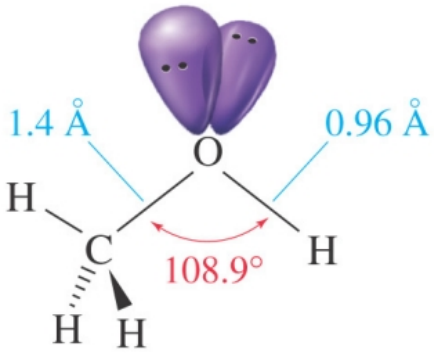
DAMIETTA UNIVERSITY

CHEM-103:

BASIC ORGANIC CHEMISTRY

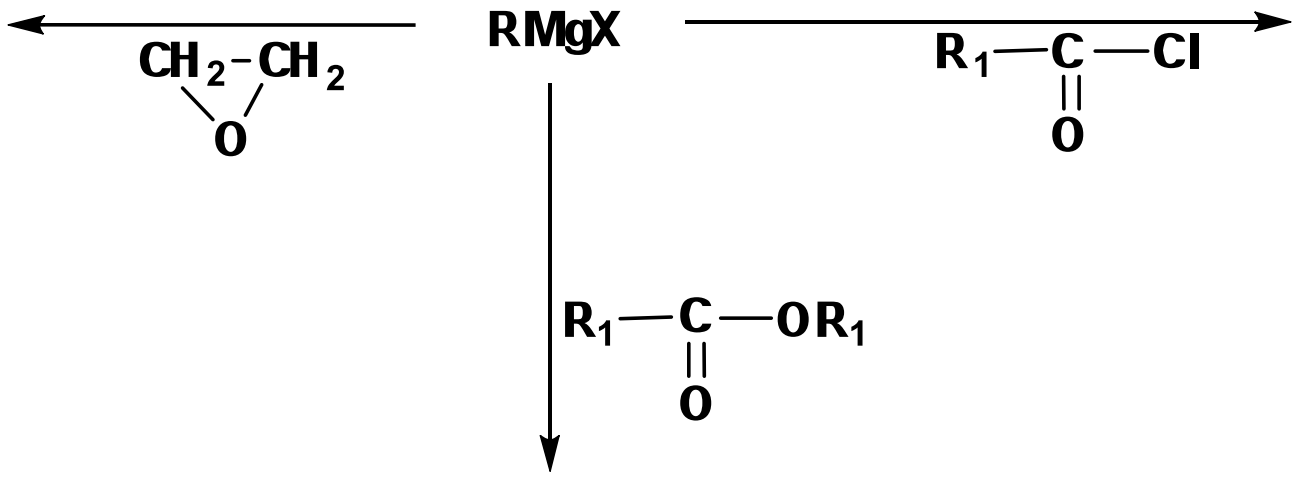
LECTURE 7

Dr Ali El-Agamey

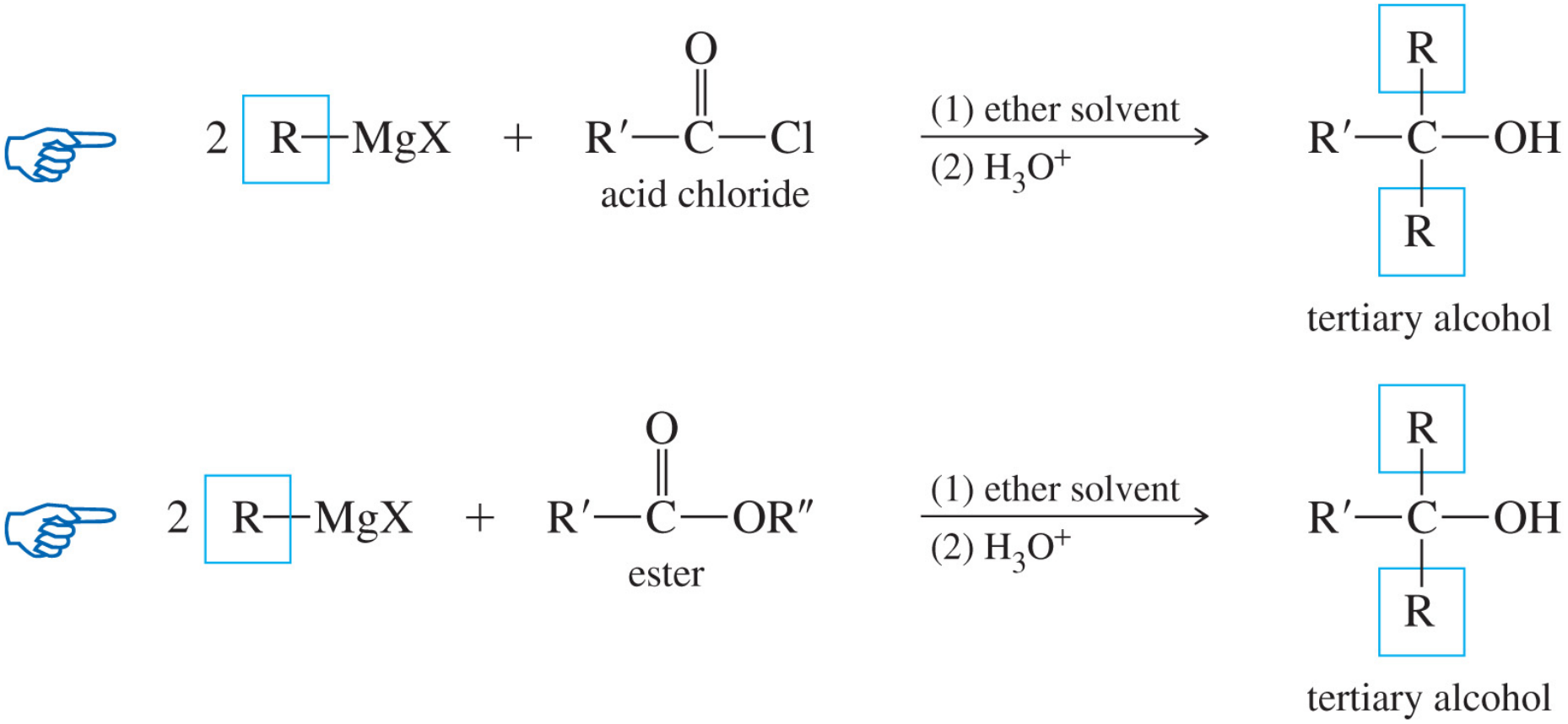


Alcohols

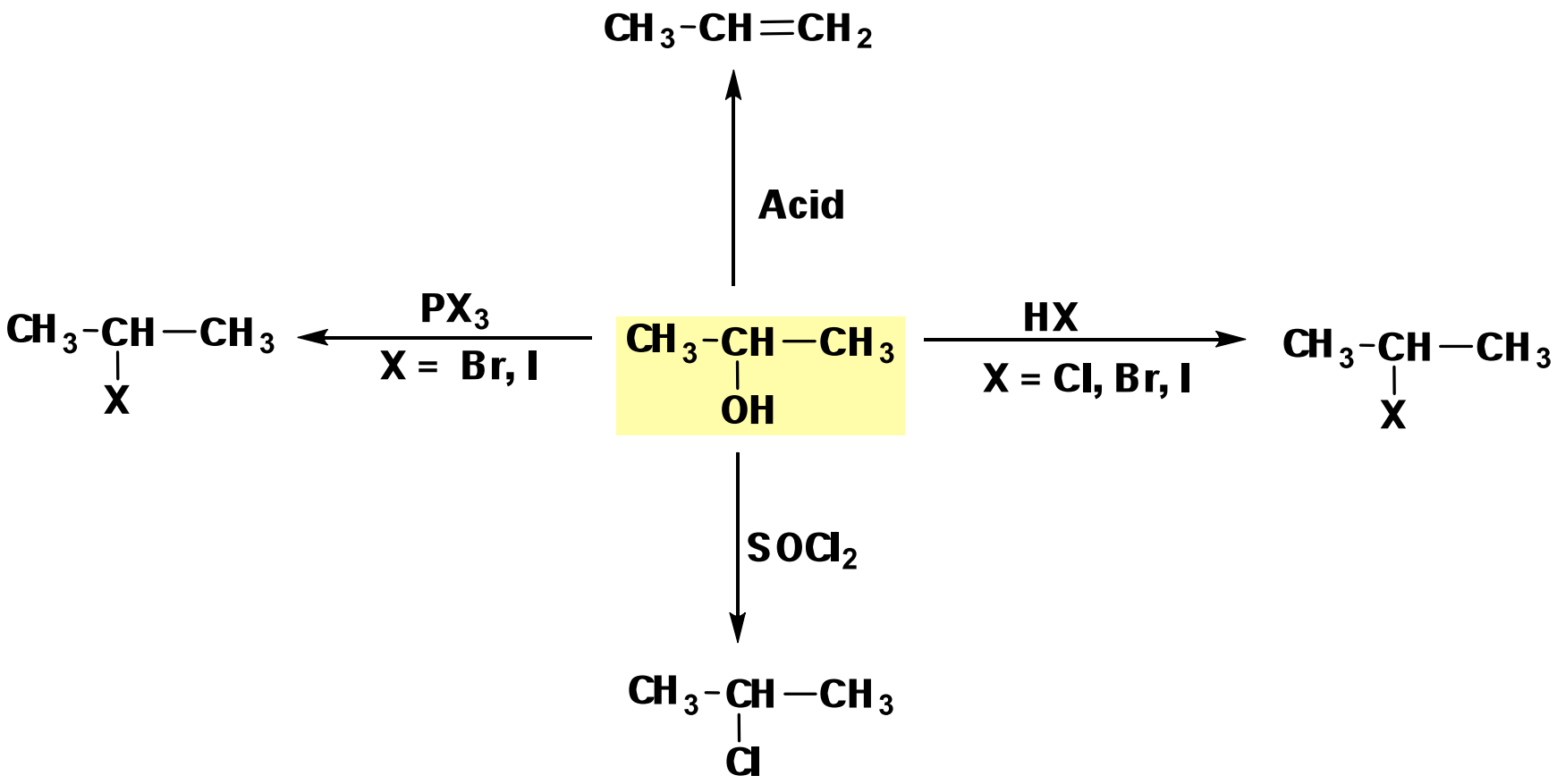
Preparation of Alcohols



Reaction of Grignards with Carboxylic Acid Derivatives

