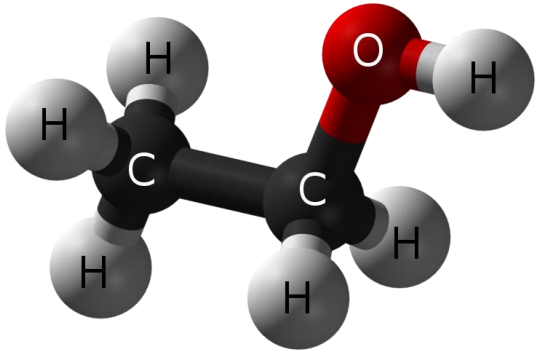
2302106 – Basic Organic Chemistry for ISE – Part II

Lecture 2-4

Alcohols – Oxidation / Reduction



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Recommended Textbook:

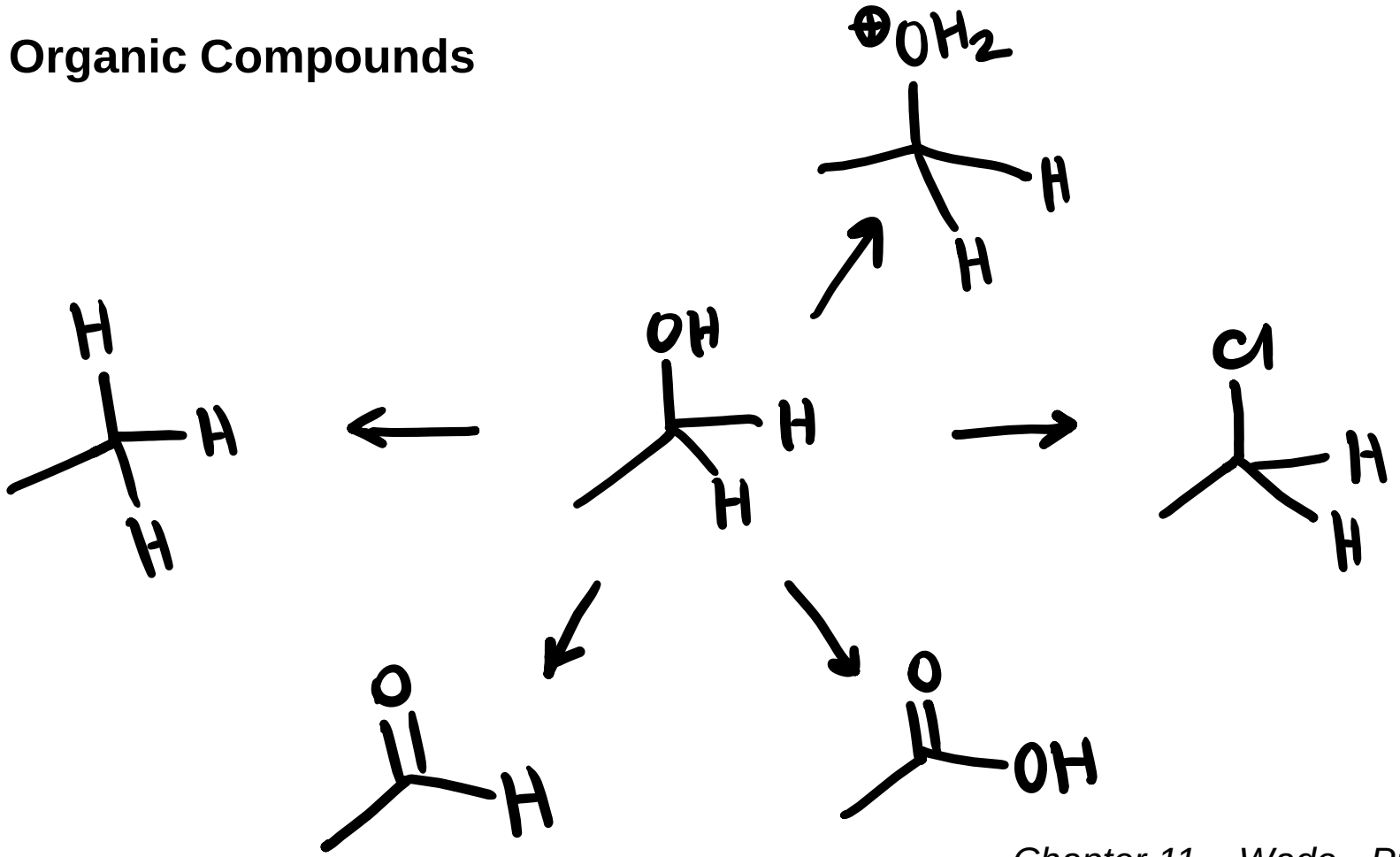
Chapter 10 and 11 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

