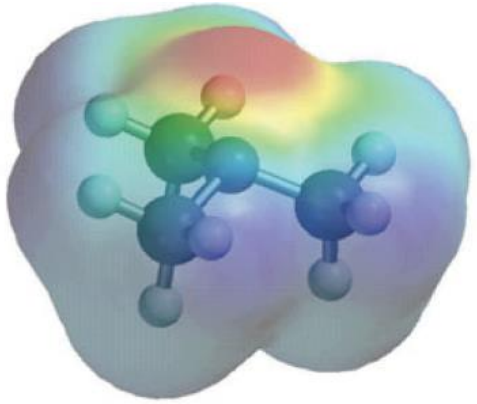
2302106 – Basic Organic Chemistry for ISE – Part II

Lecture 3-4

Amines – Amines as Electrophiles



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Recommended Textbook:

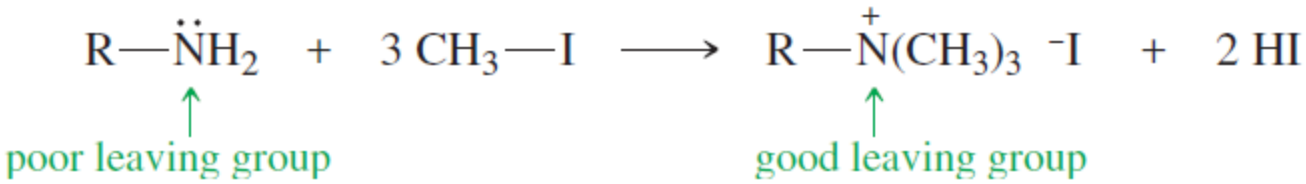
Chapter 19 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

Amines as Leaving Group – Amine vs Alcohol

Reactions of Amines – Amines as Leaving Groups

Hofmann Elimination

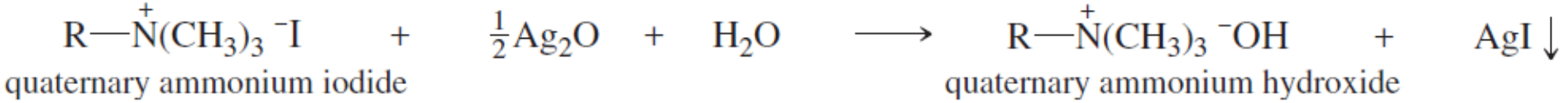
- **Exhaustive methylation** using **methyl iodide** converts amine to a **quaternary ammonium salt** that can leave as a neutral amine



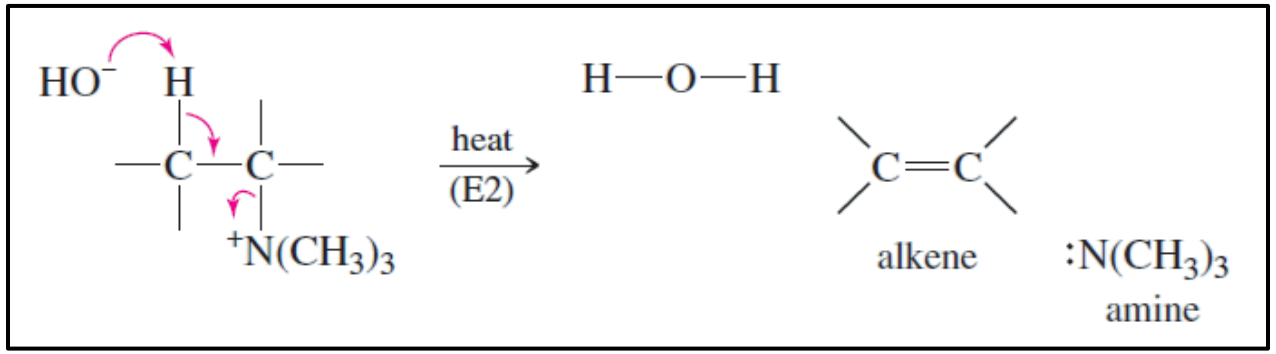
- Elimination of the quaternary ammonium salt generally takes place by the **E2** mechanism, which requires a **strong base**

Hofmann Elimination

- To provide the base, the quaternary ammonium iodide is converted to the **hydroxide salt** by treatment with **silver oxide**