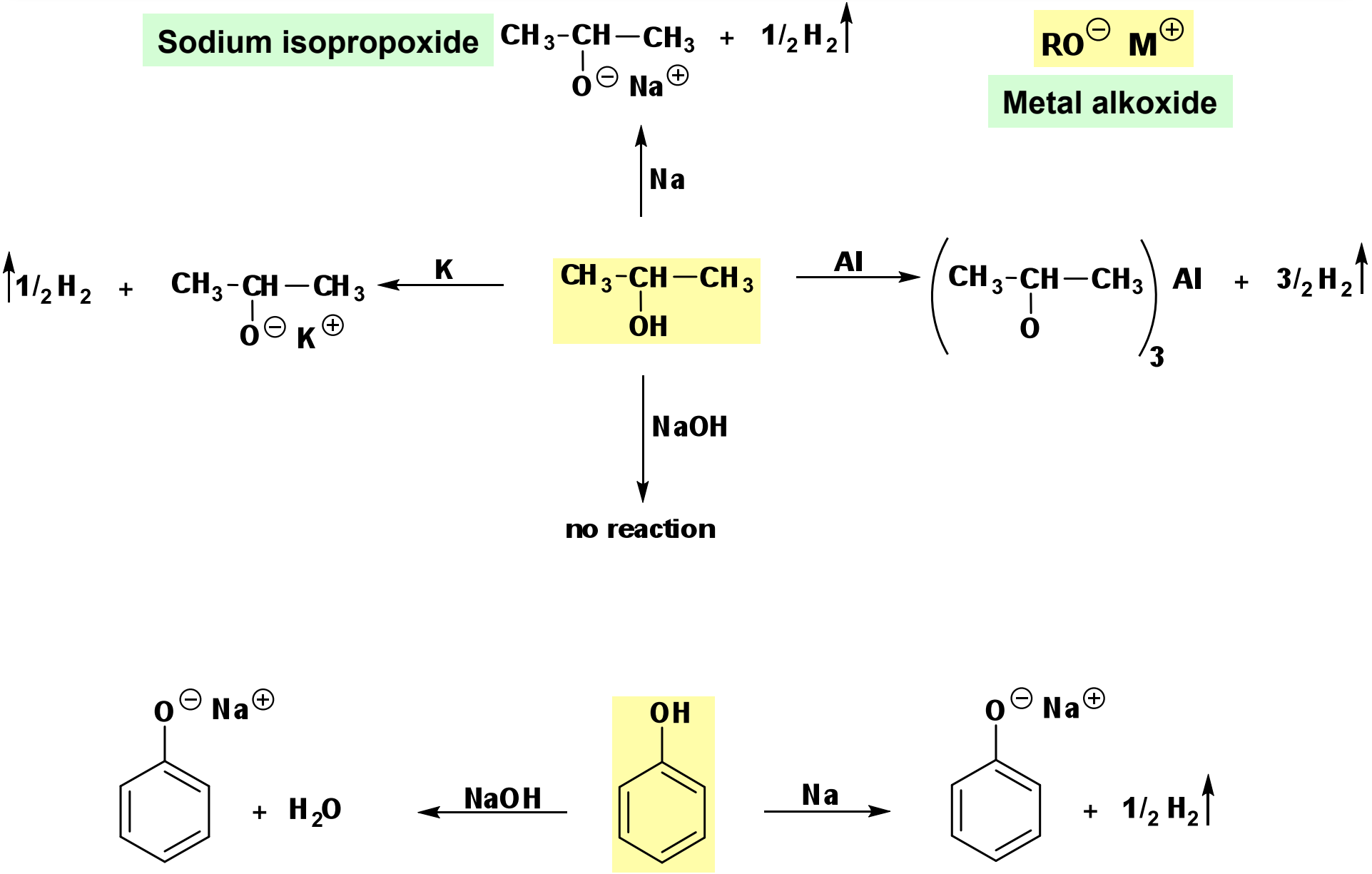


Reactions of Alcohols

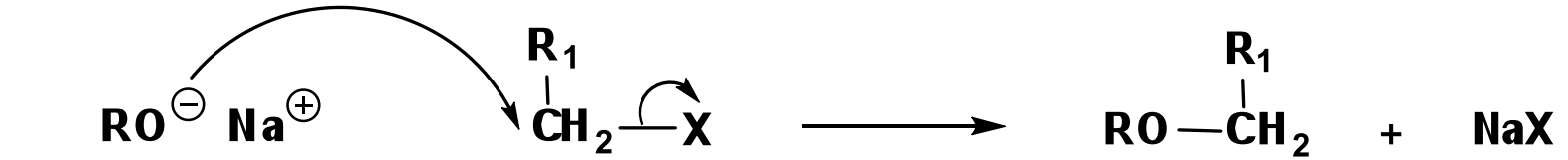


$SOCl_2$: Thionyl chloride

Reactions of Alcohols (as acids)



Alkoxide Ions: Williamson Ether Synthesis

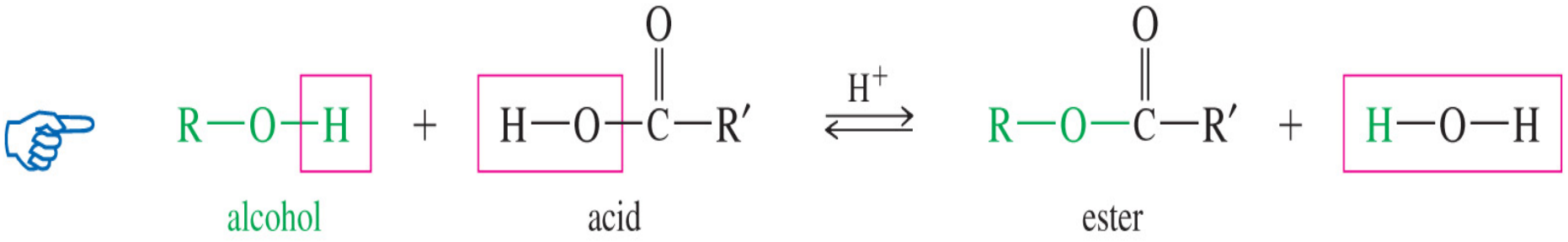


Sodium alkoxide | 1° alkyl halide | ether

