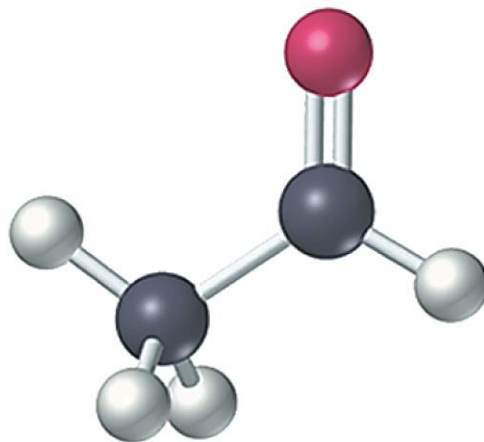


Aldehydes & Ketones – Nu. Add.-3 & Redox reactions



Instructor: Asst. Prof. Dr. Tanatorn Khotavivattana

E-mail: tanatorn.k@chula.ac.th

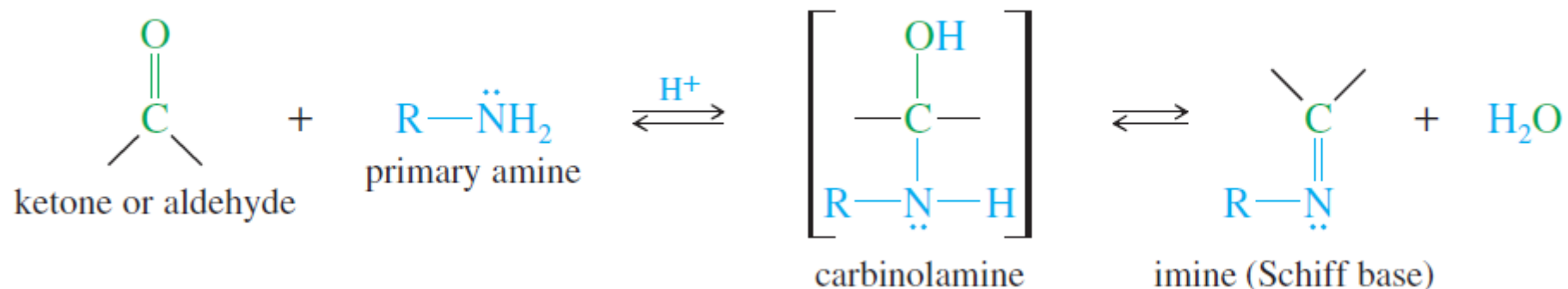
Recommended Textbook:

Chapter 18 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., 2010, Prentice Hall (Pearson Education)

Nucleophilic Addition with Weak Nucleophiles

3) Reaction with Amines (Immine formation)

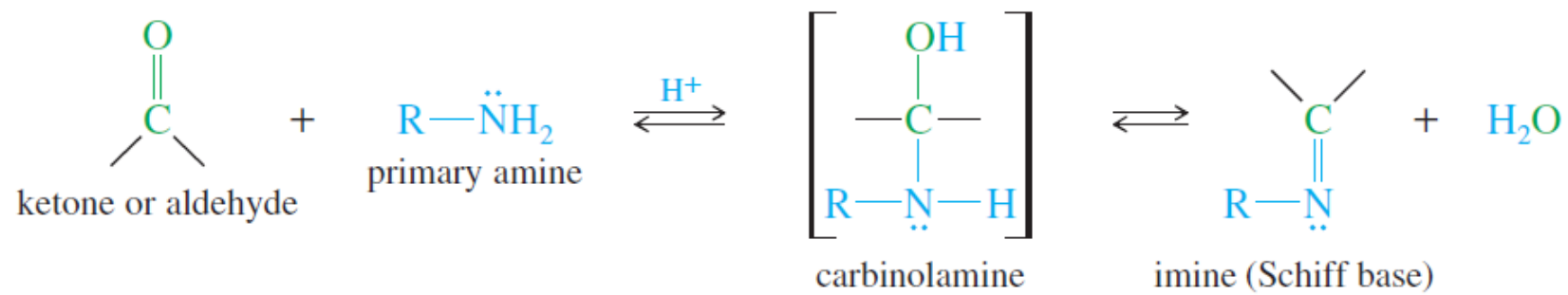
- Ammonia or a primary amine reacts with ketone or aldehyde to form an imine via condensation reaction



