Summary of Alcohol Syntheses, Ch. 10 (and Review of Old Ones).

1 $R{-}OH \xrightarrow{Na} R{-}ONa$

- Potassium (K) analogous.
- Key way to convert alcohol to alkoxide, reactive as S_N2 nucleophile and E2 base.

2 $R{-}OH \xrightarrow[2.\ R'{-}X]{1.\ Na} R{-}O{-}R'$

- Alkoxide formation-S_N2 route to ether
- The electrophile R'-X must be S_N2 reactive, preferably 1° with a good leaving group

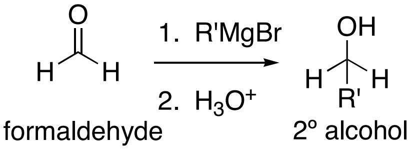
Mech?

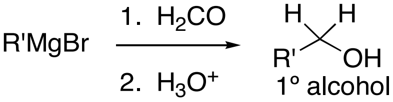
3 $R{-}Br \xrightarrow{Mg} RMgBr$

-Li is analogous for making RLi, which also act analogously.

-MgBr is spectator: $R^{\ominus}$ is key.

4

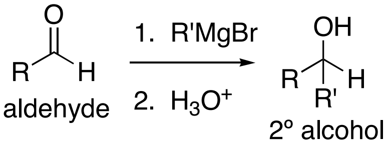


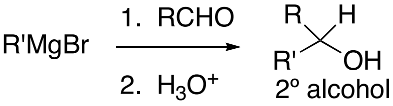


1 carbon chain extension

Mech

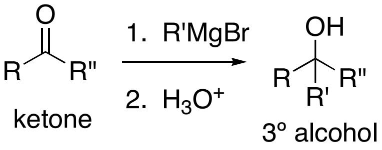
5

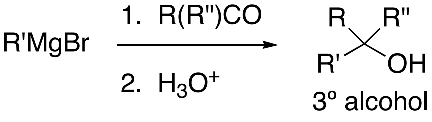




Mech

6

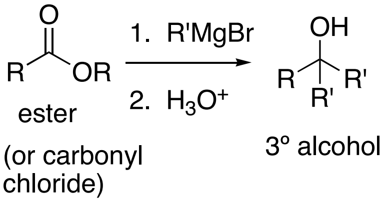


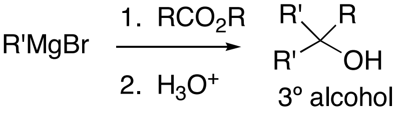


All three R groups can be different.

Mech

7

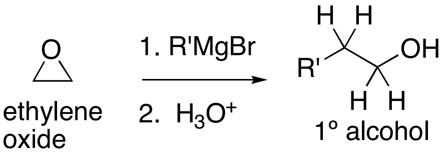


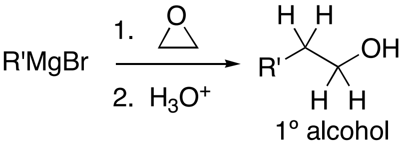


At least 2 R groups must be the same

Mech

8

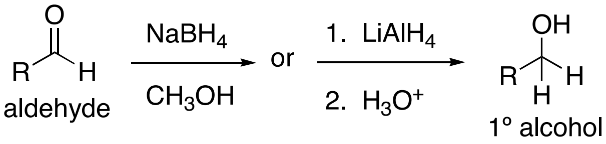




2-Carbon chain extension

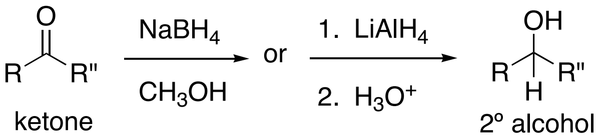
Mech

9



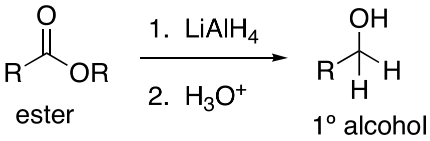
Mech

10



Mech

11

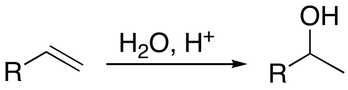


$NaBH_4$ will not react with esters

Mech

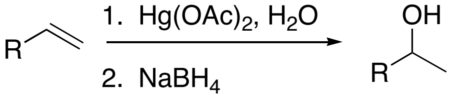
Review Routes to Alcohols

10



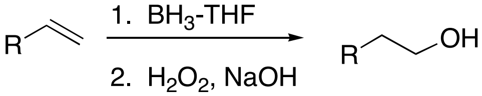
Markovnikov

11



Markovnikov

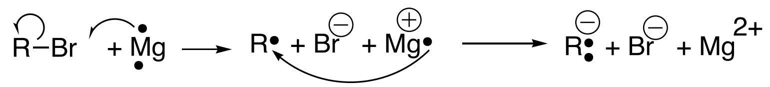
12



anti-Markovnikov

13 $R{-}X \xrightarrow{NaOH} R{-}OH$ S_N2 mech, needs 1° or 2° system and an excellent leaving group

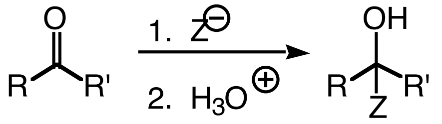
Summary of Mechanisms, Ch. 10



Not for Test

For Test:

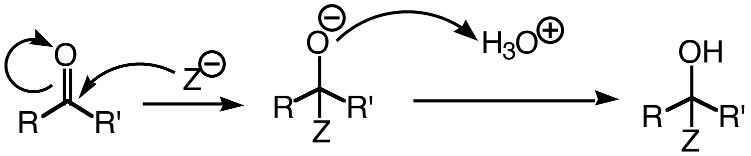
1.



aldehyde
or ketone
or formaldehyde

$Z^{\ominus}$ may be $R^{\ominus}$ (RMgBr)
or $H^{\ominus}$ ($NaBH_4$ or $LiAlH_4$)

mech:



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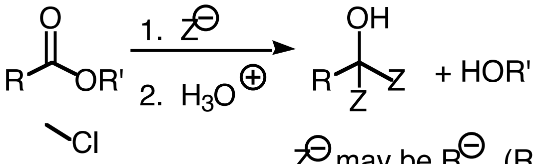
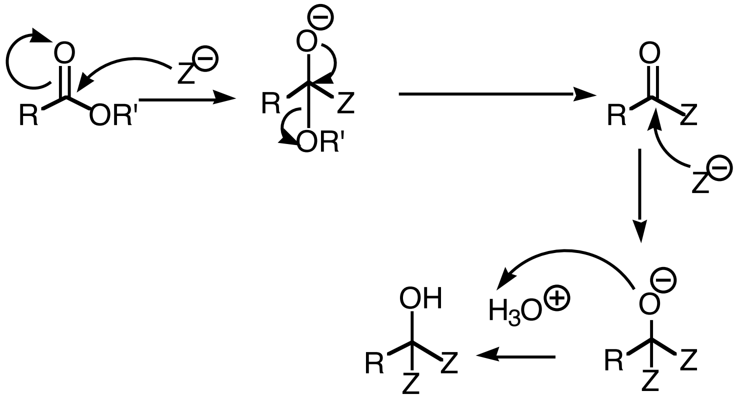


esters
or
acid chlorides

$Z^{\ominus}$ may be $R^{\ominus}$ (RMgBr)
or $H^{\ominus}$ ($LiAlH_4$)

mech:



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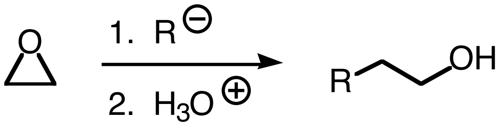
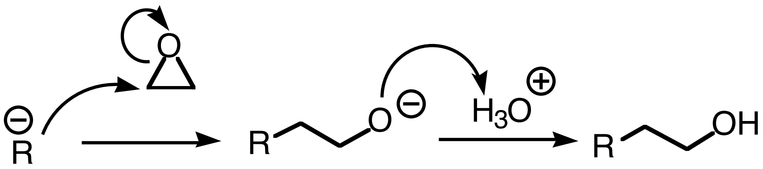


