Dr. Iverson – Missed The Wave – Monday 2/6/2017

Memorize this paragraph for 14 points on every midterm and the final
Find this on the rules of the day, Monday 1/30/2017

> **The popular medical diagnostic technique of magnetic resonance imaging (MRI) is based on the same principles as NMR, namely the flipping (i.e. resonance) of nuclear spins of H atoms by radio frequency irradiation when a patient is placed in a strong magnetic field. Magnetic field gradients are used to gain imaging information, and rotation of the gradient around the center of the object gives imaging in an entire plane (i.e. slice inside patient). In an MRI image, you are looking at individual slices that when stacked make up the three-dimensional image of relative amounts of H atoms, especially the H atoms from water and fat, in the different tissues**
> [Memorize the preceding passage, as it will be worth 14 points on every midterm and final. No I am not kidding, 14 points right there.

Mechanism Review:

- Review the first 8 pages of the mechanism packet we handed out in class
  - Also found on the website under "Mechanism Sheets Used in Class"

- Review at your class notes from Monday 1/30
  1. Arrows → show movement of electrons (Arrows do NOT show movement of atoms)
  2. Arrows start at an electron source and end at an electron sink
     a. Electron source = bond or lone pair
     b. Electron sink = atom that can accept a bond or lone pair
  3. Breaking of a bond will happen to avoid overfilling a valence

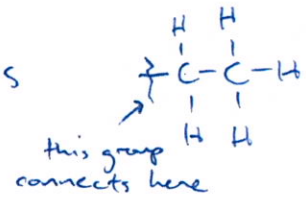
- 4 Elementary Mechanistic Steps'

The below steps always refer to the carbon-containing reagent

1. **Make a bond** between a nucleophile and an electrophile
2. **Break a bond** to generate stable molecules or ions
3. **Add a proton**
4. **Take a proton away**

2015-02-12 Missed The Wave

R = generally... - Alkyl groups

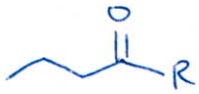


- Aryl groups

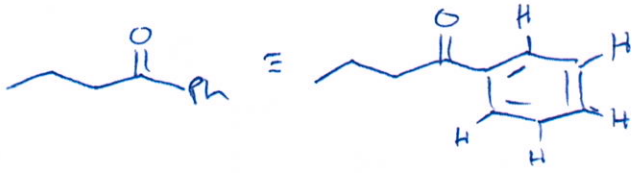
↑ Phenyl group = Ph

- Can sometimes be an H atom

R', R'', R''' => designates different R groups.