- Imines are **nitrogen analogues** of aldehydes and ketones with C=N bond in place of C=O bond
- Like amines, imines are **basic**; a substituted imine is also called a **Schiff base**

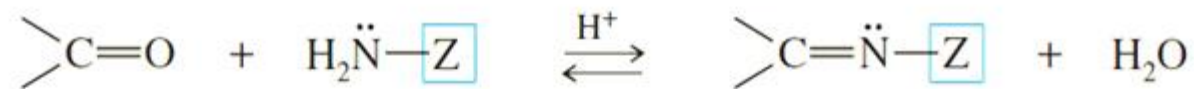
3) Reaction with **Amines** (Immine formation)

Mechanism – acid-catalysed



3) Reaction with Amines (Immine formation)

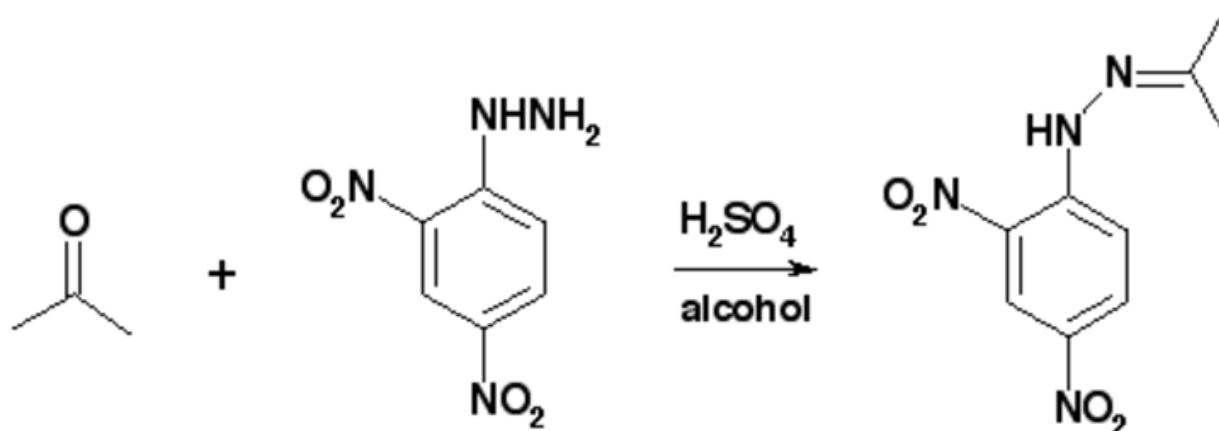
Other Types of "Amines"



<i>Z in Z—NH₂</i>	<i>Reagent</i>	<i>Product</i>
—H	$\text{H}_2\ddot{\text{N}}-\text{H}$ ammonia	$\text{>C}=\ddot{\text{N}}-\text{H}$ an imine
—R	$\text{H}_2\ddot{\text{N}}-\text{R}$ primary amine	$\text{>C}=\ddot{\text{N}}-\text{R}$ an imine (Schiff base)
—OH	$\text{H}_2\ddot{\text{N}}-\text{OH}$ hydroxylamine	$\text{>C}=\ddot{\text{N}}-\text{OH}$ an oxime
—NH ₂	$\text{H}_2\ddot{\text{N}}-\text{NH}_2$ hydrazine	$\text{>C}=\ddot{\text{N}}-\text{NH}_2$ a hydrazone
—NHPh	$\text{H}_2\ddot{\text{N}}-\text{NHPh}$ phenylhydrazine	$\text{>C}=\ddot{\text{N}}-\text{NHPh}$ a phenylhydrazone
—NHC(=O)NH_2	$\text{H}_2\ddot{\text{N}}-\text{NH}-\text{C(=O)}-\text{NH}_2$ semicarbazide	$\text{>C}=\ddot{\text{N}}-\text{NH}-\text{C(=O)}-\text{NH}_2$ a semicarbazone