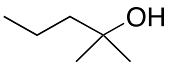
mech:



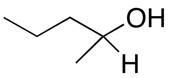
10.1,2 Intro, Classification

"**Alcohol**": OH attached to a saturated, sp^3, "alkyl" carbon

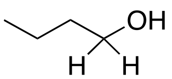
1°, 2°, 3° Alcohols: based on whether the carbon with the OH is 1°, 2°, or 3°



3°

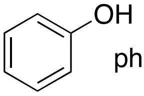


2°

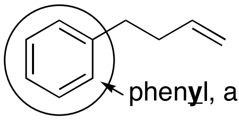


1°

"**Phenol**": OH attached to an aromatic
-Note: phen**o**l, not phen**y**l



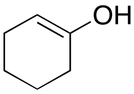
phen**o**l



4-phen**y**l-1-butene

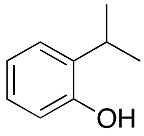
phen**y**l, as substituent

"Enol" or "vinyl alcohol": OH attached to an alkene

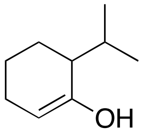


enol or vinyl alcohol

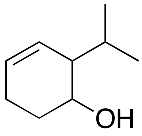
Problem: Classify each of the following either as a phenol, as a carboxylic acid, or as a 1°, 2°, 3°, or vinyl alcohol:



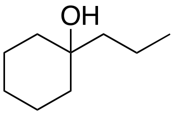
phenol



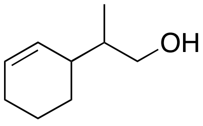
vinyl alcohol



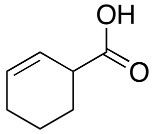
2° alcohol



3° alcohol



1° alcohol

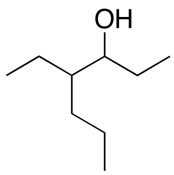


carboxylic acid

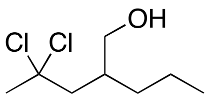
10.3 Nomenclature

A. IUPAC, when alcohol is priority functional group and is part of the core name: x-alkan**ol**

- Choose longest carbon chain **that has the OH attached**
- Remember to number!
- The oxygen itself does not count as a number

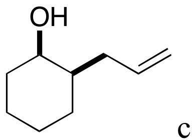


4-ethyl-3-heptanol



4,4-dichloro-2-propyl-1-pentanol

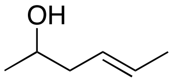
B. Cycloalkanols: The OH-carbon is automatically Number 1



cis-2-allylcyclohexanol

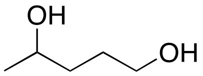
C. **x-Alken-z-ol**. When an alkene is in the main carbon chain, you need two number descriptors, one for the alkene, the second for the alcohol.

- The OH still dictates the numbering
- The OH number gets moved right before the "ol"
- The alkene number goes in front, in front of the "alken" portion
- Note: you only put the OH number right in front of the "ol" when you have an alkenol (or alkynol)



(E)-4-hexen-2-ol or trans-4-hexen-2-ol

D. Diols: x,y-alkane**diol**

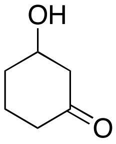


1,4-pentanediol

E. Functional Group Priority: CO_2H > C=O > OH > amine > alkene > halide

- When you have more than one functional group, the higher priority dictates the numbering
- **The higher priority is used in the "core name"**
- **The lower priority group may be forced to be named as a substituent**

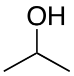
F. OH as a Substituent: "**Hydroxy**"



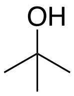
3-hydroxycyclohexanone

G. Common Names: Alkyl alcohol

CH_3OH
Methyl alcohol



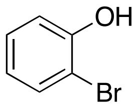
Isopropyl alcohol

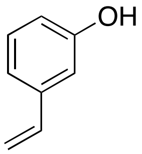


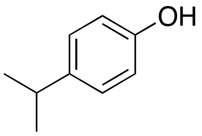
t-butyl alcohol

H. Substituted Phenols

- IUPAC: use numbers, with OH carbon #1
- Common:
  - o **Ortho: 2-position, adjacent**
  - o **Meta: 3-position, two carbons away**
  - o **Para: 4 position**
- Skill: be able to use or recognize either system



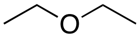


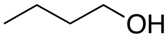


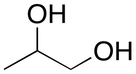
IUPAC:	2-bromophenol	3-vinylphenol	4-isopropylphenol
Common	ortho-bromophenol or o-bromophenol	meta-vinylphenol or m-vinylphenol	para-isopropylphenol or p-isopropylphenol

10.4 Physical Properties: Dominated by H-Bonding

BP: Match the boiling point for the following structures: 35°, 137°, 187°

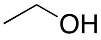

35° (no H-bond)

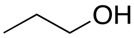

137° (H-bond)


187° (more H-bond)

Water solubility: water solubility decreases as hydrophobic R gets longer

- In general,
  - $R \leq 4$ carbons, ROH substantially water soluble
  - $R \geq 5$ carbons, ROH minimal water solubility


infinite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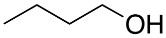
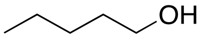
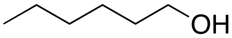
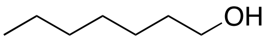

9.1g/100mL

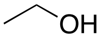
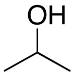

2.7g/100mL


0.6g/100mL


0.1g/100mL

10.5 Commercially Important Alcohols

- Toxic: All alcohols are "toxic" if swallowed in sufficient quantities

CH_3OH		
• Cheap • Solvent • Fuel • 100 mL → death • 15 mL → blindness	• 200 mL (7 oz) → death • Least toxic alcohol • Alcoholic beverages • Fermentation • Solvent	• Rubbing alcohol • 100 mL → death • Kills germs on skin, but not absorbed

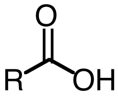
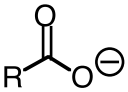
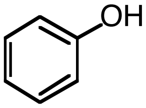
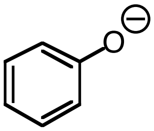
10.6 Acidity of Alcohols and Phenols

A. Alcohols are weak acids → can be ionized by stronger bases

$$ROH + B^{\ominus} \rightleftharpoons RO^{\ominus} + BH$$

- goes to the right (alkoxide) only if $RO^{\ominus}$ is more stable than $B^{\ominus}$
- ex. $^{\ominus}NH_2$, $^{\ominus}CH_3$
- ex. If a <u>less</u> stable oxygen anion can convert to a <u>more</u> stable oxygen anion

B. Acidity Table

Class	Structure	Ka	Acid Strength	Anion	Base Strength
Strong Acids	H-Cl	10^{2}	Most	$Cl^{\ominus}$	Least
Carboxylic Acid		10^{-5}			
Phenol		10^{-10}			
Water	H_2O	10^{-16}		$HO^{\ominus}$	
Alcohol	ROH	10^{-18}		$RO^{\ominus}$	
Amine (N-H)	RNH_2	10^{-33}		$RNH^{\ominus}$	
Alkane (C-H)	RCH_3	10^{-50}	Least	$RCH_2^{\ominus}$	Most

Notes/skills:

1. Be able to rank acidity.
2. Memorize/understand neutral OH acidity ranking: $RCO_2H > H_2O > ROH$
   - Reason: **resonance** stabilization of the **anion**
3. Predict deprotonation (acid/base) reactions
   - Any weak acid **will be** deprotonated by a **stronger base (lower** on table)
   - Any weak acid **will not be** deprotonated by a **weaker base (higher** on table)
4. Predict ether/water extraction problems
   - If an organic chemical is neutral and stays neutral, it will stay in ether layer
   - If an organic chemical is ionized (by an acid-base reaction), it will extract into the aqueous layer

