Objective 2. Identify and understand an organic oxidation and reduction reactions.

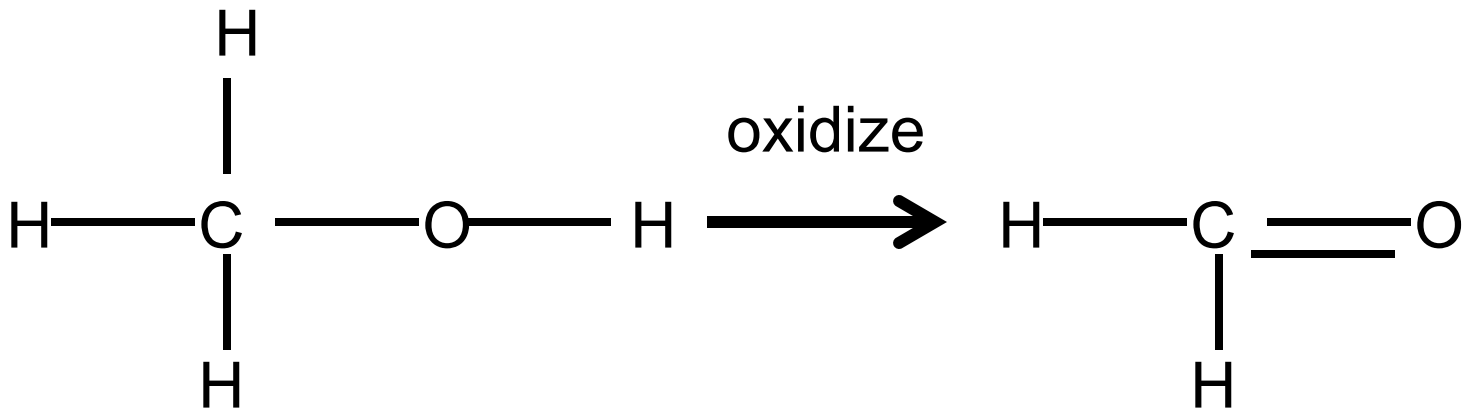
Skills: Draw structure
ID structural features and reactive sites (atom that is being oxidized or reduced)
ID Nu^- and E^+ (Note: some redox reaction do **not** involve Nu^- and E^+.)
use curved arrows to show bonds breaking and forming
show delocalized electrons with resonance structures.

Key ideas:
Oxidation = gain of O or loss of H or both at one carbon.
Reduction = gain of H or loss of O or both at one carbon.

OCHEM REDOX - ***forget about oxidation numbers***!

OChem **Oxidation** [O]: gain of O/loss of H at one Carbon
OChem **Reduction** [R]: loss of O/gain of H at one Carbon

Treat C=O double bond as 2 C-O single bonds.



C has 1 O and 3 H

C has 2 O and 2 H
Gain 1 O and Lost 1 H

Determine product of ROH oxidation
(or how to make ROH by reduction)