Oxidation / Reduction

For Inorganic Compounds

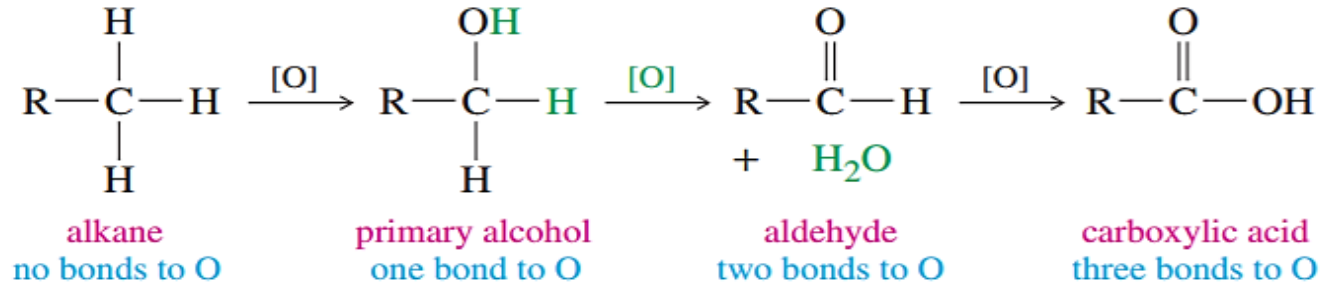
- **Oxidation**: Loss of electrons — Cr^{3+} oxidised to Cr^{6+}
- **Reduction**: Gain of electrons — Cr^{6+} reduced to Cr^{3+}

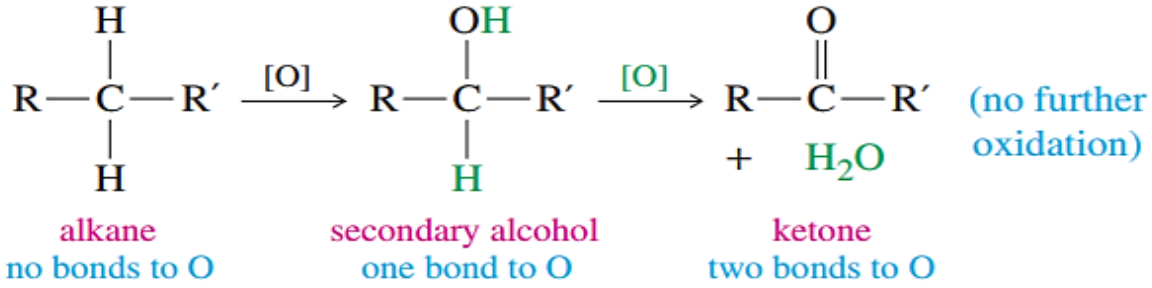
For Organic Compounds

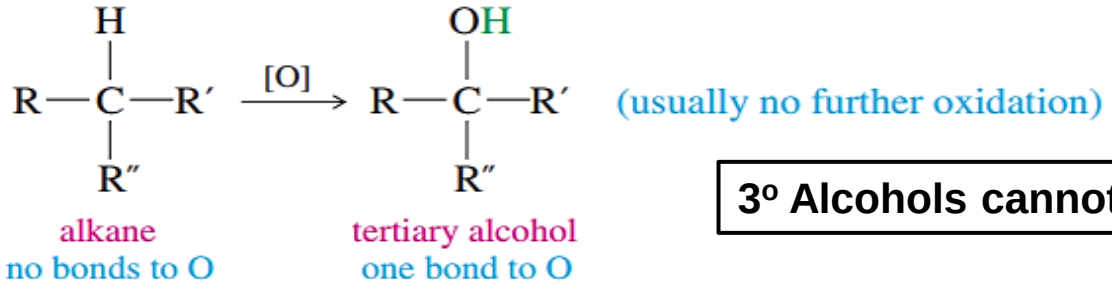


Oxidation States of Carbons

OXIDATION



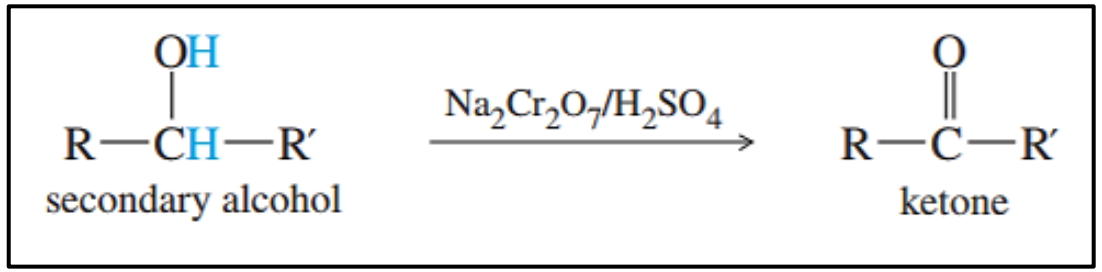




3º Alcohols cannot be oxidised !

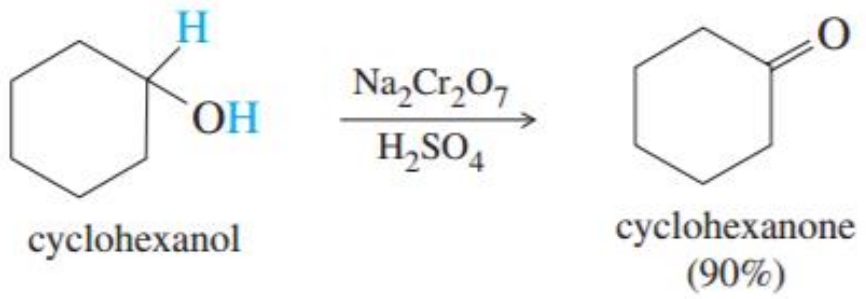
REDUCTION

Oxidation of Alcohols – 2º Alcohols



- 2° alcohol becomes a ketone
- Oxidising agent is **$Na_2Cr_2O_7/H_2SO_4$**
- Colour change is **orange** to **greenish-blue**

