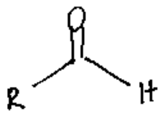
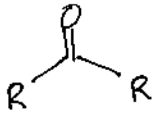
Carbonyls

Feb. 13/13





Carbonyl Double Bond

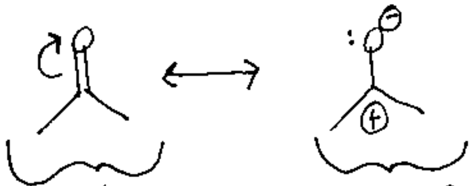
σ Bond
π Bond

π Bonds are weaker + chemistry of carbonyl involves π bonds

$\overset{\delta^+}{C}=\overset{\delta^-}{O}$ ← oxygen is more electronegative; it attracts electrons becoming more δ⁻

less electronegative
loses e⁻s becoming δ⁺

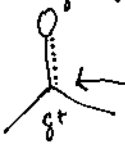
You can also analyze by resonance



Better Structure

Contributes also, as it gives a clue about reactivity

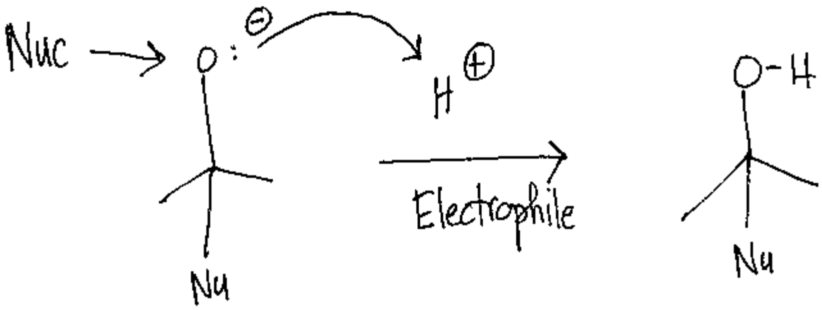
- Draw Carbonyl like this form



+'ve reagents react here
Electrophiles (Electron Loving)

-'ve reagents react at the Carbon; "Nucleophiles"
Nucleus - Loving

Feb. 13/13 Cont'd

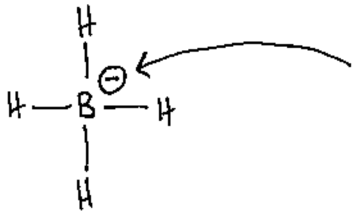


This is a Nucleophile/Electrophile Reaction
It's also an Acid/Base Reaction
It's both at the same time

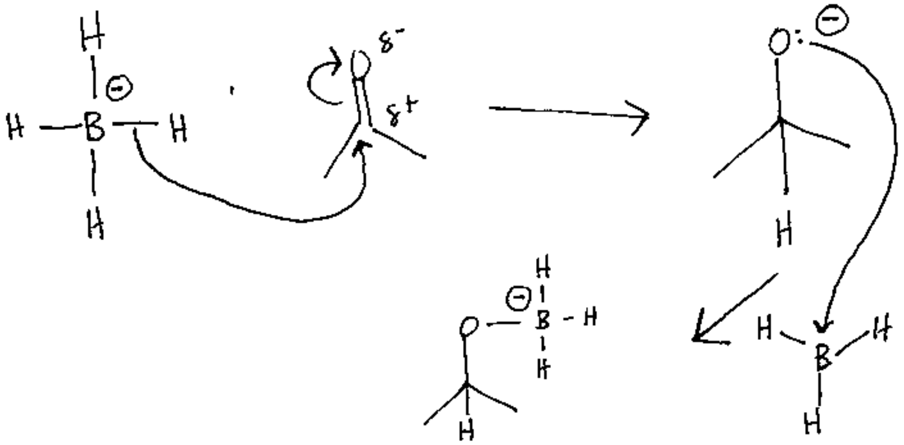
When the reaction involves H^+, you have Acid/Base