can be

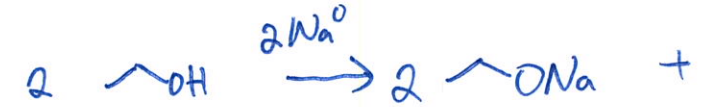


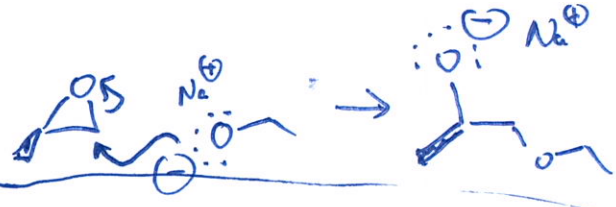
MTW

Mon 2/6/17

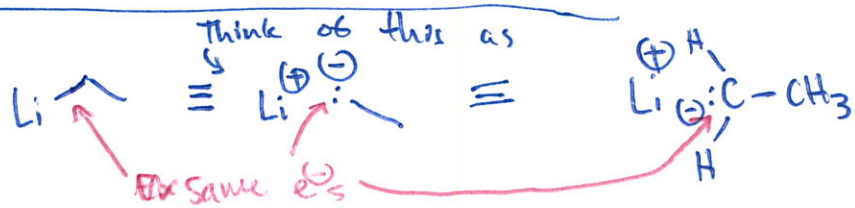
Organometallics

Recall 

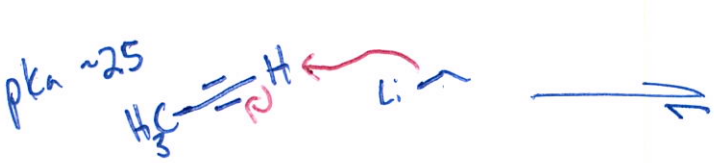


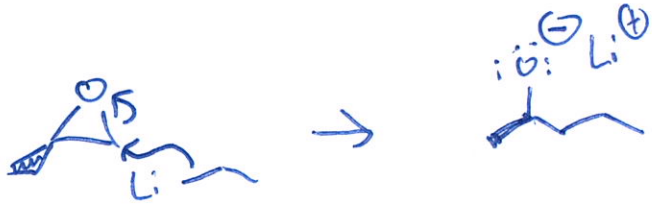


Alkyl Lithium (Organolithium) (RLi) R = something C containing

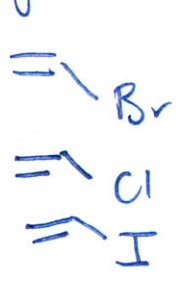


★ Extremely Basic (deprotonates $H^{\oplus}$ & pka ≤ 35)





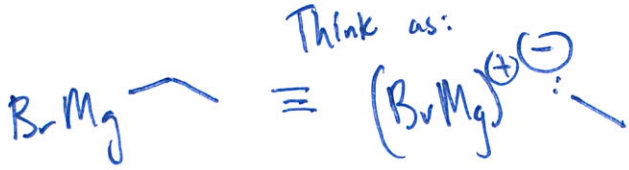
Can't react w/ 1° haloalkanes or vinyl halides

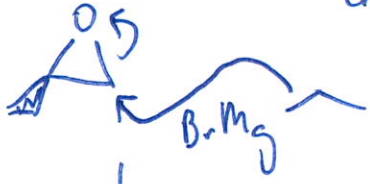


Grignard ($RMgBr$, $RMgCl$, $RMgI$)

Grignard

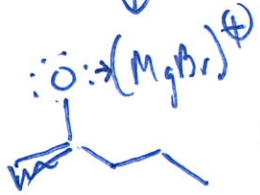
Think as:



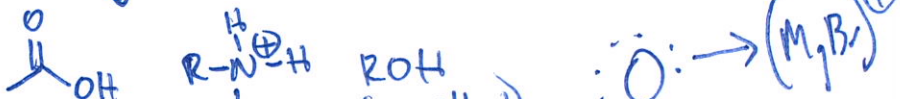


↳ Slightly Basic

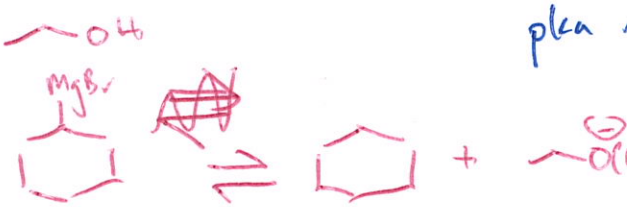
↳ Deprotonate $H^{\oplus}$ pka $\lesssim$ ~16



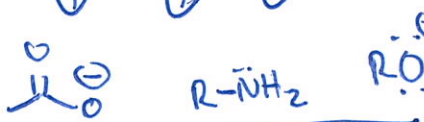
↓ examples

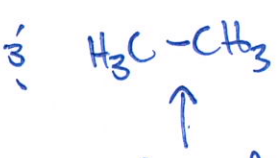


pka ~4 | ~10 | ~16 (R = alkyl, H)

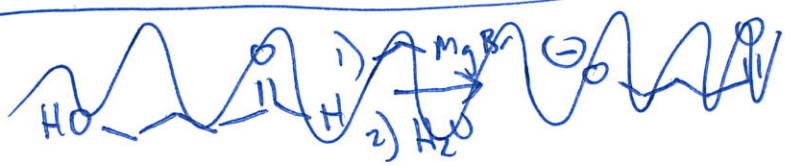


add a grignard ($-MgBr$)



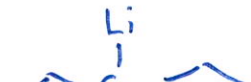


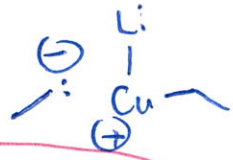
Ruined the grignard



Gilman Reagent (R_2CuLi)

No mechanism for formation for 3 organometallics

$LiCu(\text{—})_2$ = 

Think of as: 

NOT $(\text{—})_2CuLi$

$(\text{—})_2CuLi$

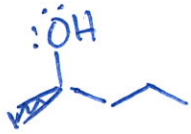
$(\text{—})_2CuLi$

Gilman

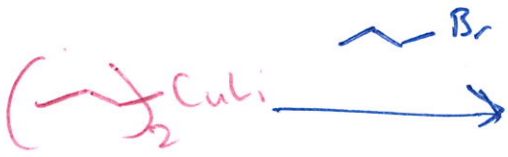
No mechanism for Reaction WITH gilman

 + $Li\,Cu(\text{—})_2$

↓ 2) HCl/H_2O (mild acid)