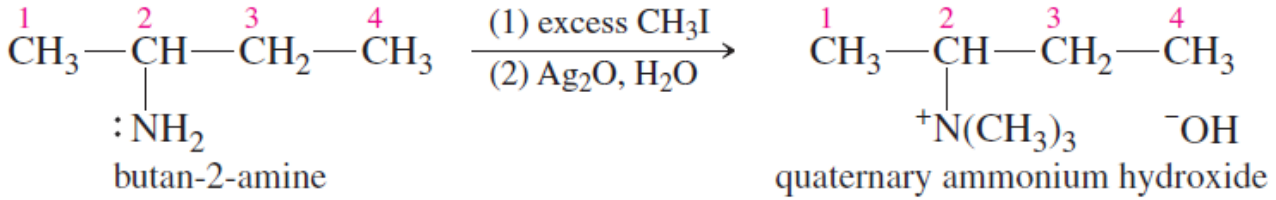
- **Heating** of the quaternary ammonium hydroxide results in **E2** elimination and formation of an alkene



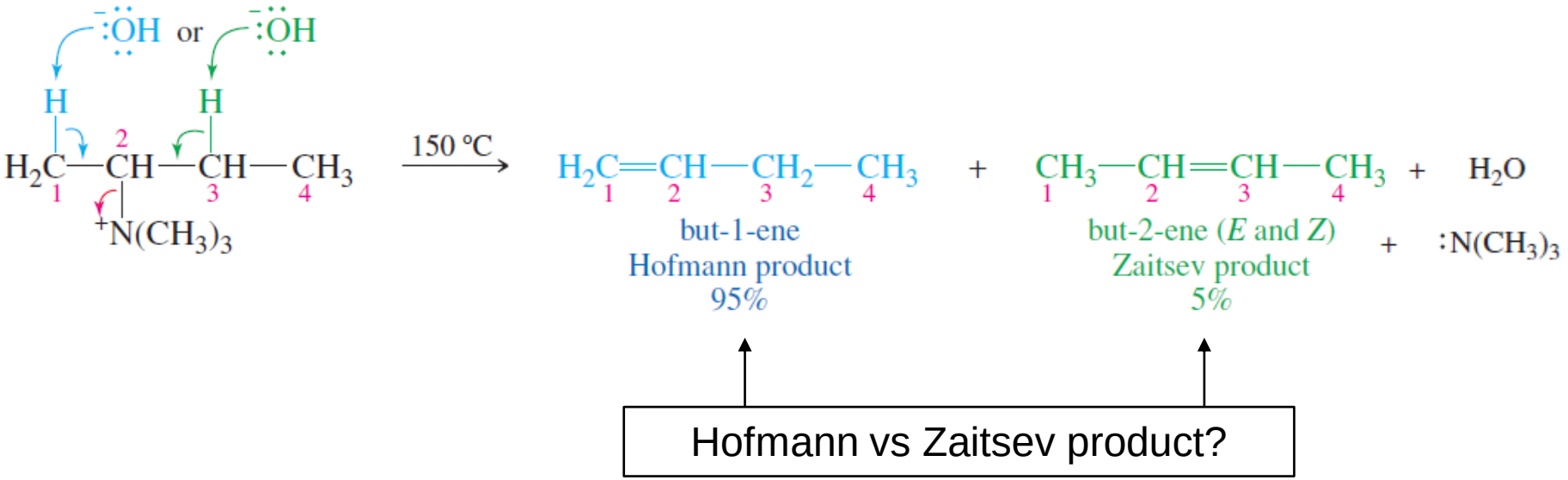
Hofmann Elimination

- **Example**

Exhaustive methylation and conversion to the hydroxide salt



Heating and Hofmann elimination



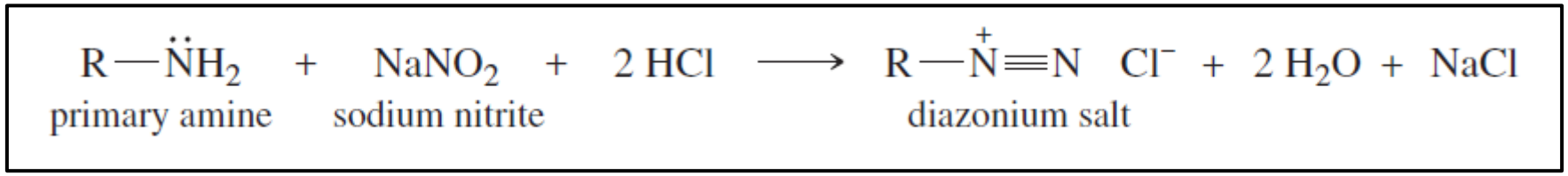
Hofmann Elimination - Example

