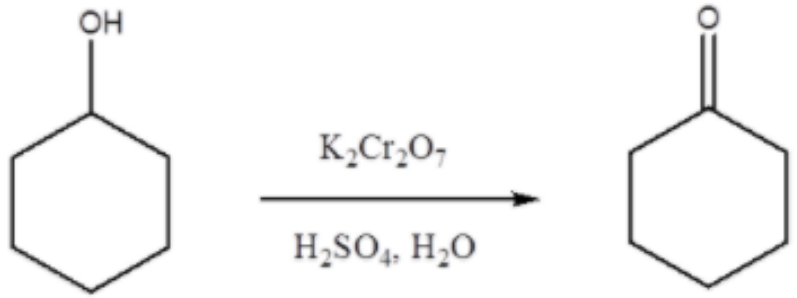


# $K_2Cr_2O_7$ oxidation

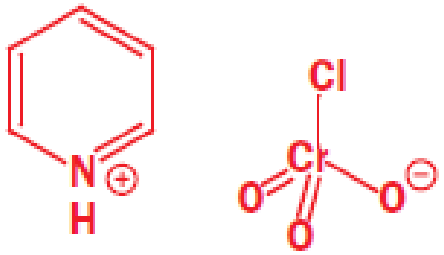
The oxidizing agent commonly shown is a solution of sodium or potassium dichromate(VI) acidified with dilute sulfuric acid. If oxidation occurs, the orange solution containing the dichromate(VI) ions is reduced to a green solution containing chromium(III) ions. The electron-half-equation for this reaction is

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$



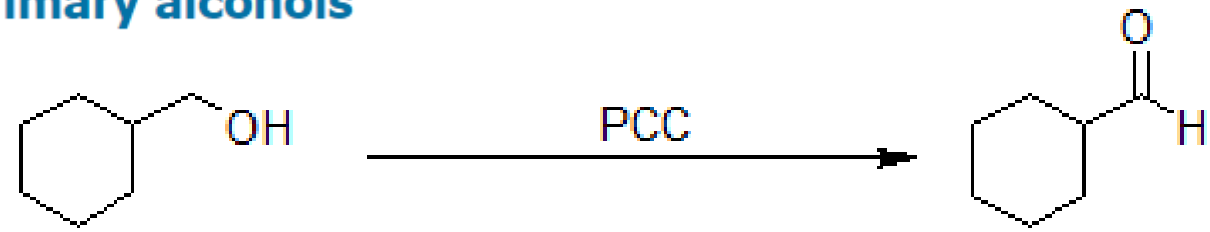



# Different form of chromate

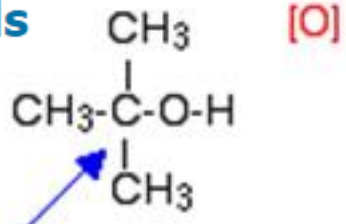



pyridinium chlorochromate, PCC

## Primary alcohols



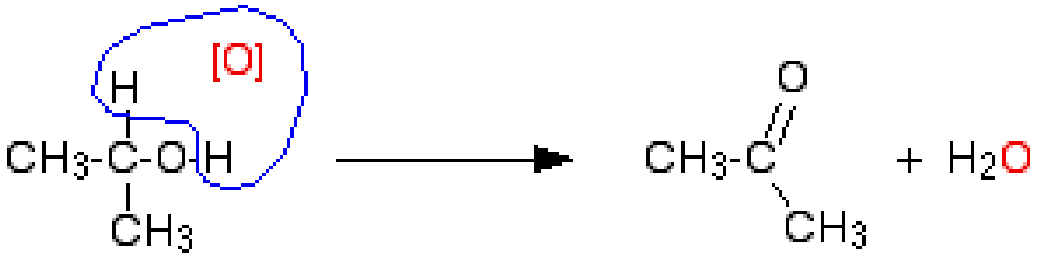

## Tertiary alcohols




[O]

There is no hydrogen attached to this carbon for the oxygen to remove.