- Ethers can be synthesized by the reaction of alkoxide ions with **primary alkyl halides** in what is known as the Williamson ether synthesis.

Reactions of Alcohols

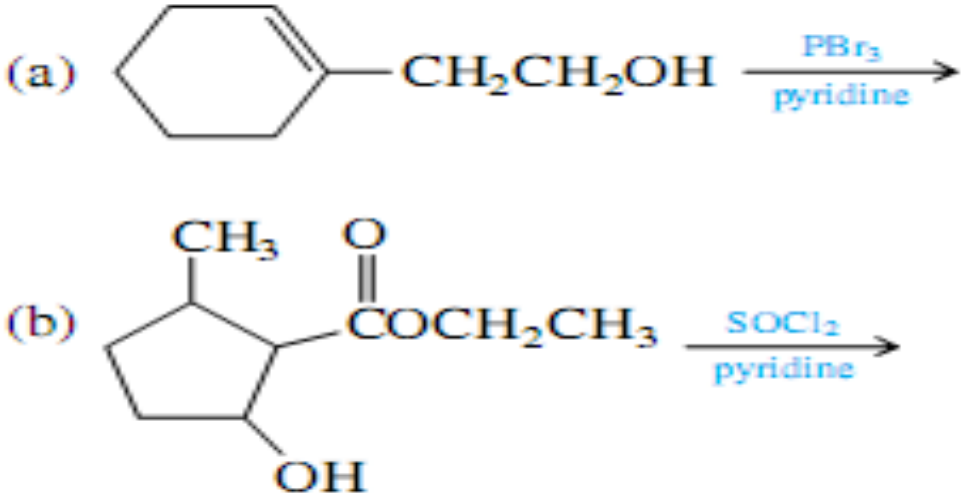
Esterification

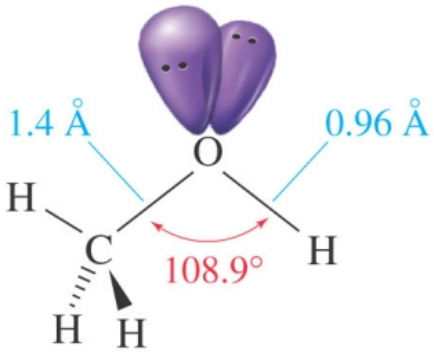


- Reaction of an alcohol and a carboxylic acid produces an ester.
- Sulfuric acid is a catalyst.