Alcohols can be Oxidized to make Aldehydes, Acids, or Ketones

1^o ROH -- [O] --> aldehyde -- [O] --> acid [O] = ox agent

2^o ROH -- [O] --> ketone

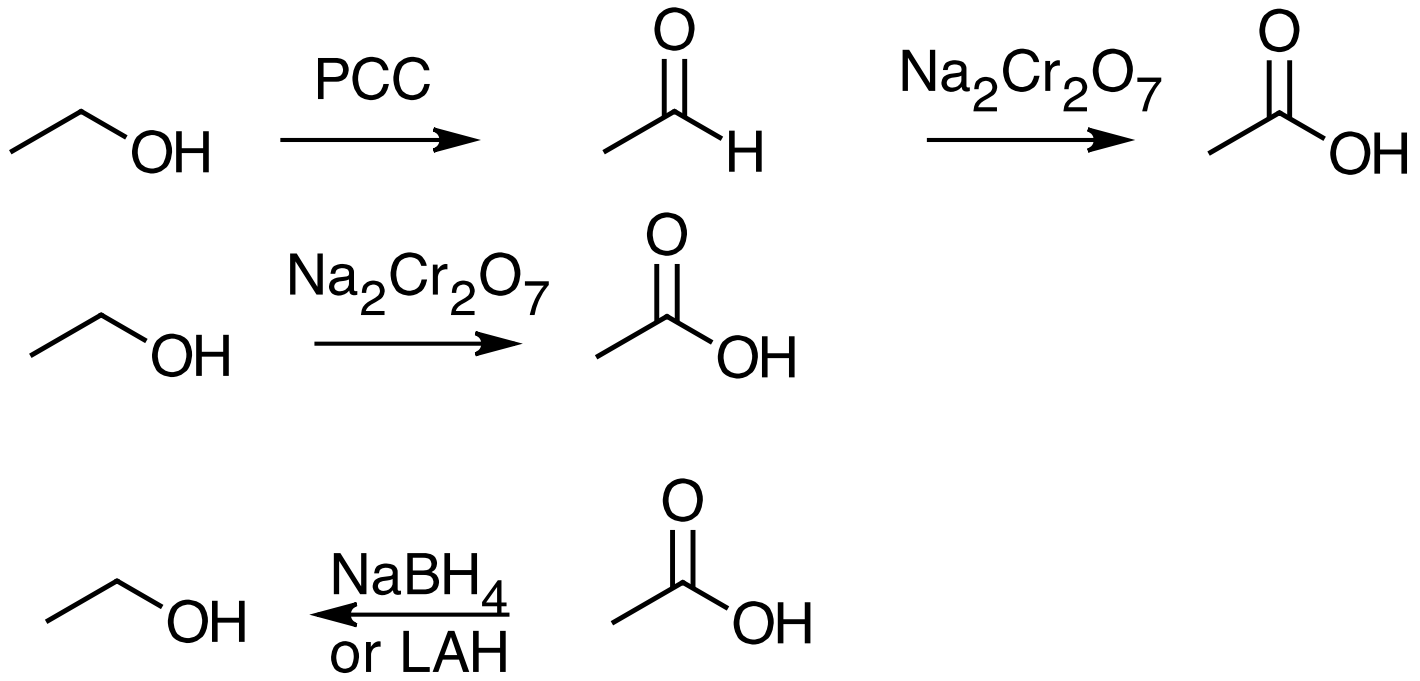
3^o ROH -- [O] --> No Reaction

<u>Common Oxidizing Agents [O]</u>:
H_2O_2 NaClO (bleach) $KMnO_4$ $Na_2Cr_2O_7$ PCC

<u>Common Reducing Agents [R]:</u>
H_2 $NaBH_4$ $LiAlH_4$

Is ethanol a 1º, 2º, or 3º alcohol?

oxidation ------>



<------reduction

Alcohol metabolism uses dehydrogenases (in liver):

$$C_2H_5OH \xrightarrow{ADH} CH_3CHO \xrightarrow{ALDH} CH_3COOH$$

hangover

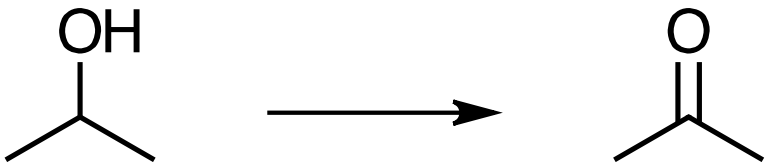
Is ethanol being oxidized or reduced?

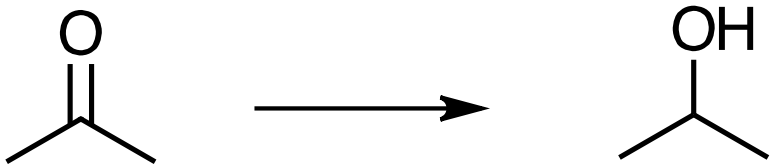
Note: acetaldehyde is toxic in our body.
Limited amount of dehydrogenase enzyme present.
When it runs out, what happens?

