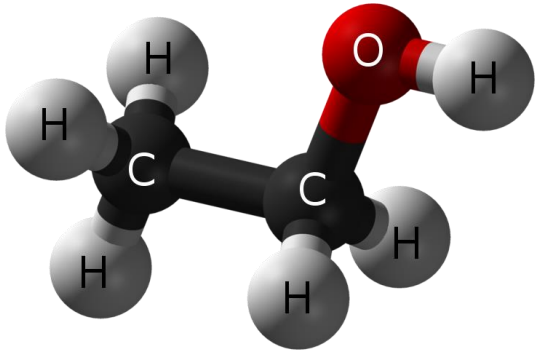
2302106 – Basic Organic Chemistry for ISE – Part II

Lecture 2-3

Alcohols - Alcohols as Electrophiles



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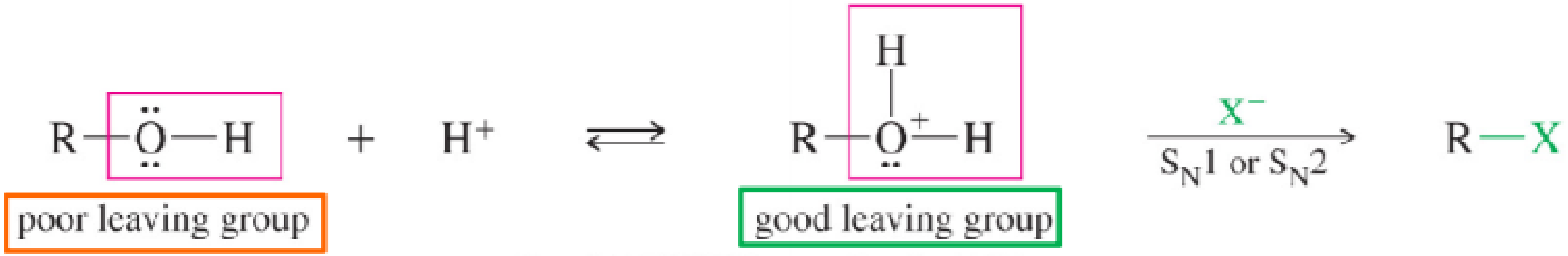
Recommended Textbook:

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

Reaction of Alcohols : Alcohols as Electrophile

- Alcohol is a **poor electrophile** because the hydroxyl group is a poor leaving group
- The hydroxyl group becomes a **good leaving** group when it is **protonated**



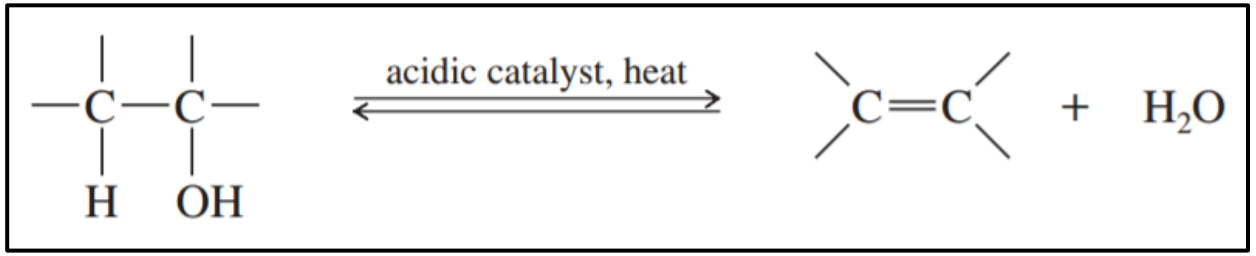
Summary:

Base : ……

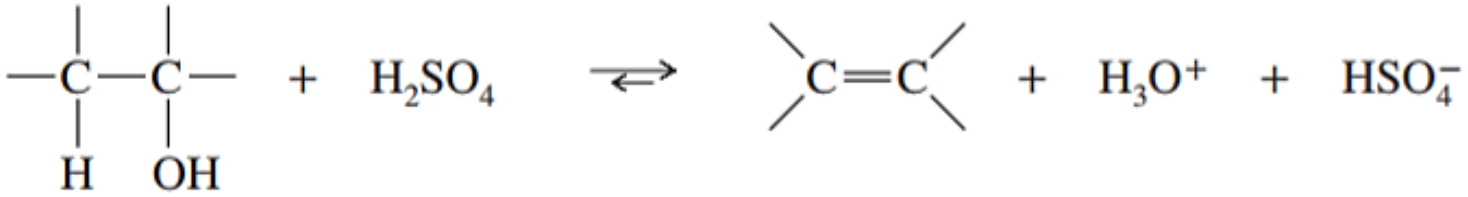
Acid : ……

Reaction of Alcohols : Alcohols as Electrophile

1) Dehydration of Alcohols



- Dehydration = "**removal of water**"
- Dehydration is a **reversible** process (hydration of alkene)
- **conc. H_2SO_4** or **conc. H_3PO_4** are the most commonly used acid (act both as **acidic catalysts** and as **dehydrating agents**)