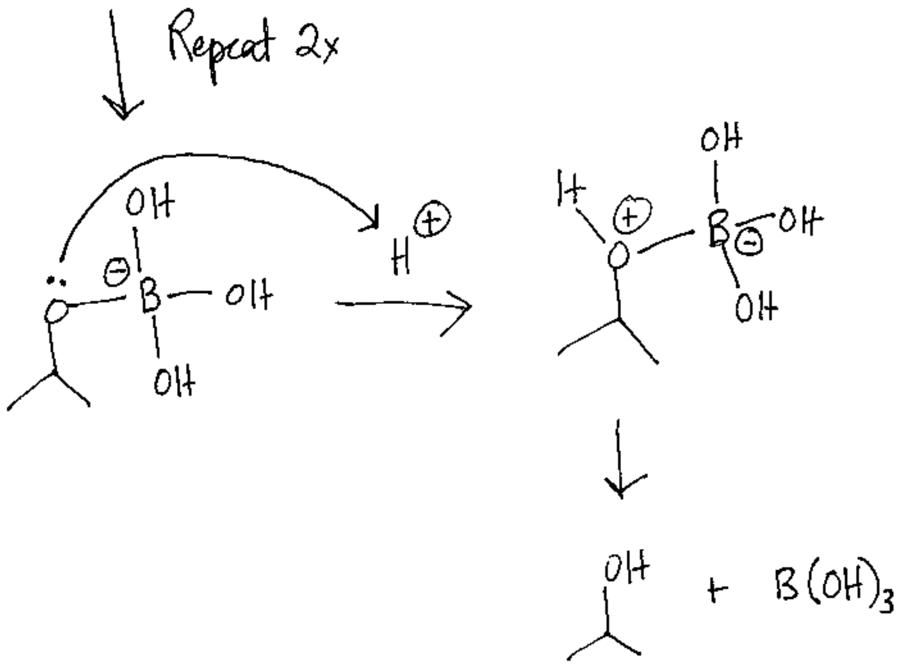
NaBH4

BH_4^- is a nucleophile
Source of H^-

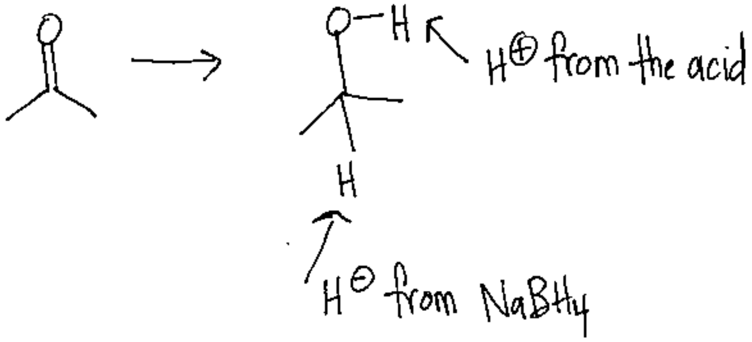


B has a -'ve formal charge
H is more electronegative than B; the -'ve charge is actually on H

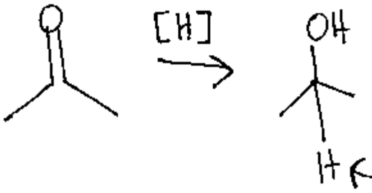




Overall, we add H_2 across the double bond:

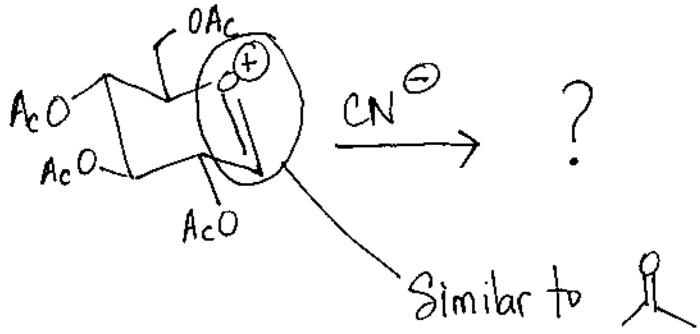


This reaction is a Reduction
- adding electrons reduces [H]
- removing electrons oxidizes [O]

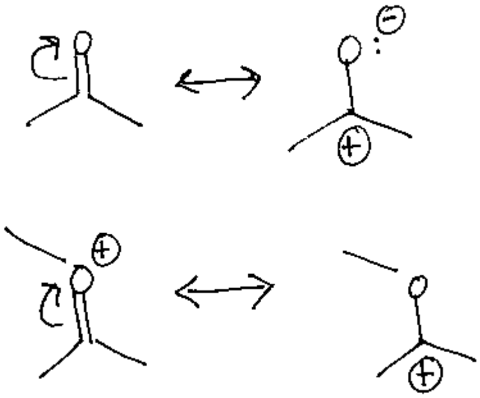


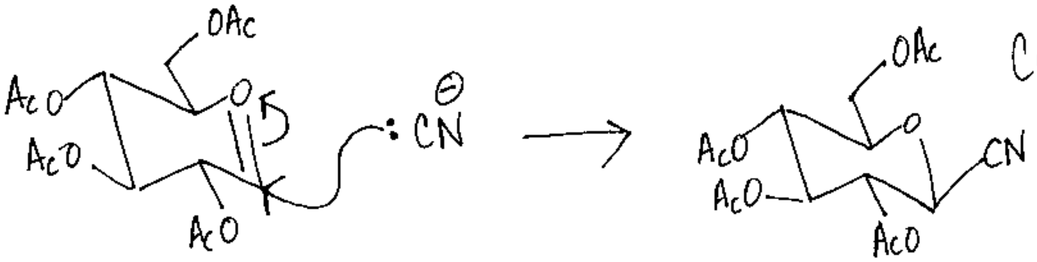
This adds H⊖, bringing a pair of e⁻ to the molecule

Add complexity...