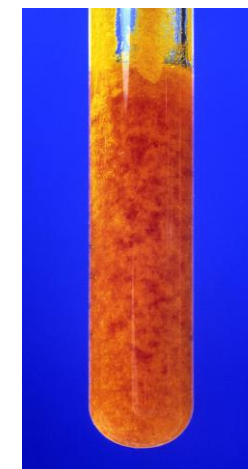
3) Reaction with **Amines** (Immine formation)

Reaction with 2,4-DNP – a qualitative test for aldehydes and ketones



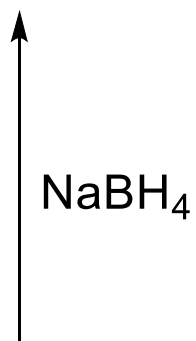
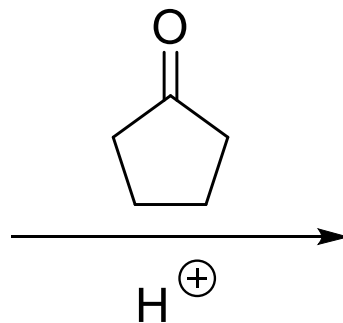
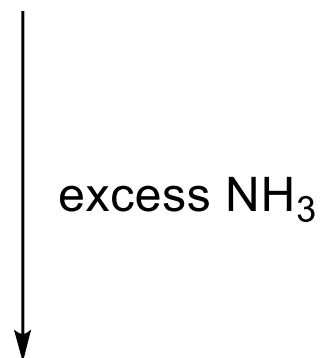
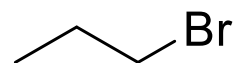
2,4-dinitrophenylhydrazine
(2,4-DNP)