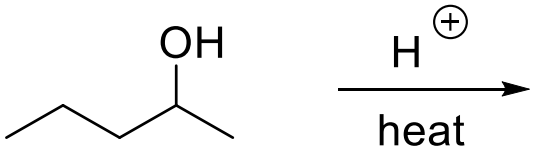
Dehydration of Alcohols – Mechanism

- **E1 mechanism**

- **Carbocation Intermediate**
  = Rearrangement possible

Dehydration of Alcohols – Example

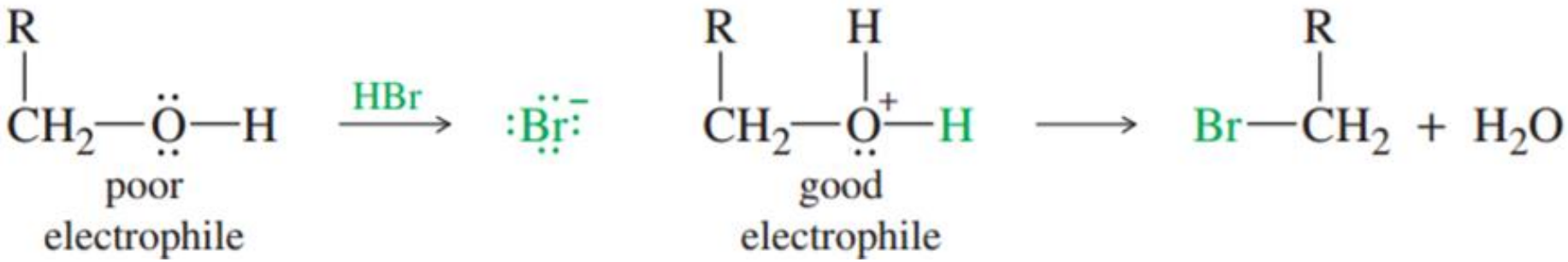
Predict the products of the following reactions:



2) Preparation of Alkyl Halides from Alcohols

2.1 Reaction with Bromide

- **1°** alcohols react via **S_N2**



- **2°** and **3°** alcohols react with Br^- via **S_N1**

2) Preparation of Alkyl Halides from Alcohols

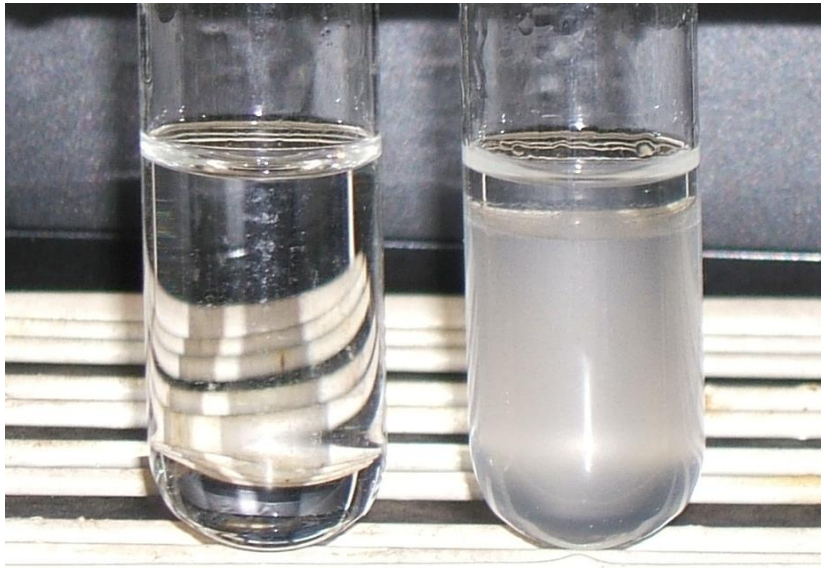
2.2 Reaction with Chloride

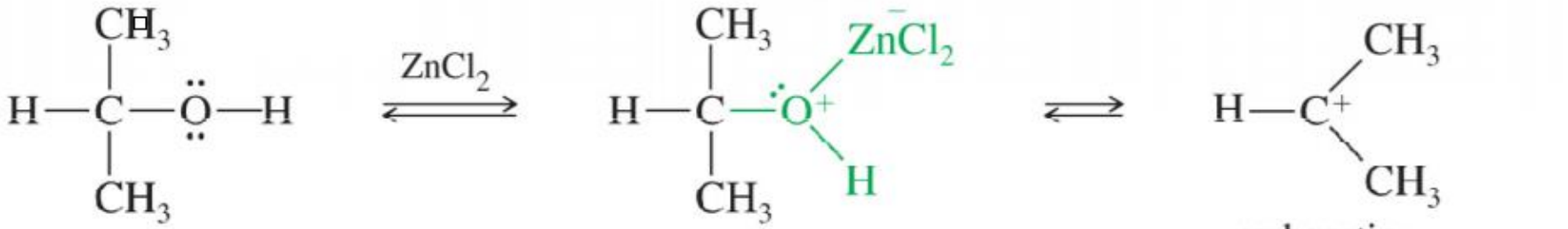
- Chloride is a **weaker nucleophile** than bromide.
- Add **$ZnCl_2$**, which bonds strongly with –OH, to promote the reaction.
- Lucas test: **$ZnCl_2$ in concentrated HCl**:

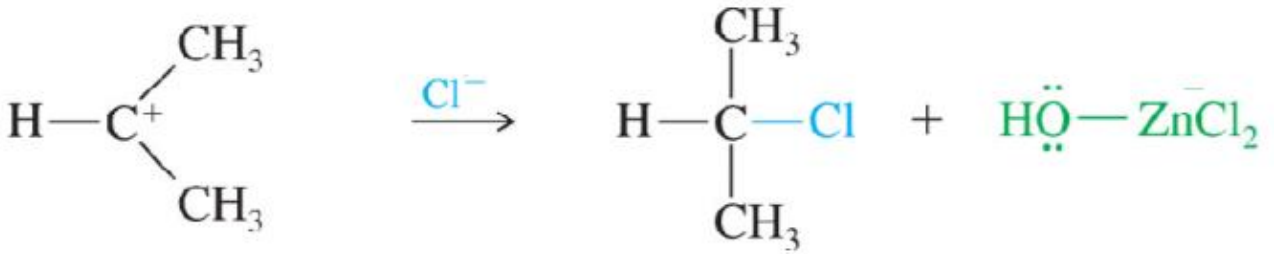
  1° alcohols react slowly or not at all (S_N2)

  2 ° alcohols react in 1-5 minutes (S_N1)

  3 ° alcohols react in less than 1 minute (S_N1)



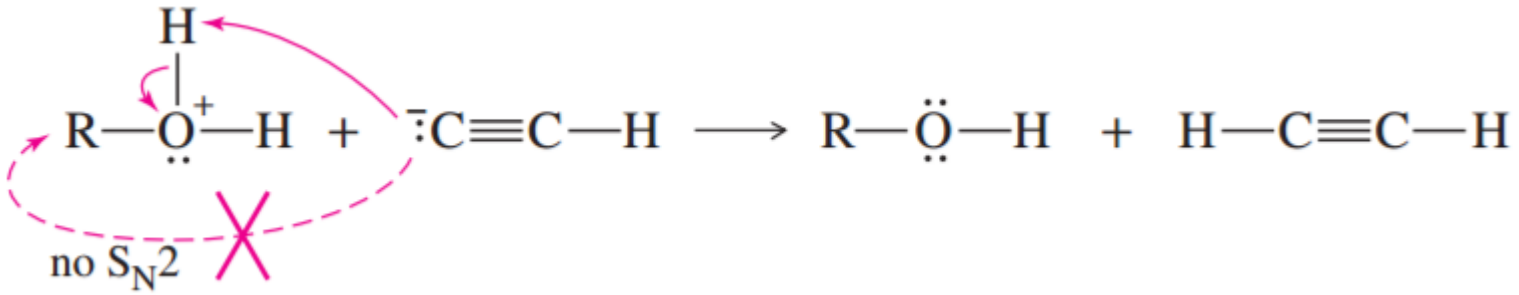




2) Preparation of Alkyl Halides from Alcohols

Limitations of HX Reactions

- **Poor yields** of alkyl halides from **primary** and **secondary** alcohols
- **Elimination** competes with substitution
- Carbocation intermediate may undergo a **rearrangement**
- **Strongly acidic solution** is required. Most strong nucleophiles are also basic and will abstract a proton in acid. Once protonated, the reagent is **no longer nucleophilic**.



