Today

Reactions with Nitrogen Nucleophiles
Section 16.8

Reactions with Oxygen Nucleophiles
Section 16.8

Protecting Groups
16.10
and
Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

Next Class

Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

Chap 17 Reactions at the α-C of a Carbonyl

Second Class from Today

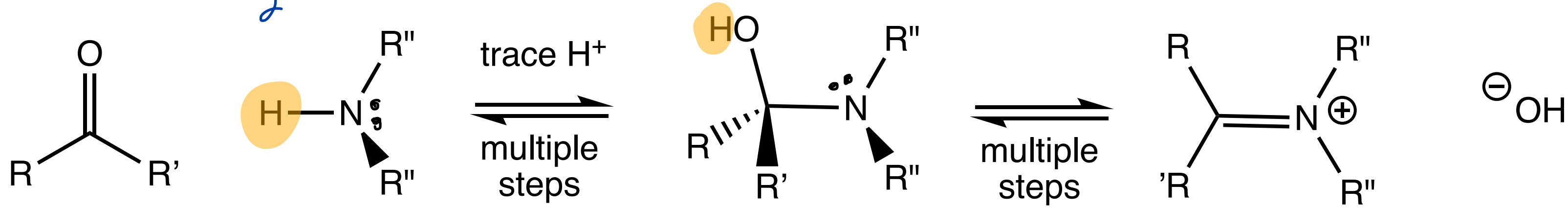
Chap 17 Reactions at the α-C of a Carbonyl

Third Class from Today

Chap 17 Reactions at the α-C of a Cabonyl

Reactions of Aldehydes and Ketones with Nitrogen Nucleophiles: 2° Amines vs 1° Amines

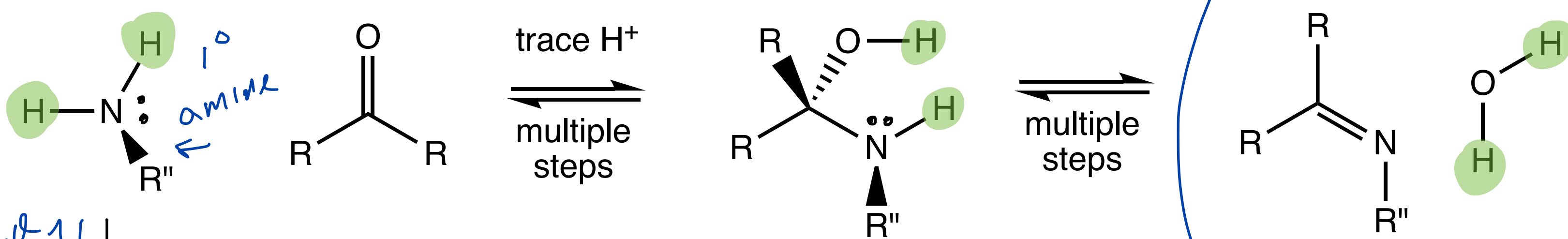
2° amine



no H+ to lose or N so OH⊖ has to be the LG and the N is still ⊕

R'' ≠ H

1° amine

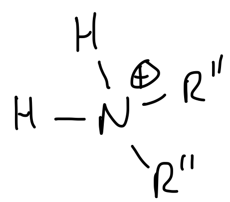


aminol

imine

trace acid

too much acid



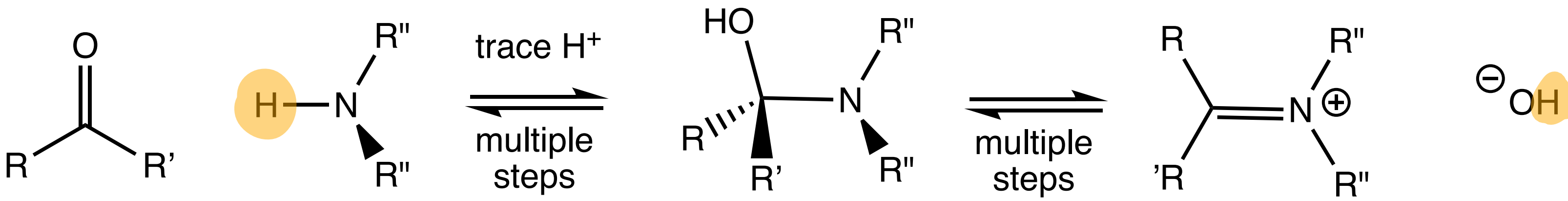
trace acid means there will be a small amount of acid to help speed up the reaction an not enough to shut it down due to protonation of the amine