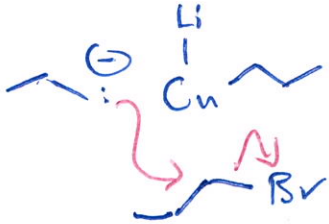


CAN React with 1° haloalknes & Vinyl halides!



new C–C bond

Think of as:



Missed the Wave

MECHANISM A: Reaction with a Strong Nucleophile

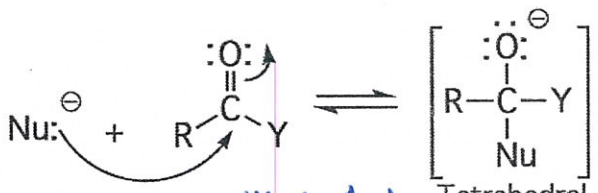
Strong Nuc:⊖

R–MgBr

⊖ :C≡N:

Na⊕ ⊖ :C≡C–R

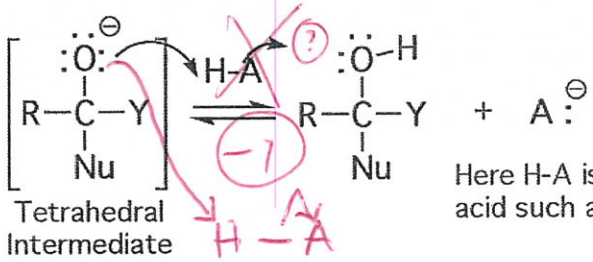
Step 1 Make a new bond between a nucleophile and electrophile



R = Y = Alkyl, Aryl, H

Aryl

Step 2 Add a proton



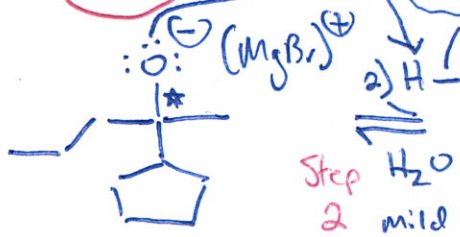
Here H-A is a weak acid such as water

Nu:⊖ ⇒ Carbonyl Geometry → Trigonal Planar

50:50 shot of Nuc attack above or below, gives rise to racemic mixture if it creates a chiral center