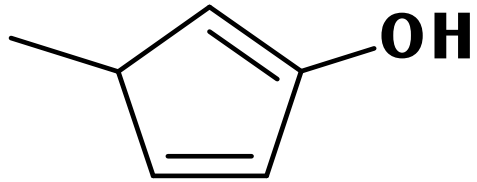
Homework: Complete the following equations

4.32





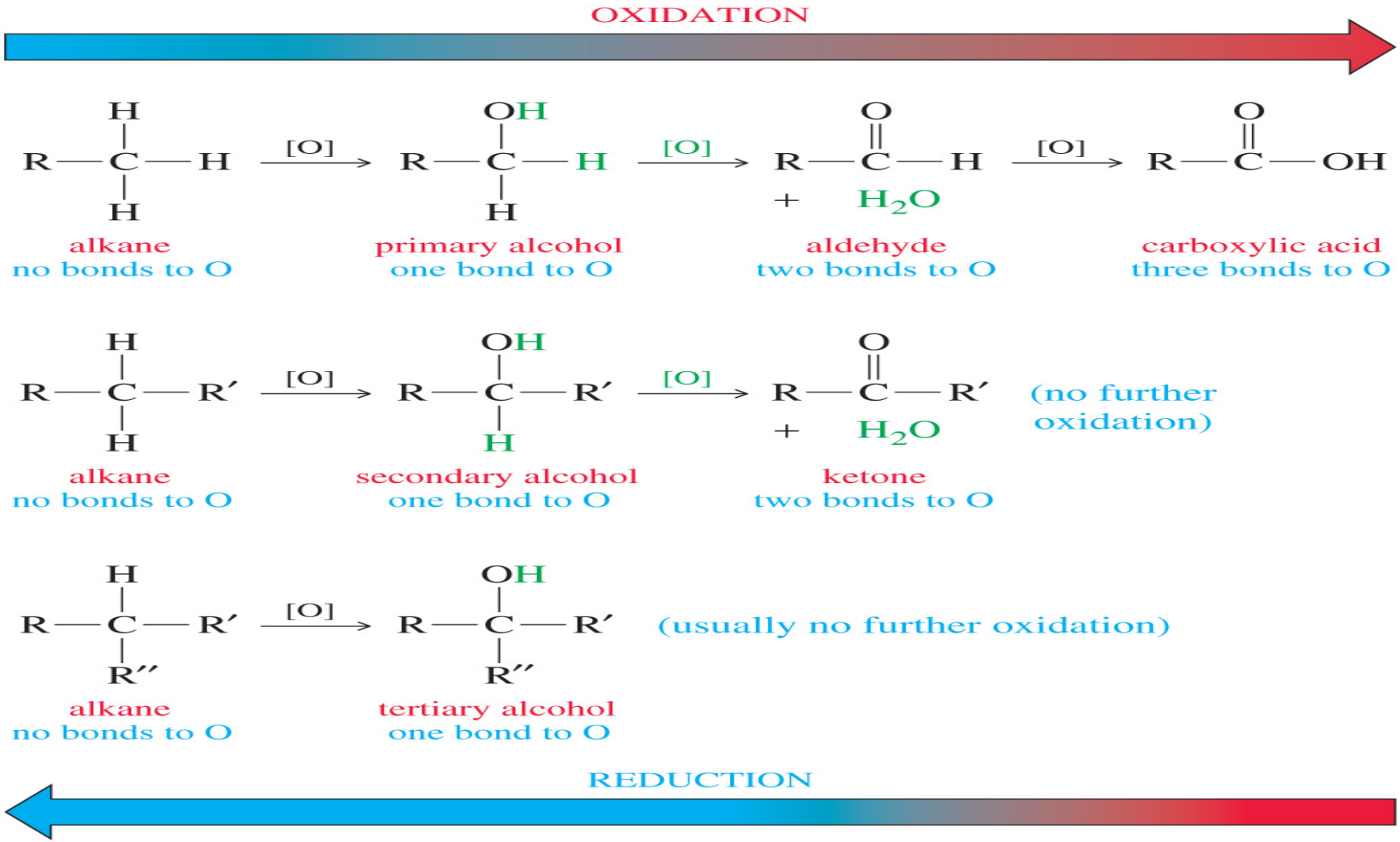
Alcohols


OH

Oxidation States

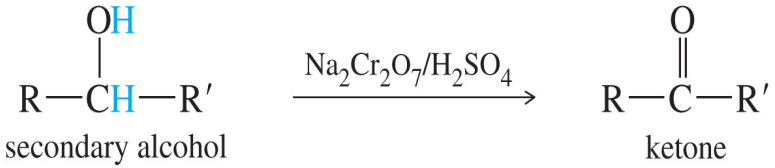
- **Easy** for inorganic salts:
  - CrO_4^{2-} reduced to Cr_2O_3.
  - $KMnO_4$ reduced to MnO_2.
- ***Oxidation***: Gain of O, O_2, or X_2; loss of H_2.
- ***Reduction***: Gain of H_2 (or H^-); loss of O or O_2; and loss of X_2.
- The gain or loss of H^+, ^-OH, H_2O, HX, etc. is neither an oxidation nor a reduction.

Oxidation States of Carbons

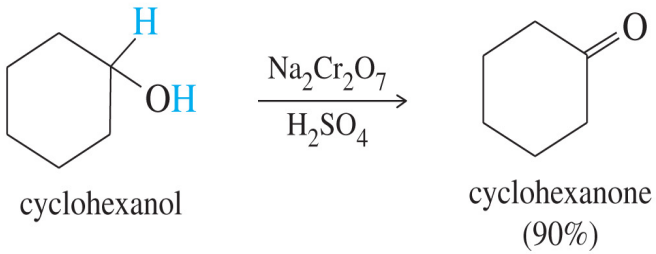


Oxidation of 2° Alcohols

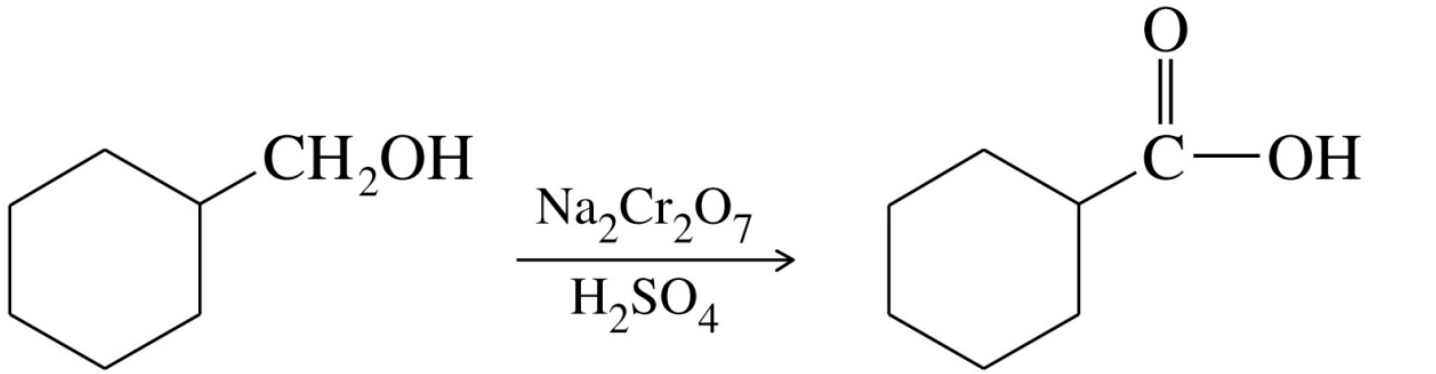
- Oxidation of 2° alcohol gives a ketone.
- Oxidizing agent is **$Na_2Cr_2O_7/H_2SO_4$** (orange color).
- Active reagent probably is **H_2CrO_4 (chromic acid)**.
- Color is changed from orange to greenish-blue **chromium (III).**