Problems

1. Draw arrow to show whether equilibrium favors products or reactants. (Why?)

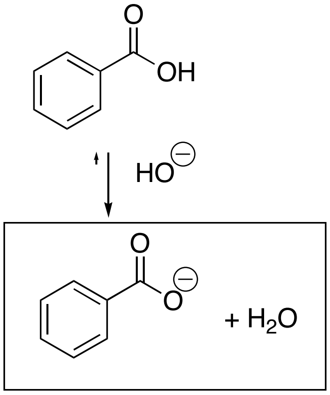
Resonance Stability

2. Which of the following will deprotonate methanol?

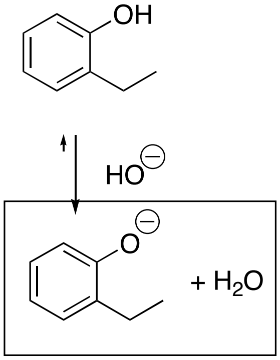
H_2O	CH_3CO_2Na	PhONa	NaOH	$NaNH_2$	CH_3MgBr
No	No	No	No	Yes	Yes

An acid (left side) will only be deprotonated by an anion/base that is **lower** on the right side

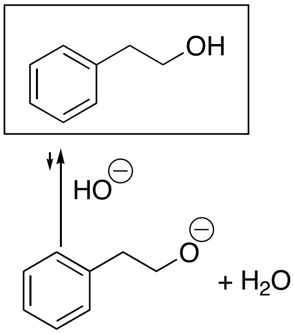
3. When the following are dissolved in ether and then treated with NaOH/water, which would extract out of the ether layer into the water layer?



Yes, converts to anion, water soluble



Yes, converts to anion, water soluble

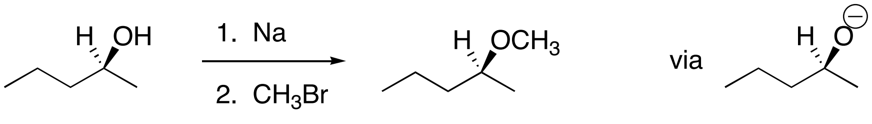


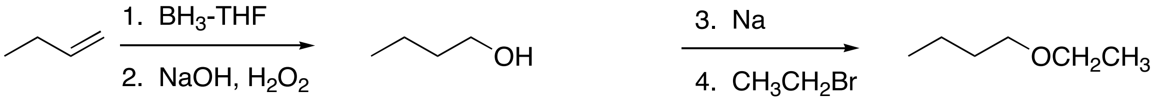
No, stays neutral, stays in ether

10.6B Formation of Sodium, Potassium Alkoxides; 2-Step Conversion of Alcohols into Ethers via the Alkoxides

1	$\left.\begin{array}{l} R{-}OH \xrightarrow{Na} R{-}ONa \\ R{-}OH \xrightarrow{K} R{-}OK \end{array}\right\} R{-}O^{\ominus}$	• Potassium (K) analogous. • Key way to convert alcohol to alkoxide, reactive as S_N2 nucleophile and E2 base.
2	$R{-}OH \xrightarrow[2.\ R'{-}X]{1.\ Na} R{-}O{-}R'$	• Alkoxide formation-S_N2 route to ether • The electrophile R'-X must be S_N2 reactive, preferably 1° with a good leaving group

Reaction 1: Key source of nucleophilic/basic alkoxides





10.7 Synthesis of Alcohols: Review: See p. 2, from Alkyl Halides (S_N2) and Alkenes

10.8 Organometallics: RM (M = Metal) = $R^{\ominus}$ $M^{\oplus}$

3

$$R{-}Br \xrightarrow{Mg} RMgBr$$

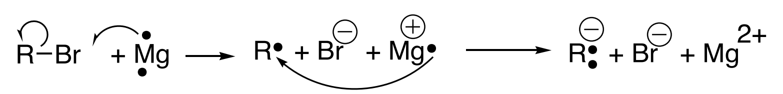
"Grignard Reagent"

$$R{-}Br \xrightarrow{2Li} RLi + LiBr$$

-Li is analogous for making RLi, which also act analogously.

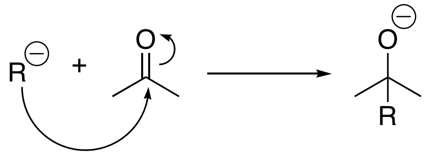
-MgBr is spectator: $R^{\ominus}$ is key.

1. We will focus on the magnesium reagents RMgBr
2. RMgBr = "Grignard Reagents" (Victor Grignard)
3. Key: This is the way to make $R^{\ominus}$, strong nucleophiles/bases
4. RMgBr are formed via redox reaction.
   - Mg gives up two electrons, is oxidized
   - Bromine is reduced to bromide anion
   - Carbon is reduced to carbanion



Not for Test

5. The formation of Grignard Reagents is completely general for all R-Halides:
   - 3°, 2°, and 1° alkyl halides all work well
   - Aryl and Vinyl halides as well as alkyl halides work well
   - RCl, RBr, and RI all work well
   - For class, we will normally use bromides, due to synthetic accessibility
6. **View as carbanions: RMgBr = $R^{\ominus}$ Super Strong Bases and Nucleophiles**
   - The counterion metal is a spectator
   - Stability-reactivity principle: very unstable → very reactive
   - This great reactivity is very useful (as nucleophile)
   - This great reactivity (as base) has implication for proper technical use (see following)
7. Solvent and handling: Grignard reactants RMgBr must be made, stored, and handled in special solvents under special conditions:
   - No water allowed
     - $R^{\ominus} + H_2O \rightarrow R{-}H + HO^{\ominus}$ Destroys carbanion
   - No alcohol or amines or acids allowed either, or carbanion will just deprotonate them too
   - If any chemicals with carbonyls are present, they too will react with the carbanion by nucleophile/electrophile reaction

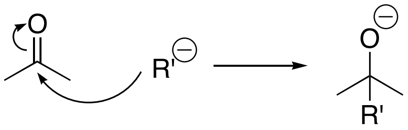


o

   - Grignards and other organometallics are made in either alkane or ether solvents.
     - These don't have any acidic hydrogens that protonate carbanions.
     - These don't have any carbonyls that react with carbanions
8. Two perspectives for dealing with organometallics in general and RMgBr in particular
   - Mechanistic Thinking: $R^{\ominus}$
   - Predict-the-product thinking: R-MgBr: easier to see source and substitution product.

$$R{-}Br \xrightarrow{Mg} R{-}MgBr \xrightarrow{Electrophile} R{-}Electrophile$$

10.9 Addition of RMgBr to Carbonyl Compounds: Alcohols are Produced



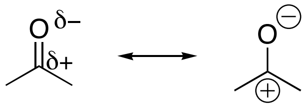
Exothermic Addition of Carbon or Hydrogen Anions:

- σ bond (made) stronger than π bond (broken)
- oxygen anion more stable than carbanion

Carbonyl is strongly electrophile

-much stronger even than a 1° alkyl iodide!

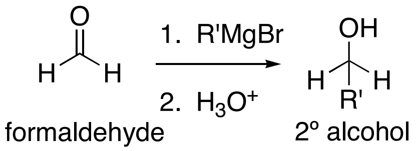
1. Breakable π bond
2. Carbonyl polarity

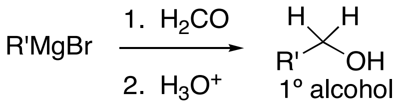


Additions of Grignard Reagents to Carbonyl Compounds

From Carbonyl's Perspective | From Grignard's Perspective

4

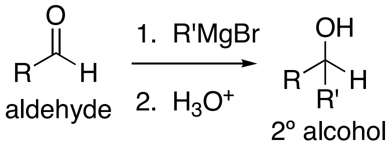


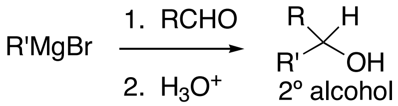


1 carbon chain extension

Mech

5





Mech

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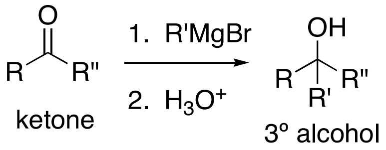
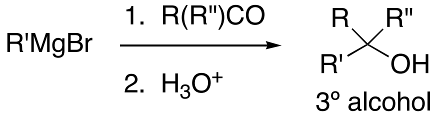
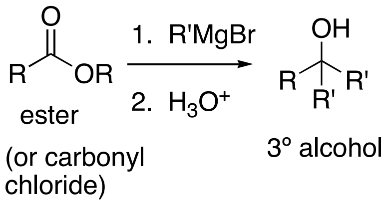


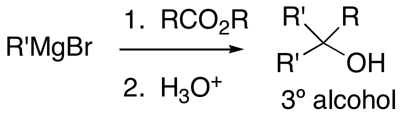


All three R groups can be different.