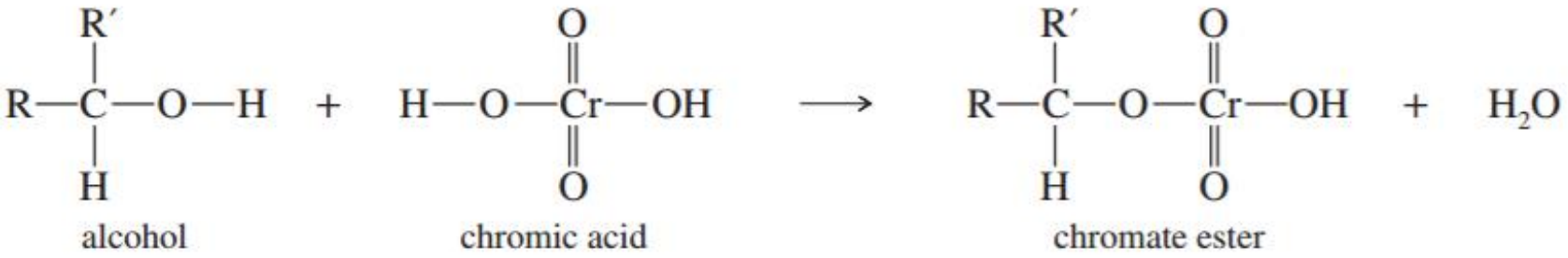
Example



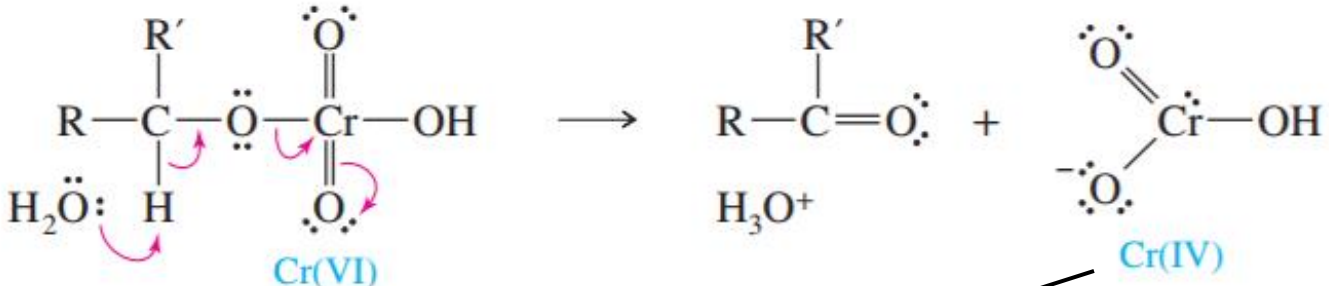
Oxidation of Alcohols – 2º Alcohols

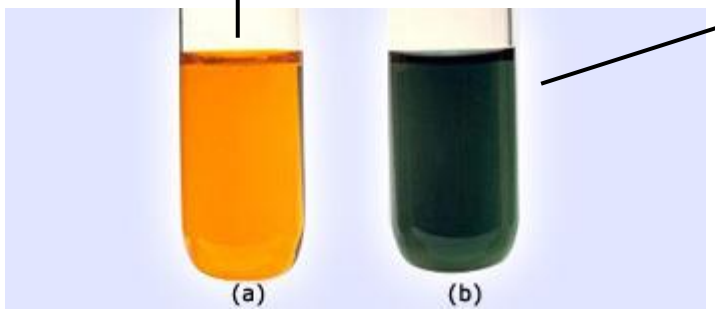
Mechanism

Formation of the chromate ester



Elimination of the chromate ester and oxidation of the carbinol carbon

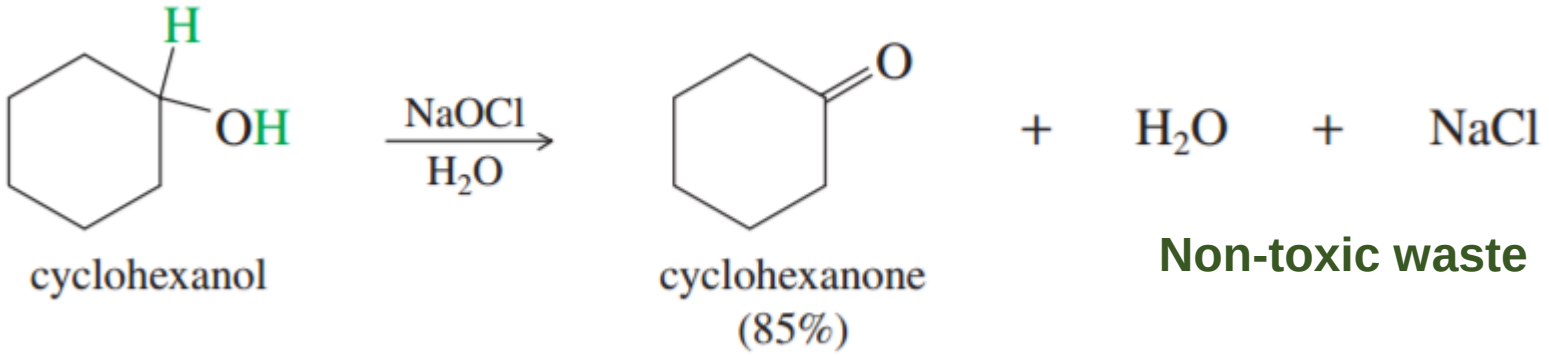




Oxidation of Alcohols – 2º Alcohols

Other Strong Oxidising Agents

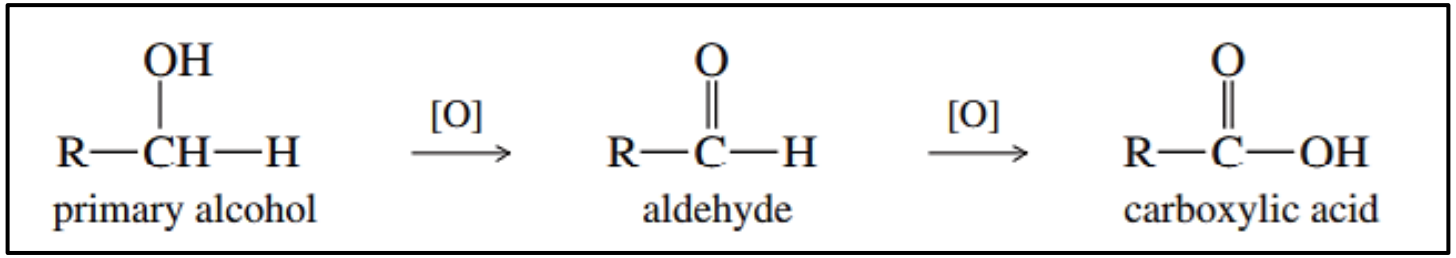
- **CuO, 300°C** (industrial dehydrogenation)
- **Collins reagent**: Cr_2O_3 in pyridine
- **Jones reagent**: chromic acid in acetone
- **$KMnO_4$** (strong oxidiser)
- **Nitric acid** (strong oxidiser)
- **Sodium hypochlorite** (NaOCl) household bleach