## Secondary alcohols

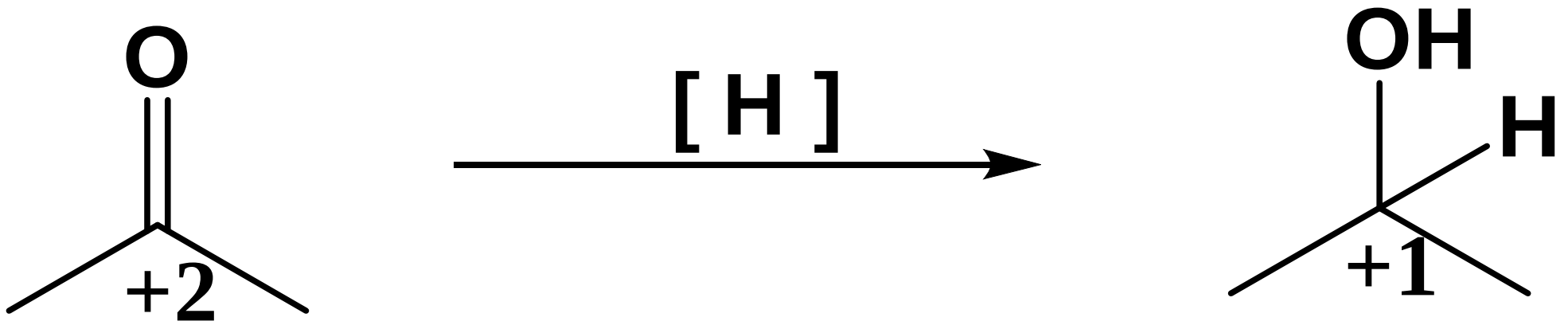



propan-2-ol

propanone

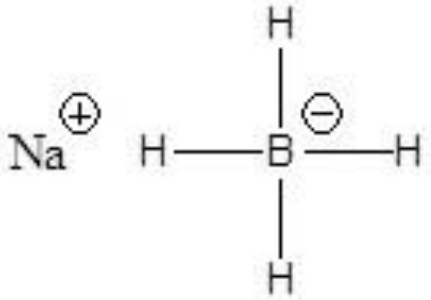
# -Reduction reaction

# Reduction reaction

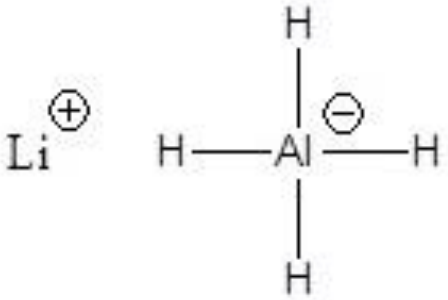



**Reduction:** decrease in  oxidation state/ addition of hydrogen related to the carbon atom

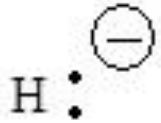
# Source of reduction



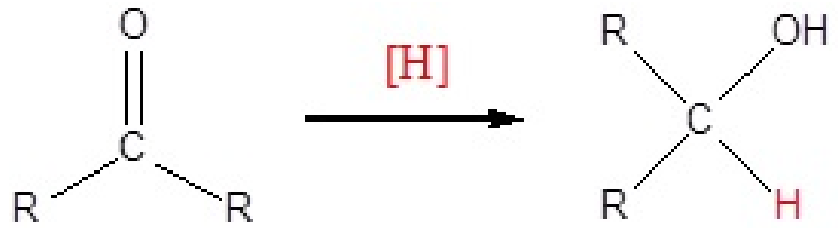

**Sodium Borohydride**




**Lithium Aluminum Hydride**

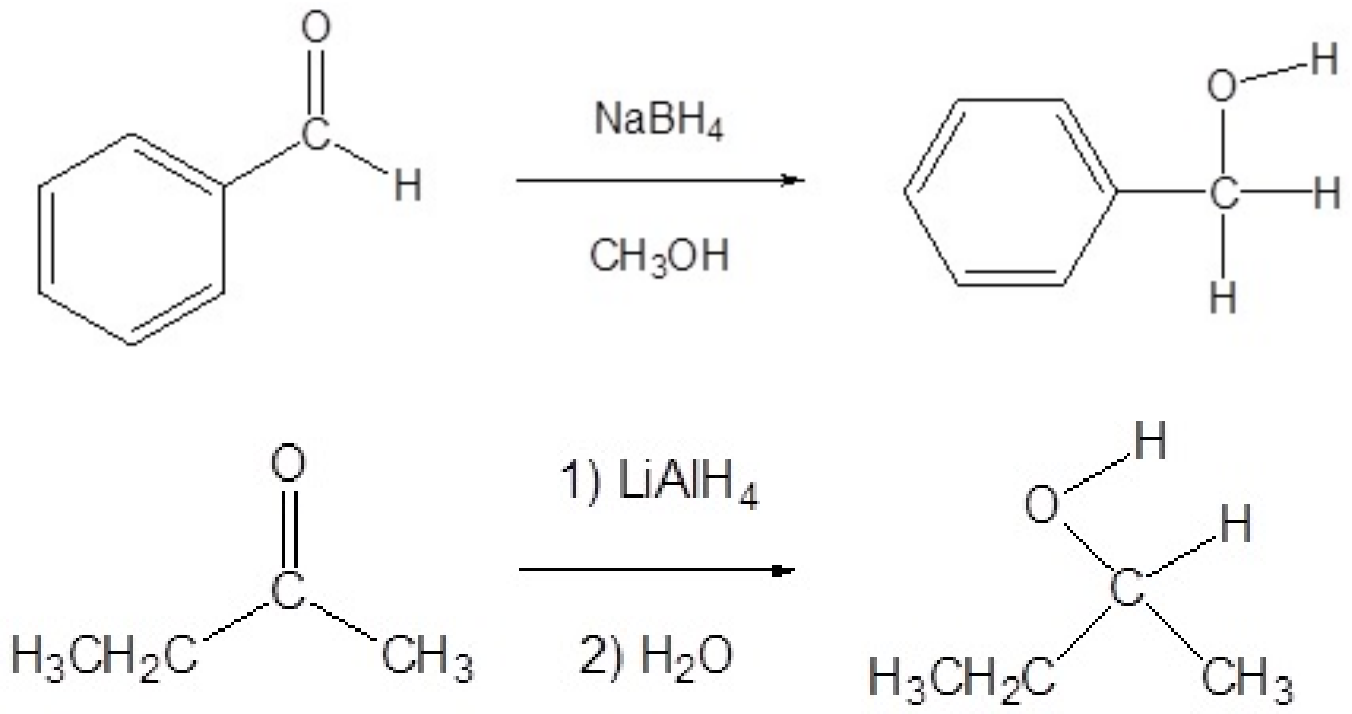