Mech

7





At least 2 R groups must be the same

Mech

Pattern:

1. After reaction, the original carbonyl carbon will have one and only one C-O single bond
2. For formaldehyde, aldehydes, and ketones, one R group adds (reactions 4-6)
3. For esters or carbonyl chlorides ("acid chlorides"), two R groups add
   - Replace not only the carbonyl p-bond, but also the "extra" C-O or C-Cl single bond
4. Product output:
   - Formaldehyde (2 H's) → 1° alcohol
   - Aldehyde (1 H) → 2° alcohol
   - Ketone (0 H) → 3° alcohol. No need for all 3 attachments to be the same.
   - Ester (0 H) → 3° alcohol. At least two common attachments at end.

Predicting Grignard Reaction Products

1. From carbonyl perspective:
   - The carbanion R' adds to the carbonyl carbon
   - The carbonyl =O gets replaced by –OH
   - For formaldehyde, aldehydes, and ketones: the two attachments on the original carbonyl carbon remain attached as spectators
   - For esters or acid chlorides: the one non-heteroatom attachment on the original carbonyl carbon remain attached as spectators.
     - The "extra" heteroatom gets replaced by a second carbanion R'

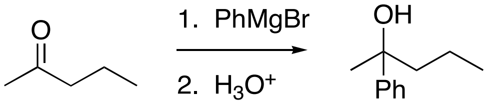
2. From Grignard perspective:
   - Where R-MgBr begins, R-C-OH ends.
     - In other words, the MgBr gets replaced by the carbonyl carbon

Note: Be sure that in the product, no carbon has more than one C-O bond

Draw products from the following reactions.

1°, 2° or 3°?

1



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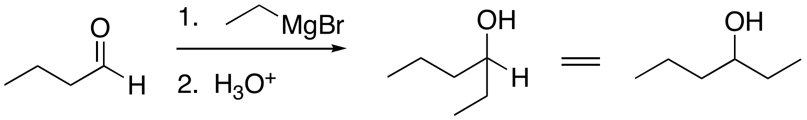

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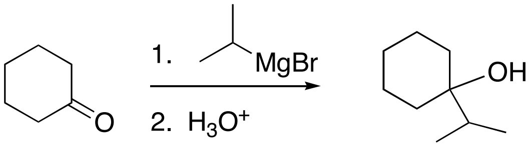

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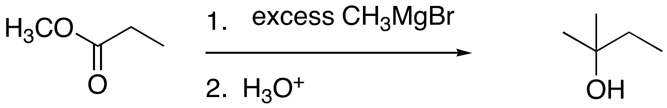

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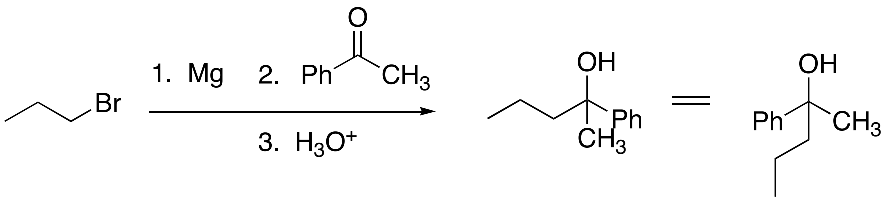

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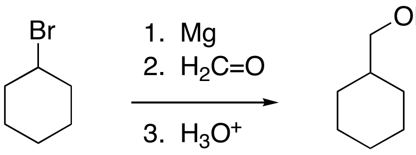
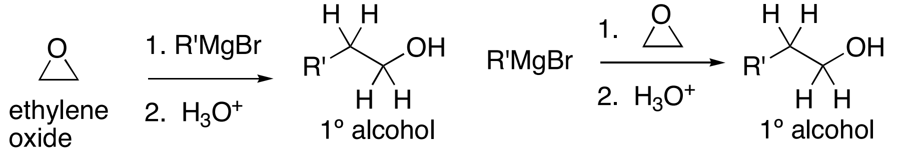


10.9E Grignard Reaction with Ethylene Oxide (Simplest Epoxide)

8



2-Carbon chain extension

Mech

Notes

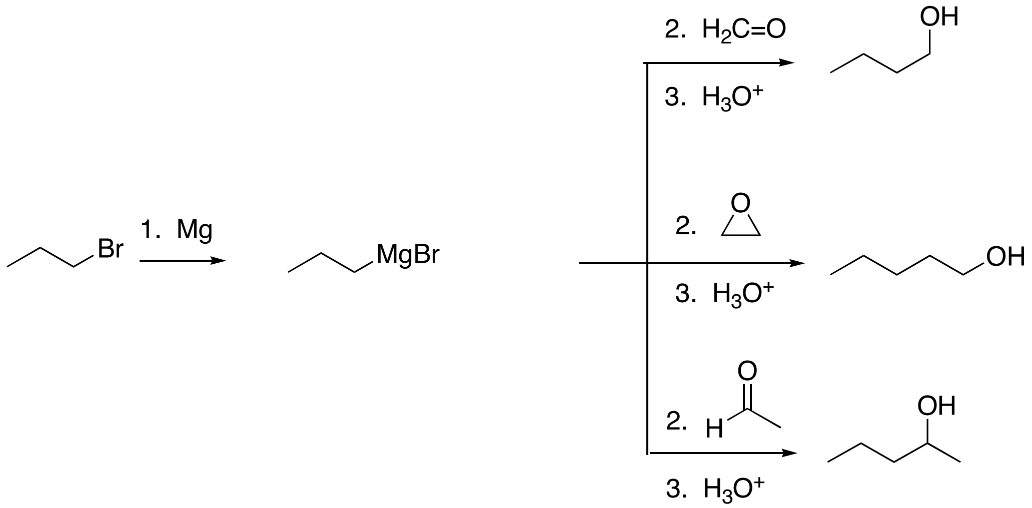
1. Results in a 1° Alcohol
2. **Predicting product: Two carbons end up in between the carbanion R’ and the OH**
3. Ethylene oxide and formaldehyde are complementary Grignard acceptors leading to 1° alcohols
   - Ethylene oxide extends the carbon chain by two (relative to the original RMgBr)
   - Formaldehyde extends the carbon chain by one (relative to the original RMgBr)
4. 2-Carbon ethylene oxide and 2-carbon ethanal give different products
   - Ethylene oxide → the OH is 1° and the OH is two carbons removed from the carbanion R
   - Ethanal→ the OH is 2° and the OH and carbanion R are both connected to the same carbon

Draw products from the following reactions.