dinitrophenylhydrazone
yellow, orange or red precipitate

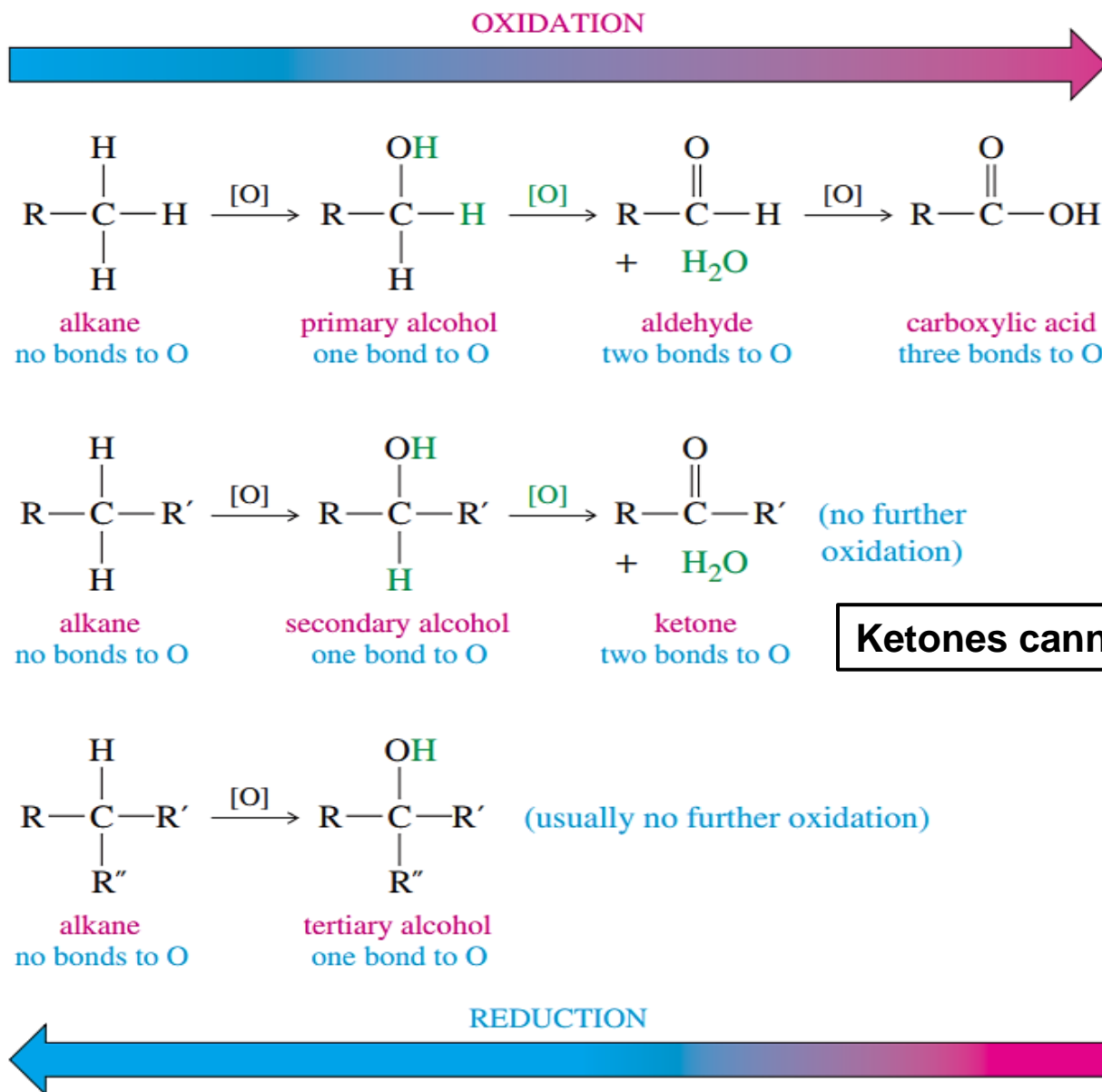


3) Reaction with Amines (Immine formation)

Examples

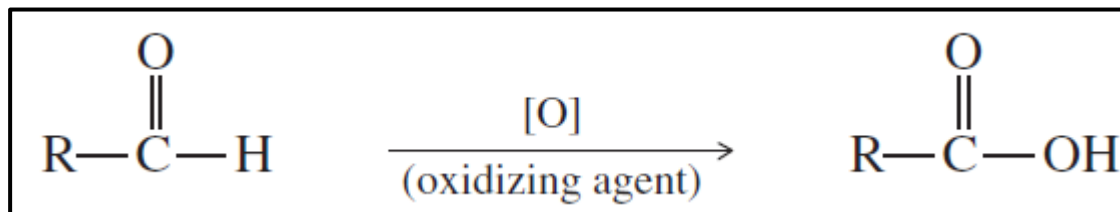


Oxidation and Reduction

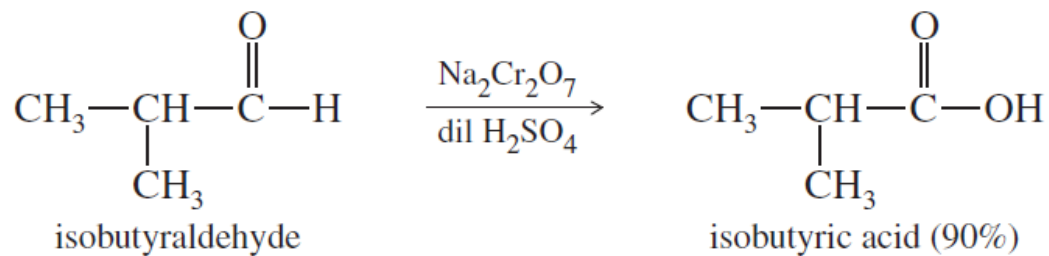


Oxidation of Aldehydes

- Common oxidants: **bleach (sodium hypochlorite)**, **chromic acid**, **permanganate**