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

Reactions of Amines – Amines as Leaving Groups

Formation of Diazonium Salts

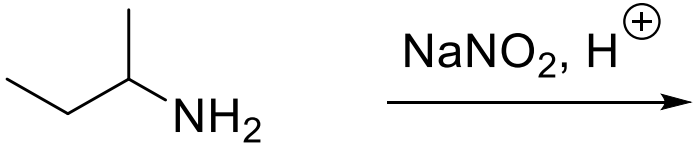
Diazotization: Primary amines react with **nitrous acid**, via the **nitrosonium ion**, to give **diazonium cations**



Diazonium Salts

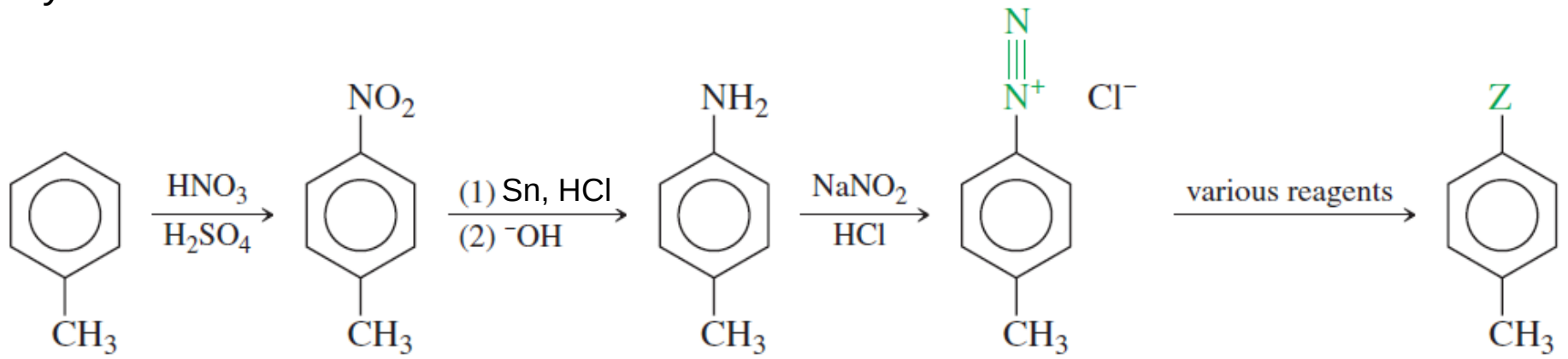
- **Alkane**diazonium salts are unstable. They decompose to give nitrogen and carbocations