Reaction of Alcohols : Alcohols as leaving group

2) Preparation of Alkyl Halides from Alcohols

Phosphorus halides; a better way to make RX from ROH

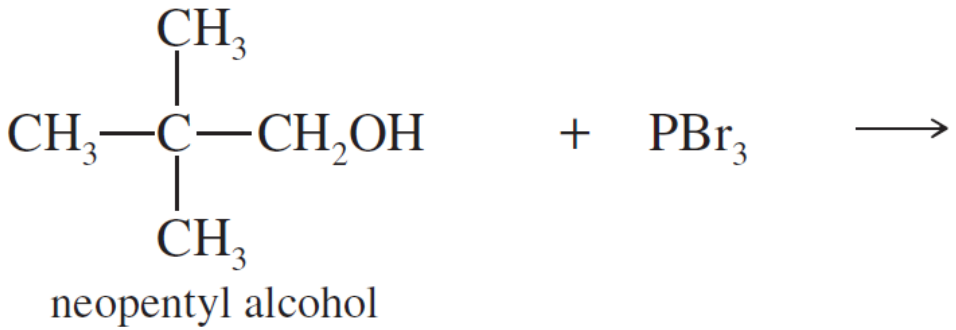
$$3\ R{-}OH + PCl_3 \longrightarrow 3\ R{-}Cl + P(OH)_3$$
$$3\ R{-}OH + PBr_3 \longrightarrow 3\ R{-}Br + P(OH)_3$$
$$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$$

- produce good yields of most **primary and secondary alkyl halides**, but none works well with **tertiary alcohols**.

Reaction of Alcohols : Alcohols as leaving group

2) Preparation of Alkyl Halides from Alcohols

Phosphorus halides – Examples

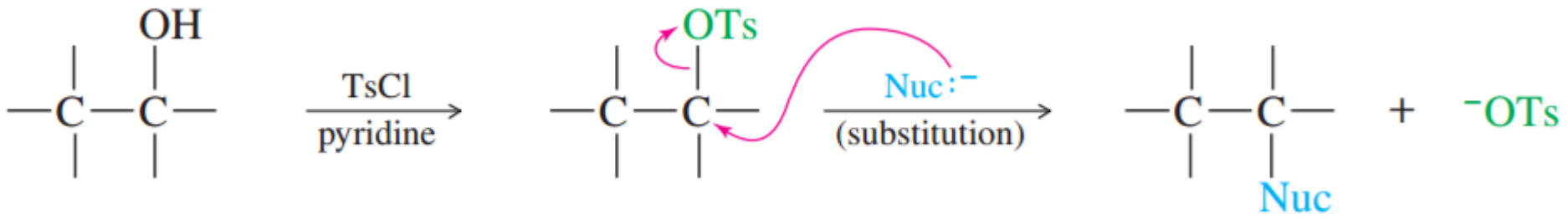


neopentyl alcohol

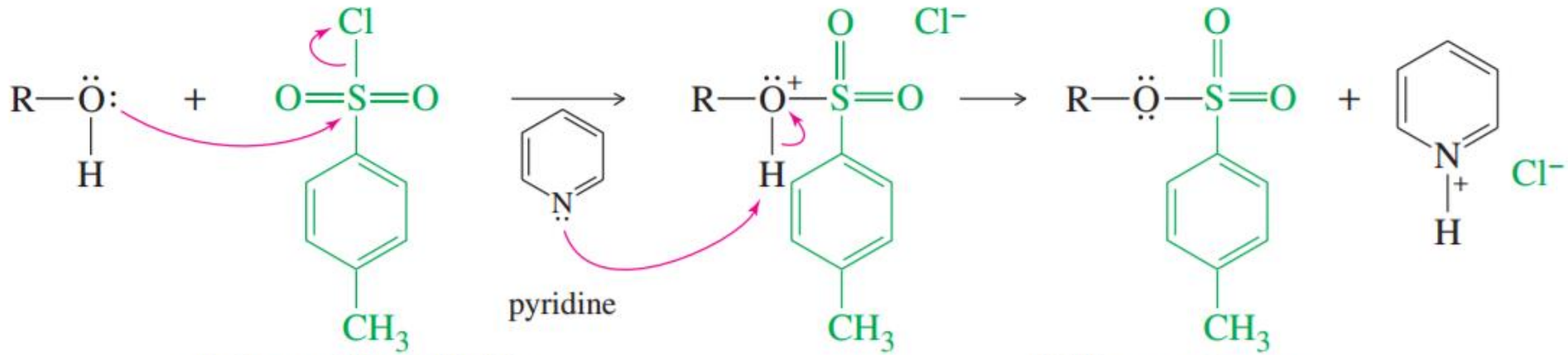
Reaction of Alcohols : Alcohols as leaving group

3) Tosylate ester

- The **tosylate group** is an excellent leaving group, and alkyl tosylates undergo substitution and elimination much like alkyl halides.