Two issues here...

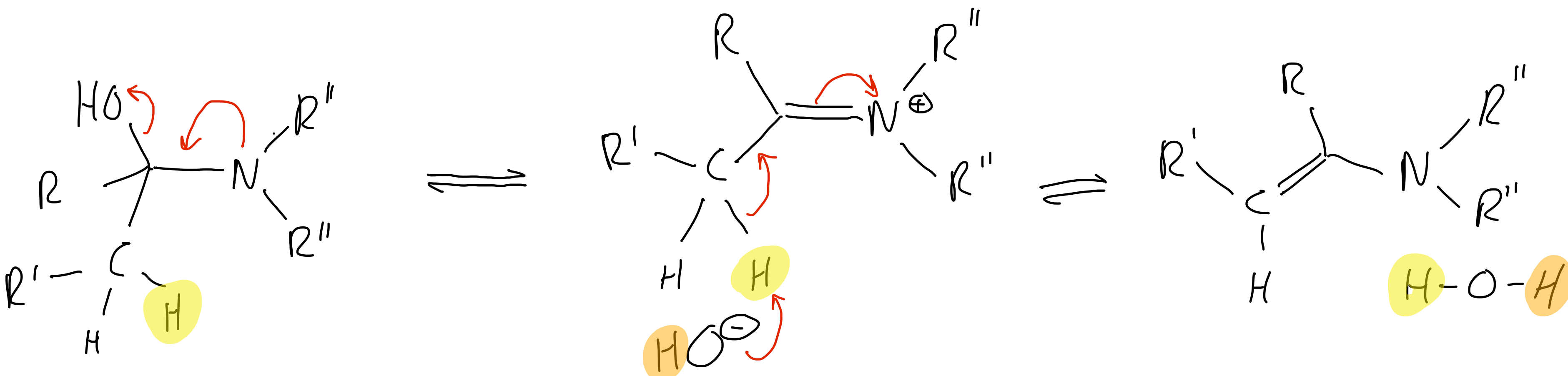
1. N is still ⊕

2. OH⊖ is a high energy ion... strong base

Reactions of Aldehydes and Ketones with Nitrogen Nucleophiles: 2° Amines vs 1° Amines