- The driving force for this reaction is the formation of an **N_2** gas



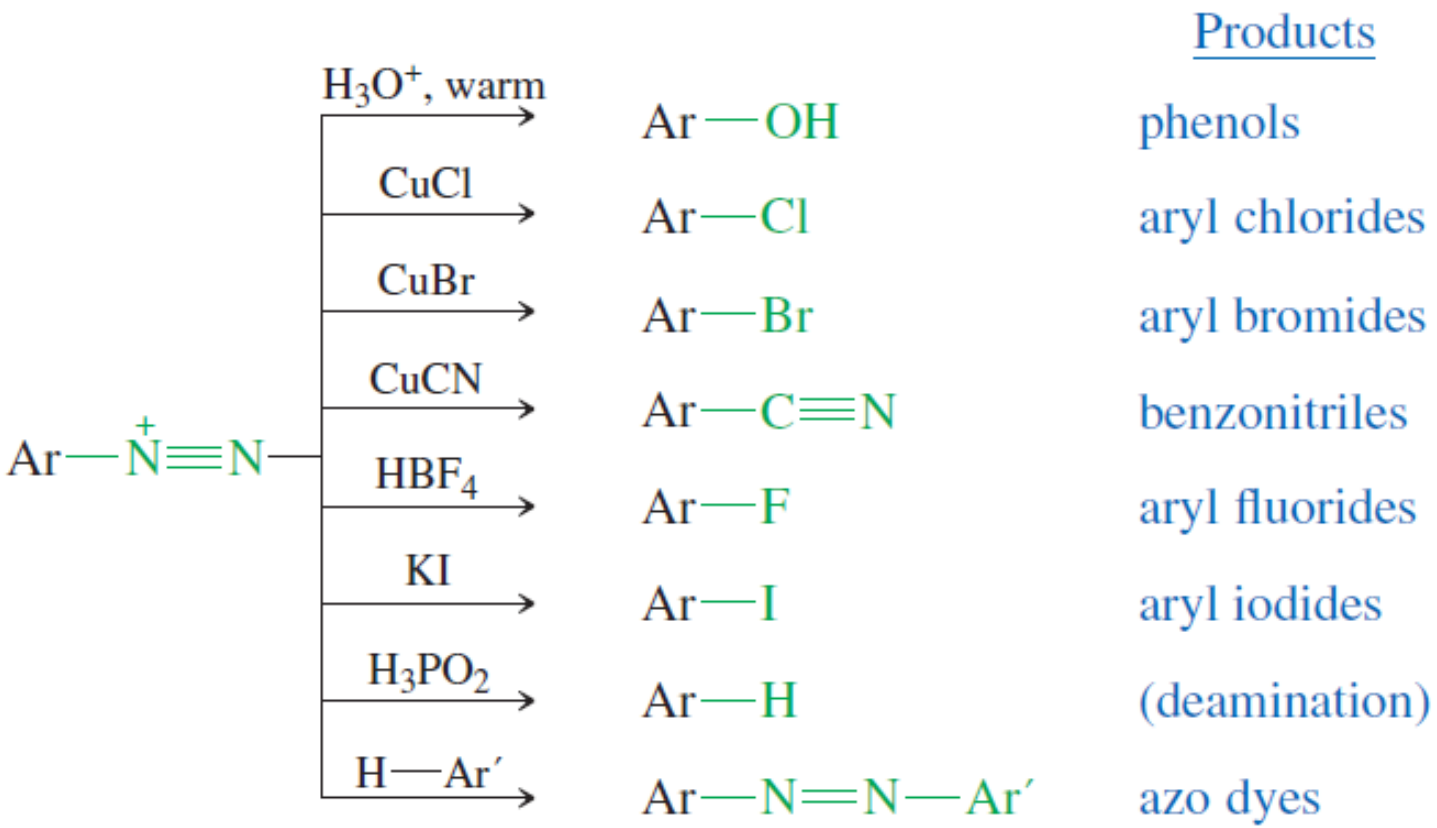
Diazonium Salts

- **Arene**diazonium salts are relatively stable around 0 - 10 °C, and they serve as **intermediates** in a variety of important synthetic reactions



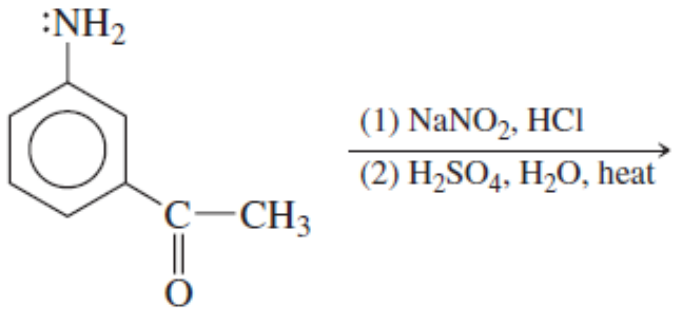
Diazonium Salts

- The following flowchart shows some of the functional groups that can be introduced via arenediazonium salts

