Overheads: - Outline

Recap Friday: Reactions of Alcohols

1) As Nu

$$R \longrightarrow H$$
 $O \longrightarrow H$ $O \longrightarrow H$ $O \longrightarrow H$ $O \longrightarrow H$ Williamson weak $Nu^ O \longrightarrow H$ $O \longrightarrow H$ Williamson $O \longrightarrow H$

2) As LG

Elimination Reactions of Alcohols

 \rightarrow Dehydration of alcohols (remove H₂O)

 \longrightarrow 1° goes by E2, but <u>much</u> slower (base = HSO₄⁻ = weak)

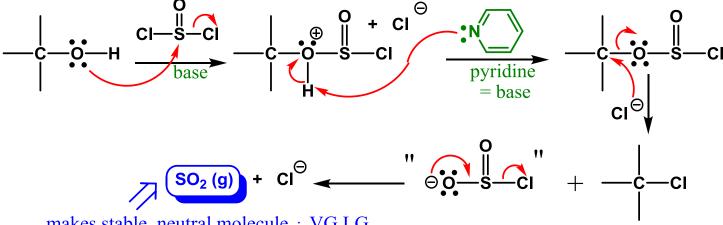
For Dehydration: $3^{\circ} ROH > 2^{\circ} ROH >> 1^{\circ} ROH$

*** Also need to consider possible rearrangements!

Other ways to turn OH into LG:

⇒ HCl etc. only good for simple ROH ⇒ rearrangements, side reactions)

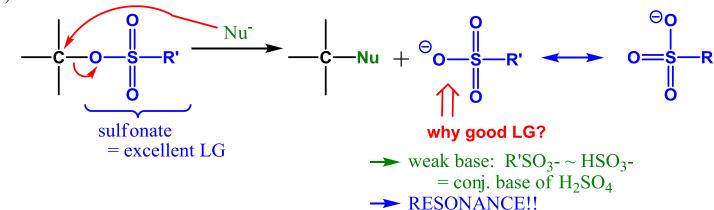
1) Turn into Cl or Br using SOCl₂ (= thionyl chloride) or SOBr₂



makes stable, neutral molecule :: VG LG also gas, :: can't go back!

⇒ PCl₃ (or PBr₃) and pyridine give same product (similar mechanism)

2) Sulfonate Esters



Common Sulfonate Esters

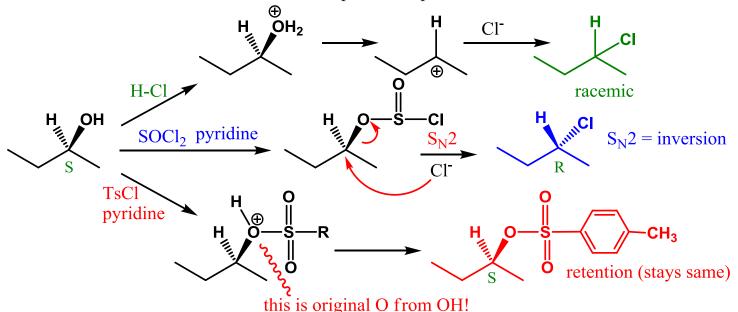
How to make Sulfonates

$$R \longrightarrow H \quad CH_3 \quad pyridine \\ = tosyl chloride (TsCl) \quad pyridine$$

$$R \longrightarrow G \quad CH_3 \quad P \longrightarrow G \quad CH_3 \quad R \longrightarrow R \longrightarrow Ts$$

Stereochemistry: R*-O-H → R*-LG

⇒if "R" is chiral center, stereochem. of product depends on how LG is added!



 $H-Cl(C+) \Rightarrow racemic$

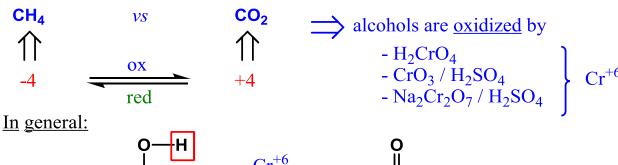
 $SOCl_2$ \Rightarrow inverts (or PCl_3 etc)

TsCl \Rightarrow retains

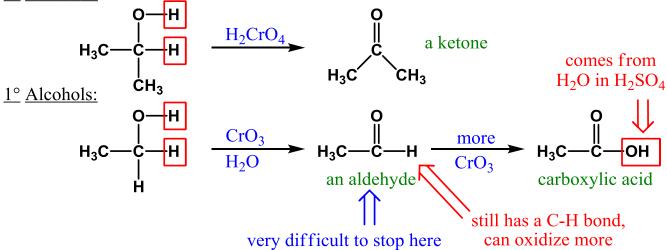
Then if we do S_N2 to replace LG, get double inversion (SOCl₂) or inversion (TsCl) $\begin{cases} \begin{cases} \begin{case$

Last Reaction of Alcohols: Oxidation

Oxidation: increase in # of C-O bonds Reduction: increase in # of C-H bonds







- to stop at aldehyde, need milder ox. agent and no H₂O

- or use "PCC" = pyridinium chlorochromate in CH_2Cl_2 (no H_2O)

<u>3° Alcohols:</u>

$$H_3C$$
 CH_3 H_2CrO_4 NO REACTION!!

How does the Oxidation work?

$$R - C - H$$
 $R - C - H$
 $O - C - OH$
 $O - C$