**Hydride Nucleophile**




**Ketone** **2° Alcohol**

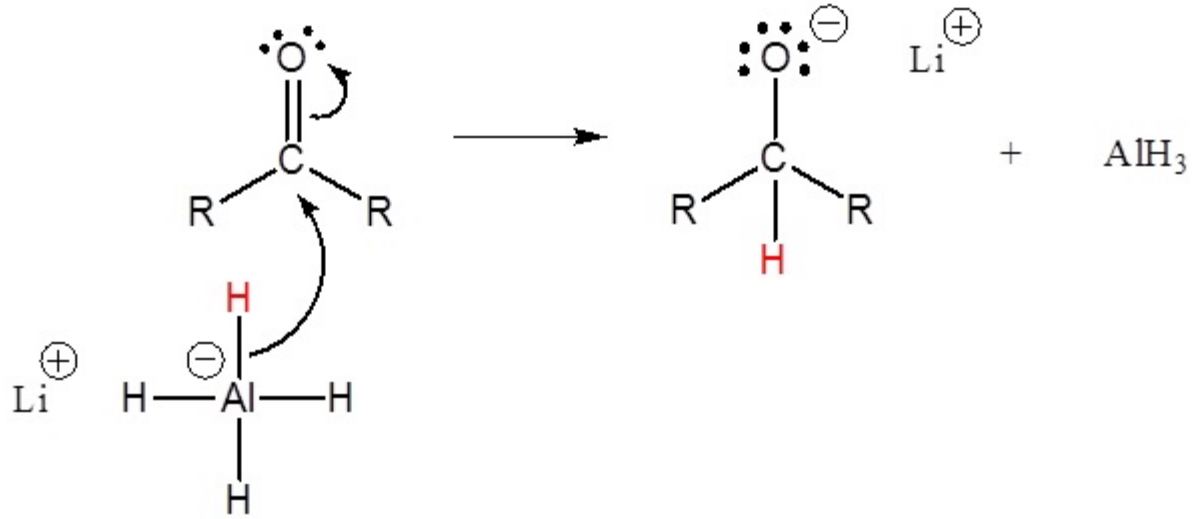
# Reactivity difference



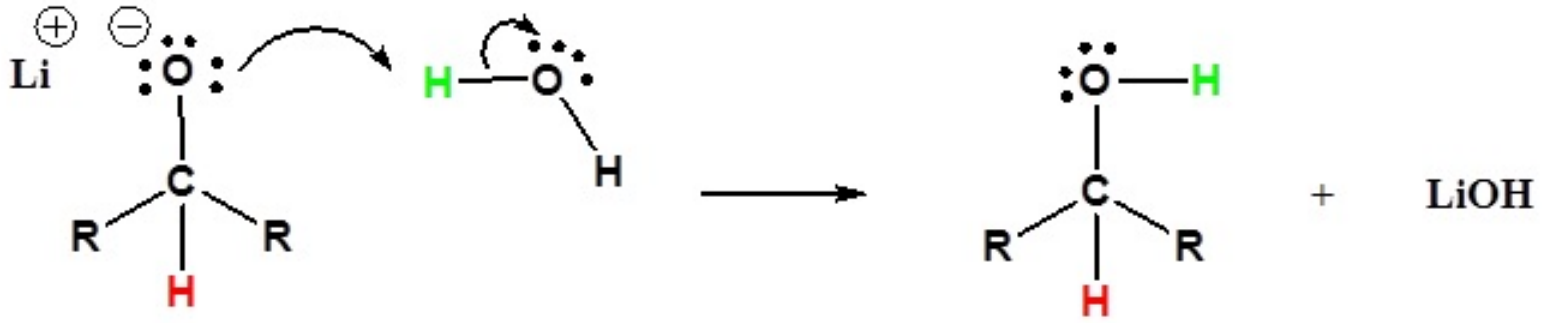

Lithium aluminium hydride (**$LiAlH_4$**) is more electropositive (more metallic) **than** boron in **$NaBH_4$**. The hydride from **$LiAlH_4$** is therefore more electron rich and thus is a **stronger** base (in reaction with water) and **stronger** nucleophile (with carbonyl group).

# Mechannism oh $LiAlH_4$ reduction

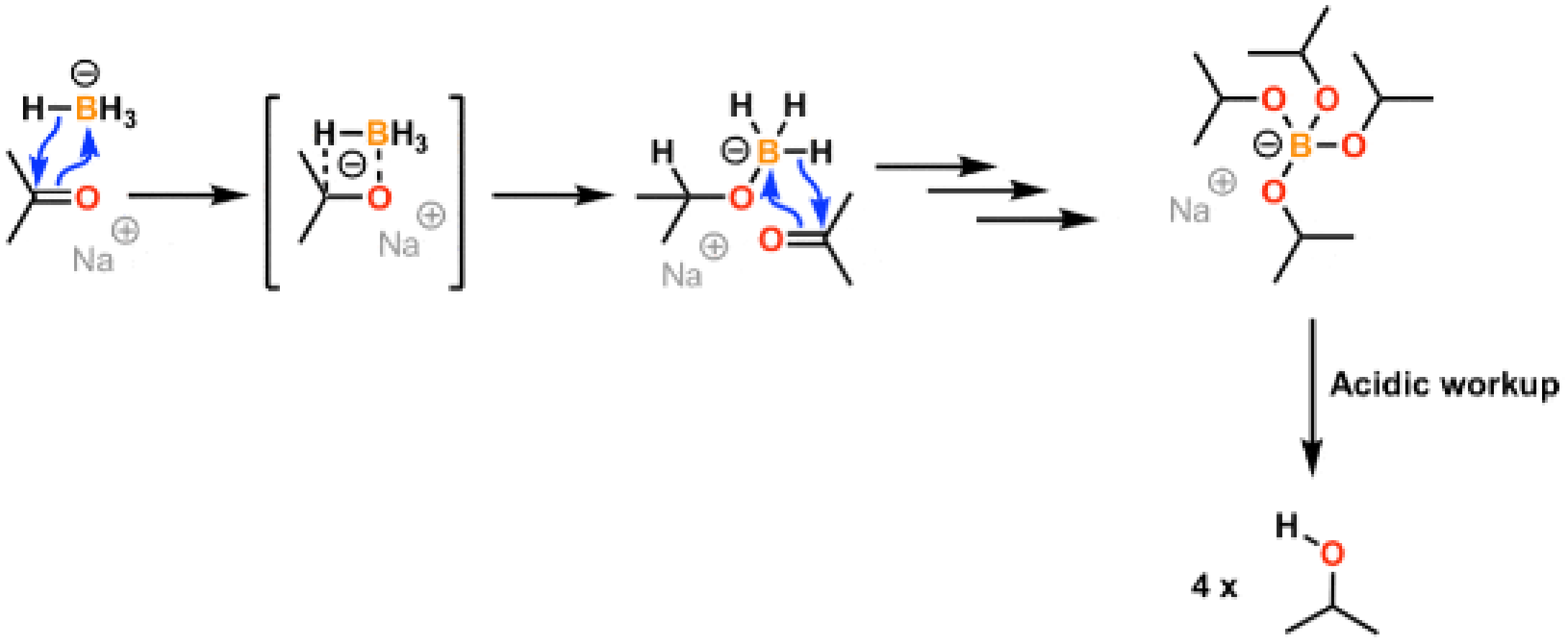
**Step 1:** Nucleophilic attack of hydride ion