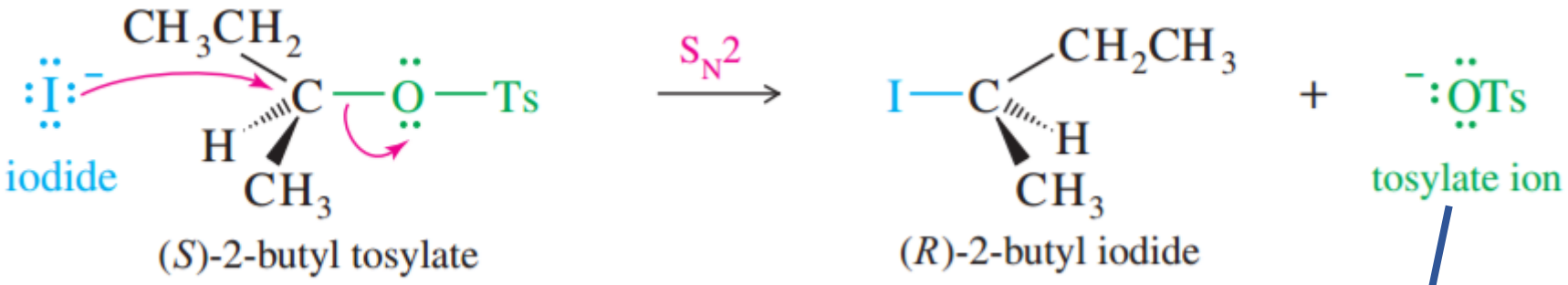
- Tosylates are made from alcohols using **tosyl chloride (TsCl) in pyridine**
- **Pyridine serves** as an **organic base** to remove the HCl formed in the reaction,



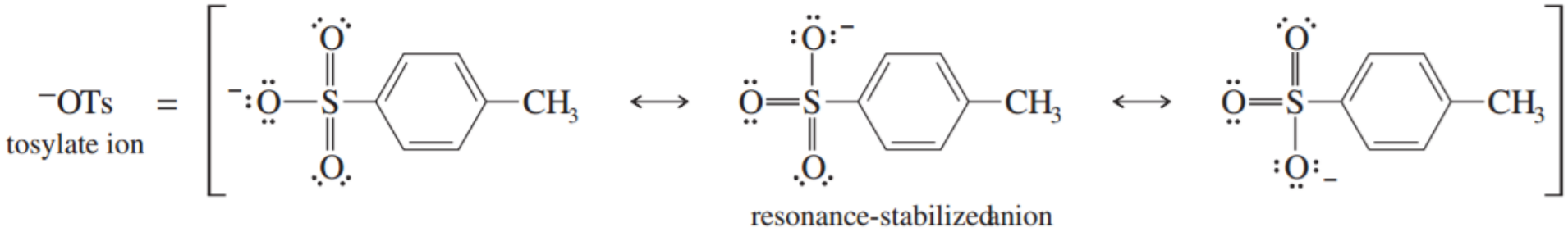
Reaction of Alcohols : Alcohols as leaving group