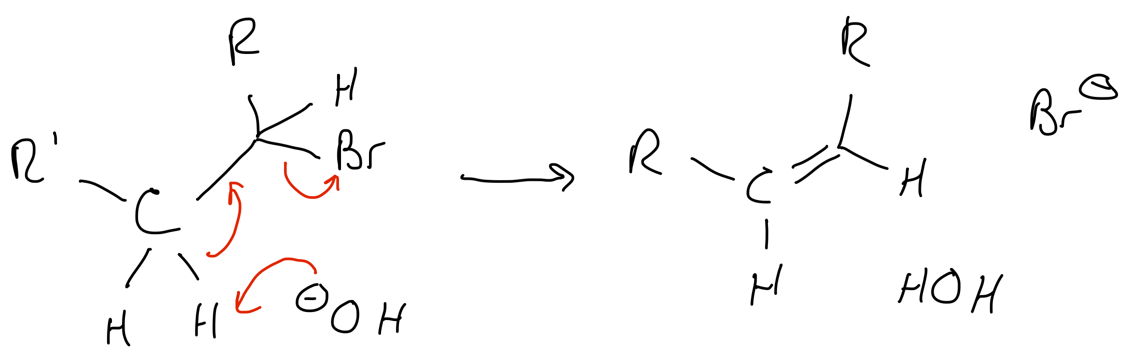


N atom is pulling e⁻'s toward itself

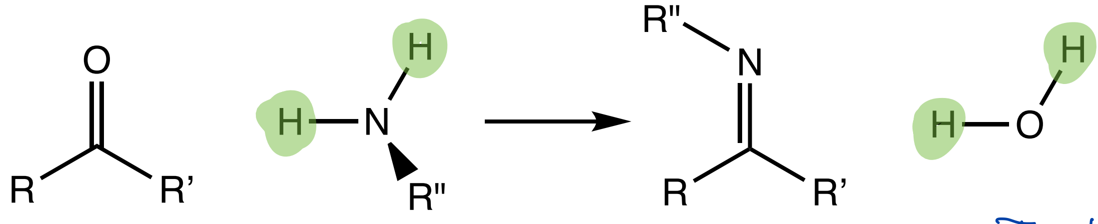


ene amine

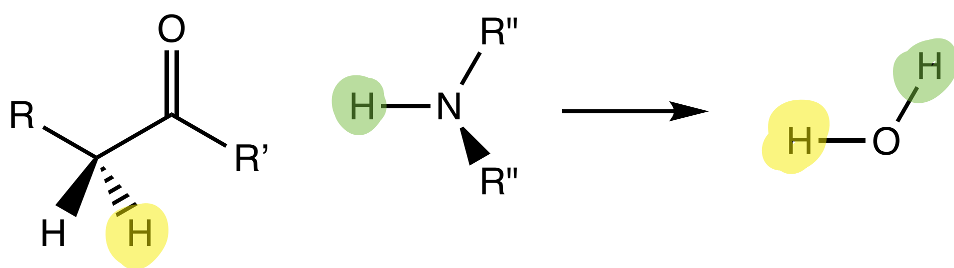
enamine