**Step 2:** Protonation of the alkoxide



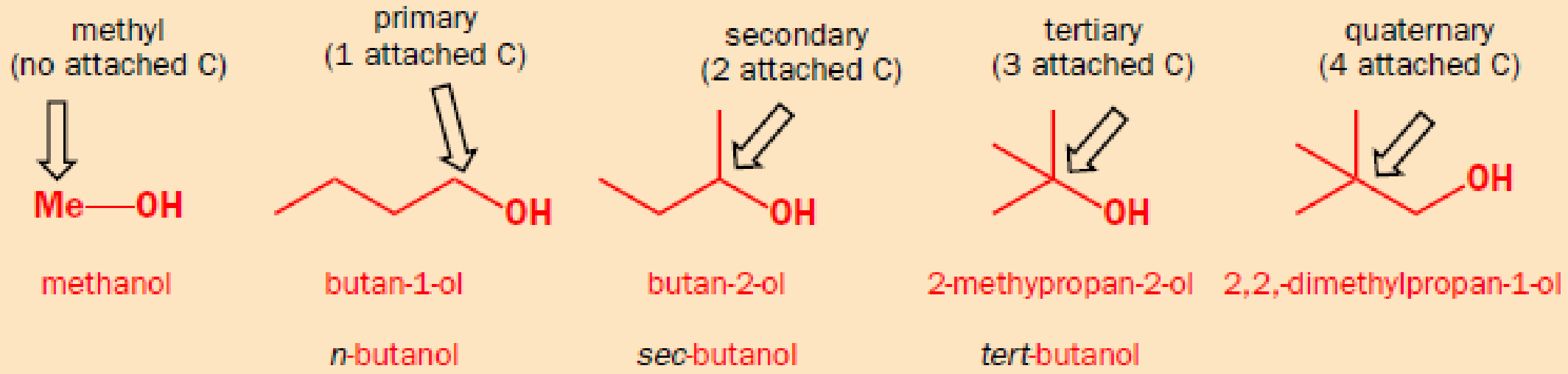
# $NaBH_4$ reduction mechanism



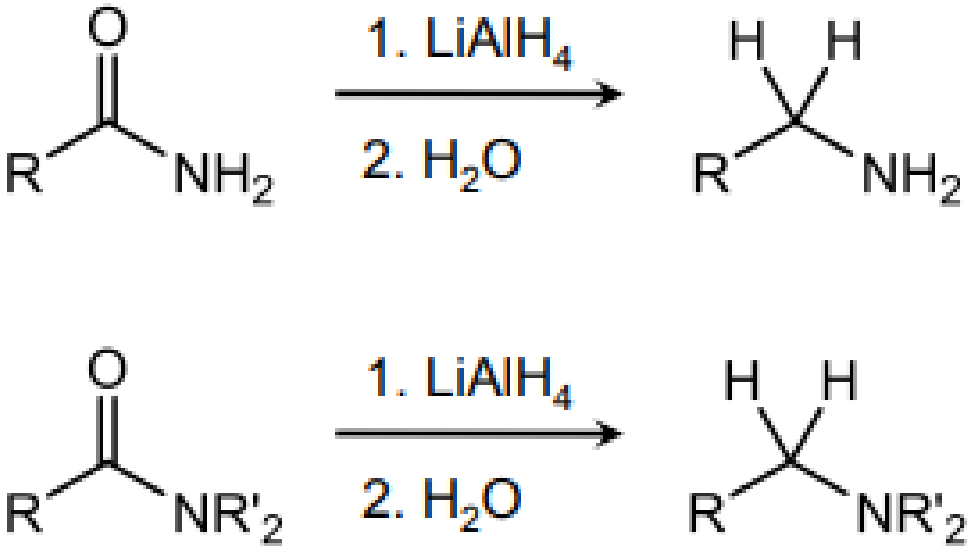
# Primary, secondary and tertiary and quarternary carbon

## Primary, secondary, and tertiary

The prefixes *sec* and *tert* are really short for secondary and tertiary, terms that refer to the carbon atom that attaches these groups to the rest of the molecular structure.



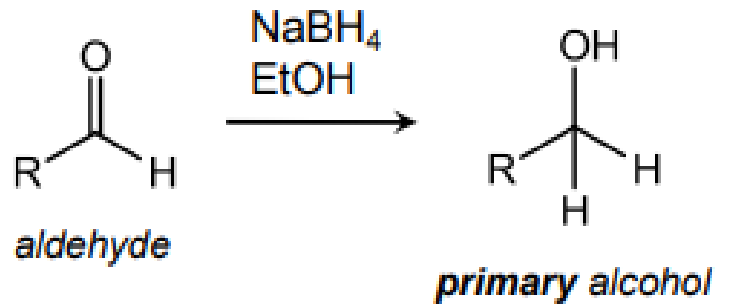
# Amide to amine




*Mechanism depends slightly on whether amide has an N-H or not.*

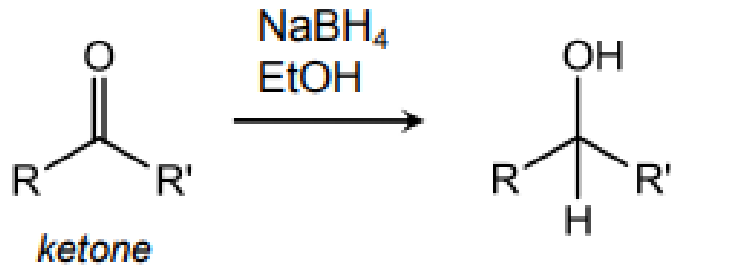
*But the result is the same.*

# Carbonyl to ketone




*aldehyde*

***primary** alcohol*




*ketone*

***secondary** alcohol*

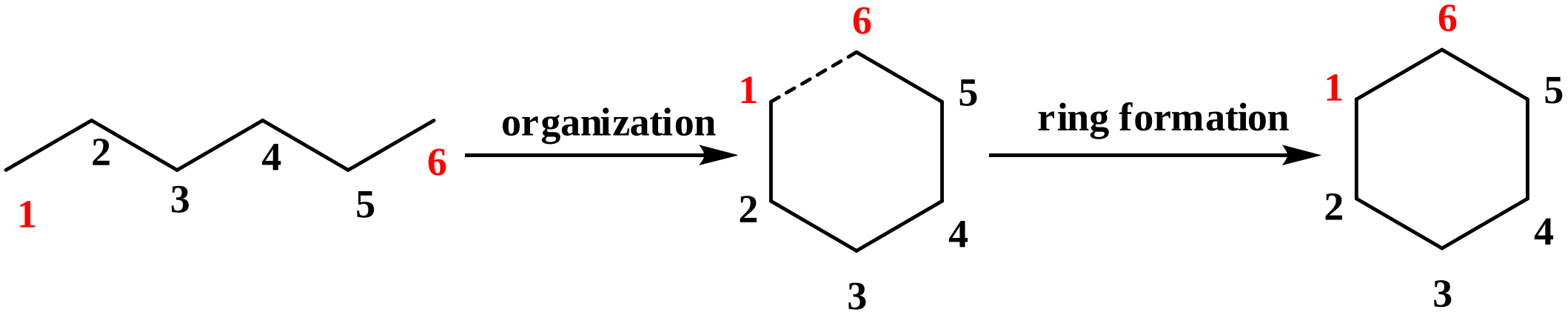
*$NaBH_4$ isn't as basic as $LiAlH_4$, so reaction can be conducted in protic solvent, and separate workup step isn't essential.*