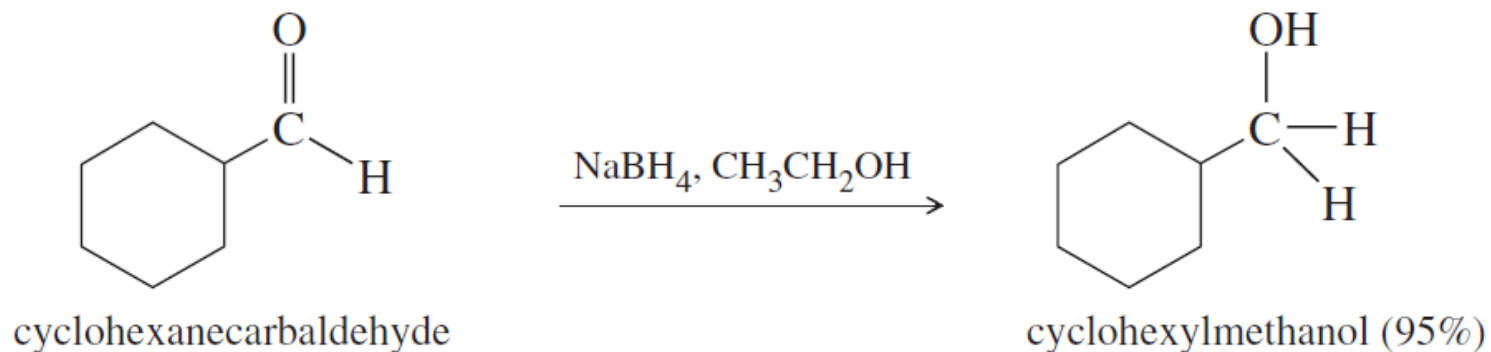


Examples



Reduction of Aldehydes and Ketones

Reduction to alcohols

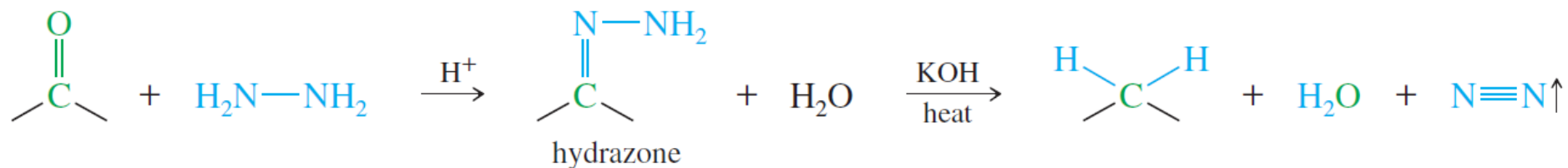


- Most commonly reduced by **sodium borohydride (NaBH₄)**
- **Lithium aluminum hydride (LiAlH₄)** also works, but it is **more powerful** (less selective), and it is much more difficult to work with

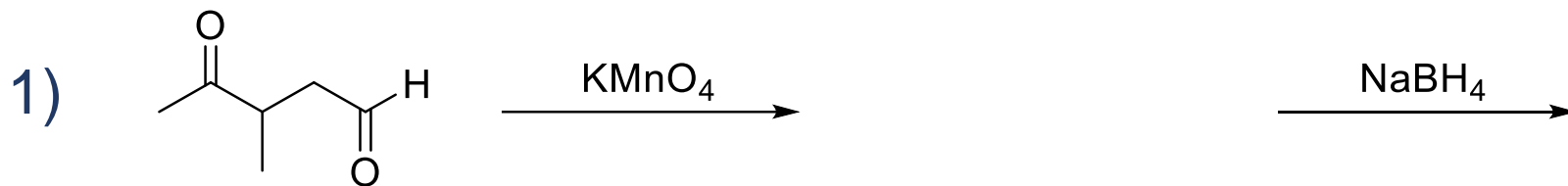
Reduction of Aldehydes and Ketones

Reduction to alkanes (Wolff–Kishner Reduction)

- The carbonyl compounds is treated with **hydrazine** to form **hydrazones**, which is heated with a **strong base** such as KOH to facilitate the elimination of N₂ gas