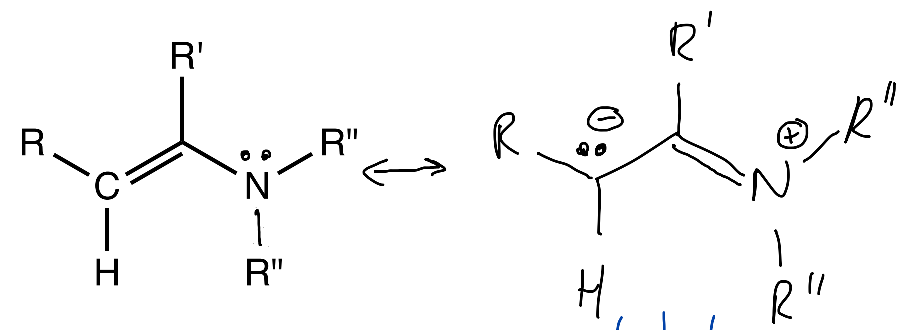


Reactions of Aldehydes and Ketones with Nitrogen Nucleophiles: summary

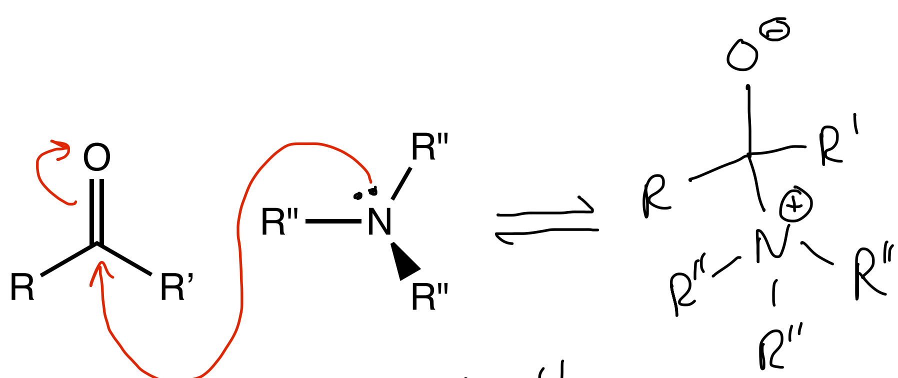


π bond adjacent to an atom with lone pair e^-'s