1

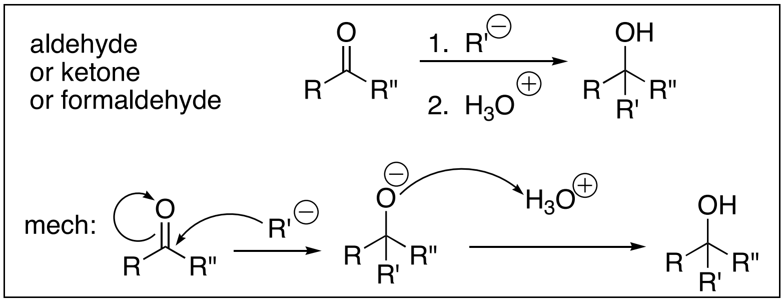
2

3



Reaction Mechanisms for Grignard Reactions

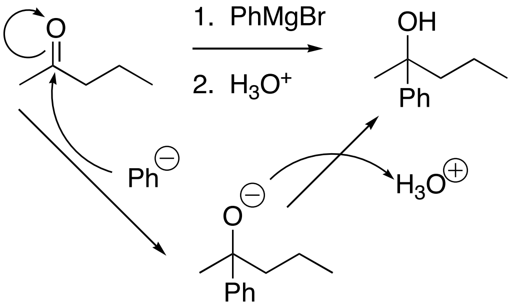
Formaldehyde, Aldehyde, or Ketone as Carbonyl Compound (Reactions 4, 5, and 6)



1. Two simple steps:
    a. **Addition**
    b. **Protonation**
2. Timing:
    a. The carbanion is added first, at one step in time, under strongly anionic conditions
    b. Later acid is added, in a second laboratory step. This provides a cationic environment
3. RMgBr = R-MgBr = $R^{\ominus}$ carbanion
    a. The $^{\oplus}$MgBr stuff is spectator, doesn't need to be drawn in
    b. Ignore in mechanisms
    c. In reality, it actually does play a nontrivial role, but we'll save that for grad school!

Draw mechanisms for the following reactions:

1



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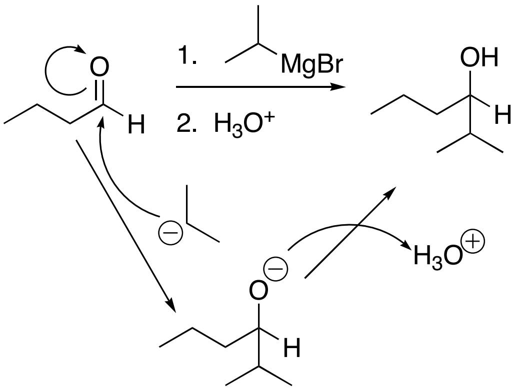
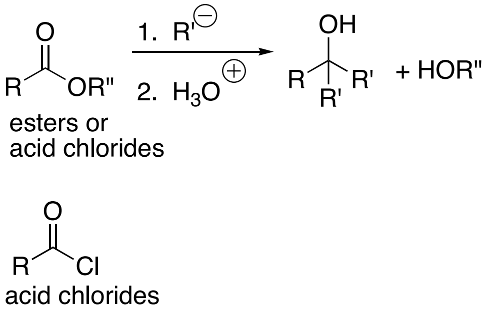
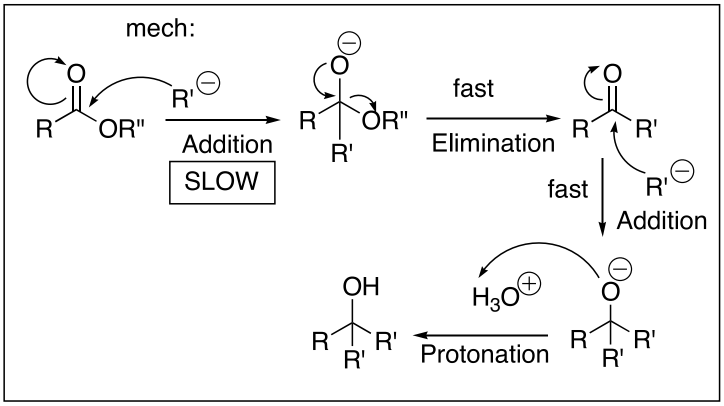
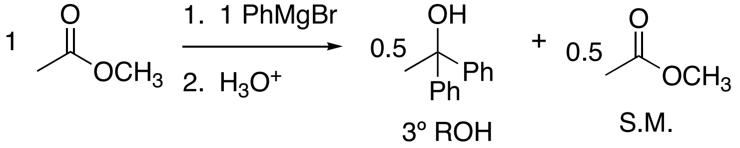


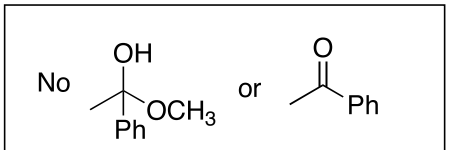
Esters or Acid Chlorides: More Complex, Needs to Explain Two Additions and More Bond Breakings





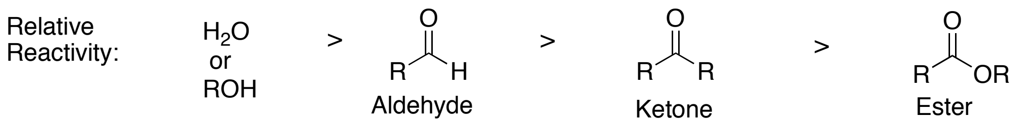
1. Four Step Mechanism:
   - **a. <u>Addition</u>**
   - **b. <u>Elimination</u>**
   - **c. <u>Addition</u>**
   - **d. <u>Protonation</u>**
2. Timing:
   - a. The carbanion is added first, at one point in time, under strongly anionic conditions
     - o The first three steps all occur under these anionic conditions
   - b. Acid is only added much later, in a second laboratory step. This gives a cationic environment.
   - c. Why don't you just protonate after the first step?
     - o There is no proton source available, and the elimination proceeds instead!
3. What if I add only one RMgBr?





After Grignard reaction, **<u>never</u>** show any products in which a carbon has more than one oxygen

Why? Kinetics and Reactivity. **<u>MEMORIZE</u>**.



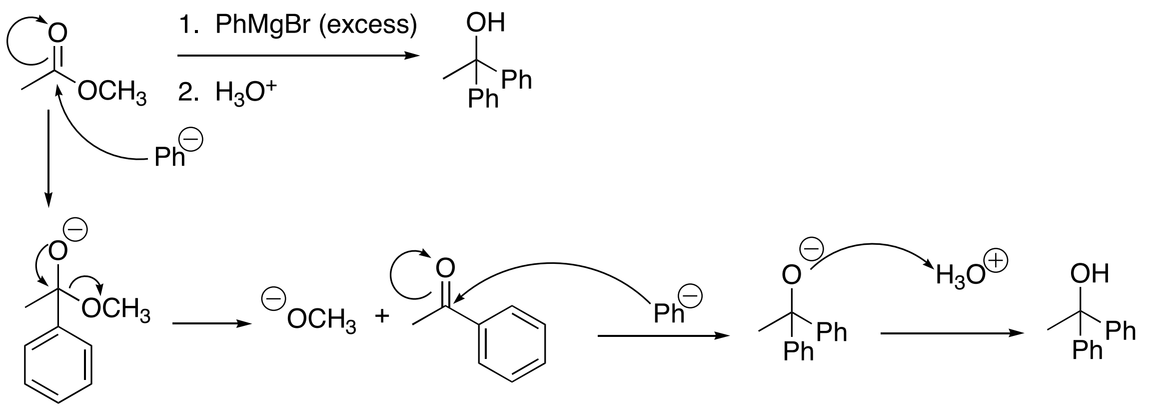
Acid/Base

Steric Advantage. Transition-state less crowded and more stable

Stablized for electronic reasons Therefore less reactive

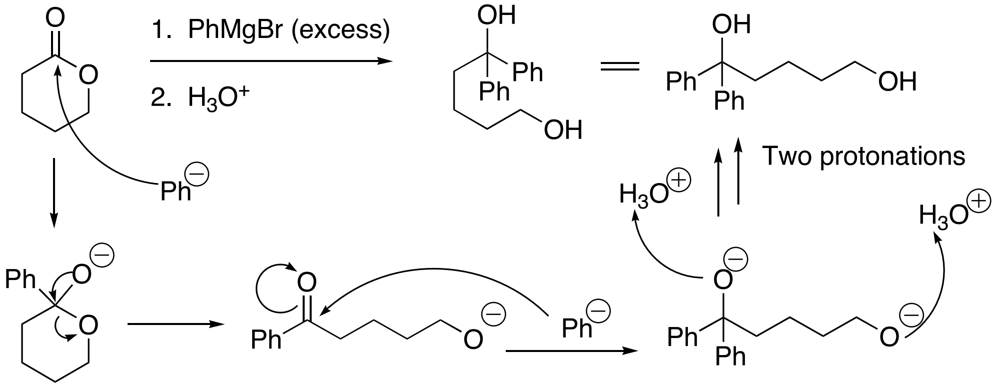
- Large differences in reactivity, with ketone > ester
- Elimination step 2 is also very fast
- Thus, under the anionic conditions, the addition is the slow step
  - o After it does happen, elimination and another addition happens bang-bang.