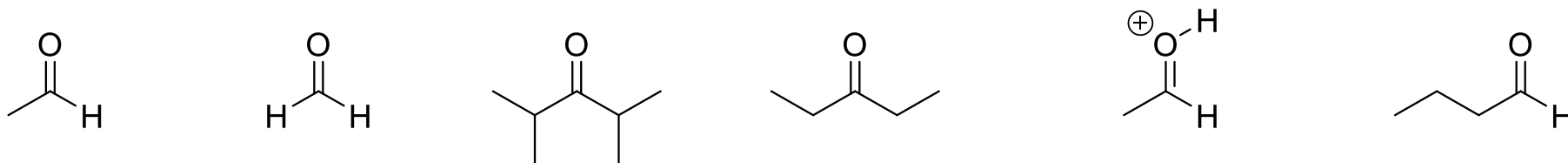


Examples



Homework – 1

1.1) Rank the following compounds in order of increasing reactivity towards nucleophilic addition reaction

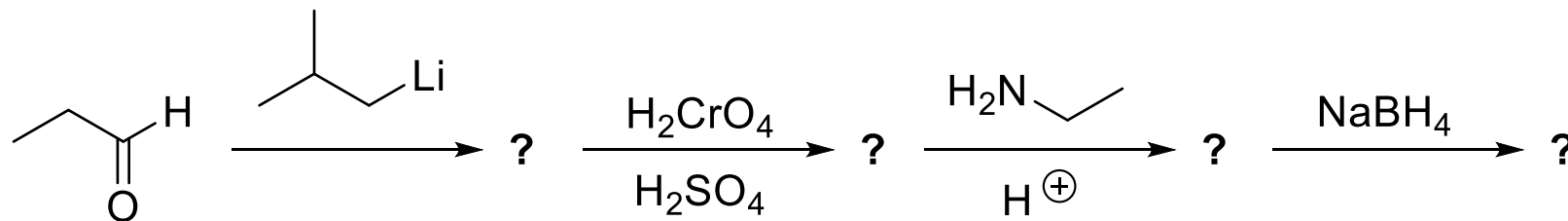


1.2) Rank the following compounds in order of increasing water solubility



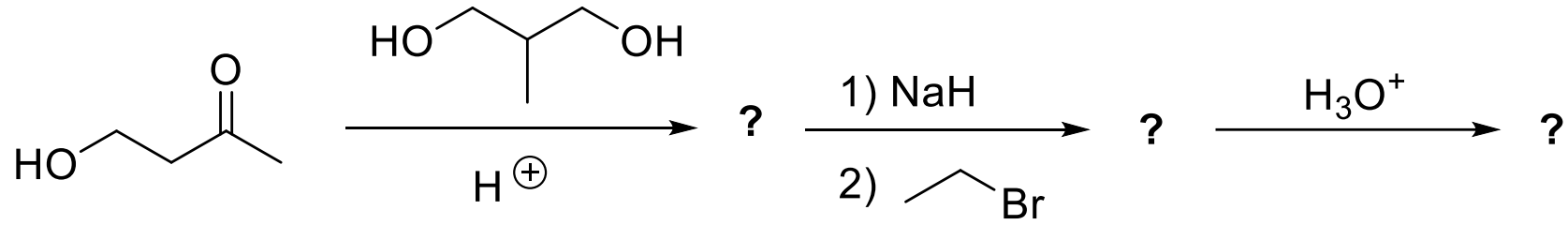
Homework – 2

Predict the products of the following reactions and draw mechanism of all steps



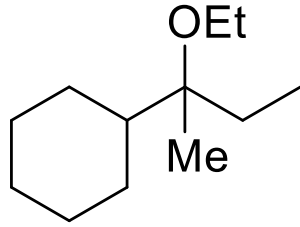
Homework – 3

Predict the products of the following reactions and draw mechanism of all steps

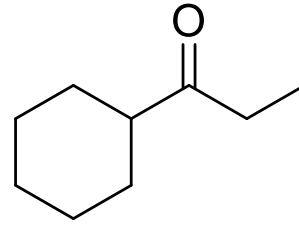


Homework – 4

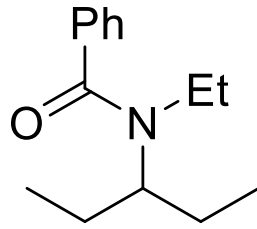
4.1) Suggest a way to synthesize



from



4.2) Suggest a way to synthesize



from