Vasopressin hormone – diuretic
Sleep – GABA and glutamate

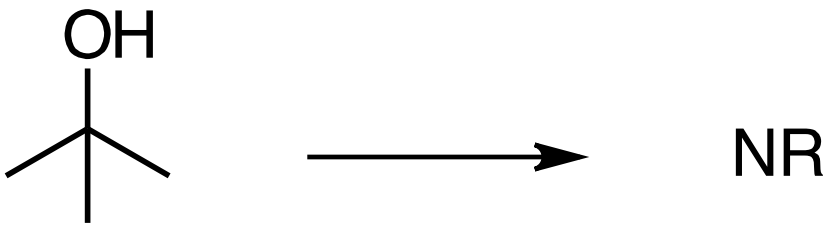
See ACS Reactions (YouTube): "How to Prevent a Hangover"

Identify each reaction as an oxidation or reduction.
What reagent would you use for each reaction?





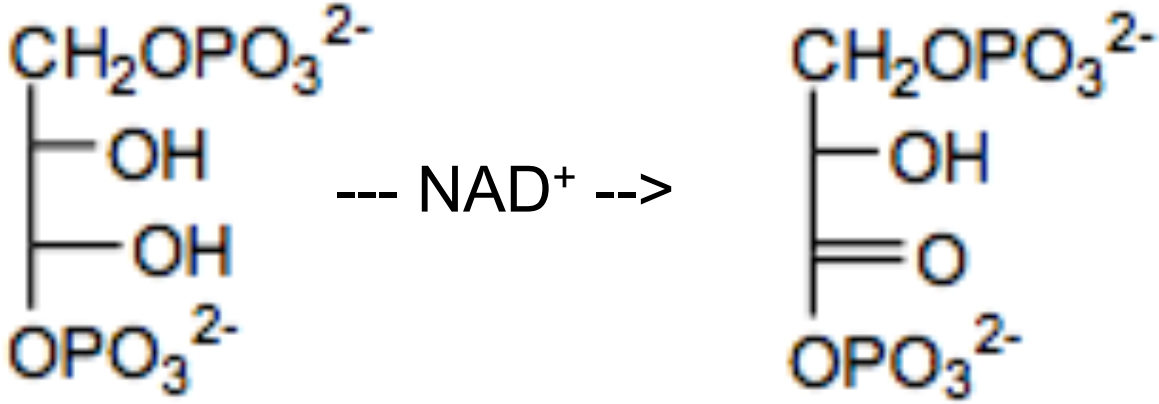
Why does this reaction not occur?



Oxidation-Reduction in Biology

Biological Oxidizing Agent: NAD^+/enzymes FAD
Biological Reducing Agent: NADH/enzymes $FADH_2$
for C-O, C-N for C-C

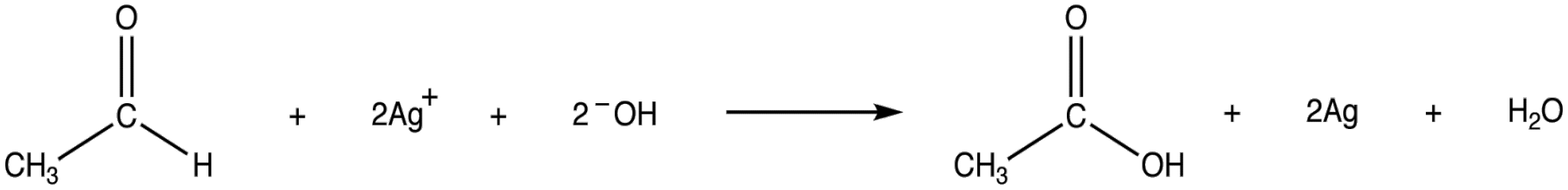
Glycolysis Step 6:



Is this reaction an oxidation or reduction?
Which C is oxidized or reduced?