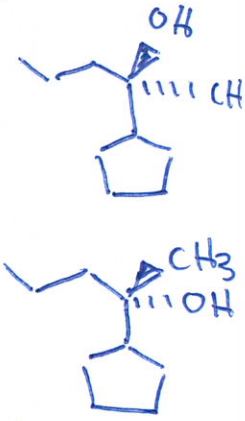
Example

Step 1 ⇌



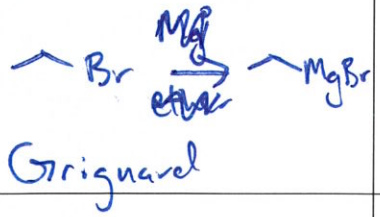
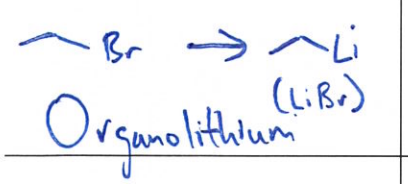
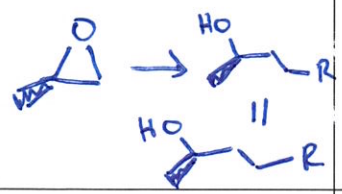
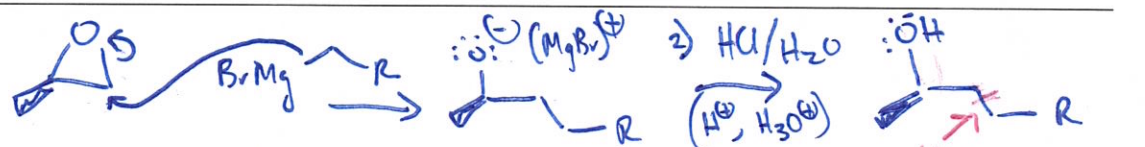
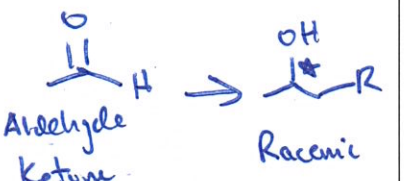
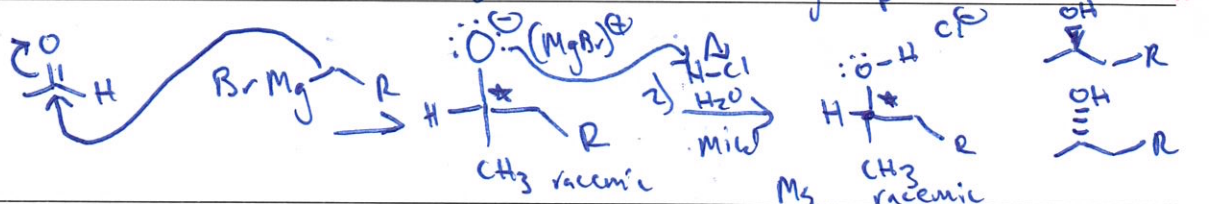
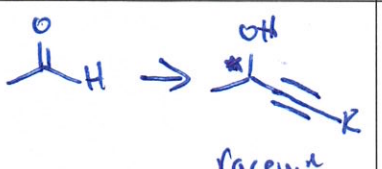
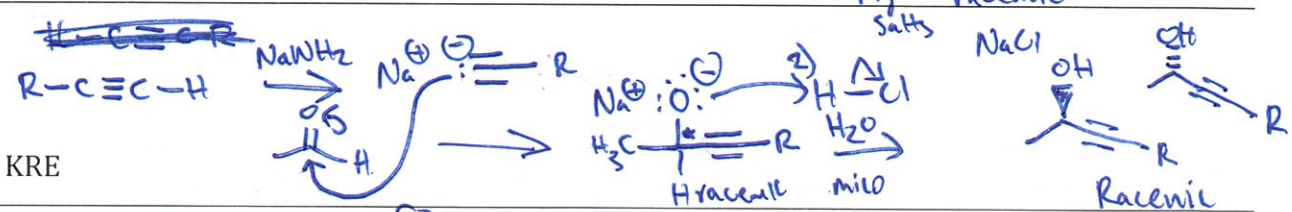
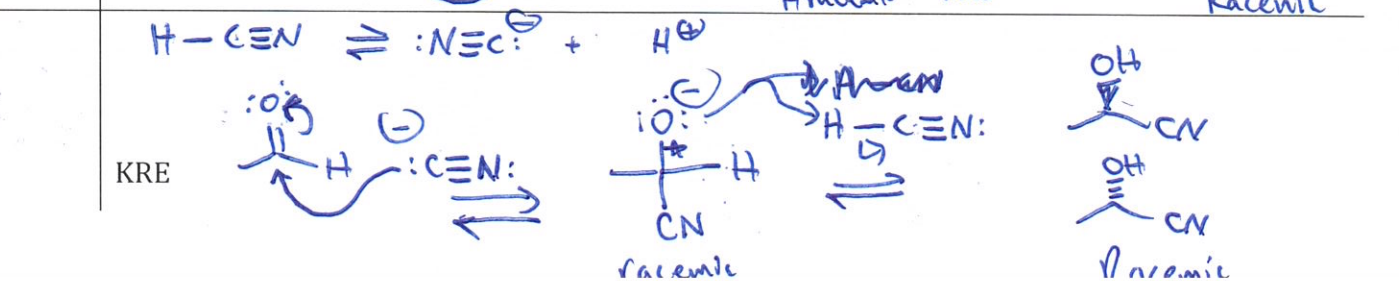
Step 2 H_2O mild

Racemic



Racemic

Nuc:⊖ ‖ Nu:⊖

Transformation	Reagent	Mechanism
 Grignard	Mg^0 * ether	None KRE
 Organolithium	2 Li^0	None KRE
 Gilman	CuI	None KRE
	1) R–Li, R–MgBr, $(R)_2CuLi$ 2) H_2O/HCl (mild acid)	 KRE New C–C bond adjacent to –OH group
 Aldehyde Ketone	1) R–MgBr 2) HCl/H_2O (mild)	 KRE
 Racemic	1) $Na^{\oplus}$:C≡C–R 2) HCl/H_2O mild	 KRE
	H–C≡N	 KRE