Draw Mechanism:

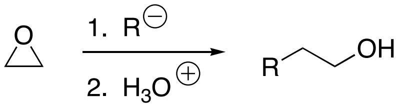


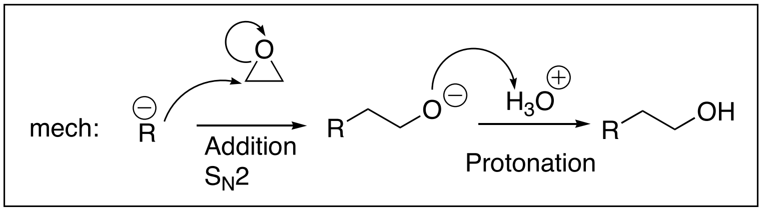
Cyclic Ester: The O-Carbonyl single bond breaks, but the other C-O single bond does **not** break -the result is formation of a dialcohol

Draw product and mechanism for the following:

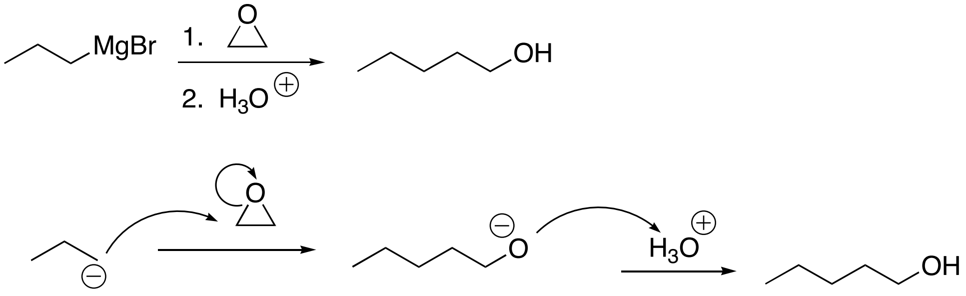


Ethylene Oxide Mechanism



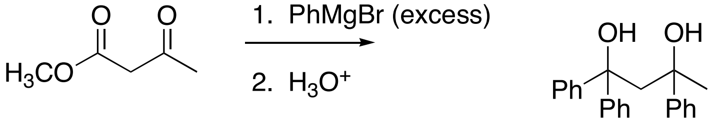


Draw product and mechanism for the following:



More Grignard Practice. Including polyfunctional Molecules: (Know relative reactivity)

1



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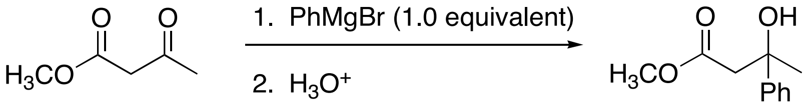

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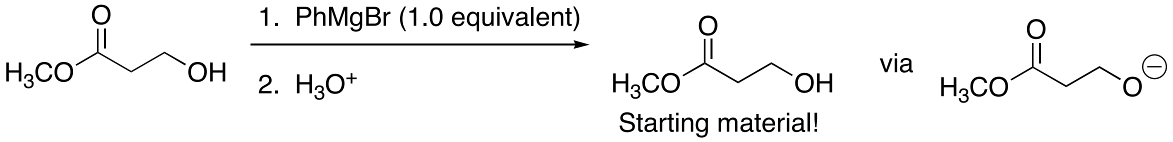

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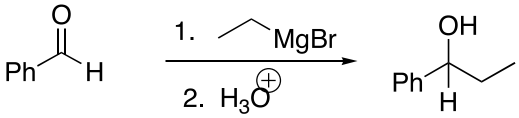

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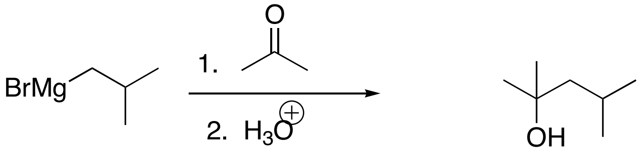

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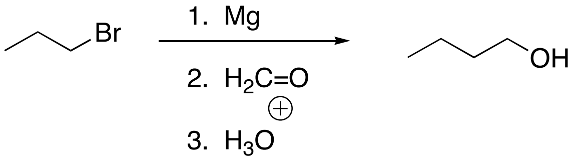

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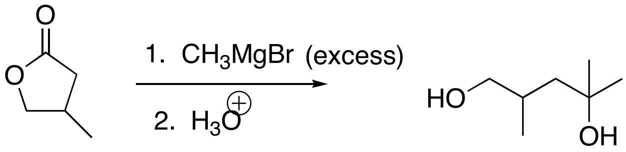

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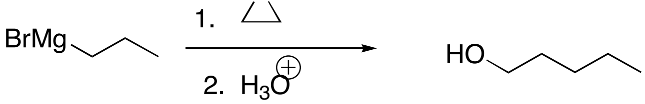
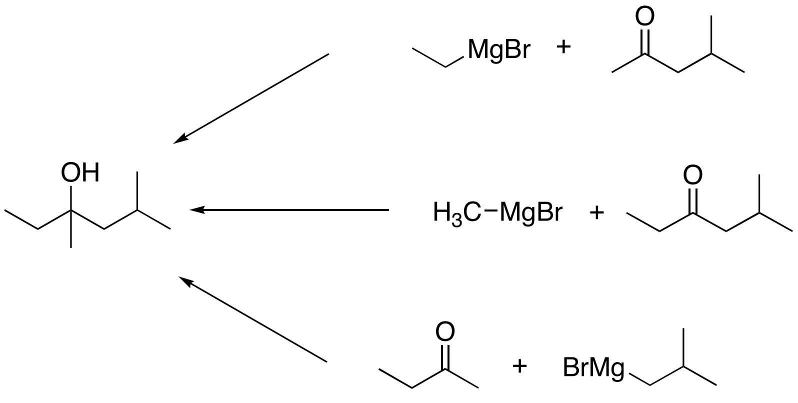
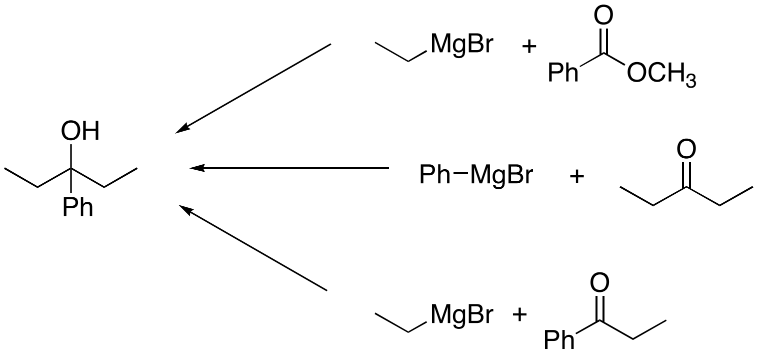


Grignards in Synthesis: Provide Precursors.

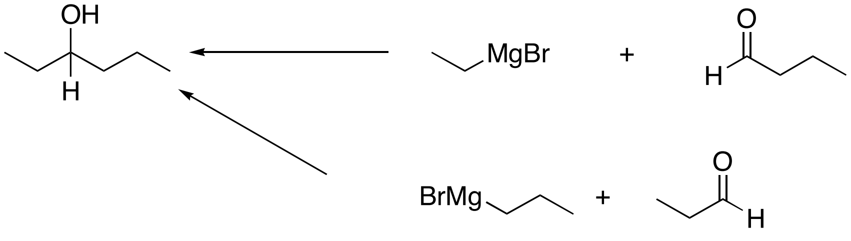
- **Think backwards from Targets to Reactants.**
- Identify possible Grignards and Grignard acceptors
- **Pattern:**
    - **3° alcohol, all three attachments different ← Ketone Precursor**
    - **3° alcohol, two (or more) of the attachments identical ← Ester**
    - **2° alcohol ← Aldehyde**
    - **1° alcohol ← Formaldehyde or ethylene oxide**



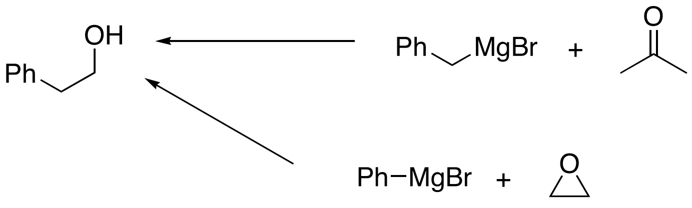
a.



b.



c.



d.