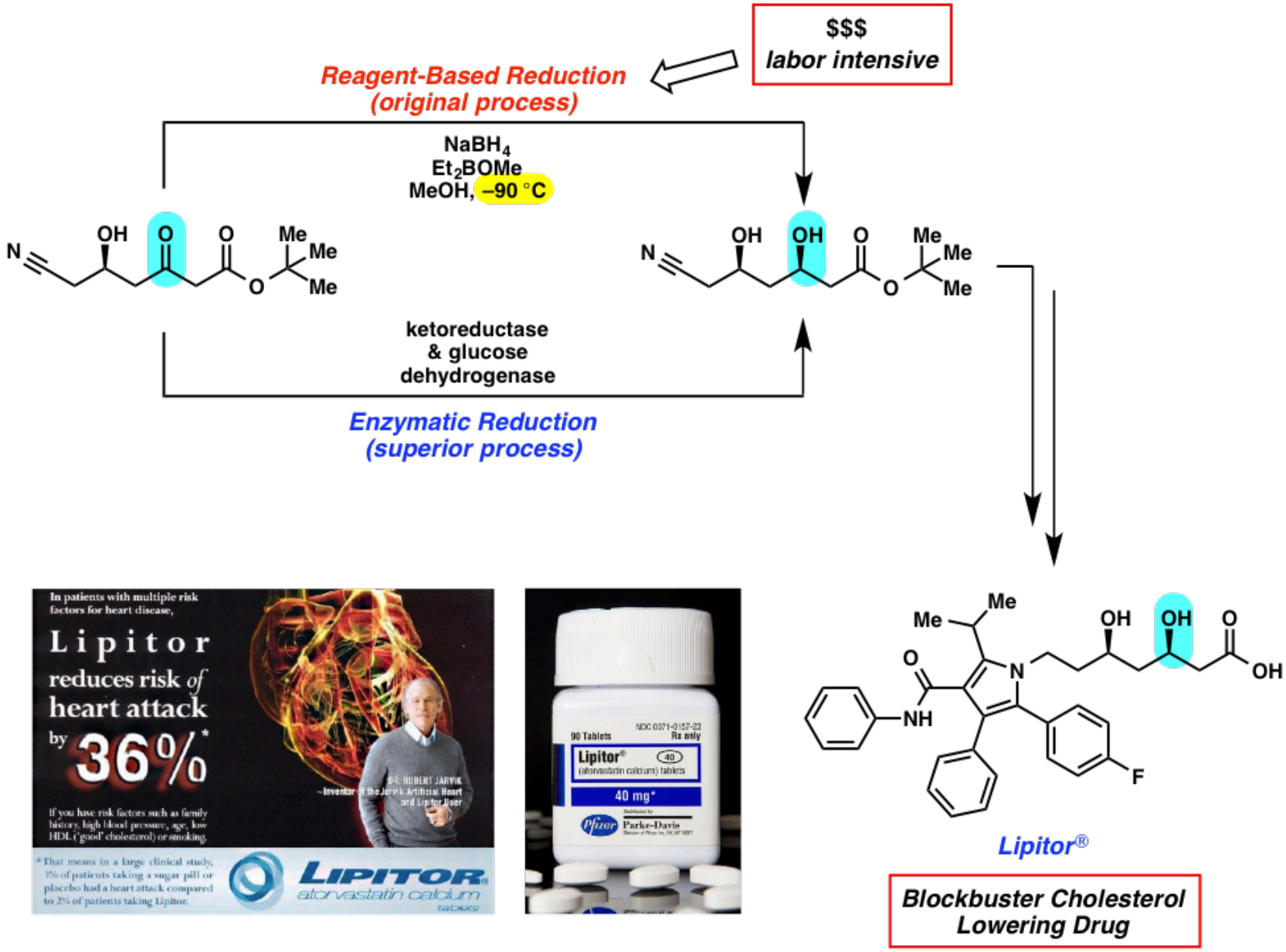
Tollens' reagent, Fehlings' reagent, Benedict's reagent test for **Reducing Sugars** (a reducing sugar *reduces* the test reagent):
Aldoses and Ketoses are Reducing Sugars.

Tollens' test (http://science.uvu.edu/ochem/index.php/alphabetical/s-t/tollens-test/)



Benedict's test – glucose in urine (diabetes)
(http://www.harpercollege.edu/tm-ps/chm/100/dgodambe/thedisk/carbo/bened/benedict.htm)

Is the reducing sugar oxidized or reduced?