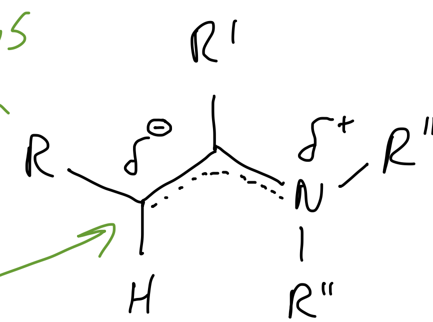
resonance contributors



tertiary amines don't make stable products

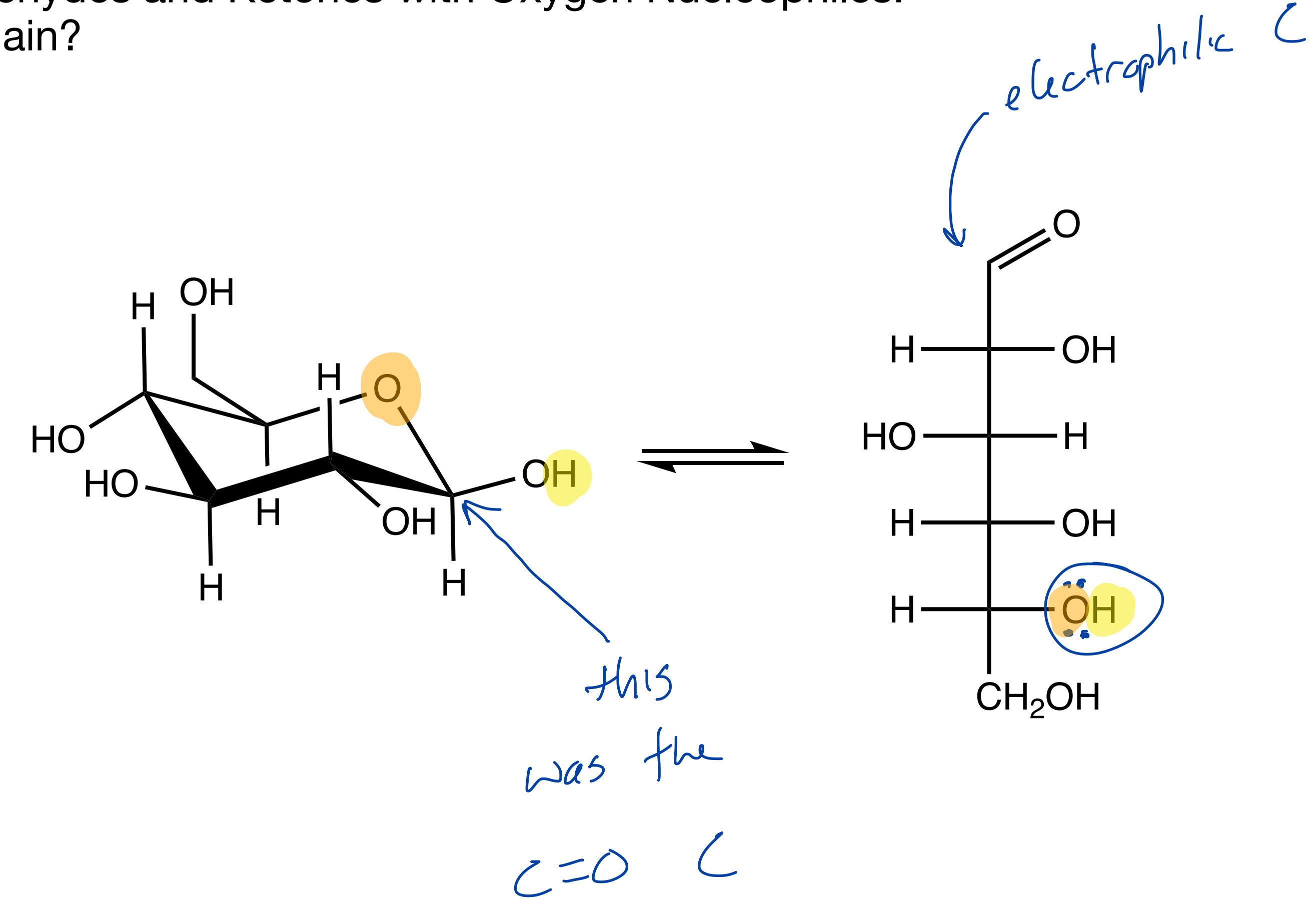
R" ≠ H

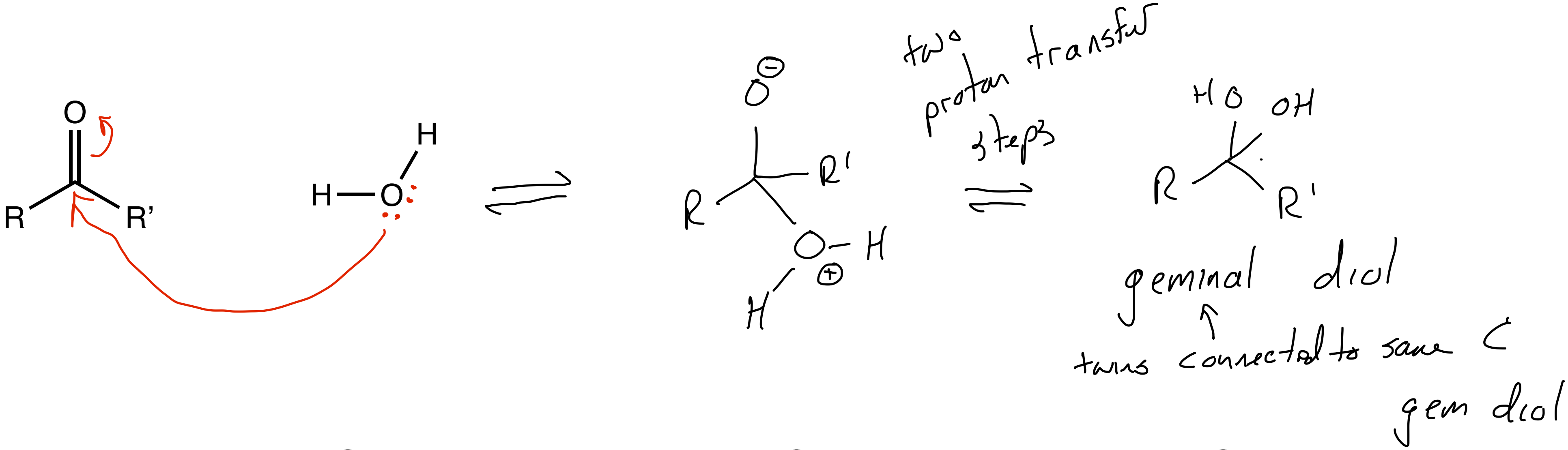