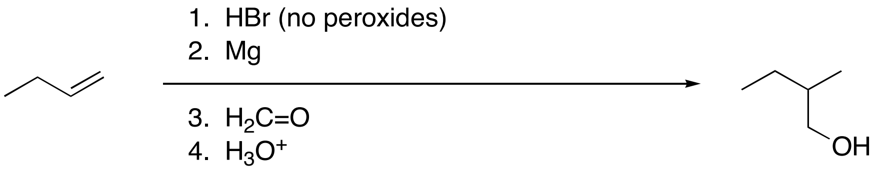
Provide Reagents for the Following Transformations. You may use whatever reagents, including ketones or aldehydes or Grignards or esters, that you need.

- Key: Try to identify key C-C connection in the product that wasn't present to start with
- Try to identify the where the reactant carbons are in the final product
- Numbering your carbon chains is very helpful.
- Usually best to work backwards from the product

a.

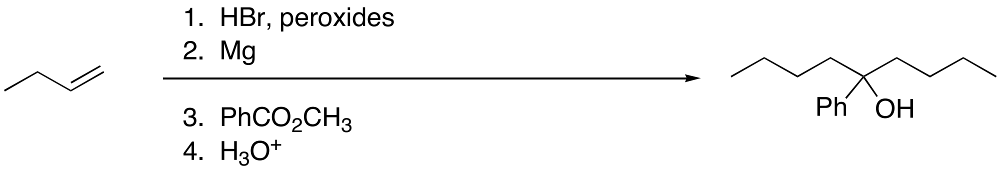
2 steps plus H_3O^+ workup

b.



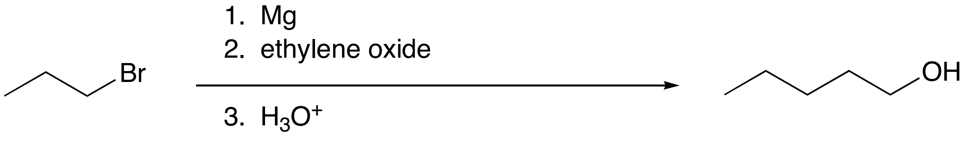
3 steps plus H_3O^+ workup

c.

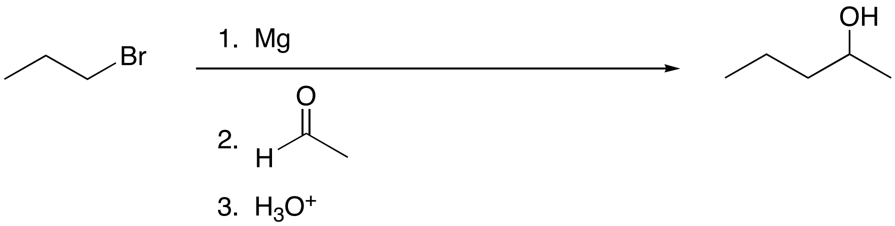


3 steps plus H_3O^+ workup

d.

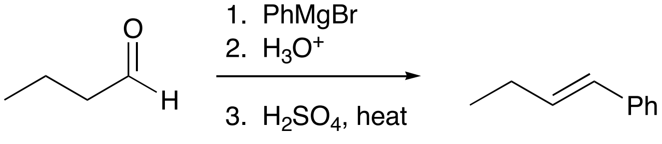


e.

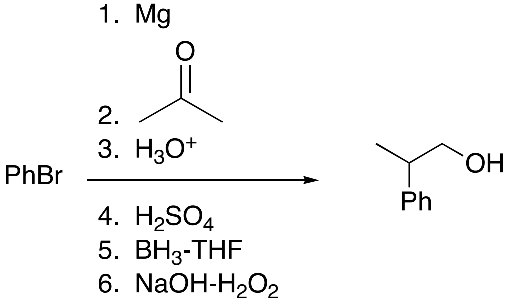


Combining Grignard Reactions with Other Reactions

a.



b.

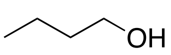


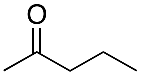
10.10 Restrictions on Grignard Reactions

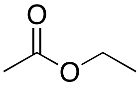
- RMgBr = $R^{\ominus}$ carbanion, highly unstable, highly reactive.
- Unstable in the presence of:
  1. OH's (get proton transfer reaction)
  2. Carbonyls (get Grignard-type nucleophilic addition)

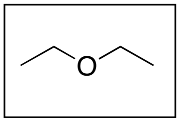
1. Solvent limitations. RMgBr cannot be formed and used in the presence of
   - H2O
   - ROH
   - Any solvent with a C=O

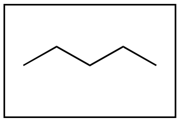
Which Solvents (if any) Would be OK for Handling RMgBr?,





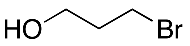


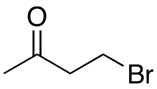


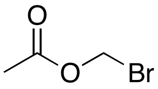


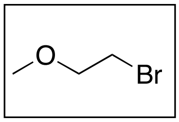
2. Substrate limitations. Any organohalide that also contains an OH or C=O bond can't be converted into a useful RMgBr, because it will self-destruct.

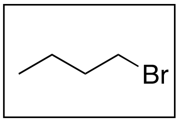
Which substrates could be converted into RMgBr, and subsequently reacted with CH_3CHO?







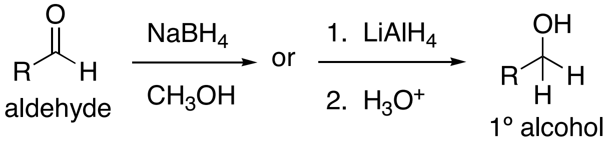




3. Atmosphere/Glassware/Storage limitations. Make, store, and use in:
   - water-free dried glassware
   - moisture-free atmosphere. (Dried air, or else under nitrogen or argon atmosphere)
   - When stored for extended periods, must have very good seals so that no air can leak in.

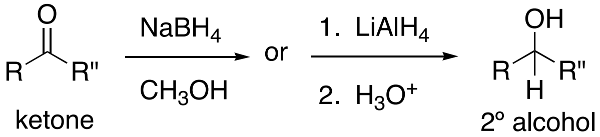
10.11 Alcohols by Reduction of Carbonyls: $H^{\ominus}$ Addition