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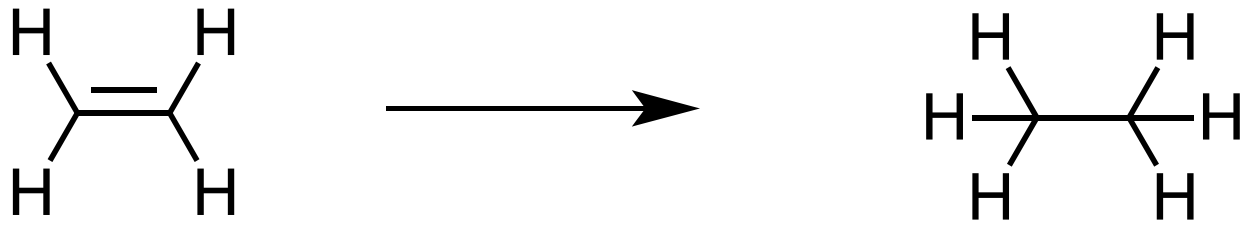
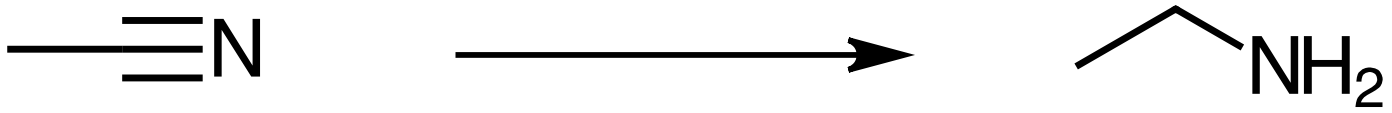
Other Functional Groups are Oxidized or Reduced

E.g., Hydrogenation (Addition of H_2 to alkene)



C gains 1 H ==> reduction

Nitrile ---> Amine



Oxidation or Reduction?
What reagent to use?

OCHEM REDOX - ***forget about oxidation numbers***!

OChem **Oxidation**: gain of O/loss of H at one Carbon
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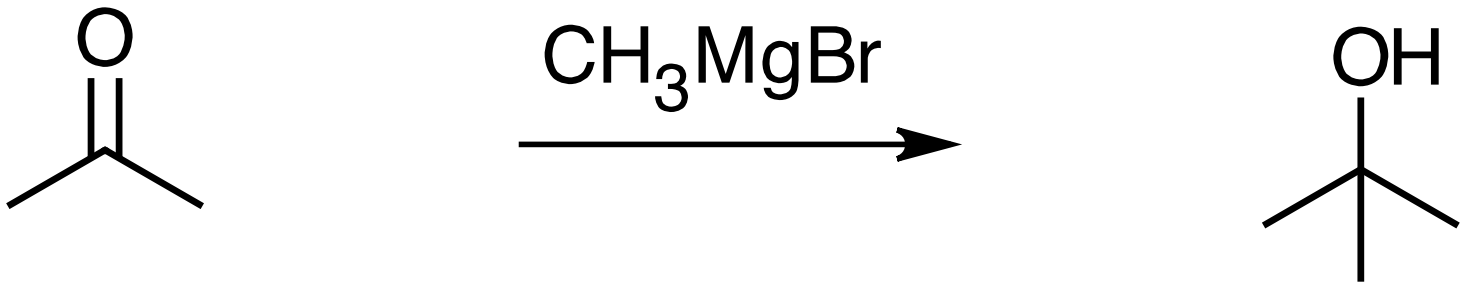
Grignard Reaction:

RCOR/RCHO ---> ROH



Oxidation or Reduction?

New way to make a C-C bond.

Grignard Reaction is used to prepare ROH (Nu:$^-$ addition rxn):

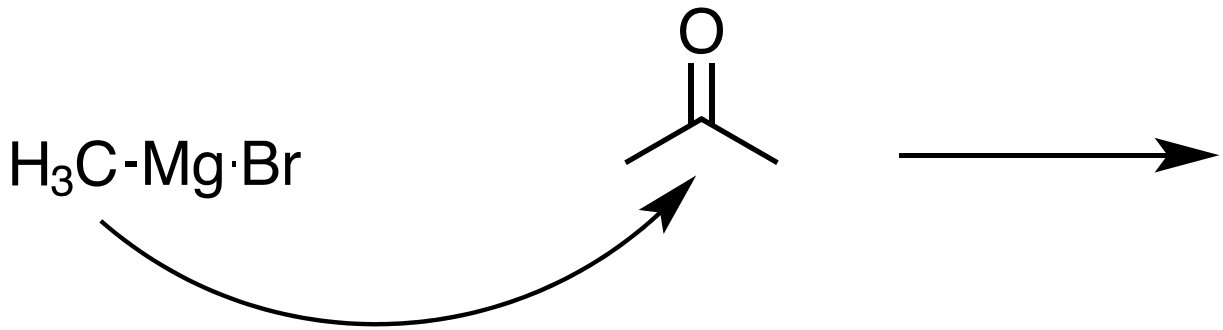
- Starting Material is RCHO or RCOR
- Form C-C bond (add R group to α-C) to make bigger molecule