-Cyclization
-Ring opening reactions

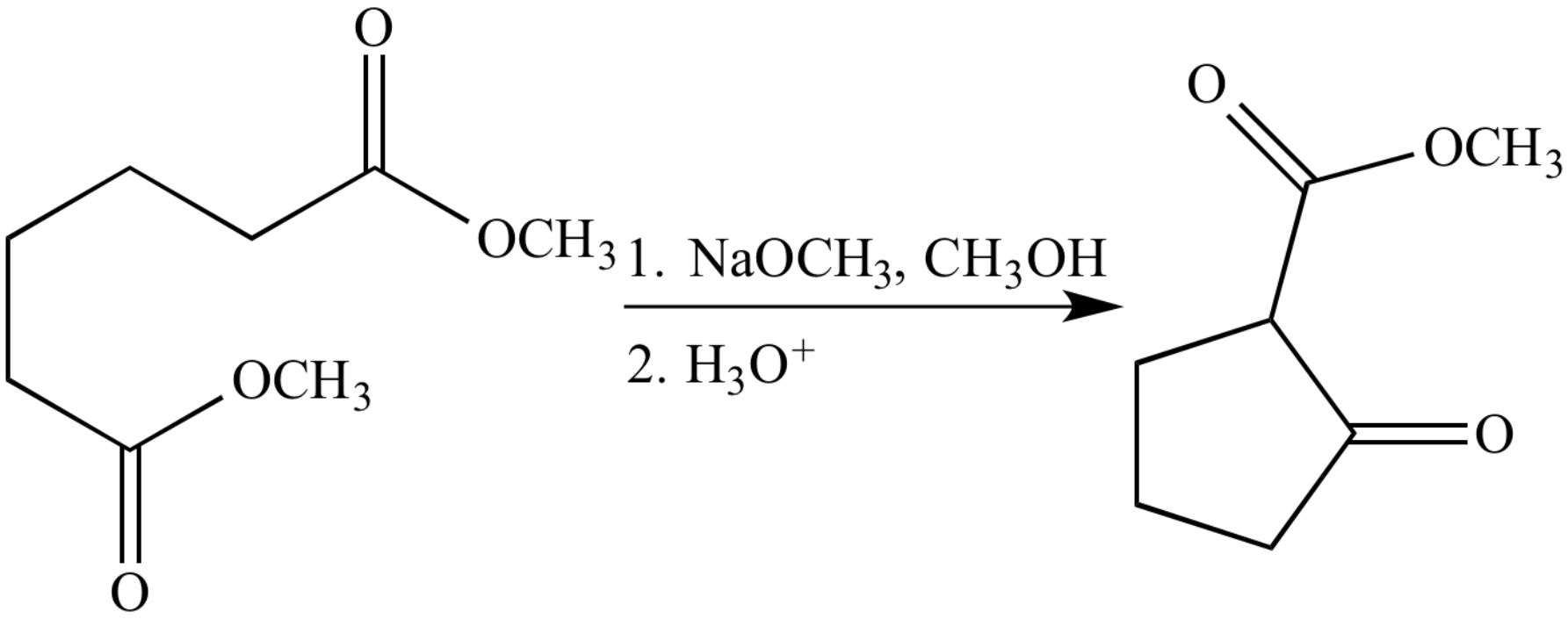
# Cyclization

**formation of a ring in a chemical compound**

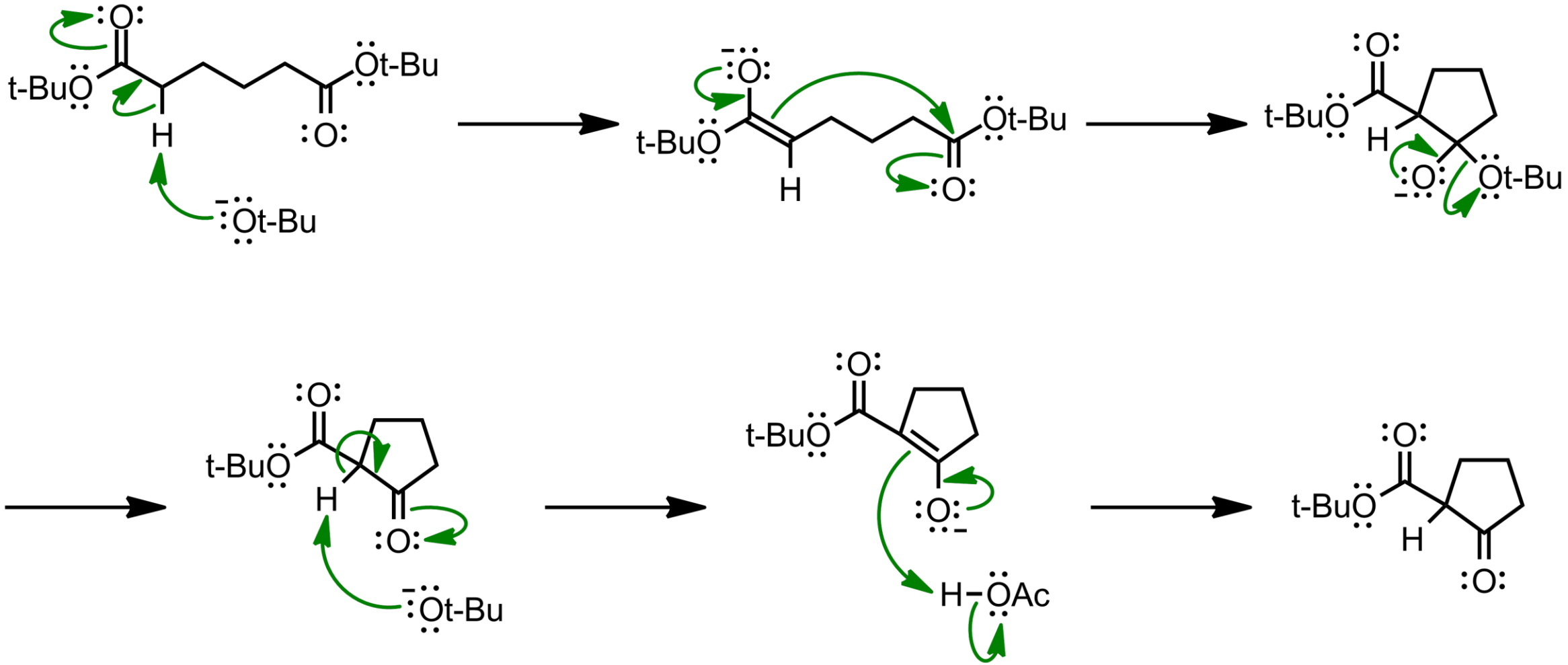
**intramolecular reaction**



# Dieckmann Condensation



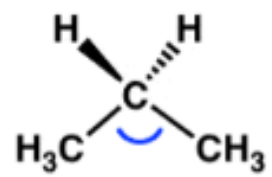
# Mechanism


t-BuO
Ot-Bu
H
O
Ot-Bu
t-BuO
Ot-Bu
H
O
t-BuO
H
O
Ot-Bu
t-BuO
H
O
Ot-Bu
t-BuO
H
O
t-BuO
O
H
OAc
t-BuO
H
O