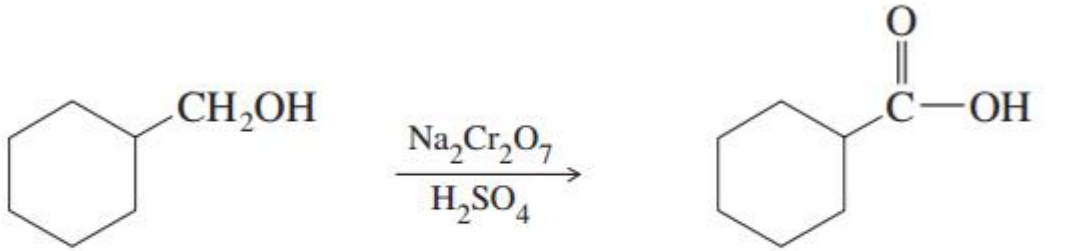
cyclohexanol → cyclohexanone (85%) + H_2O + NaCl

Non-toxic waste

Oxidation of Alcohols – 1º Alcohols



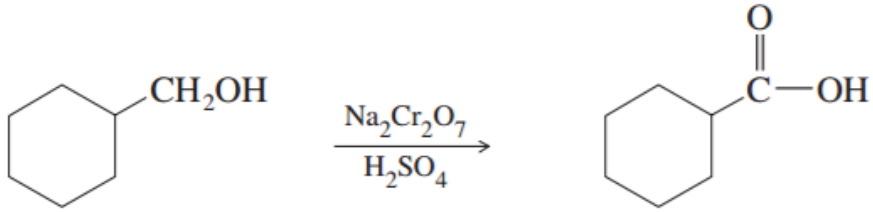
Oxidation of 1º Alcohols to Carboxylic Acid



- Chromic acid reagent or other **strong oxidising agents** will oxidise primary alcohols to carboxylic acids
- The oxidising agent is **too strong to stop at the aldehyde**.
  How can we stop the reaction at the aldehyde stage?

Oxidation of Alcohols – 1º Alcohols

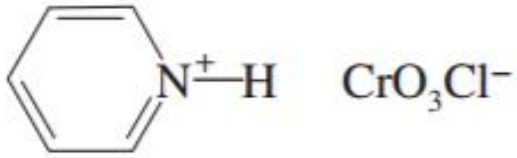
Oxidation of 1º Alcohols to Carboxylic Acid



Oxidation of Alcohols – 1º Alcohols

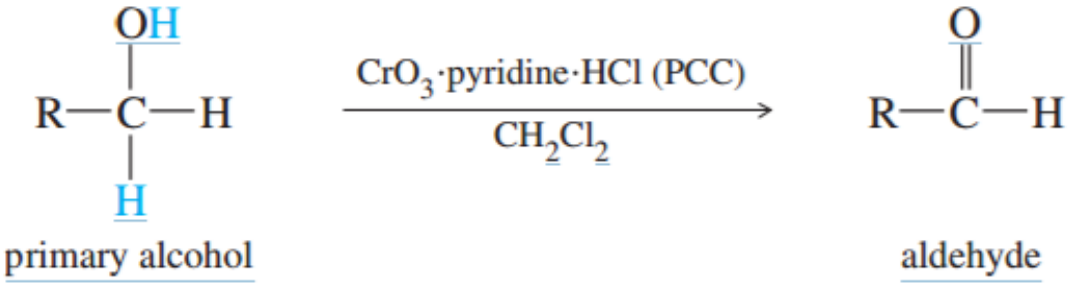
Oxidation of 1º Alcohols to Aldehyde – PCC