1. Make Grignard reagent: RMgX

$CH_3Br + Mg \rightarrow H_3C\text{-}Mg\cdot Br$

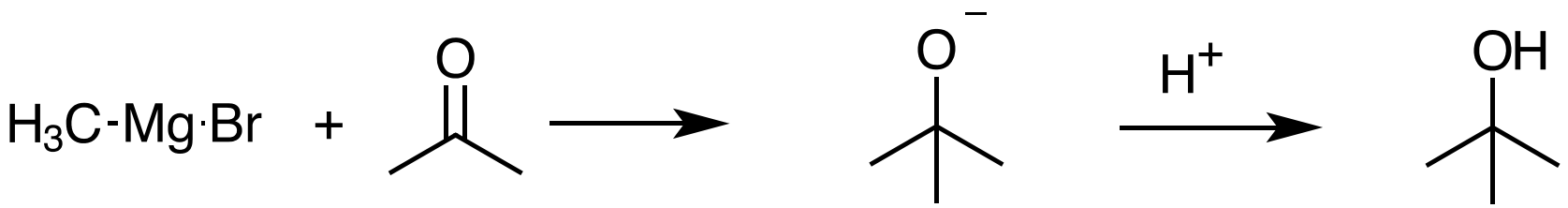
C is Nu:$^-$. Why?

2. RMgX reacts with C=O (carbonyl carbon is E^+)



Use curved arrows to show product

Nu:$^-$ addition reaction (more on this reaction later in Chem 12B)

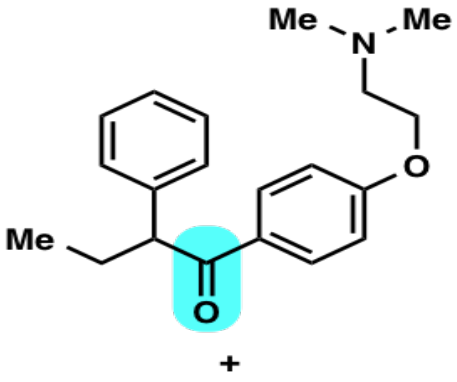


Carbonyl carbon in ketone becomes α-carbon in alcohol.

New C-C bond forms on carbonyl carbon/α-carbon.

Compare Nu:$^-$ addition reaction to E^+ addition reaction.

Electrophilic C in C=O Nucleophilic pi bond in C=C



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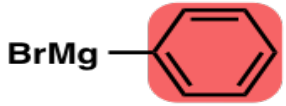
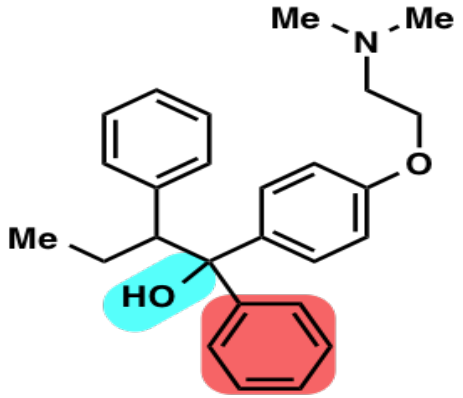
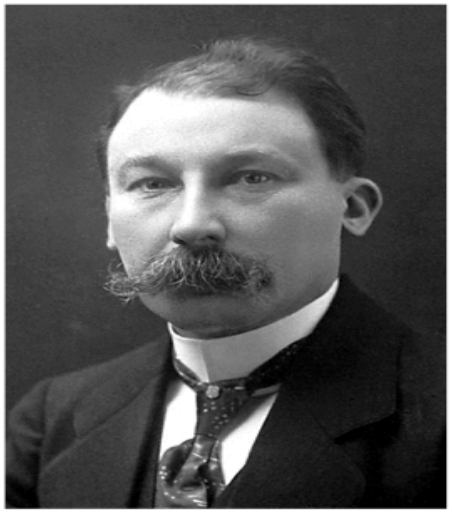
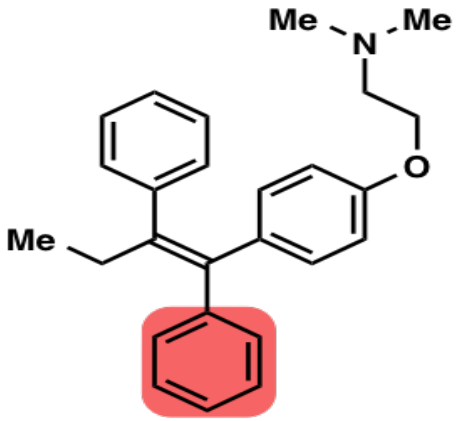