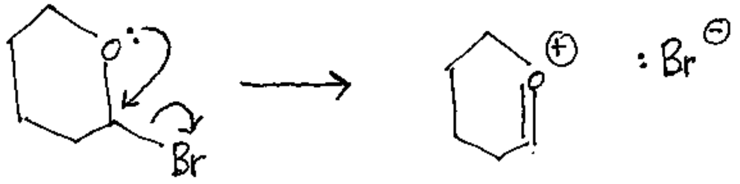
Similar to





Cyanohydrin

Use this to get electron flow :



Organometallic Reactions

"Organo" → Carbon
"Metallic" → Metal i.e. Mg, Li, Na, K, Pd, Zn

- Formation of C–C Bonds

Grignard Reagents

- The metal is <u>always</u> magnesium $\boxed{\mathrm{Mg}}$

Ex. $\mathrm{CH_3-Br}\quad \mathrm{Mg} \longrightarrow \mathrm{CH_3-Mg-Br}$

Mg inserts into C–Br Bond

Oxidation state of Mg starts at 0 then ends up at +2 which changes the polarization of the carbon

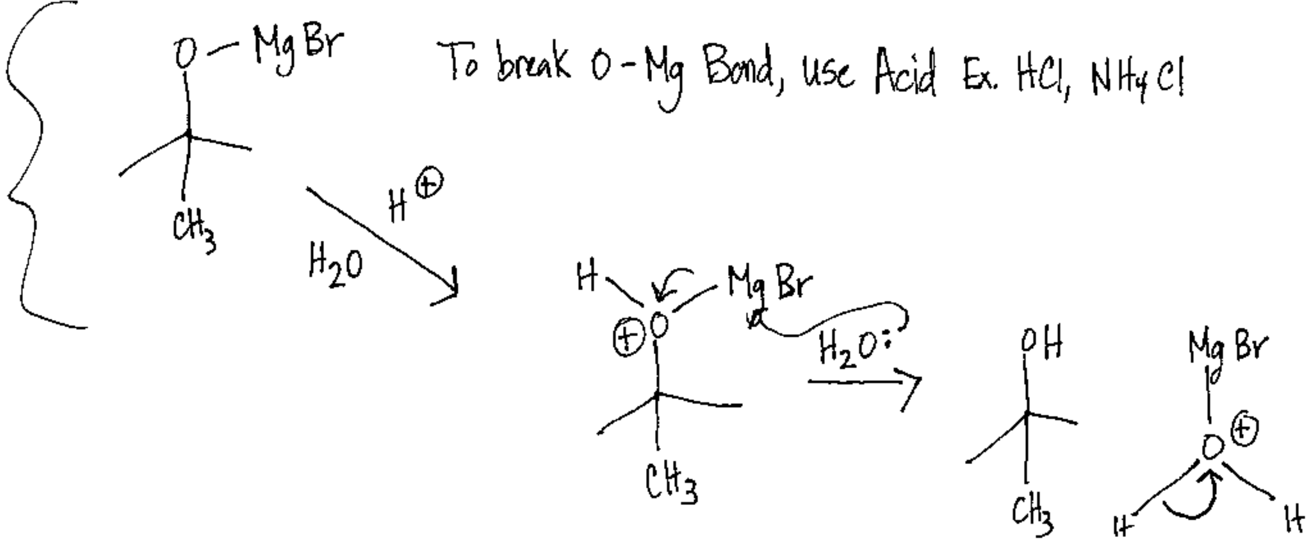
$$\overset{\delta^+}{\mathrm{CH_3}} - \overset{\delta^-}{\mathrm{Br}}$$

$$\underbrace{\overset{\delta^-}{\mathrm{CH_3}}}_{\text{Nucleophile}} \longleftarrow \overset{\delta^+}{\mathrm{Mg\,Br}} \qquad \text{Reacts like } {}^{\ominus}\!:\mathrm{CH_3}\ {}^{\oplus}\mathrm{Mg\,Br}$$