Pyridinium chlorochromate (PCC):



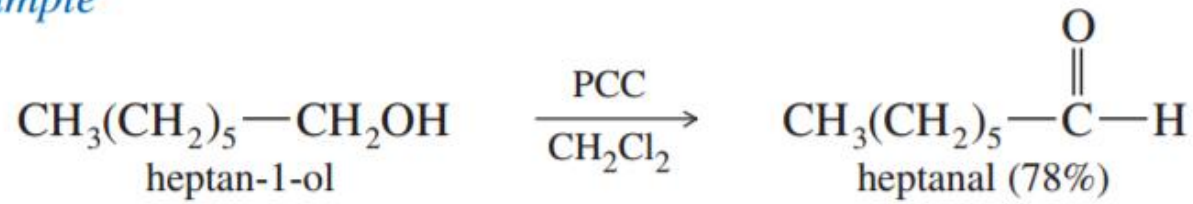
$CrO_3 \cdot$ pyridine $\cdot$ HCl
or $pyH^+ CrO_3Cl^-$

- complex of chromium trioxide with pyridine and HCl
- **Milder** oxidizing agent
- PCC is soluble in **nonpolar solvents** such as dichloromethane (CH_2Cl_2)



primary alcohol — aldehyde

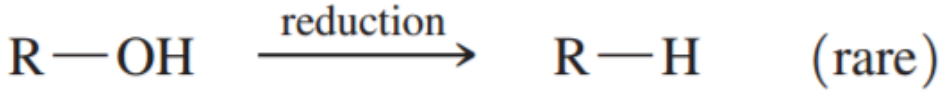
Example



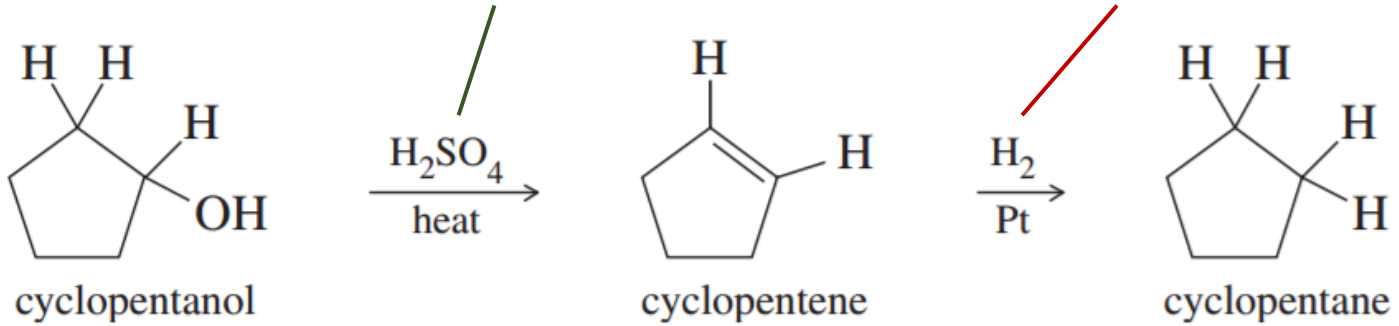
Reaction of Alcohols

Reduction of Alcohols

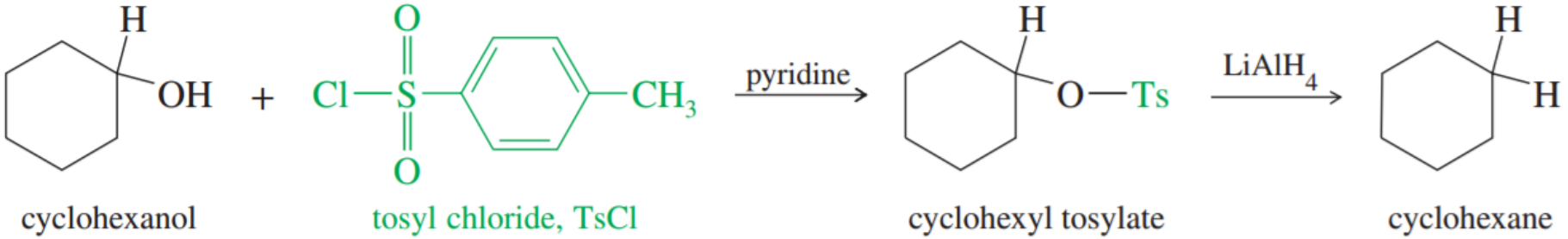
Reduction of alcohols to alkanes is rare