enamines have an e^- rich C atom

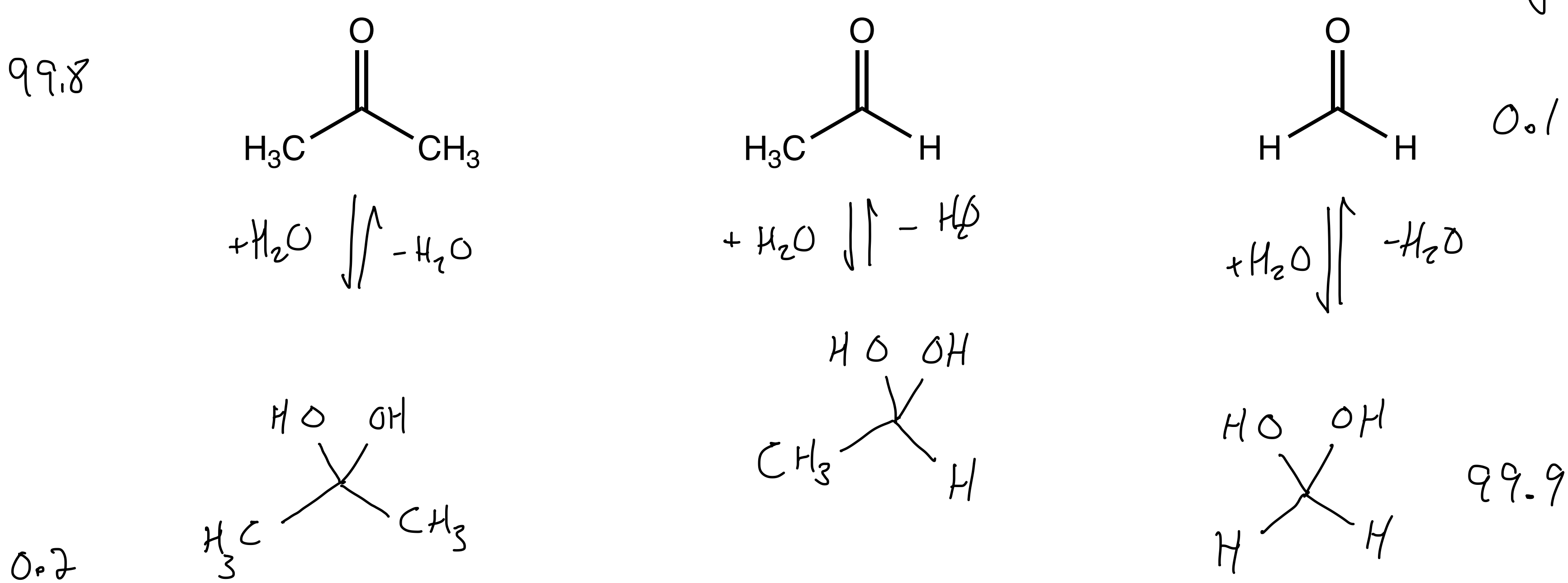


resonance hybrid = actual molecule

Reactions of Aldehydes and Ketones with Oxygen Nucleophiles: Why do I care again?