Work-up to break C-Mg Bond

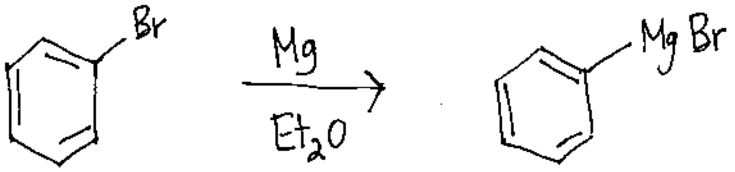
Find out where e's go

To break O-Mg Bond, use Acid Ex. HCl, NH_4Cl

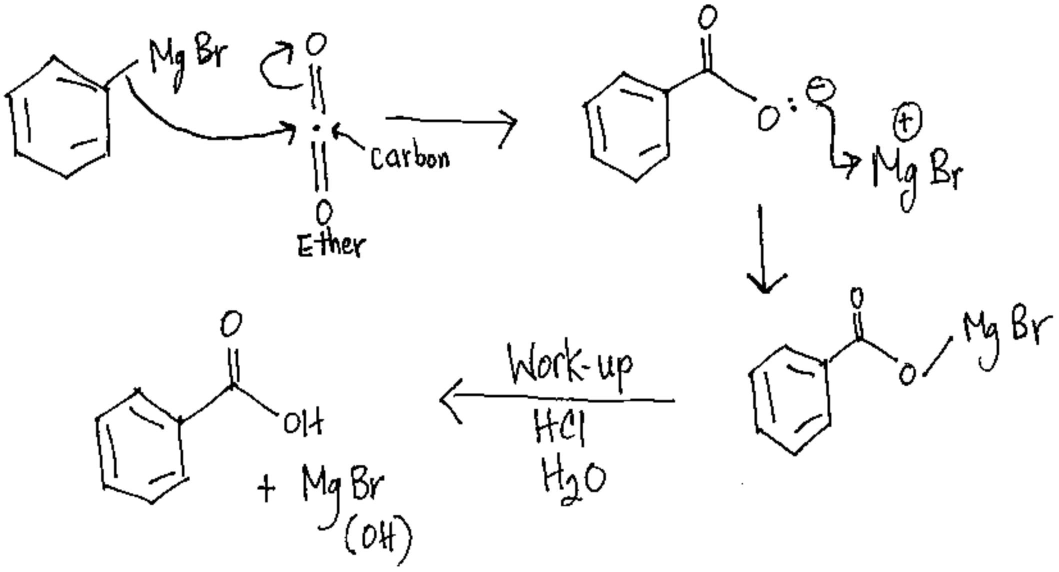


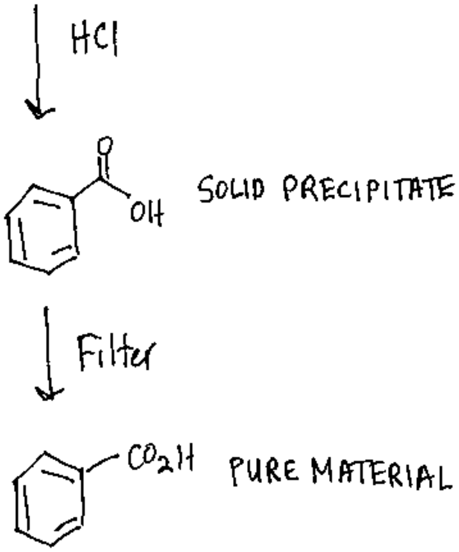
Ex.

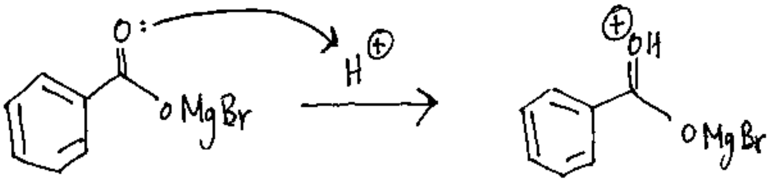
Et₂O = Ether



O=·=O is CO_2

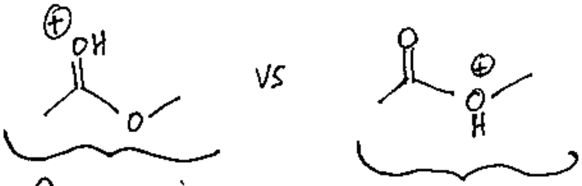






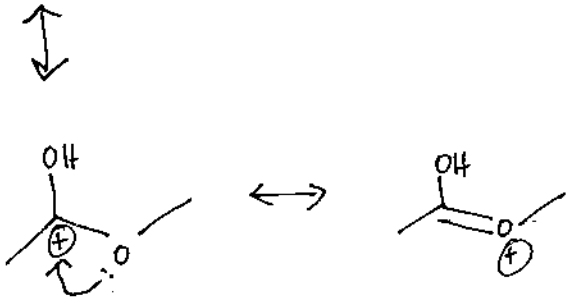
Why This?

* Protonation happens at the Carbonyl Oxygen

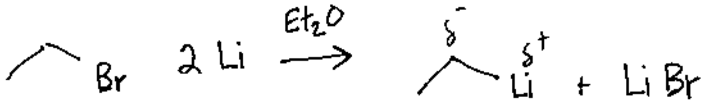


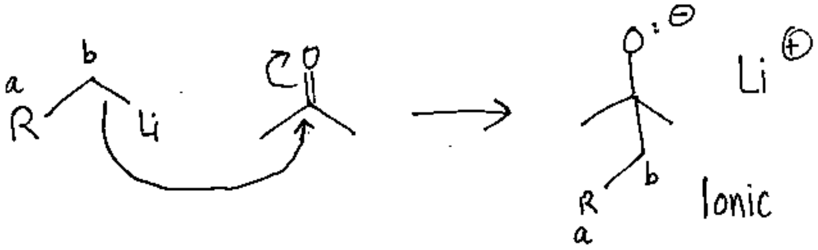
Resonance is possible for this structure!

Resonance is Not Possible for this structure

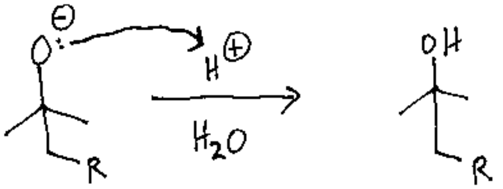


Organolithiums





Work-up:



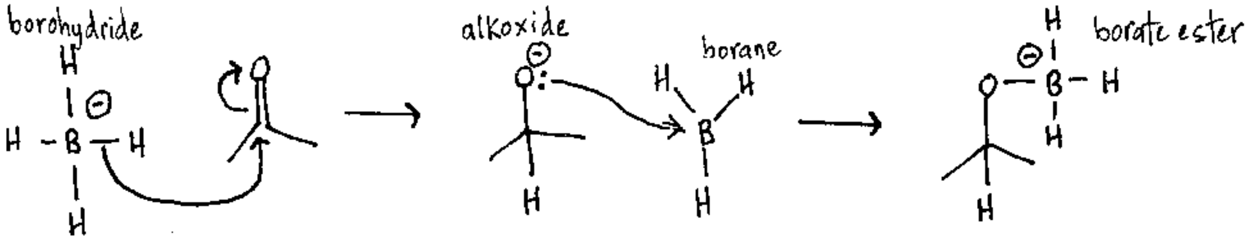
Very Strong Bases! pka > 45

→ OH
NH
SH } Acid/Base

In special cases, it's possible to remove an H from a C

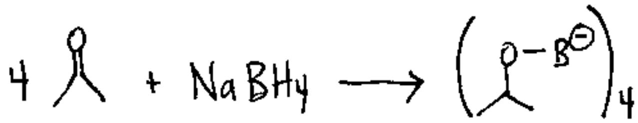
Butyllithium (Strong Base)
"BuLi"

Reduction of Carbonyls with NaBH$_4$

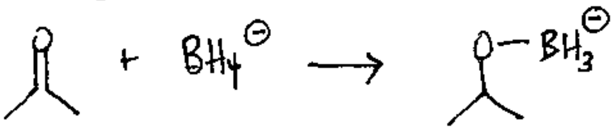


It can react with 3 more  groups

The overall reaction has the following stoichiometry:



For assignments + tests, just use the 1st stage:



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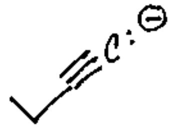
pKa & Hybridization

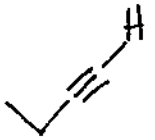
- S orbitals are lower energy than p
- electrons in S orbitals impart lower energy than p
- hybrid orbitals with more S character stabilize -'ve charges better