9



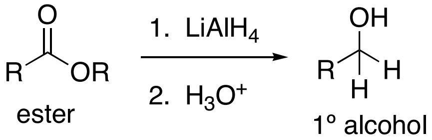
Mech

10



Mech

11



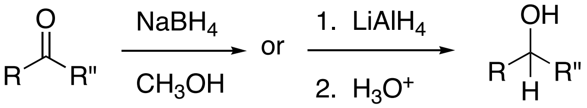
$NaBH_4$ will not react with esters

Mech

Mechanism

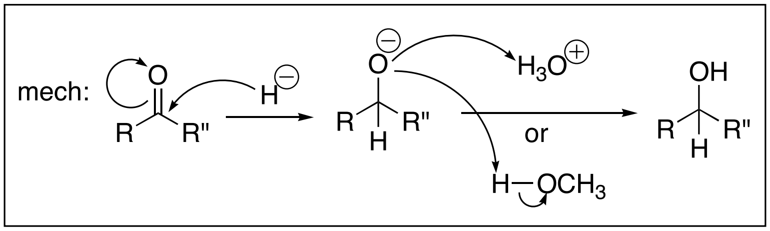
Aldehydes and Ketones

aldehyde
or ketone
or formaldehyde

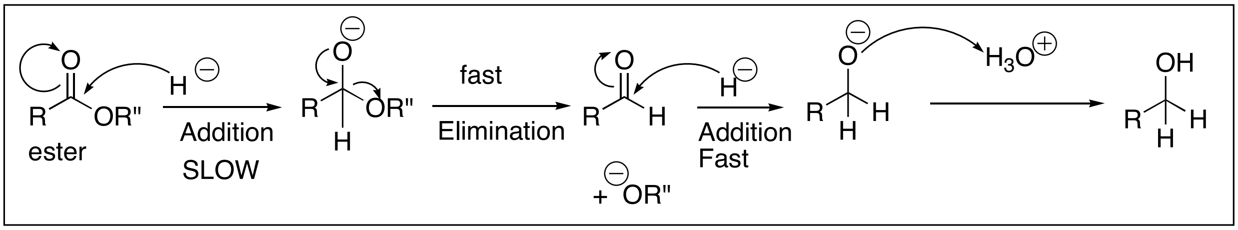


$NaBH_4 = H^{\ominus}$

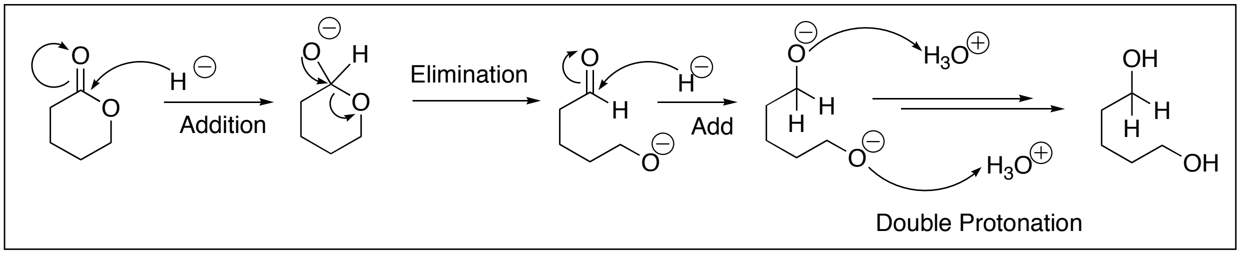
$LiAlH_4 = H^{\ominus}$



Esters

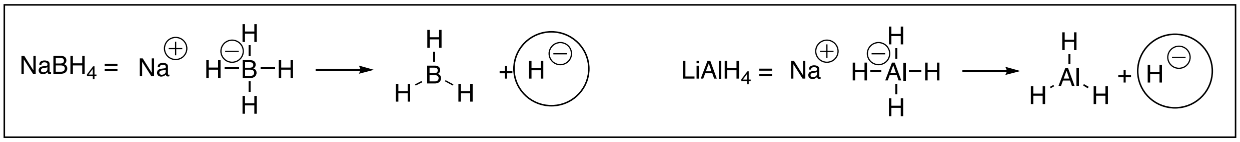


Cyclic Esters



Notes:

- Mechanisms are exactly like with Grignard reactions
- $LiAlH_4$ and $NaBH_4$ function as hydride anions $H^{\ominus}$
- For mechanisms, just draw $H^{\ominus}$ rather than trying to involve the Li and Al and Na and B…



- Boron is one row higher than aluminum, and in keeping with normal periodic patterns is more electronegative
    - Because boron is more electronegative, the $BH_4^{\ominus}$ anion is more stable, and less reactive.
        - The boron holds the $H^{\ominus}$ more tightly.
    - Aluminum being less electronegative doesn't attract and hold the $H^{\ominus}$ as well, and thus is considerably more reactive.

Reactivity

	Aldehydes	Ketones	Esters
$LiAlH_4$	Yes	Yes	Yes
$NaBH_4$	Yes	Yes	No

$LiAlH_4$ is much stronger, $NaBH_4$ much weaker

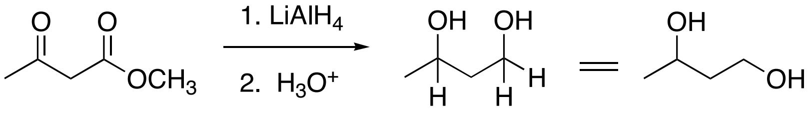
1. $LiAlH_4$ is strong enough to react with esters, $NaBH_4$ isn't
2. **Selective reduction**: if both an ester and an aldehyde/ketone are present:
    - $LiAlH_4$ reduces both
    - $NaBH_4$ selectively reduces the aldehyde/ketone but leaves the ester untouched
3. **$LiAlH_4$ is strong enough to react with and be destroyed by water or alcohol; $NaBH_4$ isn't**

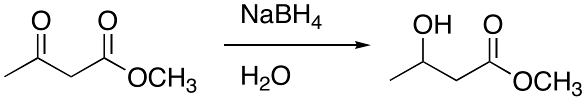
$$LiAlH_4 + H_2O \rightarrow H_2(\text{gas}) + LiOH + AlH_3 + \text{heat}$$

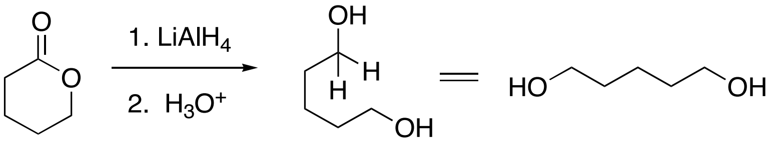
    a. As a result, $LiAlH_4$ is harder to use and store
    b. Acid has to be added in a subsequent step with the $LiAlH_4$; (thus, 2-step recipe)
    c. $NaBH_4$ can be run in alcohol solvent which serves as a proton source for protonating alkoxide
    d. Solvent restrictions, glassware must be dry, wet air must be excluded, etc.
    e. Because $NaBH_4$ is stable to water, it's easier to handle in air, easier to store, much easier to work with
    f. **Default: for a simple aldehyde or ketone reduction, normally use $NaBH_4$ because it's so much easier**

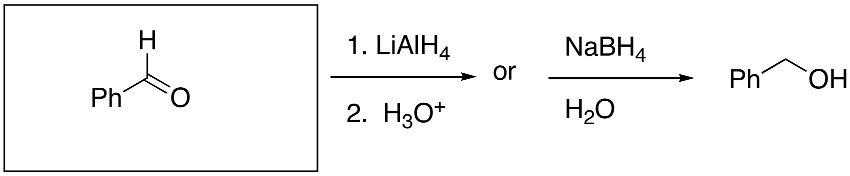
4. $LiAlH_4$ is strong enough to react with esters, $NaBH_4$ isn't

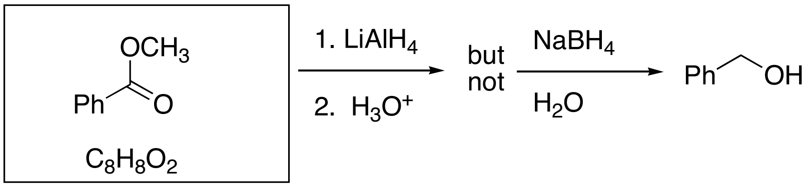
Draw the products for the following reactions.

1. 

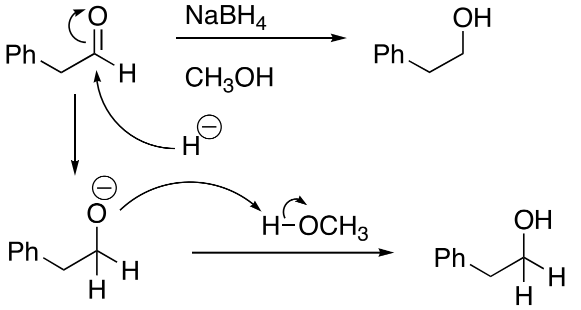
2. 

3. 

4. 

5. 

Draw the mechanism for the following reaction.

6. 

7.