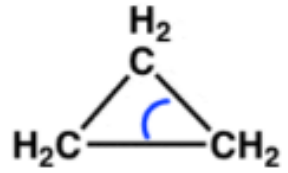
# Ring opening reactions

# Cyclopropane ring

C**yclopropane  has** large **ring strain** due to a mixture of angle **strain** and torsional **strain**



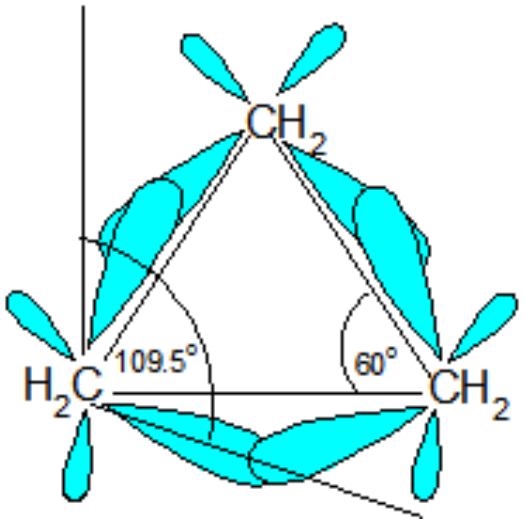

C–C–C bond angle 109.5°



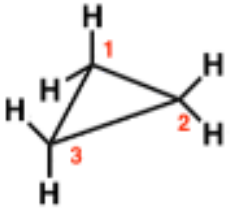

interior bond angle 60°

**(~ 49° less than ideal of 109°)**

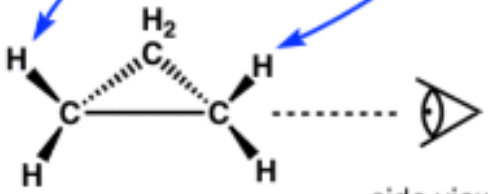
**Orbital overlap**




**Torsional Strain in Cyclopropane**

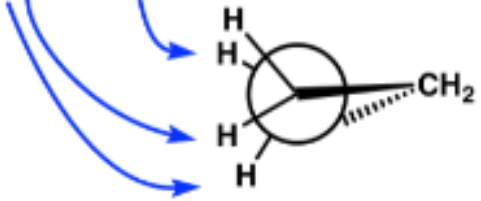