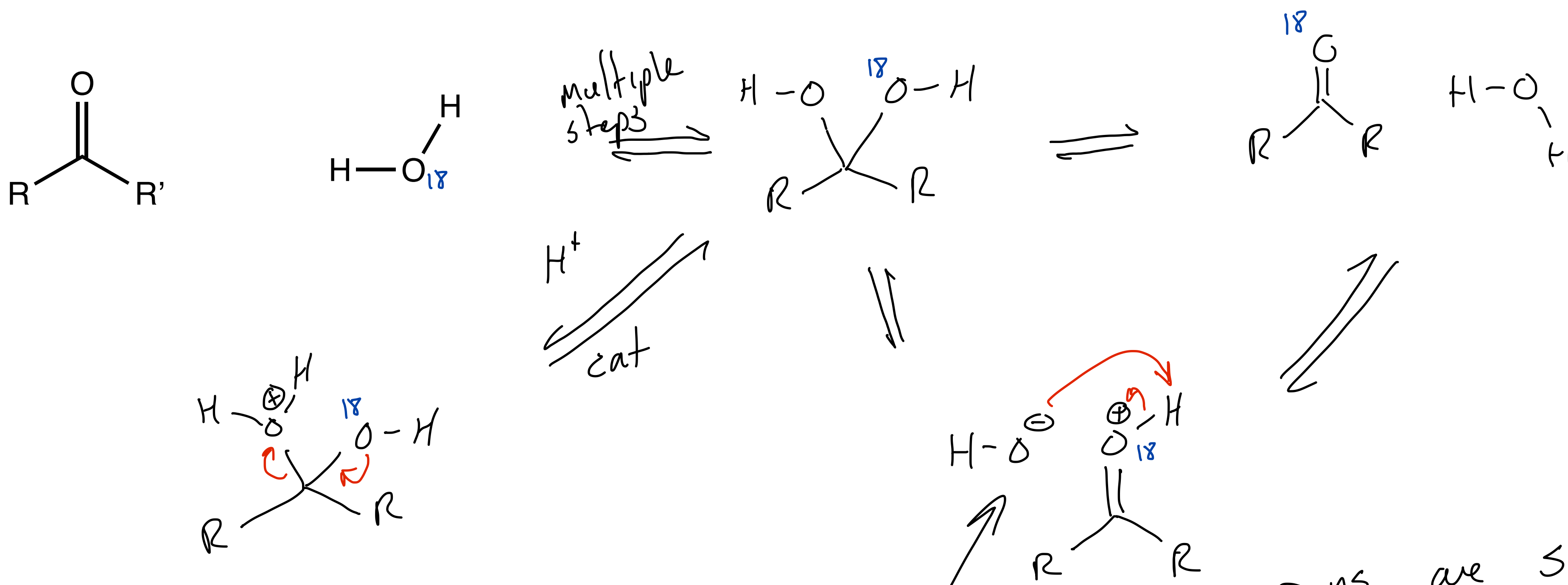


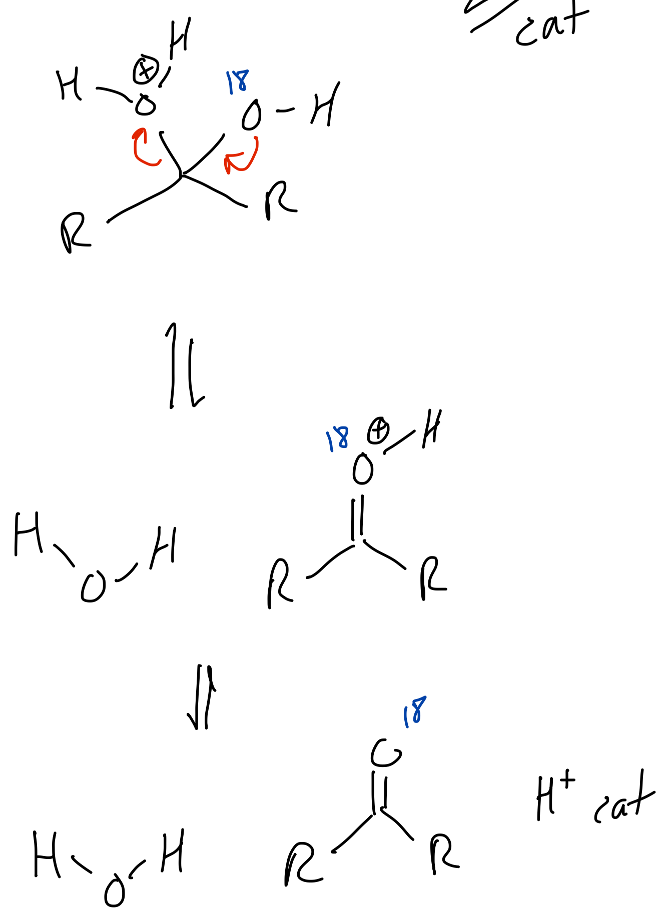
99.8 : 0.2

42 : 58

0.1 : 99.9

M 10^{-7} $H_3O^{\oplus}$ 10^{-7} $OH^{\ominus}$

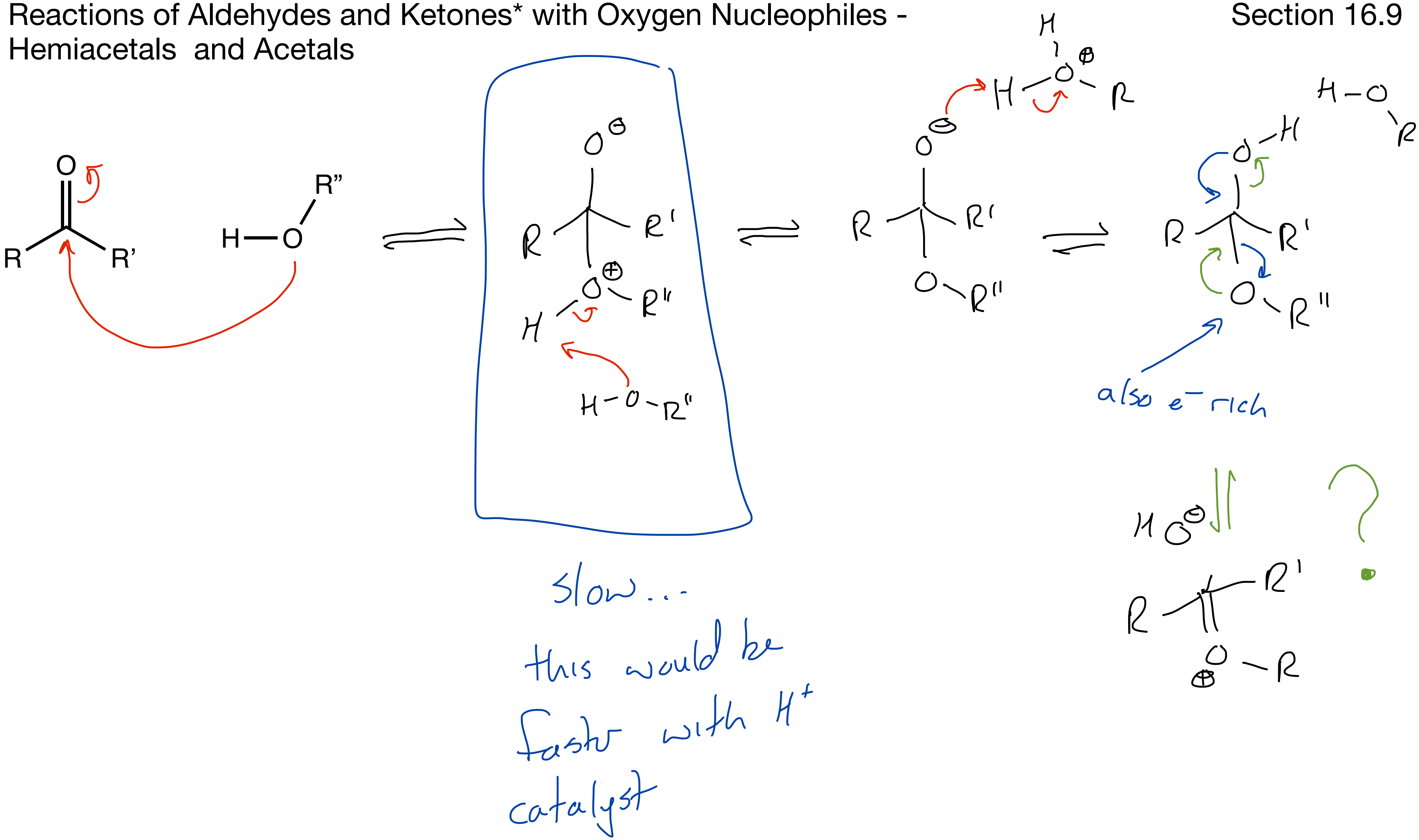




without catalyst rxns are slow because $H-O^{\ominus}$ is a very poor LG and proton transfers to create a good H_2O LG have low probability of occurring

H^+ catalyst speeds up reaction

Reactions of Aldehydes and Ketones* with Oxygen Nucleophiles - Hemiacetals and Acetals



*Even though, nomenclature-wise, ketones form hemiketals and ketals chemists typically refer to the entire class of molecules as hemiacetals and acetals.