Example



Oxidation of 1° Alcohols to Carboxylic Acids



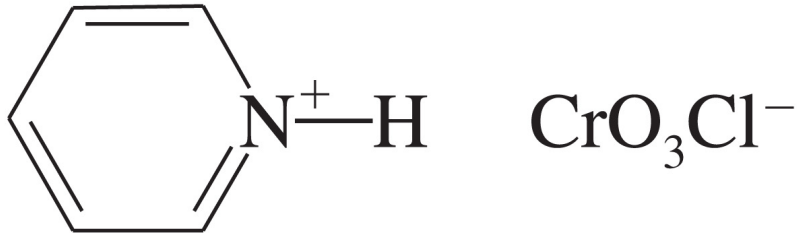
cyclohexyl methanol

cyclohexanecarboxylic acid (92%)

- Chromic acid reagent (or $KMnO_4$) oxidizes primary alcohols to carboxylic acids.
- The oxidizing agent is **too strong** to stop at the aldehyde.

Pyridinium Chlorochromate (PCC)

Pyridinium chlorochromate (PCC):

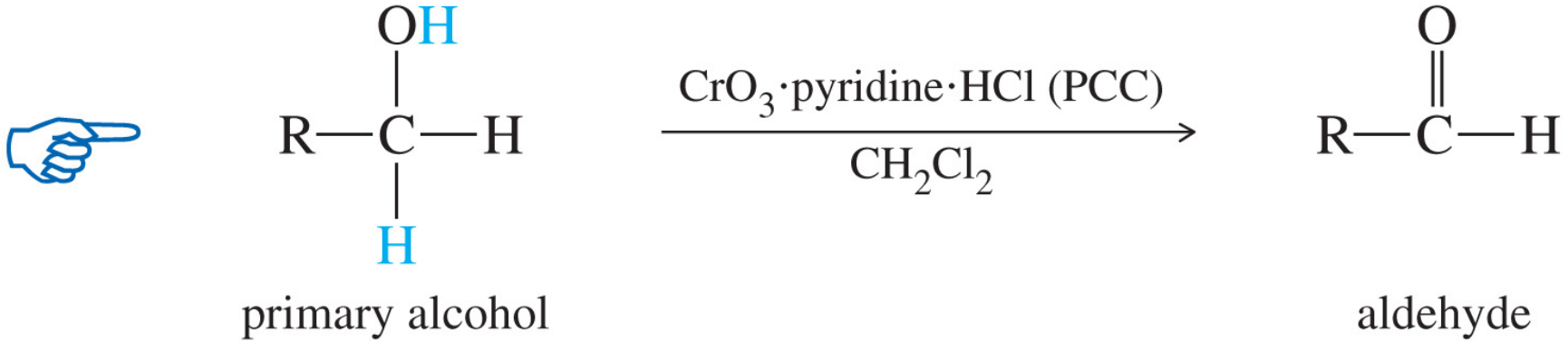


$CrO_3 \cdot \text{pyridine} \cdot HCl$

or $pyH^+ CrO_3Cl^-$

- PCC is a complex of chromium trioxide, pyridine, and HCl.
- **Oxidizes primary alcohols to aldehydes**.
- Oxidizes secondary alcohols to ketones.

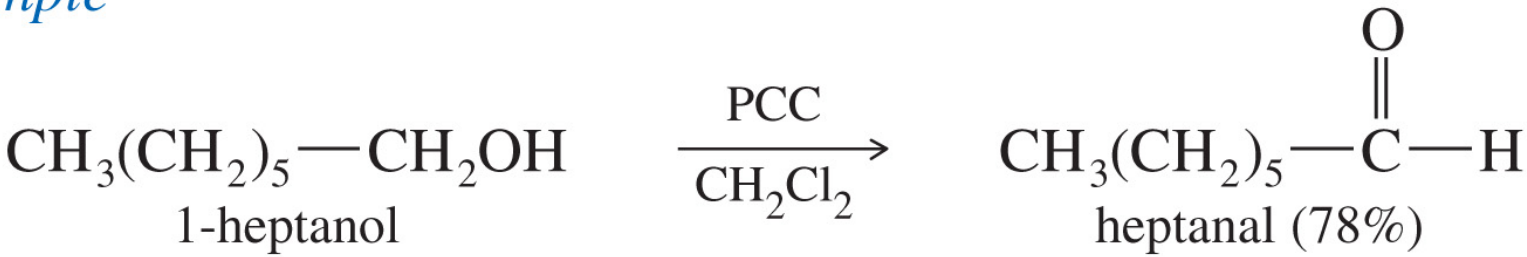
Pyridinium Chlorochromate (PCC)



primary alcohol

aldehyde

Example



1-heptanol

heptanal (78%)

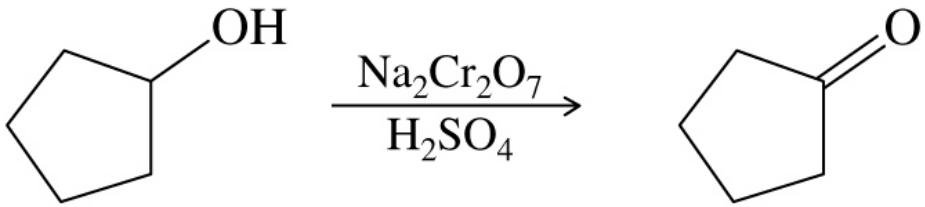
3° Alcohols Cannot Be Oxidized

- Carbon does not have hydrogen, so oxidation is difficult and involves the breakage of a C—C bond.
- Chromic acid test is for **primary and secondary** alcohols because tertiary alcohols do not react.