same as




side view

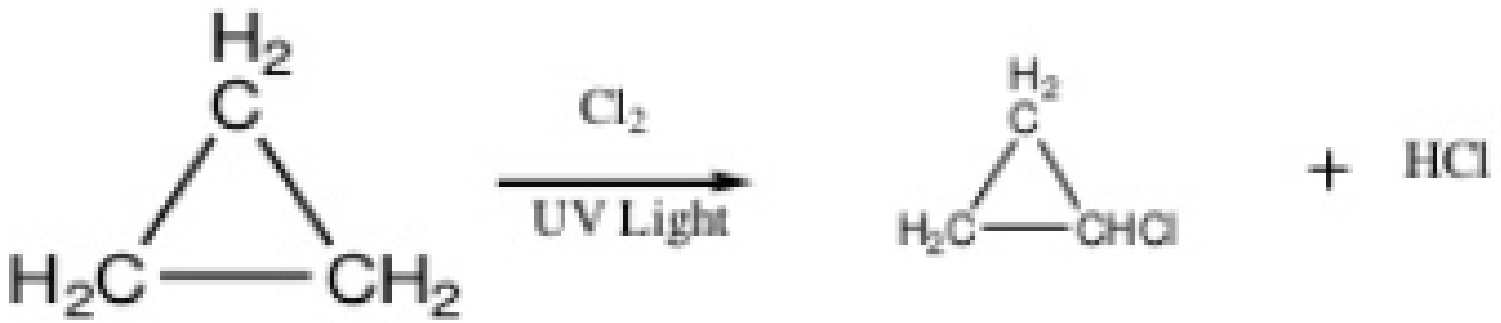
**note how hydrogens are eclipsed !**



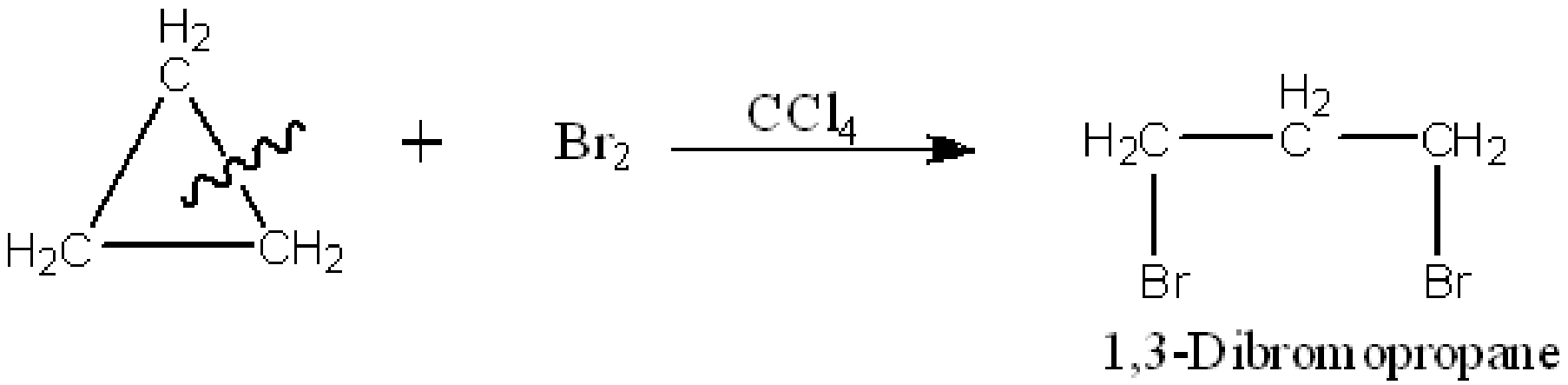

*Newman projection*

# Formation of cyclopropane ring

# Chlorination

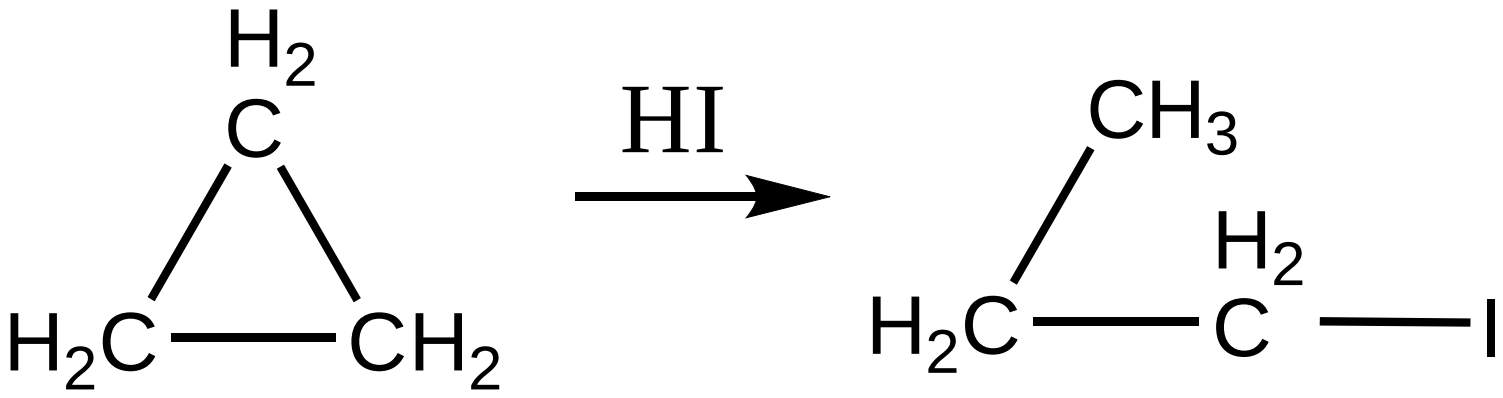



# Bromination

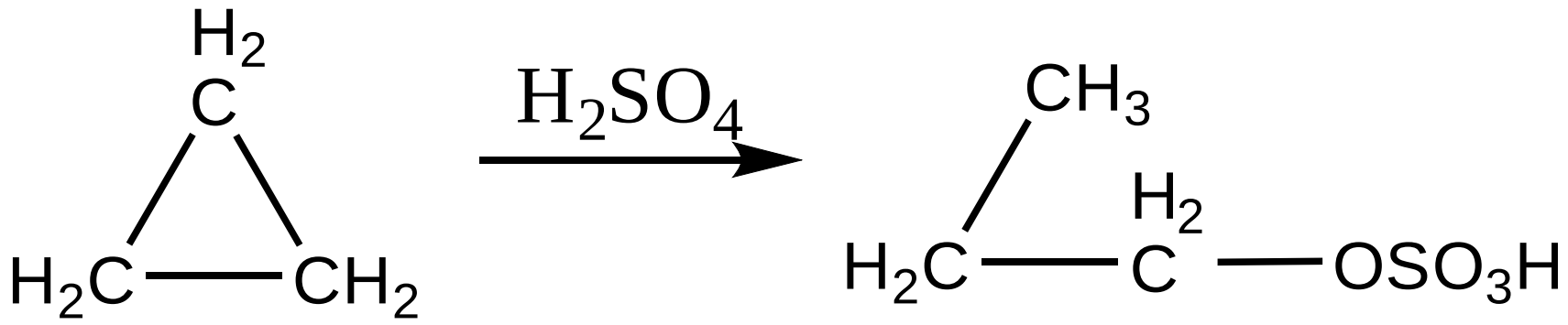



1,3-Dibromopropane

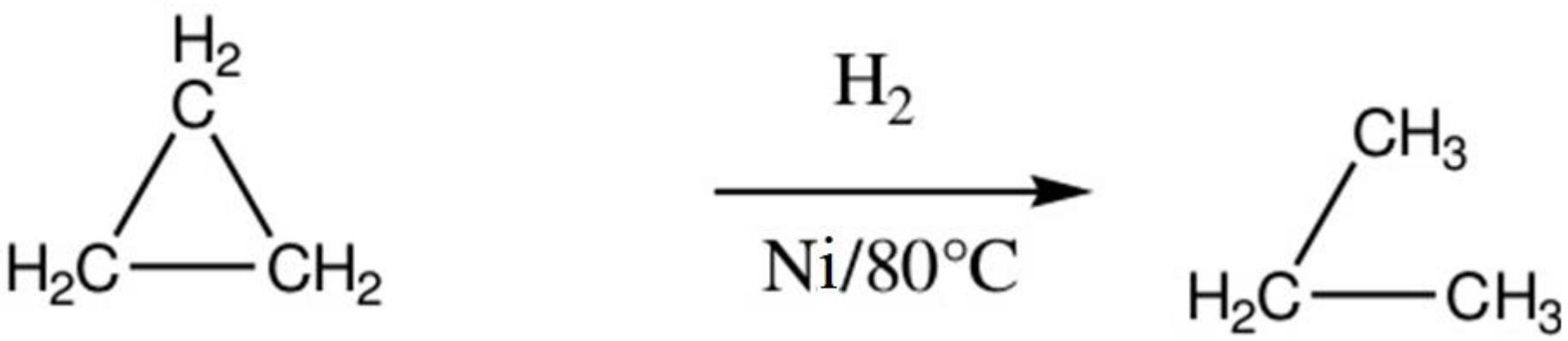
# Addition of HI (hydrogen iodide)