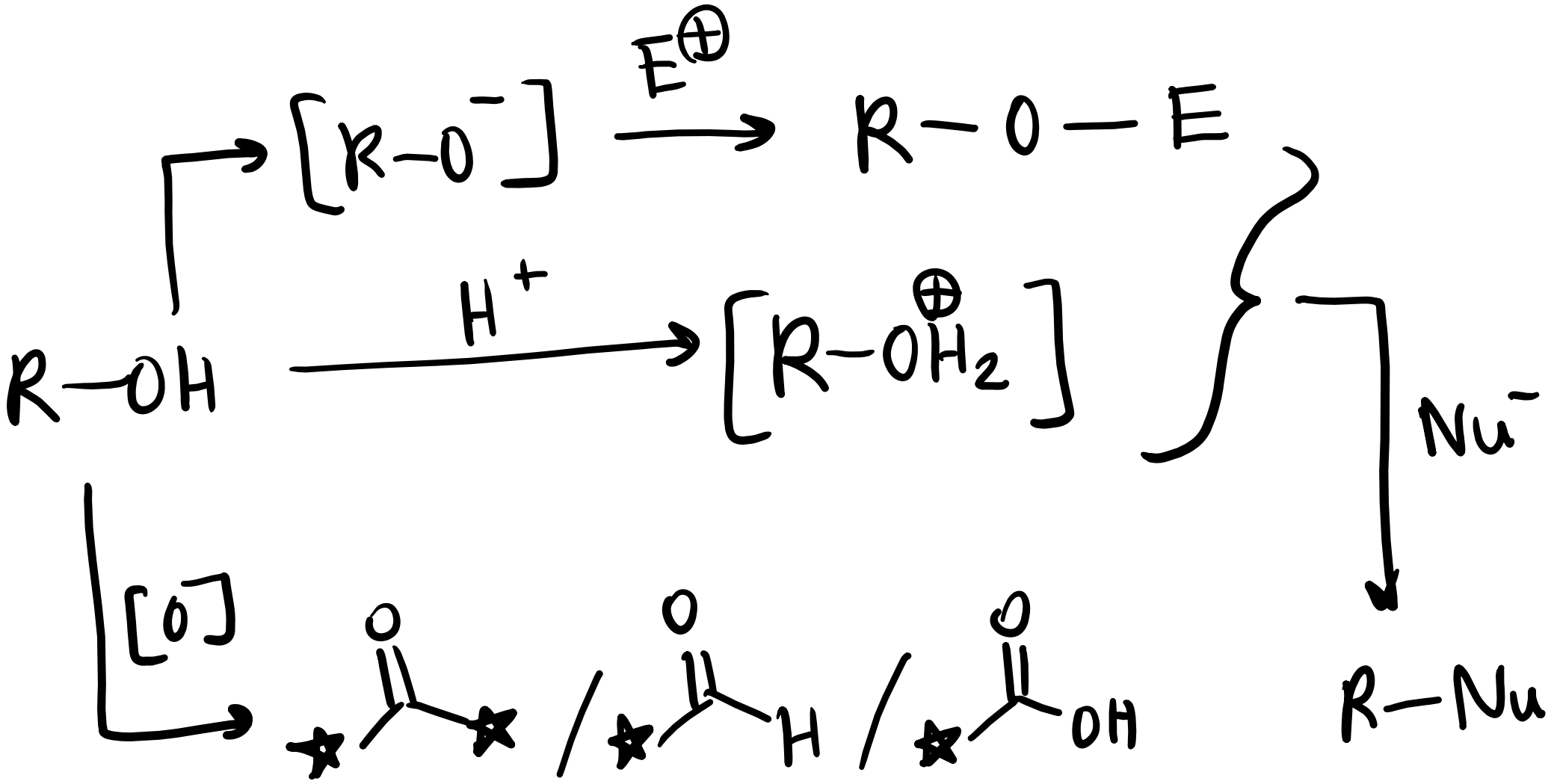
- Alcohol can be reduced by **dehydrating** it to an alkene, then **hydrogenating** the alkene



- Another method for reducing an alcohol involves converting the alcohol to the **tosylate ester**, then using a **hydride** reducing agent to displace the tosylate leaving group

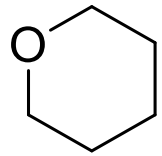


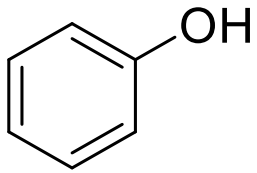
Reaction of Alcohols - Summary

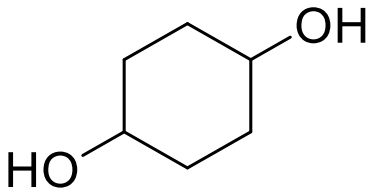


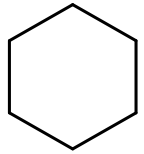
Homework – 1

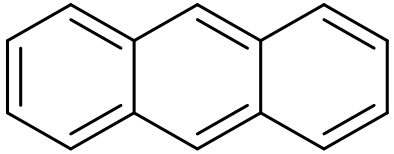
a) Rank the compound from the one with lowest to highest boiling point