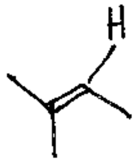
Sp
Most Stable

Sp2

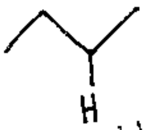
Sp3
Least Stable



Strongest Acid
pKa ≈ 25



pKa 44



Weakest Acid
pKa >50

Hydrate & Hemiacetal Formation

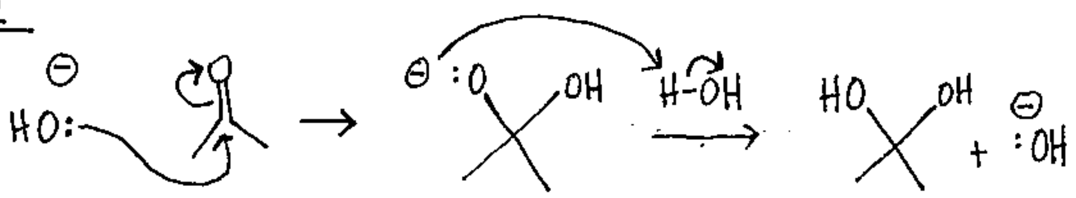
↙ H_2O

↘ HO-R

H_2O adds reversibly to carbonyl groups

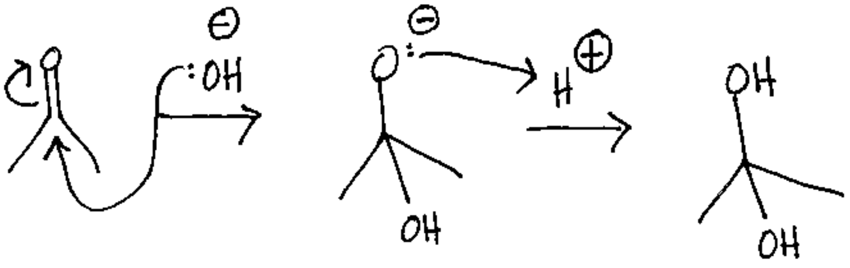
- Acids are base catalyst

Base

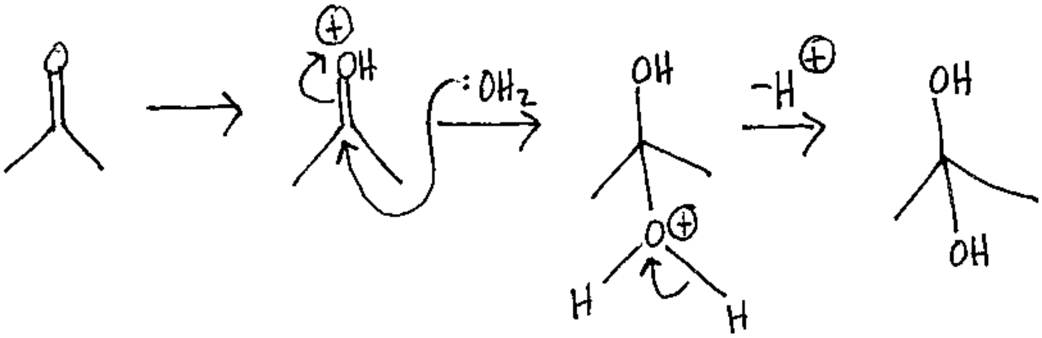


$OH^{\ominus}$ is a catalyst → consumed + replaced ; accelerates the rxn

Base

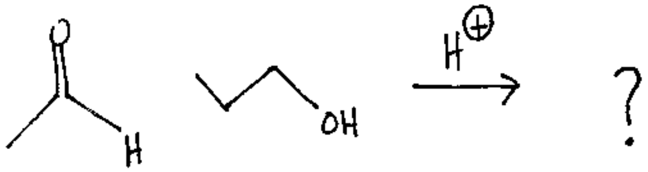


Acid

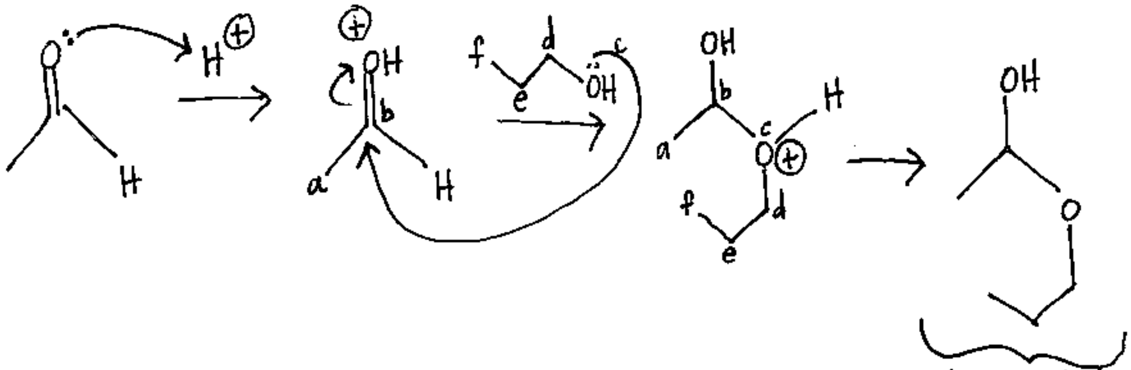


Intramolecular Forces

- within the same molecule is intramolecular
- intermolecular is between different molecules

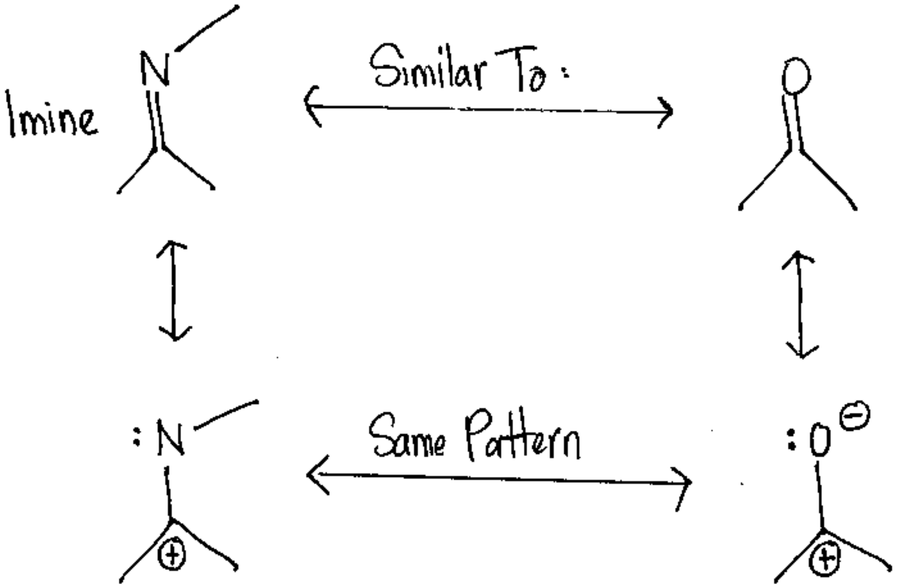


Intermolecular:

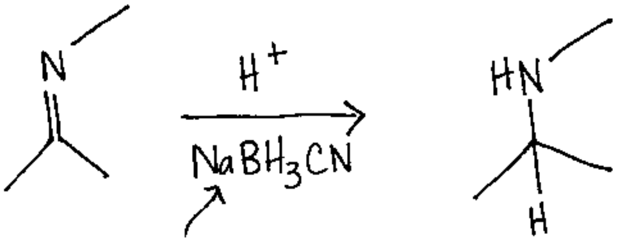


Hemiacetal
(a carbon with
2 O's)

Reaction of Imines



- Nitrogen is less electronegative than Oxygen
- contribution of charged resonance form is less
- Imines are *less* stable than C=O
- Imines require activation with weak Nucleophiles