Grignard reagent





Victor Grignard (1871–1935)
Nobel Prize in Chemistry (1912)



Tamoxifen

Treatment of Breast Cancer

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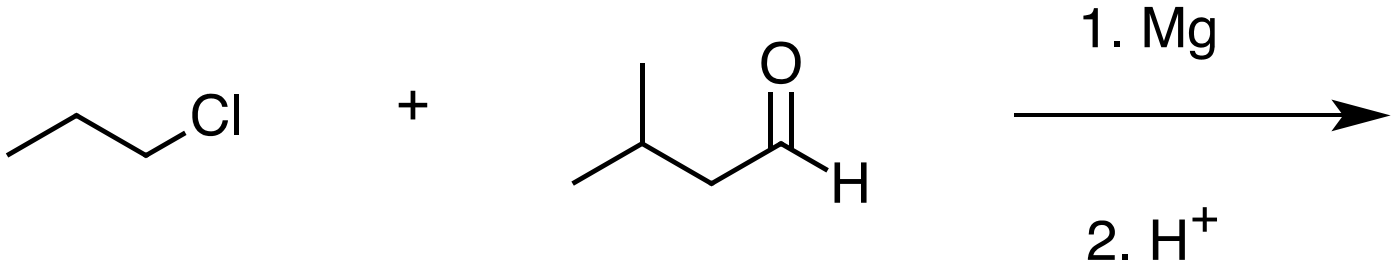
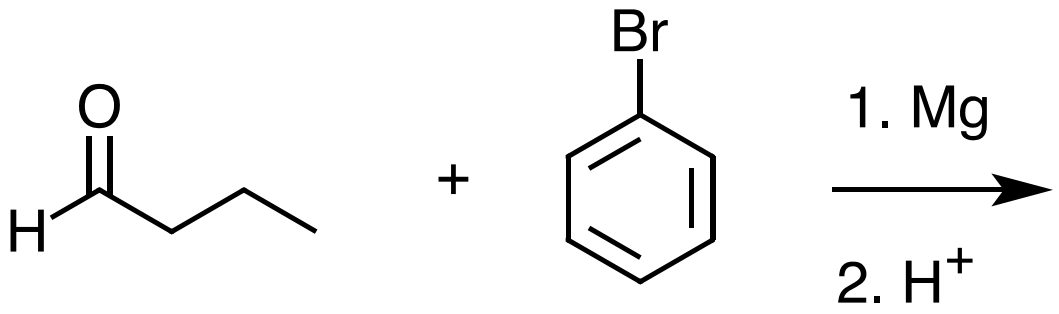
Predict product of Grignard reaction