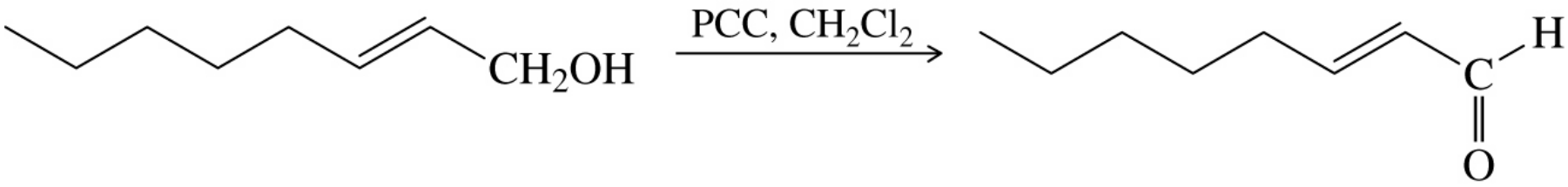
Summary of Alcohol Oxidations

To Oxidize	Product	Reagent
2° alcohol	ketone	chromic acid (or PCC)
1° alcohol	aldehyde	PCC
1° alcohol	carboxylic acid	chromic acid

Examples



cyclopentanol (or PCC,) cyclopentanone



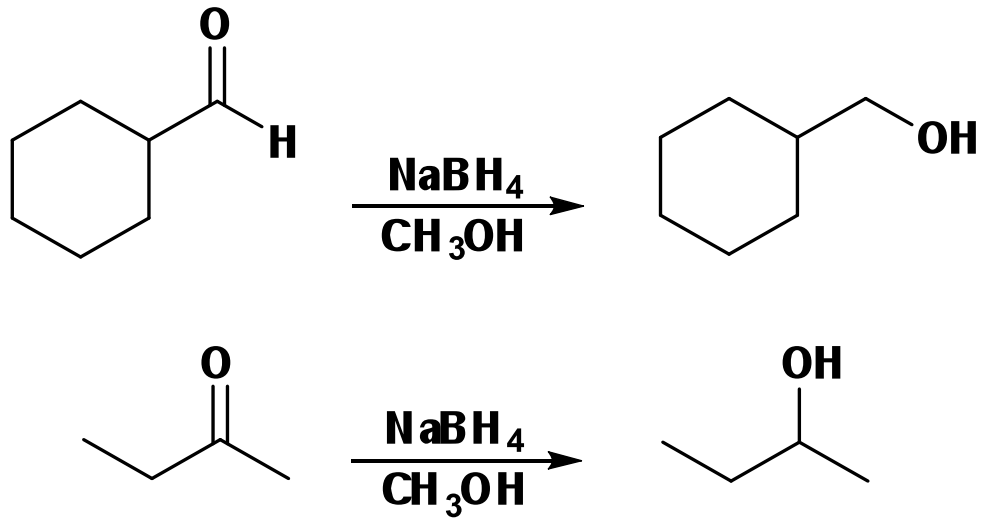
2-octen-1-ol 2-octenal

Reduction of Carbonyl

- Reduction of aldehyde yields 1º alcohol.
- Reduction of ketone yields 2º alcohol.
- Reagents:
  - Sodium borohydride, $NaBH_4$
  - Lithium aluminum hydride, $LiAlH_4$
  - Raney nickel

Sodium Borohydride

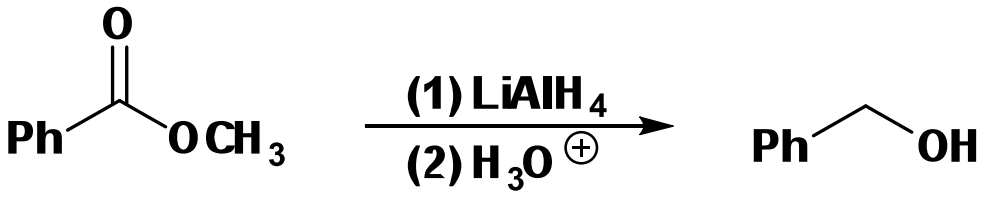
- $NaBH_4$ is a source of hydrides (H^-)
- Only reacts with carbonyl of aldehyde or ketone, **not** with carbonyls of esters or carboxylic acids.

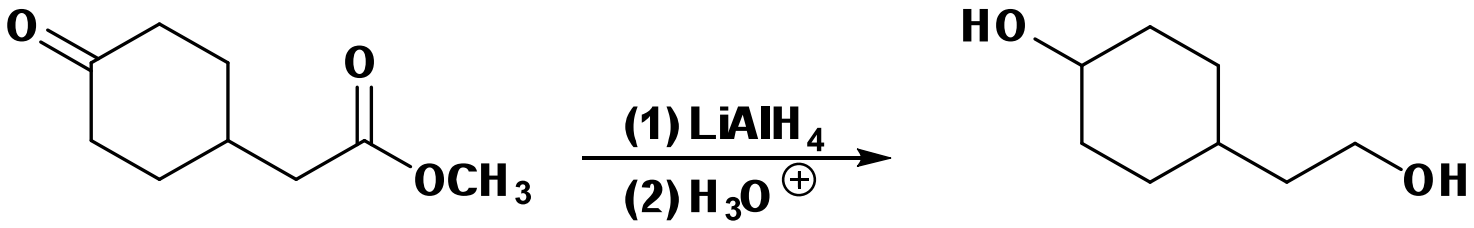


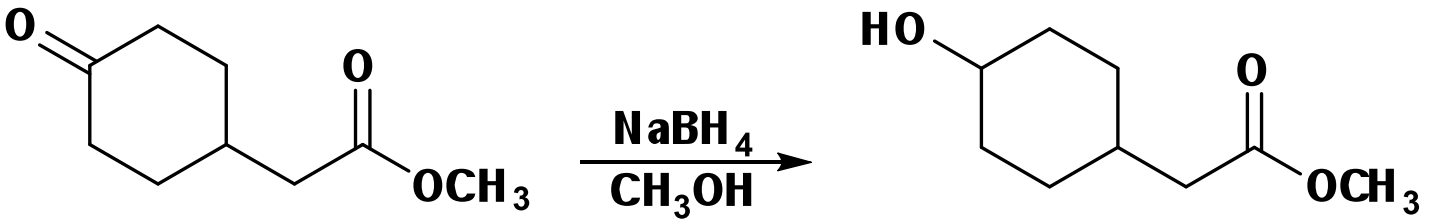
Lithium Aluminum Hydride

- $LiAlH_4$ is source of hydrides (H^-)
- **Stronger** reducing agent than sodium borohydride, but dangerous to work with.
- Reduces ketones and aldehydes into the corresponding alcohol.
- Converts esters and carboxylic acids to **1º alcohols**.