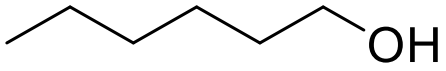


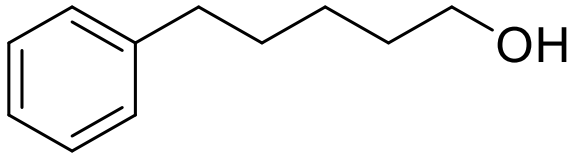


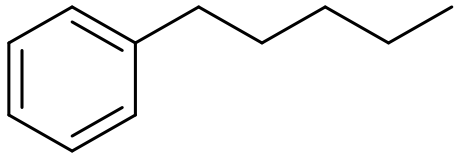


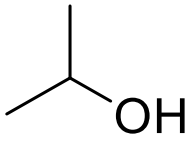


b) Rank the compound from the one with lowest to highest solubility in water

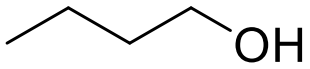


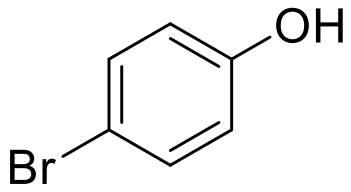


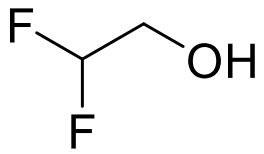


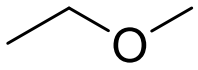


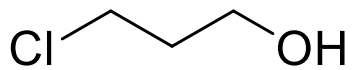
c) Rank the compound from the one with lowest to highest acidity





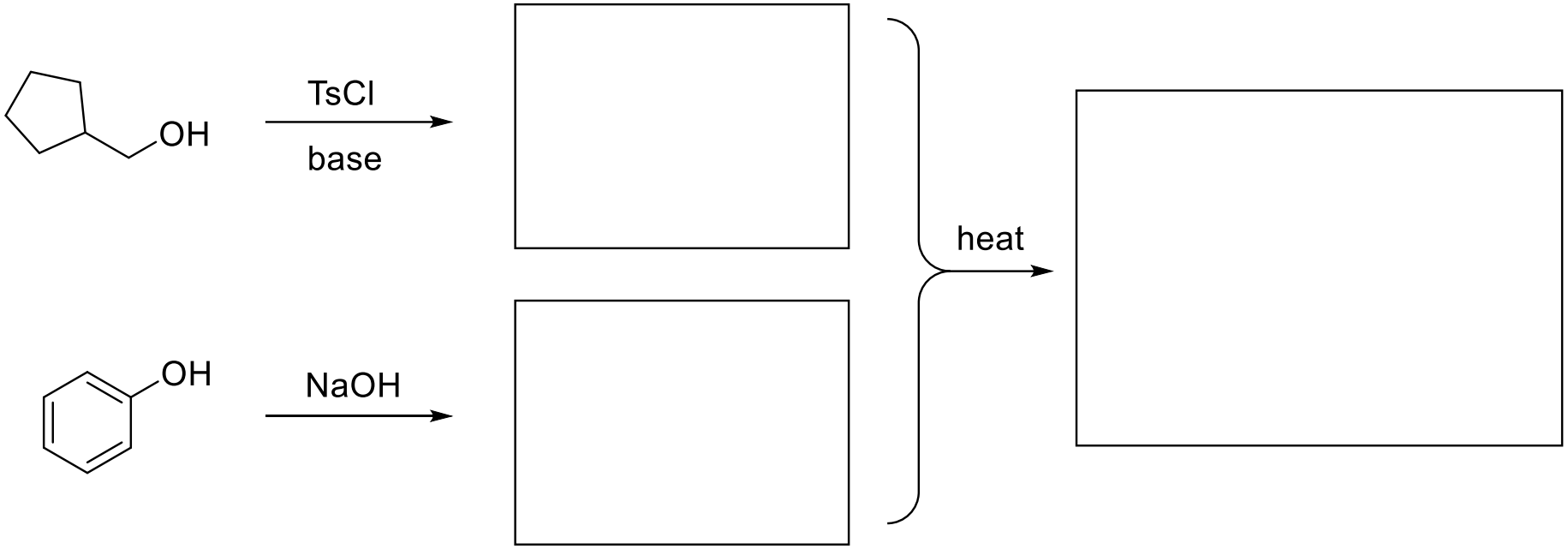






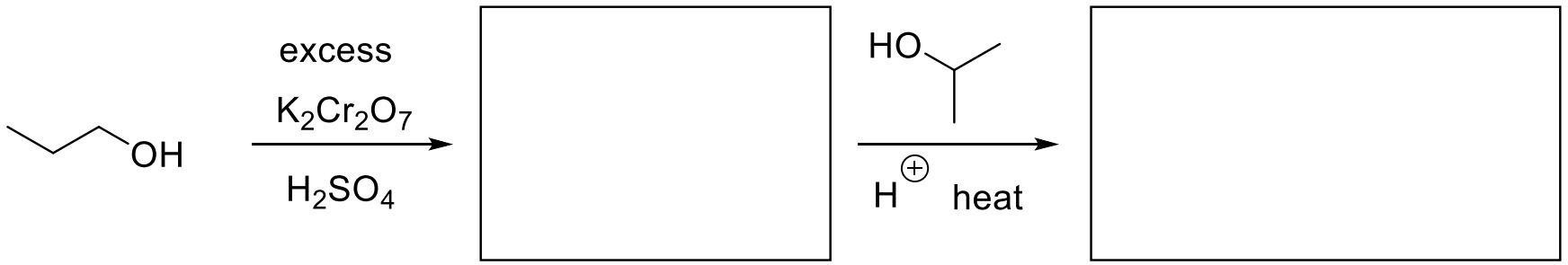
Homework – 2 Predict the product and draw the mechanism of the following reaction