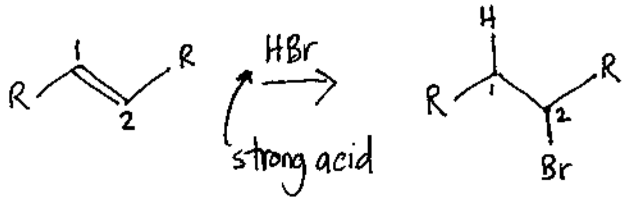


stable to acid
⇒ less reactive than $NaBH_4$
destroyed by acid

Reactions of Alkenes

March 1/13

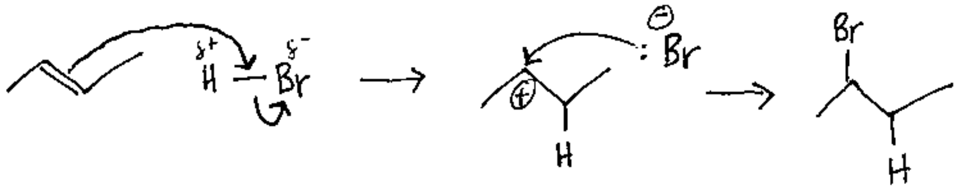
Electrophilic Addition



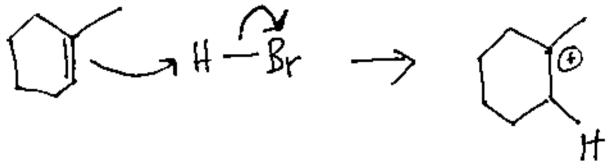
Add HBr across the double bond:
H adds to C1
Br adds to C2

π Bond acts as a Nucleophile

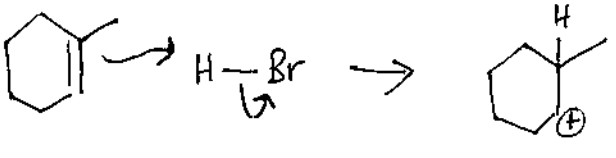
HBr is an acid → source of H^+



Depending on the substitution patterns, you can get different products



3° Carbocation (very stable)

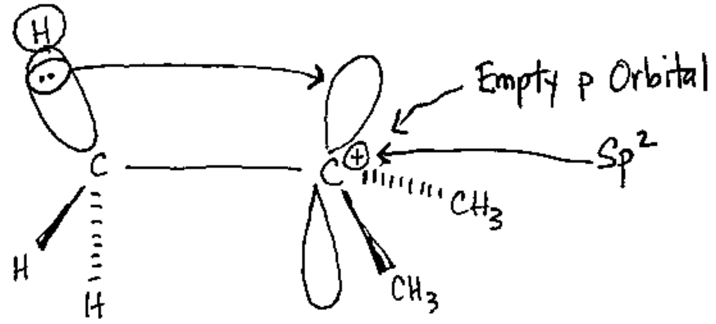


2° Carbocation (less stable than 3°)

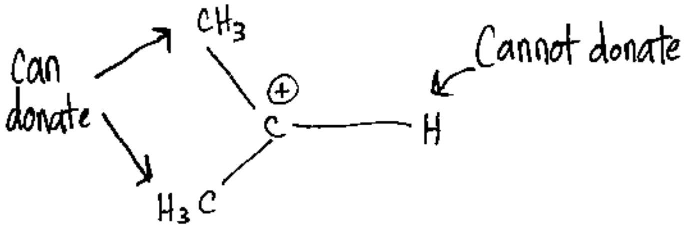
The H^+ will add such that the most stable carbocation is formed
→ This leads to the Major Product in the Reaction
(form in largest amount)

Hyperconjugation

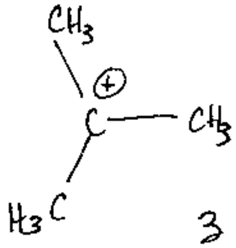
C–H and C–C σ Bonds on the Alkyl groups donate electrons into empty p orbital on C⊕



Donation of electrons from C–H and C–C bonds into C⊕ reduces effective charge and increase stability

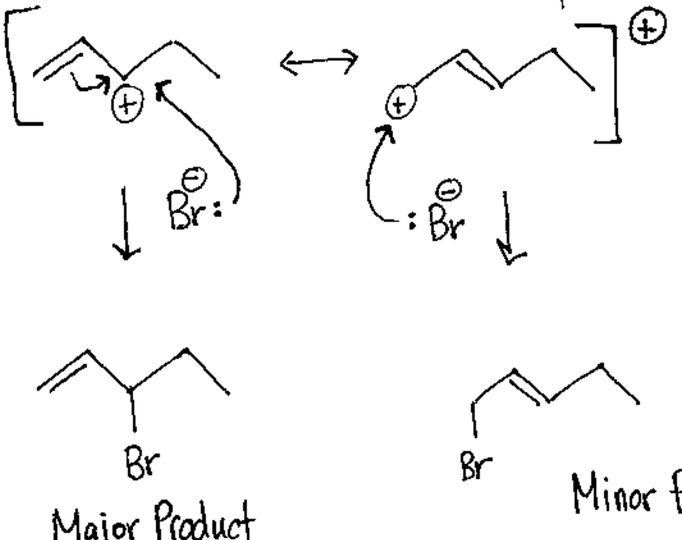


2 Alkyl groups on C⊕



3 Alkyl groups on C⊕

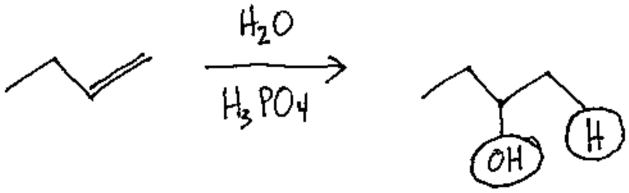
Use $C^{\oplus}$ Structure to predict the product