Reduction with $LiAlH_4$

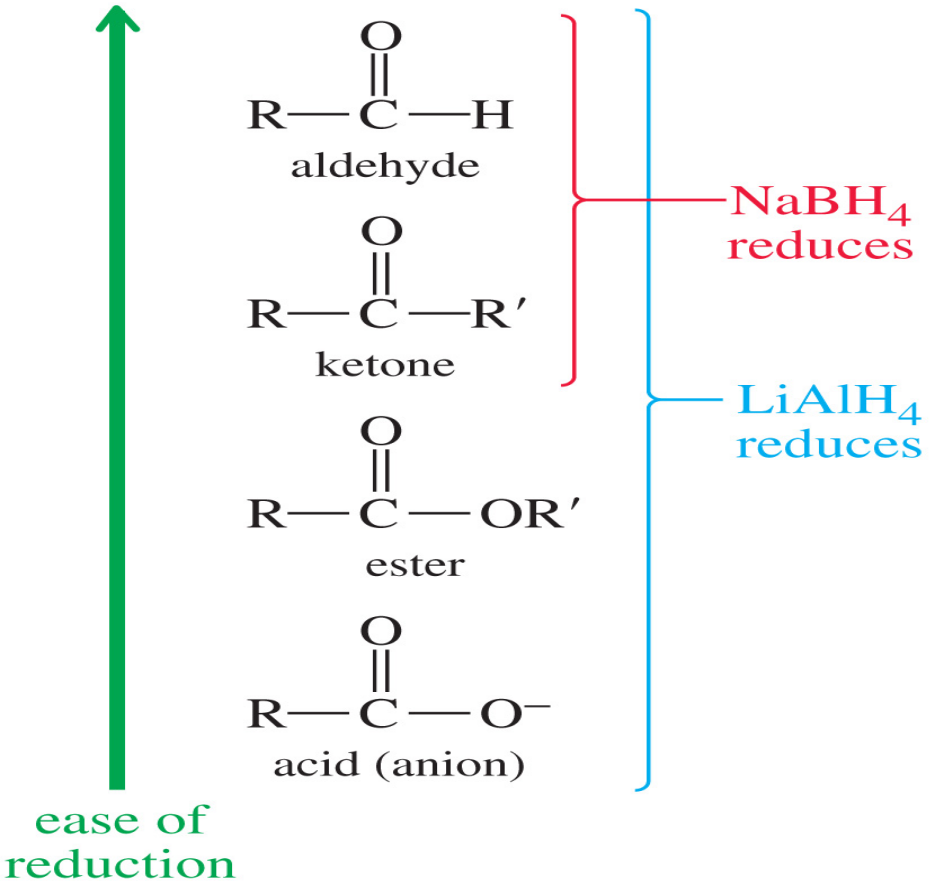




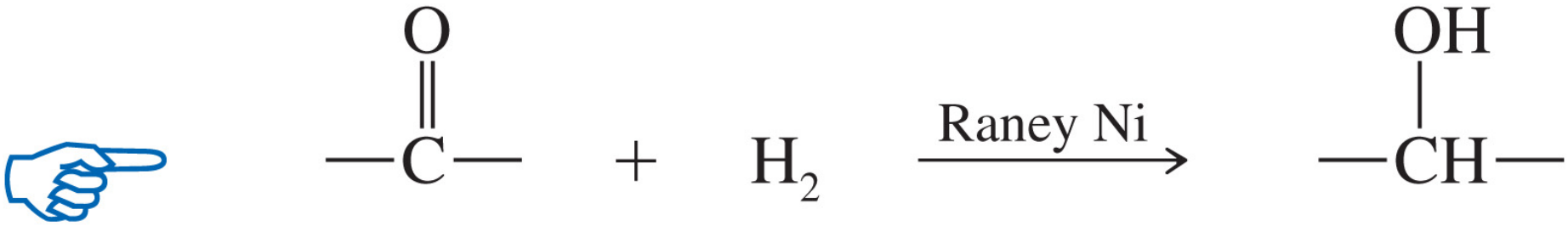


Reducing Agents

- $NaBH_4$ can reduce aldehydes and ketones but not esters and carboxylic acids.
- $LiAlH_4$ is a stronger reducing agent and will reduce all carbonyls.