# Addition of sulfuric acid



# Reduction of Cycloalkane/ hydrogenation

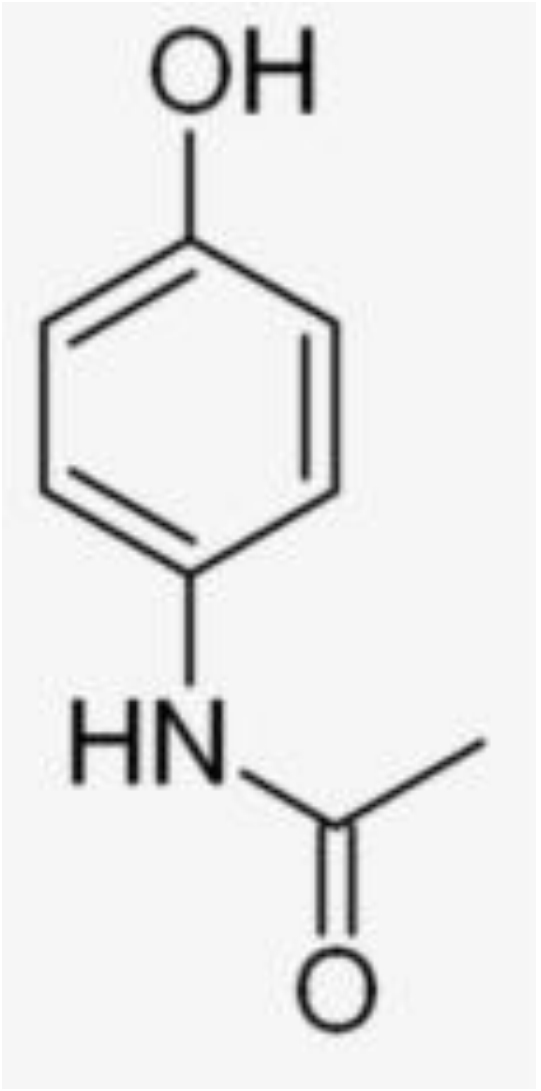


# Drug synthesis

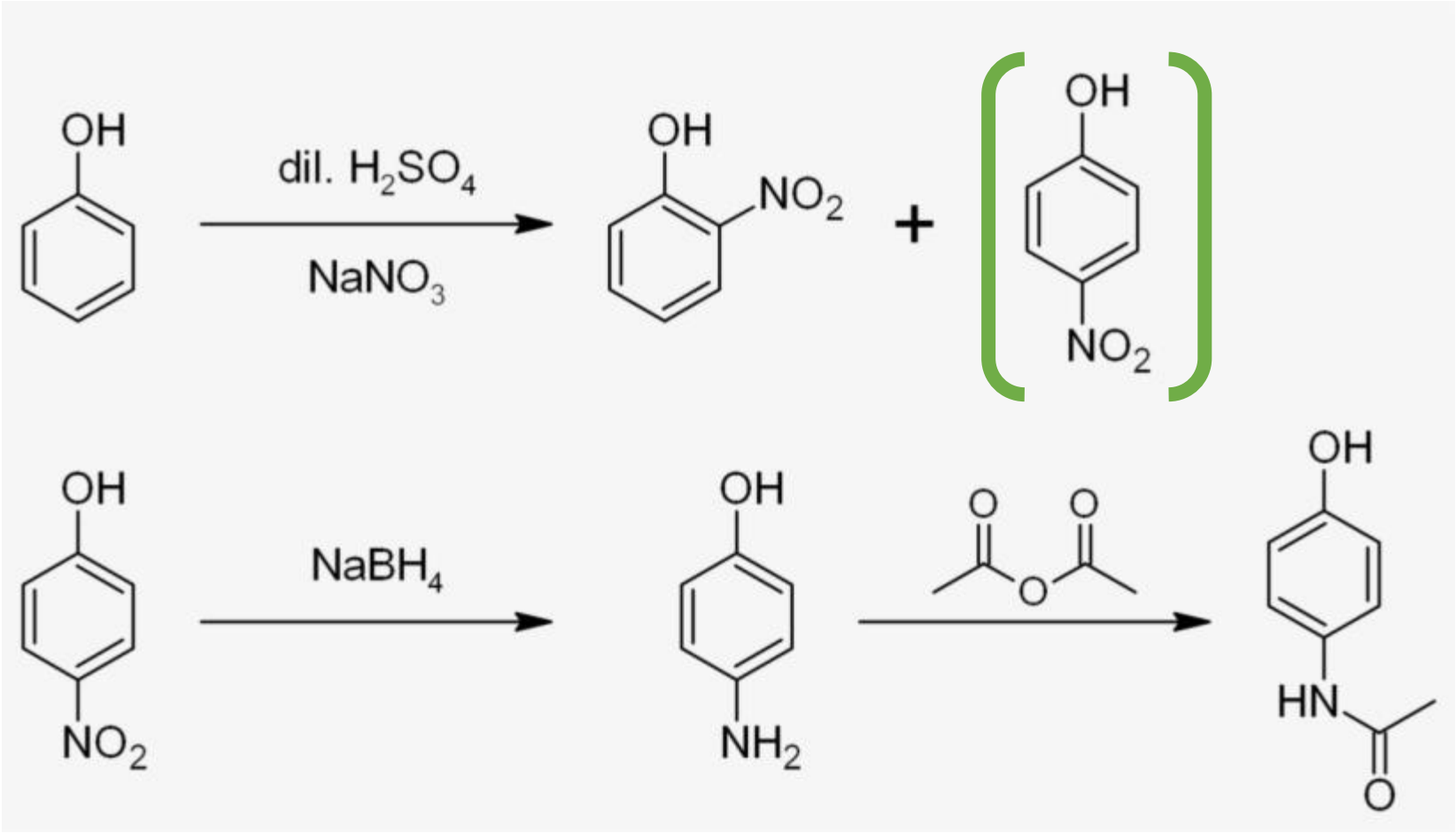
# Paracetamol


**Antipyretic**

**Analgesic**

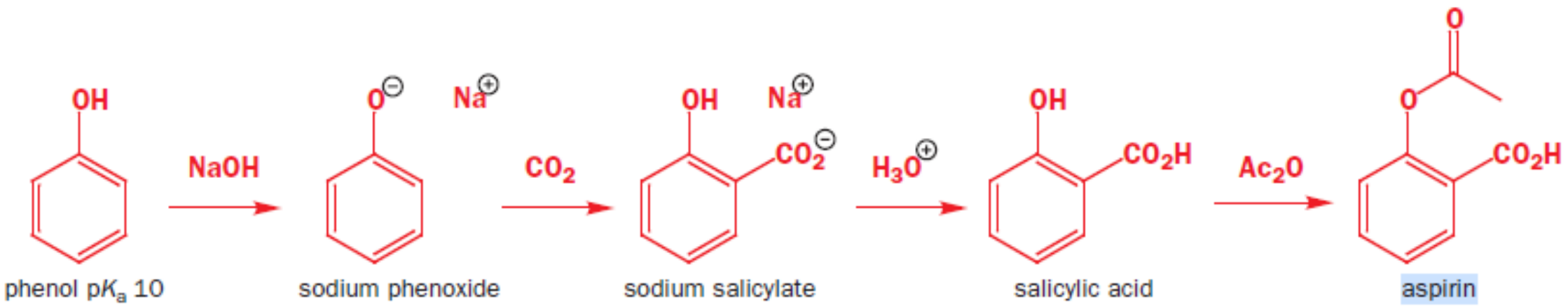


# SLO-2 Synthesis of a commonly used drug molecule-Introduction



# Synthesis of Aspirin and its uses

**Aspirin, also known as acetylsalicylic acid, is a medication used to reduce pain, fever, or inflammation**



# THANK YOU