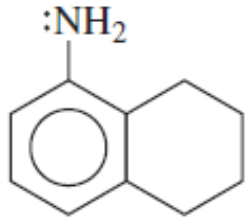


Diazonium Salts

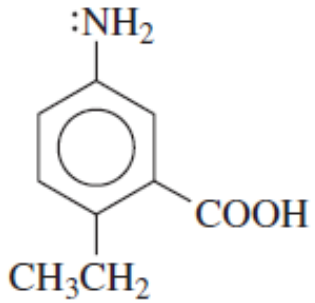
Example



$\xrightarrow[(2)\ H_2SO_4,\ H_2O,\ heat]{(1)\ NaNO_2,\ HCl}$



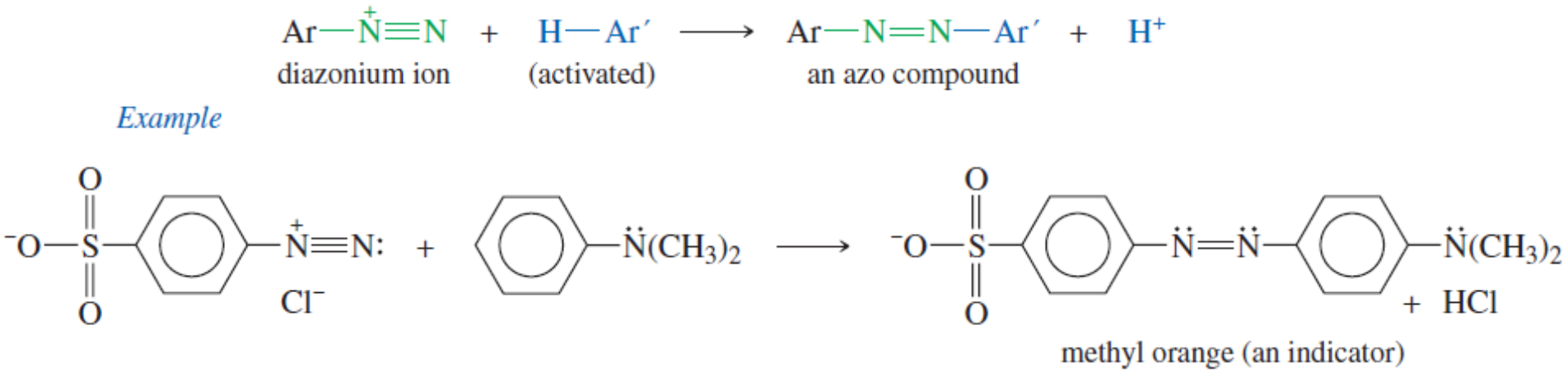
$\xrightarrow[(2)\ CuCl]{(1)\ NaNO_2,\ HCl}$



$\xrightarrow[(2)\ H_3PO_2]{(1)\ NaNO_2,\ HCl}$

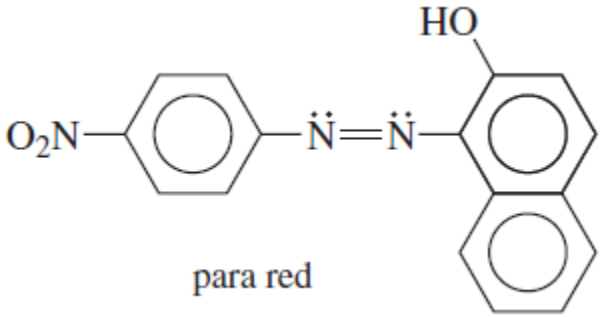
Diazonium Salts

- **Diazocoupling:** Arenediazonium ions act as **weak electrophiles** in electrophilic aromatic substitutions; react only with **strongly activated rings**



Diazonium Salts

Suggest a synthesis for para red

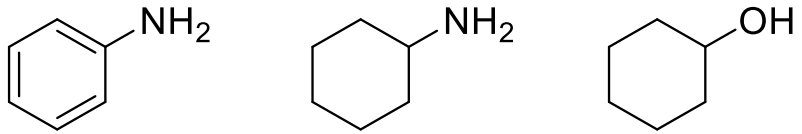


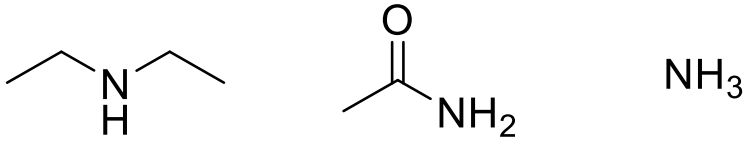
para red

Reactions of Amines - Summary

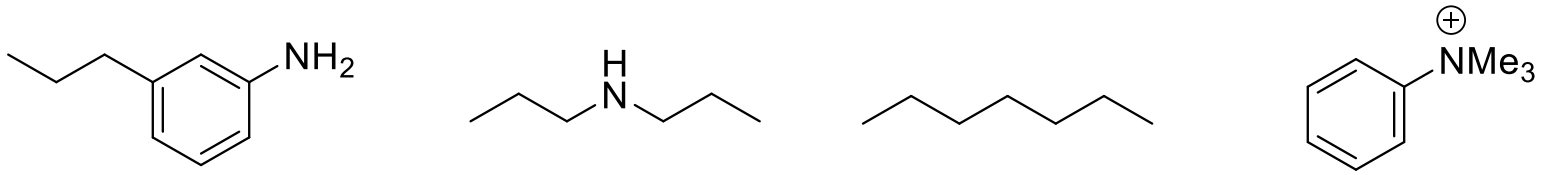
Homework – 1

a) Rank the following compounds in order of increasing basicity

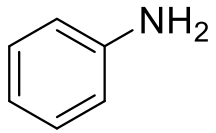
i) 

ii) 