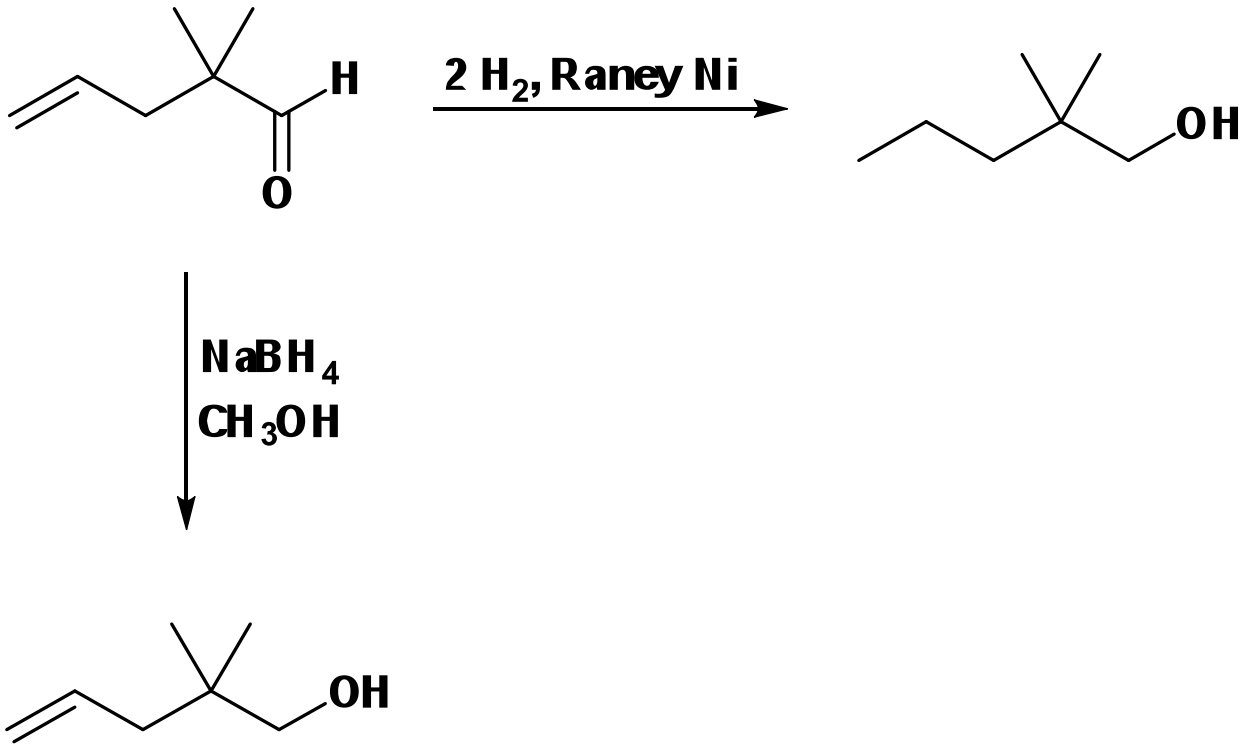


Catalytic Hydrogenation



- Raney nickel is a hydrogen rich nickel powder that is more reactive than Pd or Pt catalysts.
- This reaction **is not commonly** used because it will **also reduce double and triple bonds** that may be present in the molecule.
- Hydride reagents ($NaBH_4$ and $LiAlH_4$) are **more selective** so they are used more frequently for carbonyl reductions.

Catalytic Hydrogenation



Haloform reaction

- **Reagent used:**

X_2, NaOH (NaOX)

e.g. NaOCl; NaOBr; NaOI

Sodium hypohalite

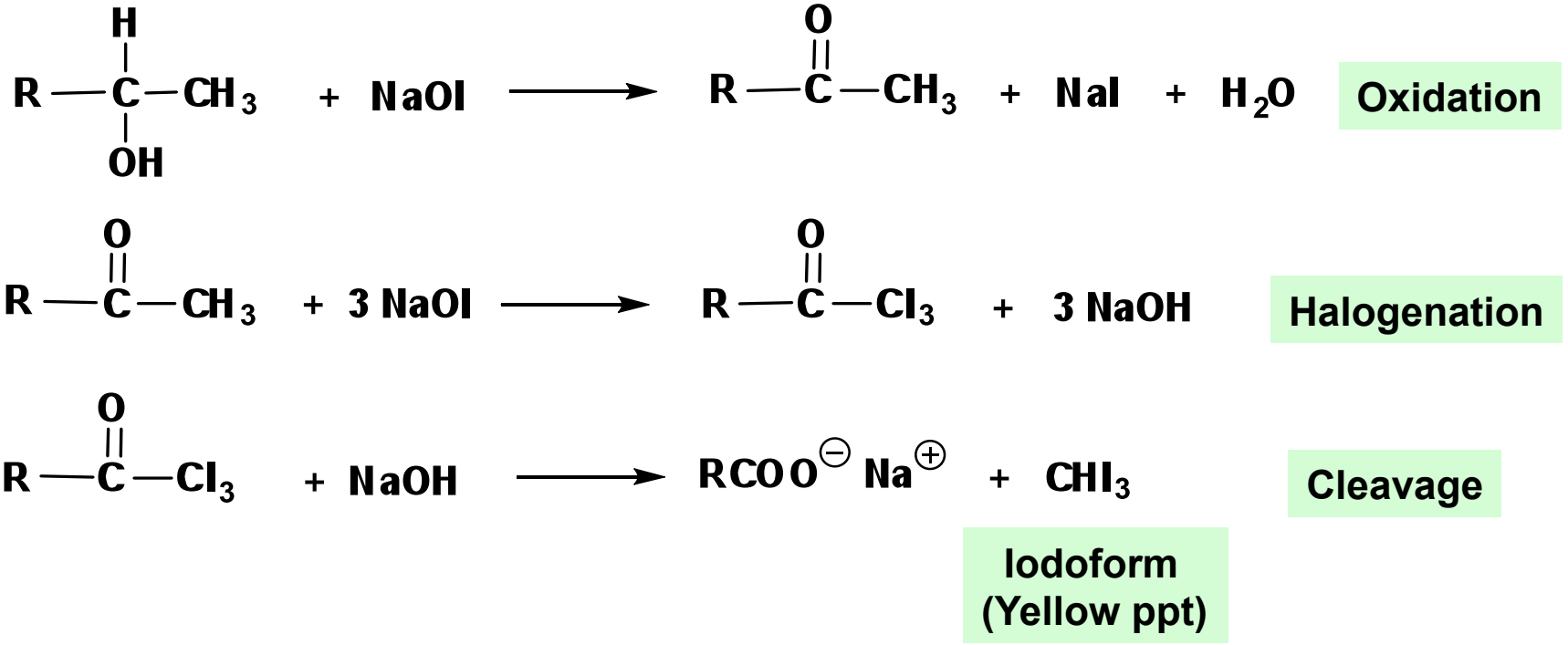
X_2, KOH (KOX)

e.g. KOCl; KOBr; KOI

Potassium hypohalite

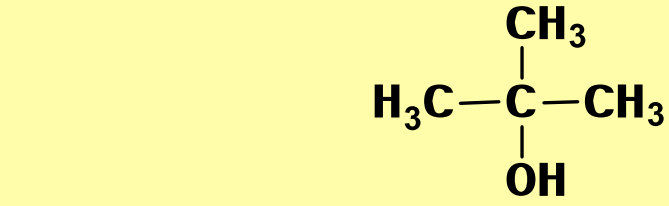
Haloform reaction

- **Mechanism:**



- Haloform reaction can convert an alcohol to a carboxylic acid **with one less carbon atom**.

Homework: Which of the following compounds will give a **positive iodoform test**?



(ii)

(iv)

Homework

15.28 Write the structure of the principal organic product formed in the reaction of 1-propanol with each of the following reagents:

(b) Sulfuric acid (catalytic amount), heat at 200°C

(d) Pyridinium chlorochromate (PCC) in dichloromethane

(e) Potassium dichromate ($K_2Cr_2O_7$) in aqueous sulfuric acid, heat

(f) Sodium amide ($NaNH_2$)

(g) Acetic acid ($CH_3\overset{\overset{O}{\|}}{C}OH$) in the presence of dissolved hydrogen chloride

Homework

15.27 Show how each of the following compounds can be synthesized from cyclopentanol and any necessary organic or inorganic reagents. In many cases the desired compound can be made from one prepared in an earlier part of the problem.

(c) 2-Phenylcyclopentanol

(f)