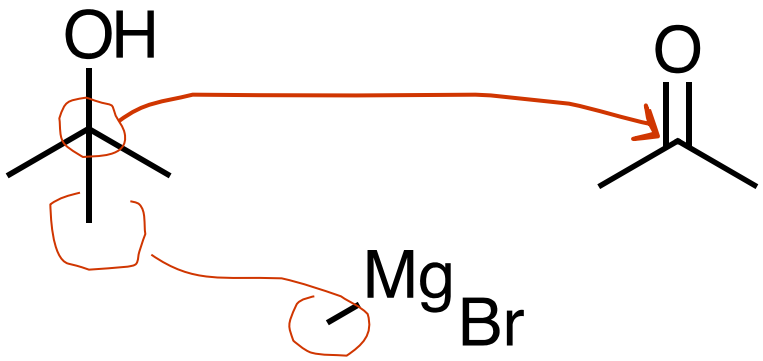


Predict product of Grignard reaction

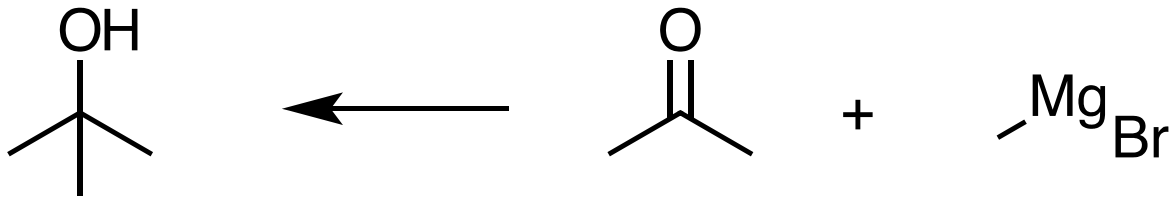


2. ID reactants to make ROH using Grignard reaction

Make t-butanol by Grignard reaction:

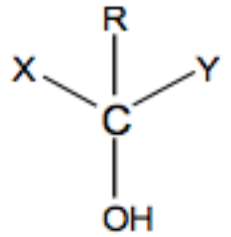


α-carbon in alcohol comes from carbonyl carbon in ketone or aldehyde.
Grignard reagent comes from a C bonded to α-carbon.

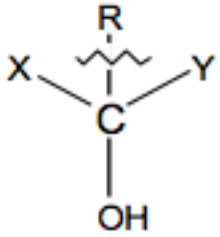


Retrosynthetic Analysis: How to Work Backwards to Determine Reactants to Make a Target Molecule

Step 1: Start with target molecule

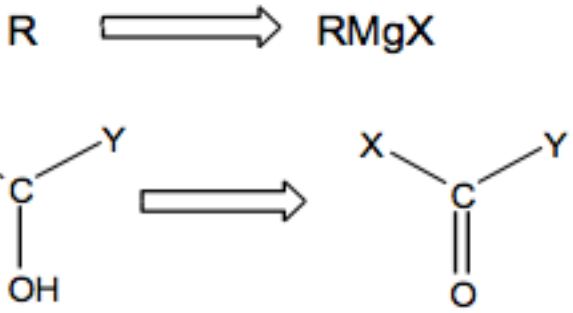


Step 2: Break/Disconnect the C-R bond

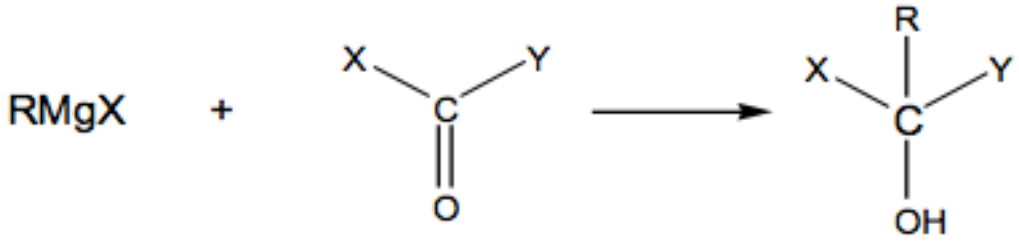


Note: bond between α-C and R

Step 3: Use the R fragment to make a Grignard reagent and the C-OH fragment to make an aldehyde/ketone



Step 4: Grignard and aldehyde/ketone --> target molecule



Retrosynthesis: working backwards	Grignard reaction: Working forwards
IDENTIFY Functional Group(s) How do you make this group?	IDENTIFY Functional Group(s) How does this group react?
Step 1: Break one of the C-C bonds that is bonded to C-OH ***Hint***: see starting material	Step 4: C=O becomes C-OH
Step 2: C fragment comes from RMgX	Step 3: R from RMgX forms C-C bond to C=O in RCHO or RCOR
Step 3: C-OH comes from RCHO or RCOR	Step 2: RMgX reacts with RCHO or RCOR
	Step 1: RX + Mg --> RMgX

Propose a synthesis using a Grignard reaction:
(Hint: there are at least two ways to make the alcohol.)