2.1



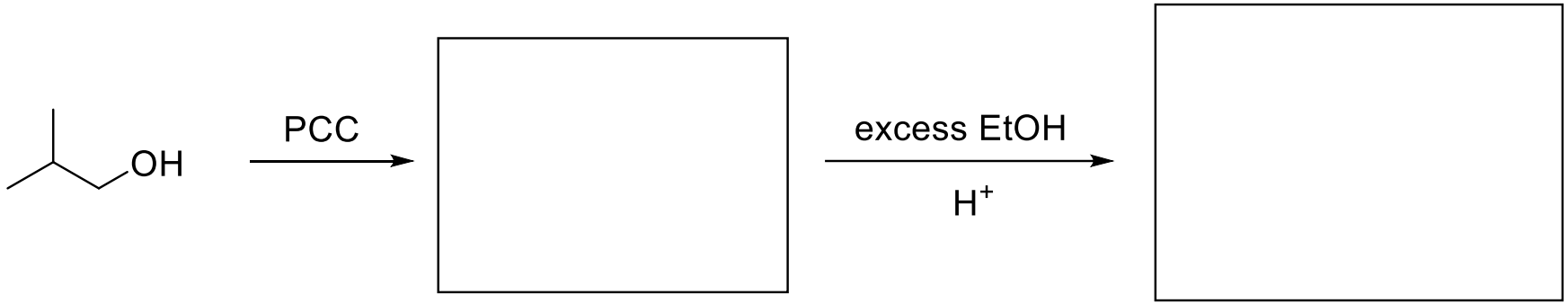
Homework – 2 Predict the product and draw the mechanism of the following reaction

2.2

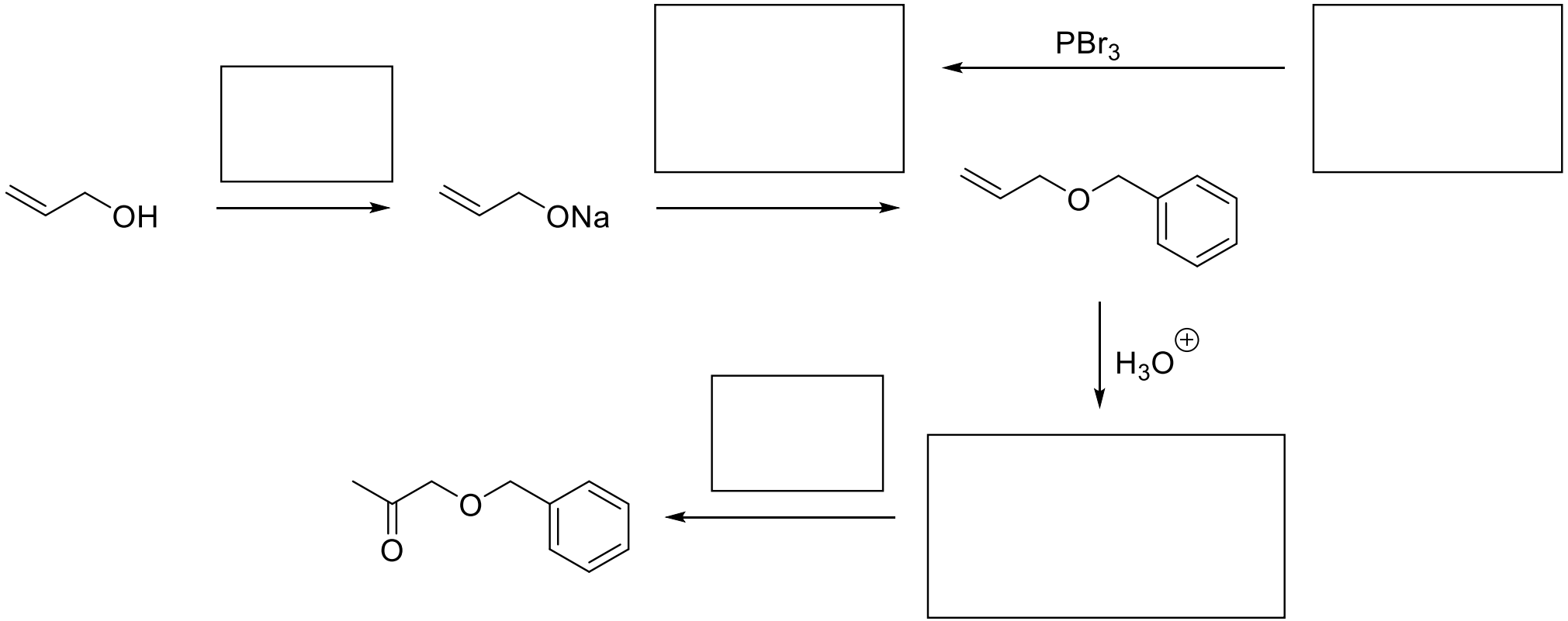


Homework – 3 Fill in the boxes with appropriate compound (if you want to practice, draw the mechanism too)

a)



b)



Homework – 4

The synthesis of a fluorescence nanoparticle was performed using the following sequence. Suggest the structure of the products in each step. (if you want to practice, draw the mechanism too)