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

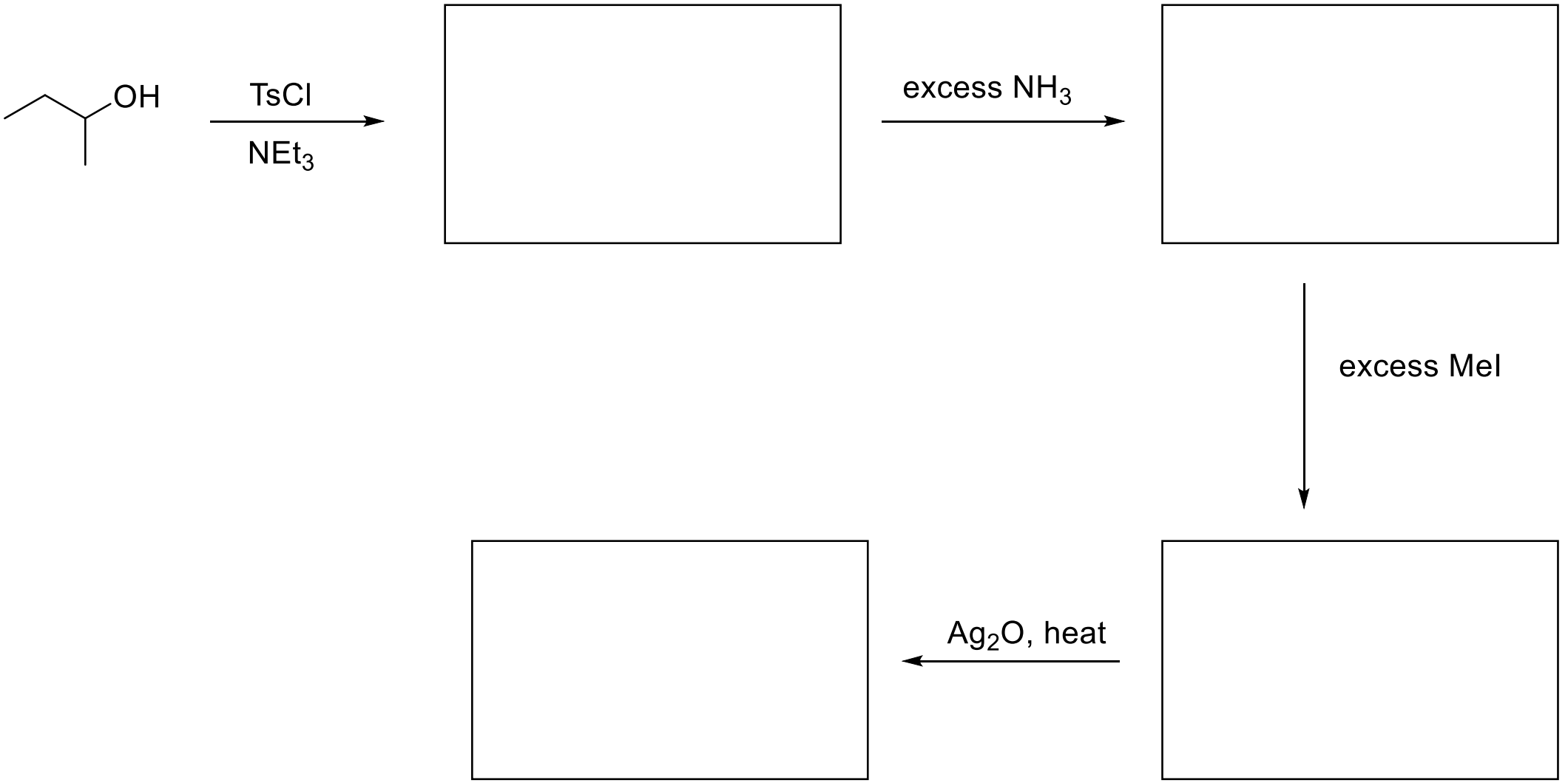


Homework – 2

Suggest a way to separate aniline  from a mixture of aniline and benzene

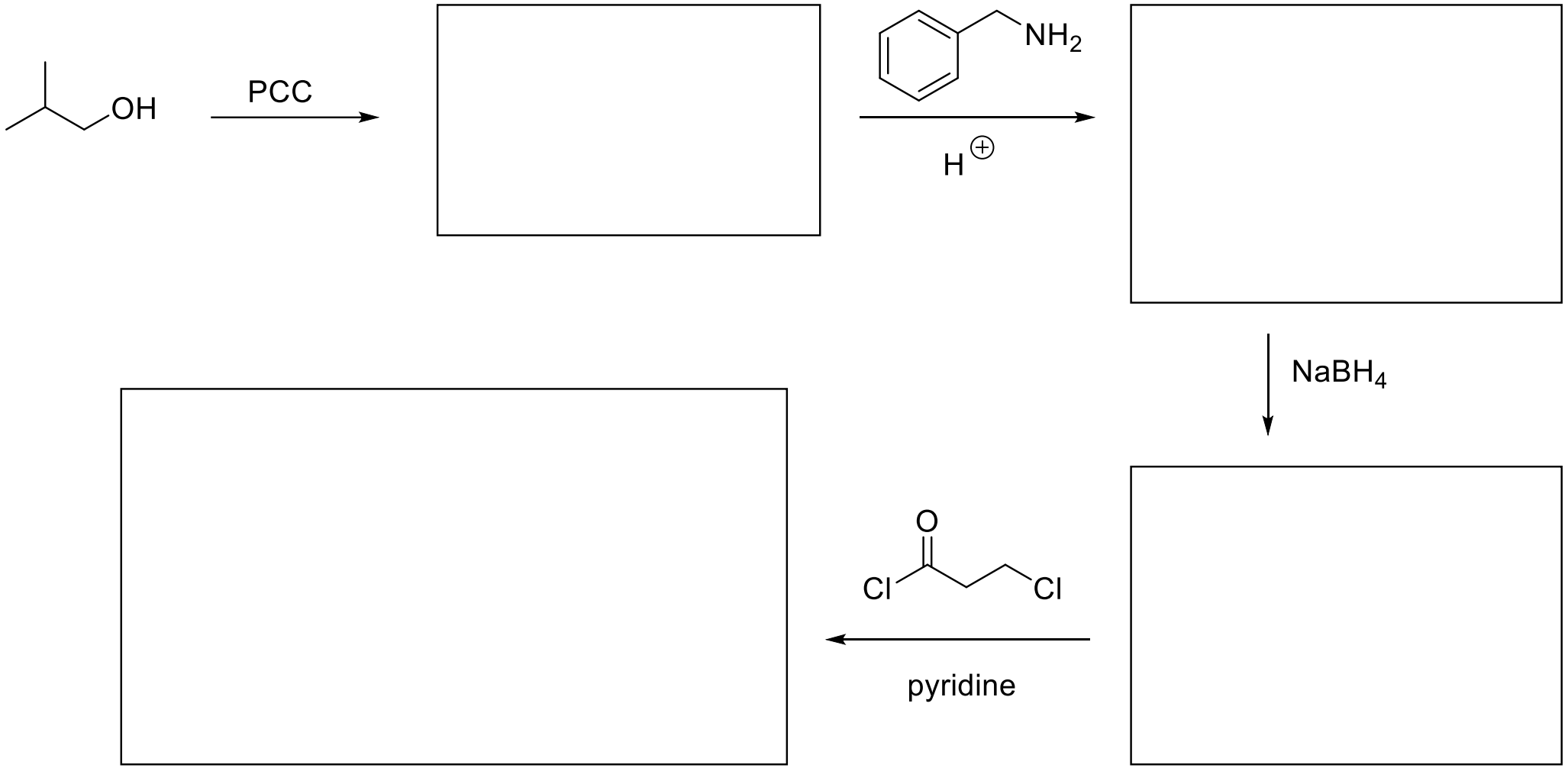
Homework – 3

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



Homework – 4

Predict the products of the following reactions:



Homework – 5

A synthesis of coloured nanoparticles was performed using the following sequence. Suggest the structure of the products in each step.