3) Tosylate ester

- The following reaction shows the **S_N2 displacement** of tosylate ion



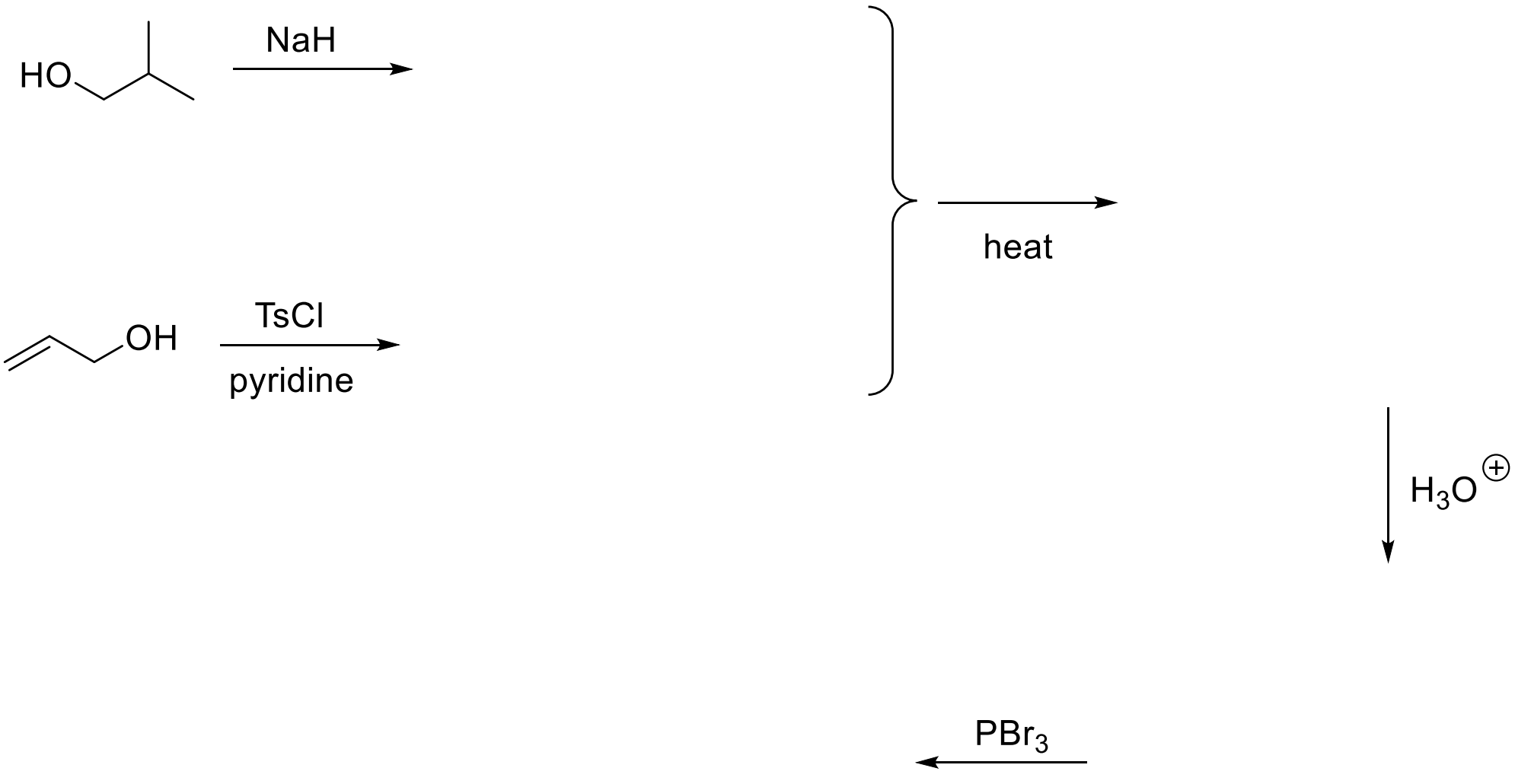
- The tosylate ion is a particularly **stable anion**, with its negative charge delocalised over three oxygen atoms.



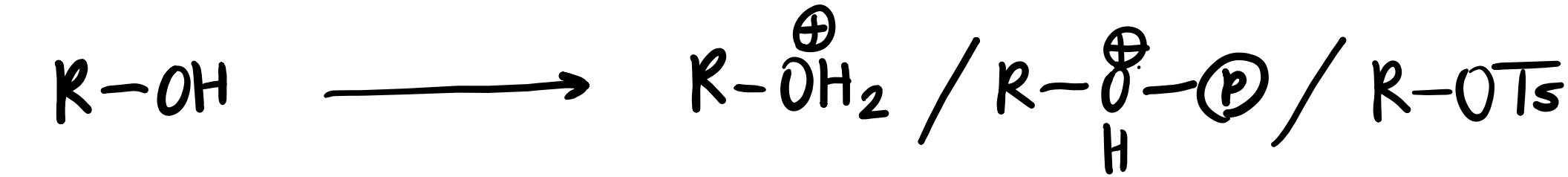
- The tosylate leaving group is displaced by a wide variety of nucleophiles

Reaction of Alcohols : Alcohols as leaving group

Example: Predict the product of the following reactions



Reaction of Alcohols : Alcohols as leaving group



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