Major Product

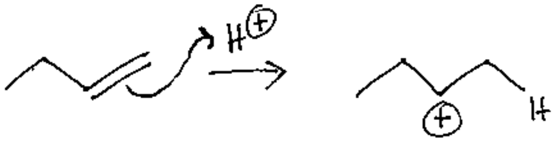
Minor Product

Addition of Water Using Acid

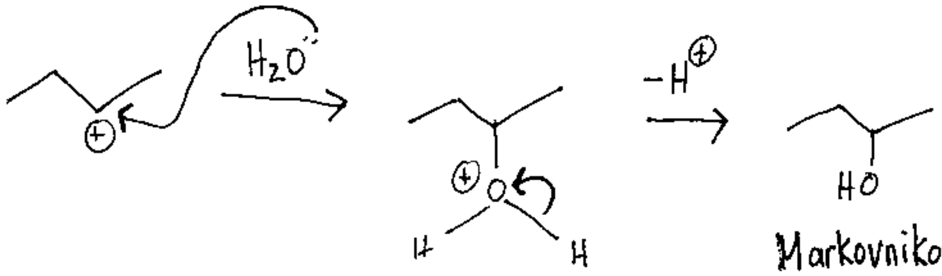


Markovnikov
(the oxygen heteroatom is in the more substituted position)

Mechanism:

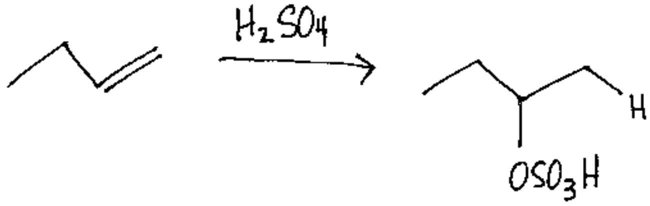


H adds to the side that gives the most stable $C^{\oplus}$



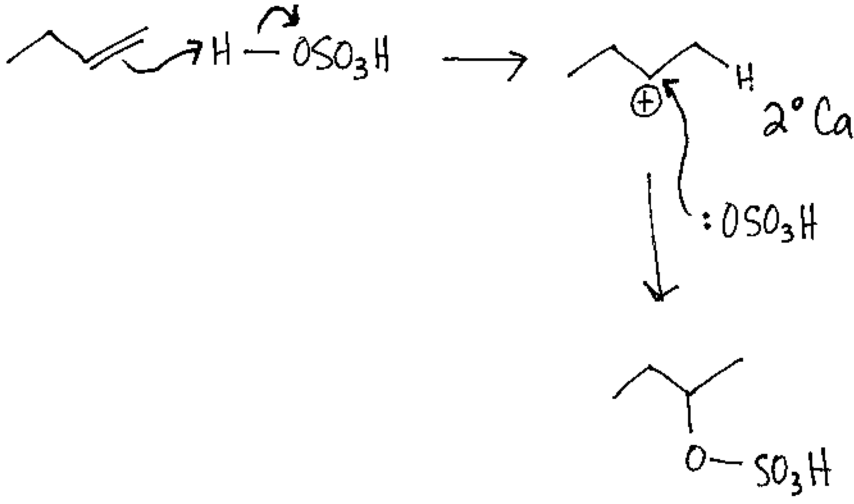
Markovnikov Product

Sulfuric Acid Can Make Sulfates



Markovnikov

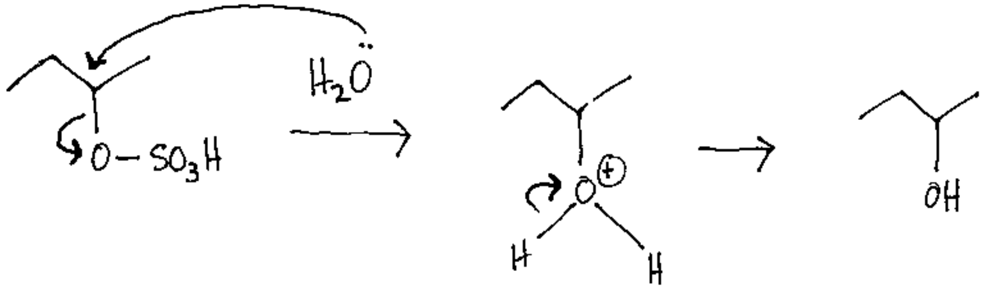
Mechanism:



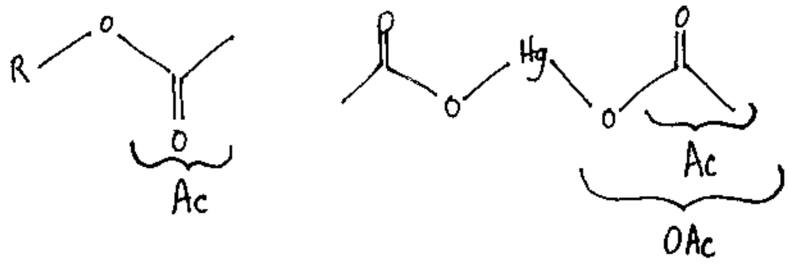
2° Carbocation

Markovnikov

Sulfates Are Converted to Alcohols Using Water



OAc :



Mechanism: