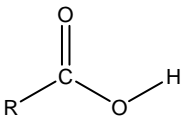
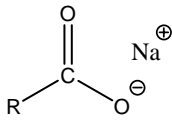
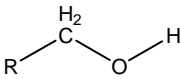
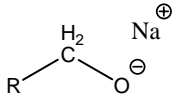
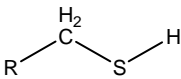
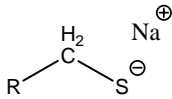

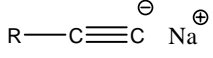
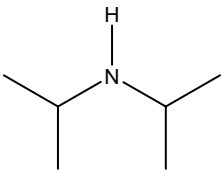
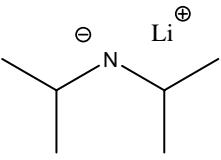
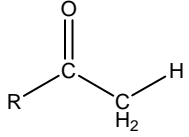
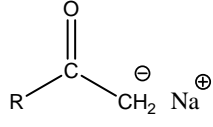


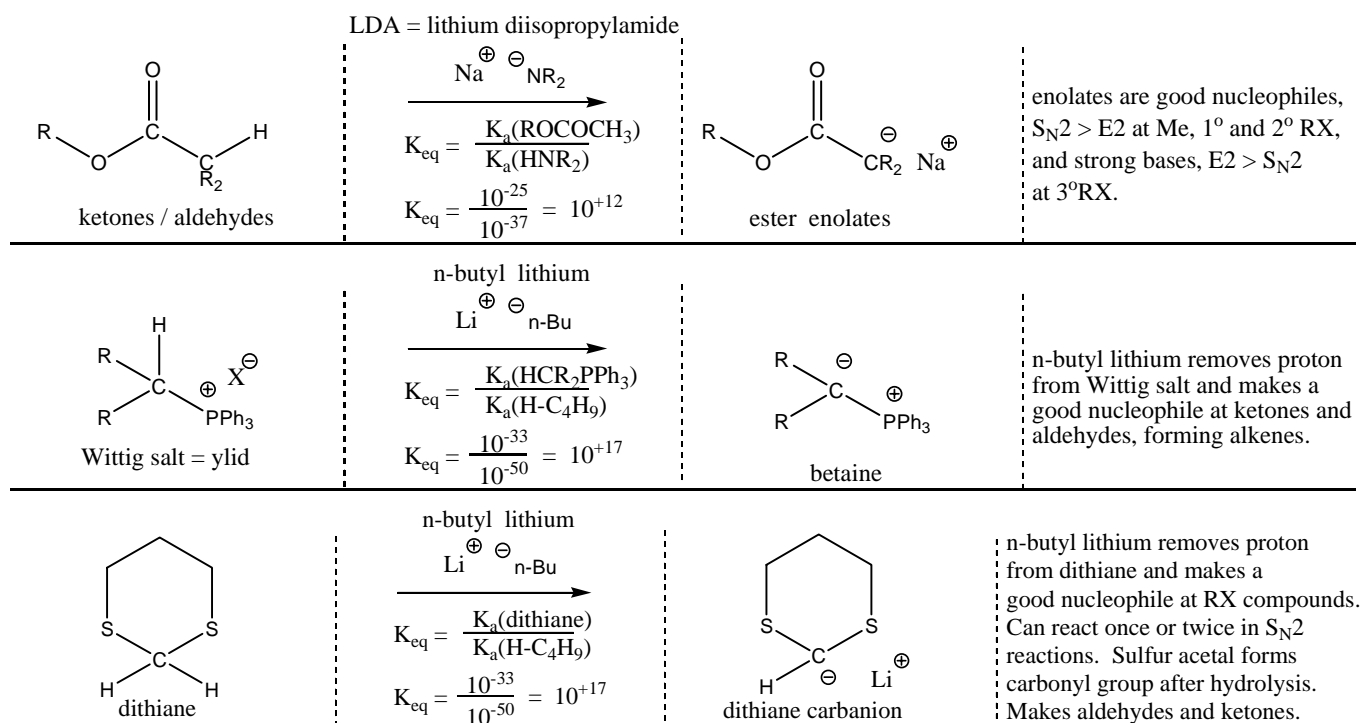
# Reactions Study List Through Chem 315

For Use as a Study Guide

Beauchamp

Important acid/base reactions used in the examples below.

<u>Acid</u>	<u>Base</u>	<u>New Base</u>	<u>Comments</u>
 <p>carboxylic acids</p>	<p>sodium hydroxide</p> $\text{Na}^{\oplus} \text{O}^{\ominus}\text{---H}$ $K_{\text{eq}} = \frac{K_a(\text{RCO}_2\text{H})}{K_a(\text{H}_2\text{O})}$ $K_{\text{eq}} = \frac{10^{-5}}{10^{-16}} = 10^{+11}$	 <p>carboxylates</p>	<p>Carboxylates are good nucleophiles,  <math>S_{\text{N}}2 &gt; \text{E}2</math> at Me, 1° and 2° RX</p>
 <p>alcohols</p>	<p>sodium hydride</p> $\text{Na}^{\oplus} \text{H}^{\ominus}$ $K_{\text{eq}} = \frac{K_a(\text{ROH})}{K_a(\text{H}_2)}$ $K_{\text{eq}} = \frac{10^{-17}}{10^{-35}} = 10^{+18}$	 <p>alkoxides</p>	<p>alkoxides are OK nucleophiles,  <math>S_{\text{N}}2 &gt; \text{E}2</math> at Me and 1° RX, and strong bases, <math>\text{E}2 &gt; S_{\text{N}}2</math> at 2° and 3°RX.</p>
 <p>thiols</p>	<p>sodium hydroxide</p> $\text{Na}^{\oplus} \text{OH}^{\ominus}$ $K_{\text{eq}} = \frac{K_a(\text{RSH})}{K_a(\text{H}_2\text{O})}$ $K_{\text{eq}} = \frac{10^{-8}}{10^{-16}} = 10^{+8}$	 <p>thiolates</p>	<p>thiolates are good nucleophiles,  <math>S_{\text{N}}2 &gt; \text{E}2</math> at Me, 1° and 2° RX, and strong bases, <math>\text{E}2 &gt; S_{\text{N}}2</math> at 3°RX.</p>
 <p>terminal alkynes</p>	<p>sodium amide</p> $\text{Na}^{\oplus} \text{NR}_2^{\ominus}$ $K_{\text{eq}} = \frac{K_a(\text{RCCH})}{K_a(\text{HNR}_2)}$ $K_{\text{eq}} = \frac{10^{-25}}{10^{-37}} = 10^{+12}$	 <p>terminal acetylides</p>	<p>terminal acetylides are OK nucleophiles, <math>S_{\text{N}}2 &gt; \text{E}2</math> at Me and 1° RX, and strong bases, <math>\text{E}2 &gt; S_{\text{N}}2</math> at 2° and 3°RX.</p>
 <p>diisopropylamine</p>	<p>n-butyl lithium</p> $\text{Li}^{\oplus} \text{n-Bu}^{\ominus}$ $K_{\text{eq}} = \frac{K_a(\text{HNR}_2)}{K_a(\text{H-C}_4\text{H}_9)}$ $K_{\text{eq}} = \frac{10^{-37}}{10^{-50}} = 10^{+13}$	 <p>LDA = lithium diisopropylamide</p>	<p>LDA is a very strong base that is also very sterically hindered, it always acts as a base in our course.</p>
 <p>ketones / aldehydes</p>	<p>LDA = lithium diisopropylamide</p> $\text{Na}^{\oplus} \text{NR}_2^{\ominus}$ $K_{\text{eq}} = \frac{K_a(\text{RCOCH}_3)}{K_a(\text{HNR}_2)}$ $K_{\text{eq}} = \frac{10^{-20}}{10^{-37}} = 10^{+17}$	 <p>ketone enolates</p>	<p>enolates are good nucleophiles,  <math>S_{\text{N}}2 &gt; \text{E}2</math> at Me, 1° and 2° RX, and strong bases, <math>\text{E}2 &gt; S_{\text{N}}2</math> at 3°RX.</p>

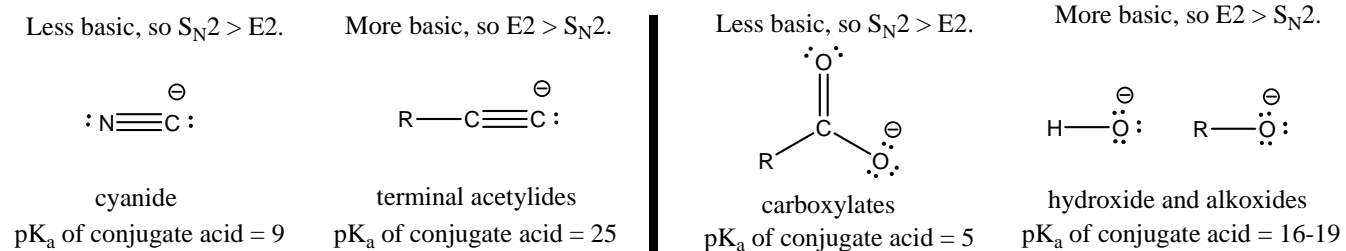


### $S_N2$ versus $E2$ choices at $2^\circ$ RX.


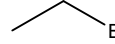
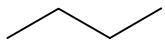
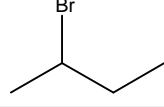
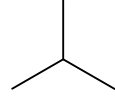
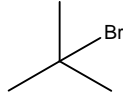
At secondary RX (X= OTs, I, Br, Cl)  $S_N2$  and  $E2$  products are in close competition with each other. Anions whose conjugate acids have higher  $pK_a$ 's (stronger bases have weaker acids) generally produce more  $E2$  relative to  $S_N2$ . The two examples that we will emphasize at  $2^\circ$  RX centers are carboxylates ( $S_N2 > E2$ ) vs hydroxide and alkoxides ( $E2 > S_N2$ ), and cyanide ( $S_N2 > E2$ ) vs terminal acetylides ( $E2 > S_N2$ ). Steric hindrance in RX or the electron pair donor also favors  $E2 > S_N2$ .

Similar looking base/nucleophiles (used in our course) that react differently with  $2^\circ$  RX structures. (They all react by  $S_N2$  at methyl and  $1^\circ$  RX and they all react by  $E2$  at  $3^\circ$  RX.)

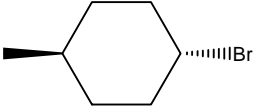
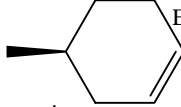
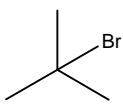
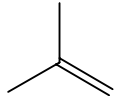
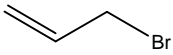
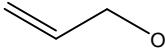
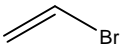
### $2^\circ$ RX structures



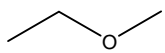

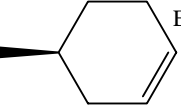
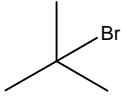
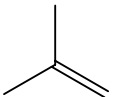
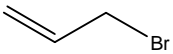
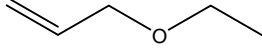
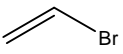
Alkanes with  $\text{Br}_2 / h\nu$ . (Synthesis of RX compounds, X = Br, Cl.)

$\text{CH}_4$	$\xrightarrow{\text{Br}_2 / h\nu}$	$\text{H}_3\text{C}-\text{Br}$	free radical halogenation achiral
	$\xrightarrow{\text{Br}_2 / h\nu}$		free radical halogenation achiral
	$\xrightarrow{\text{Br}_2 / h\nu}$		free radical halogenation enantiomers (R and S)
	$\xrightarrow{\text{Br}_2 / h\nu}$		free radical halogenation achiral

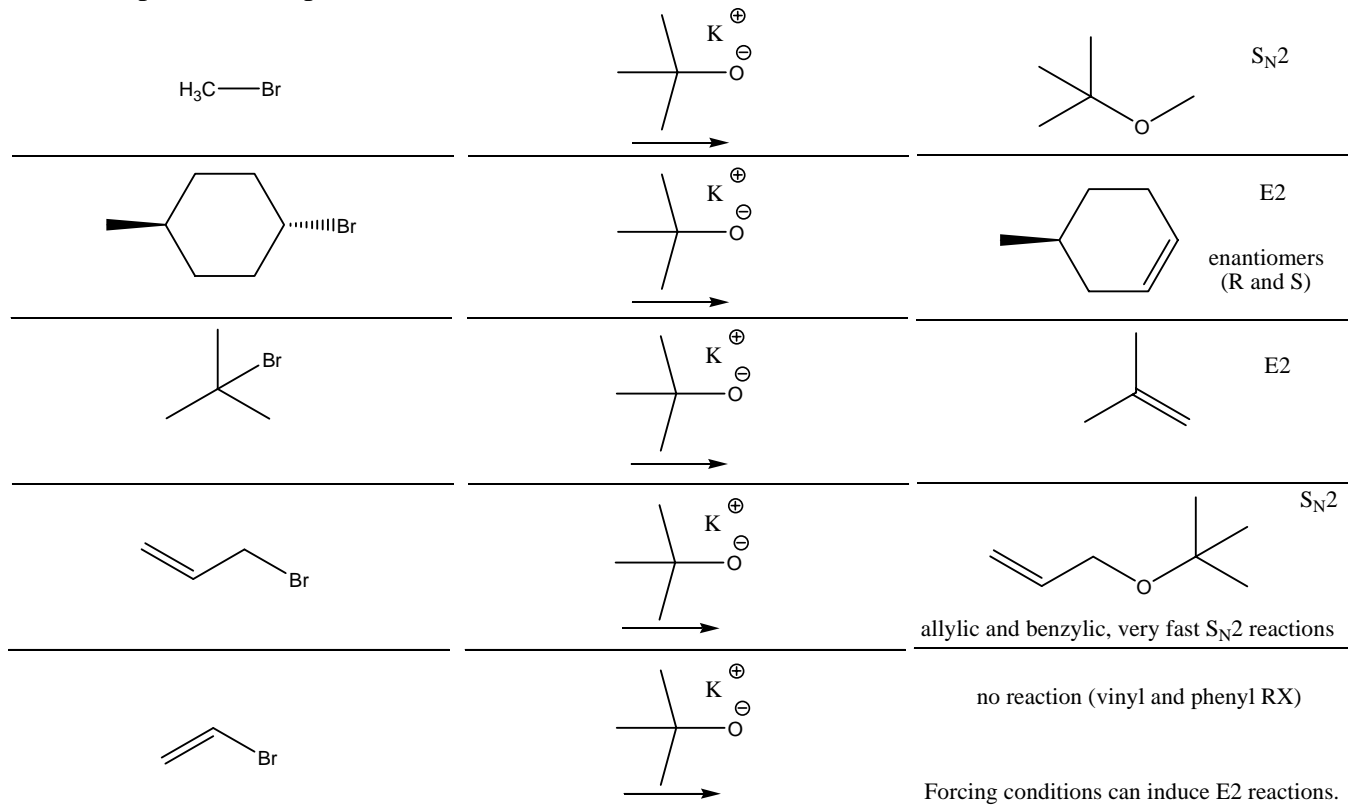
1. a. RX compounds with  $\text{NaOH} / \text{H}_2\text{O}$ . (Alcohol synthesis.)

$\text{H}_3\text{C}-\text{Br}$	$\xrightarrow{\text{NaOH} / \text{H}_2\text{O}}$	$\text{H}_3\text{C}-\text{OH}$	$\text{S}_{\text{N}}2$
	$\xrightarrow{\text{NaOH} / \text{H}_2\text{O}}$	 $\text{S}_{\text{N}}2$	major enantiomers (R and S)
	$\xrightarrow{\text{NaOH} / \text{H}_2\text{O}}$		E2
	$\xrightarrow{\text{NaOH} / \text{H}_2\text{O}}$	 $\text{S}_{\text{N}}2$	allylic and benzylic, very fast $\text{S}_{\text{N}}2$ reactions
	$\xrightarrow{\text{NaOH} / \text{H}_2\text{O}}$		no reaction (vinyl and phenyl RX) Forcing conditions can induce E2 reactions.

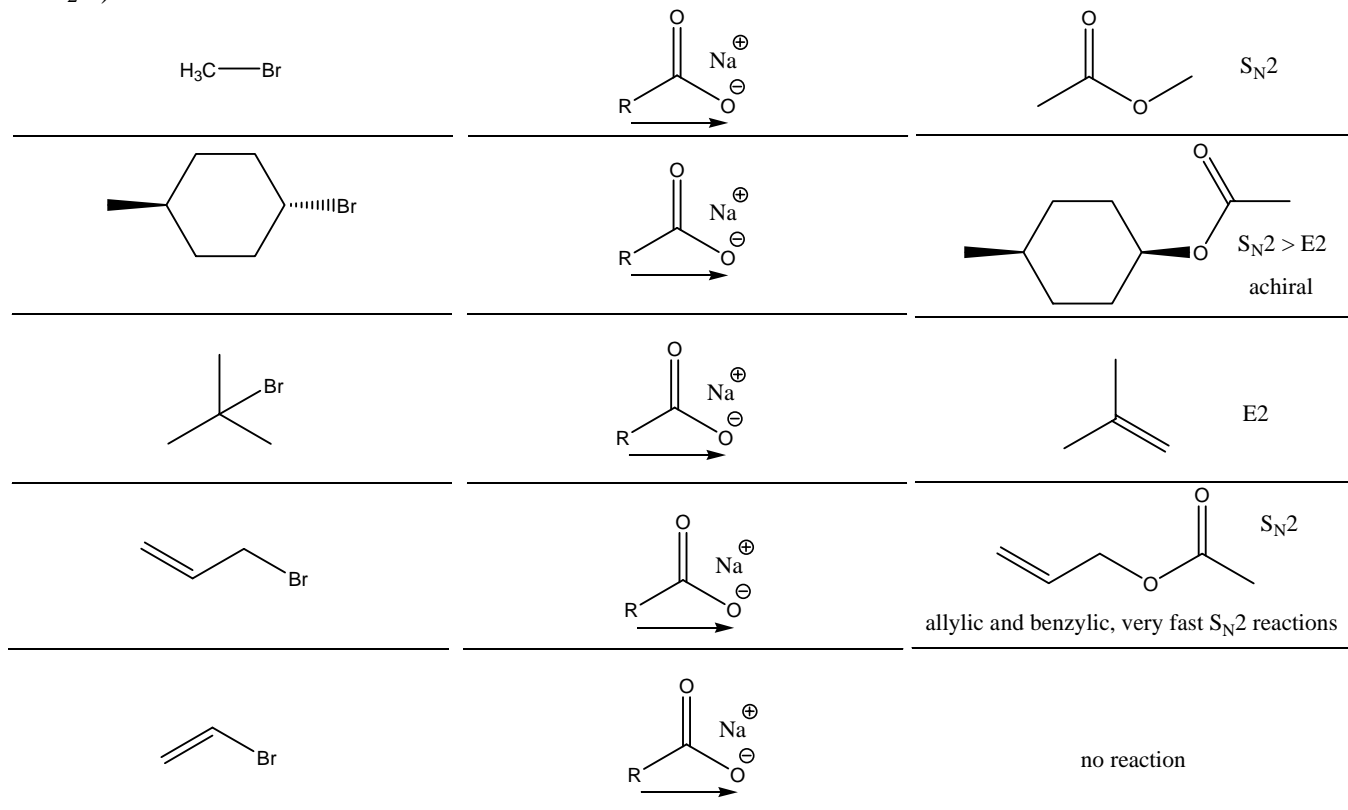
b. RX compounds with  $\text{NaOR} / \text{ROH}$ . (Ether synthesis, need to make  $\text{RO}^-$ ,  $\text{Na}^+$ .)

$\text{H}_3\text{C}-\text{Br}$	$\xrightarrow{\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+}$	 $\text{S}_{\text{N}}2$	
	$\xrightarrow{\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+}$	 $\text{S}_{\text{N}}2$	major enantiomers (R and S)
	$\xrightarrow{\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+}$		E2
	$\xrightarrow{\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+}$	 $\text{S}_{\text{N}}2$	allylic and benzylic, very fast $\text{S}_{\text{N}}2$ reactions
	$\xrightarrow{\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+}$		no reaction (vinyl and phenyl RX) Forcing conditions can induce E2 reactions.

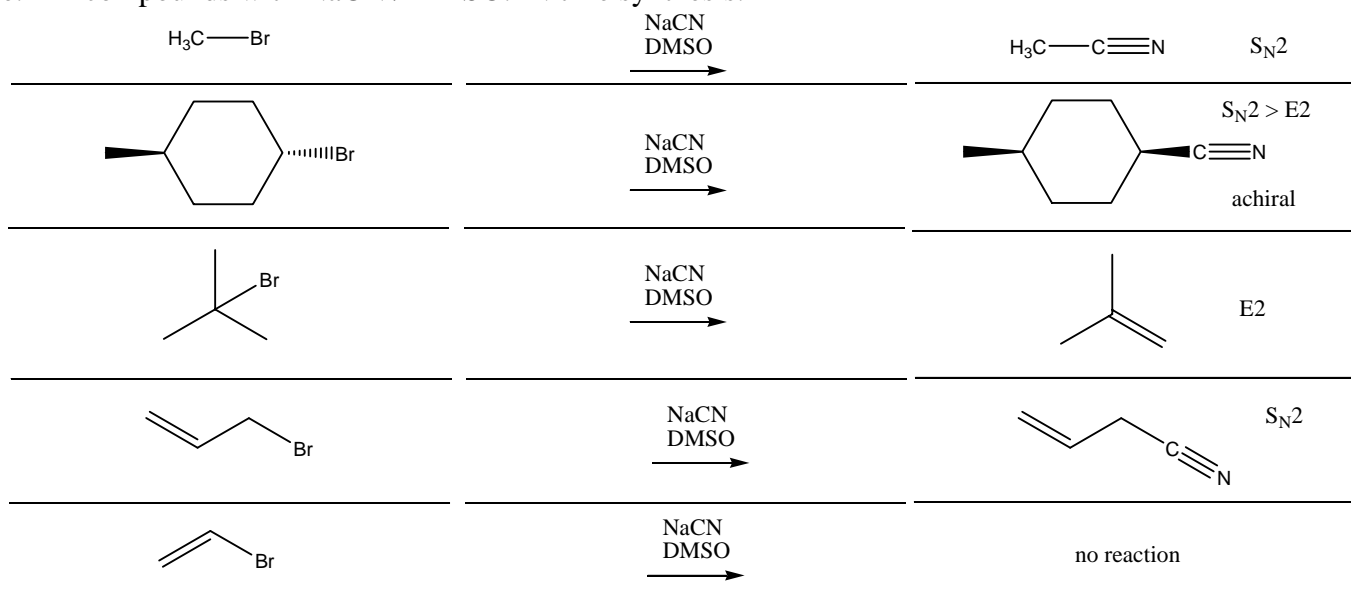
c. RX compounds with potassium t-butoxide (favors E2 > S<sub>N</sub>2).



d. RX compounds with sodium carboxylates. Ester synthesis (can hydrolyze with base to ROH and RCO<sub>2</sub>H).

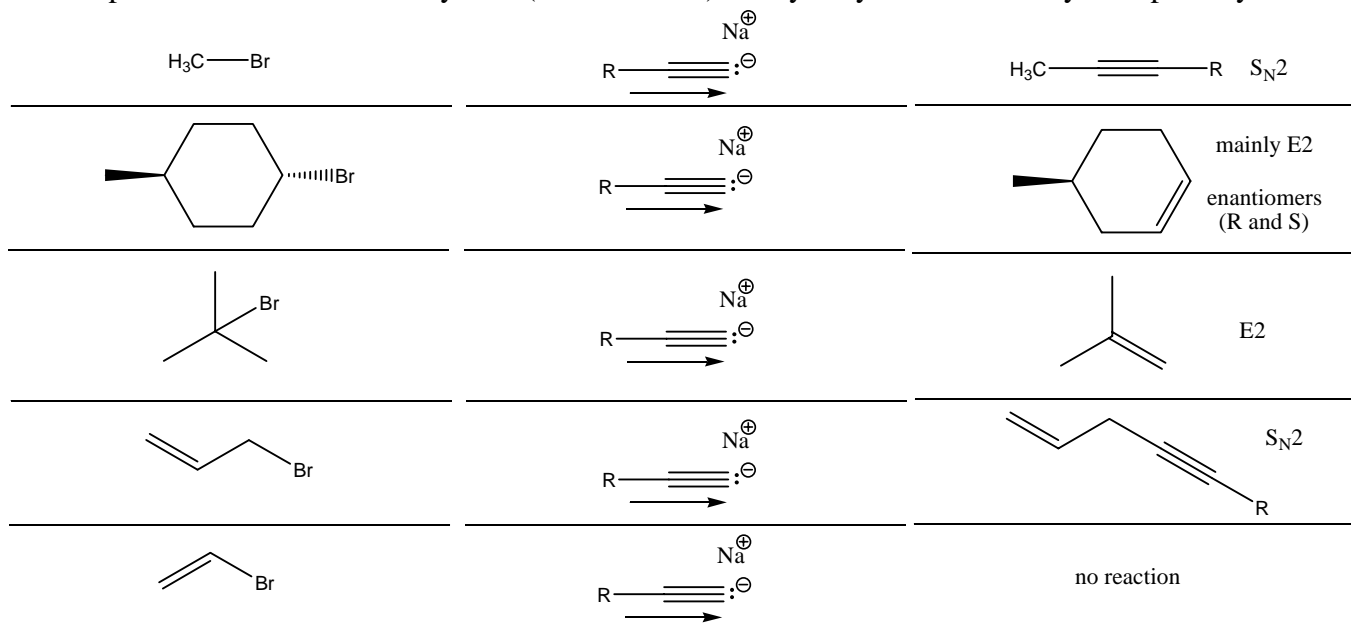


e. RX compounds with NaCN / DMSO. Nitrile synthesis.



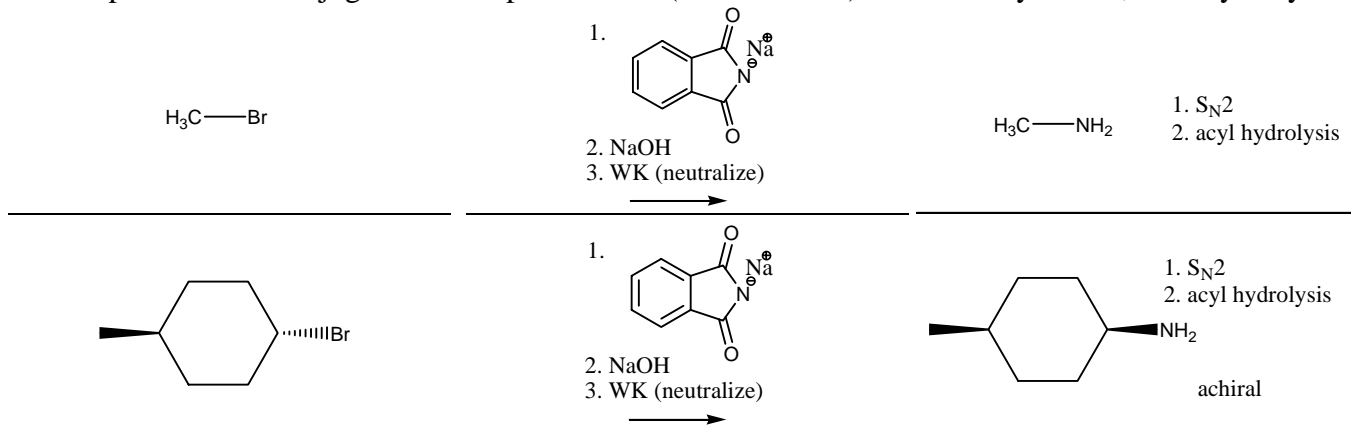
f.

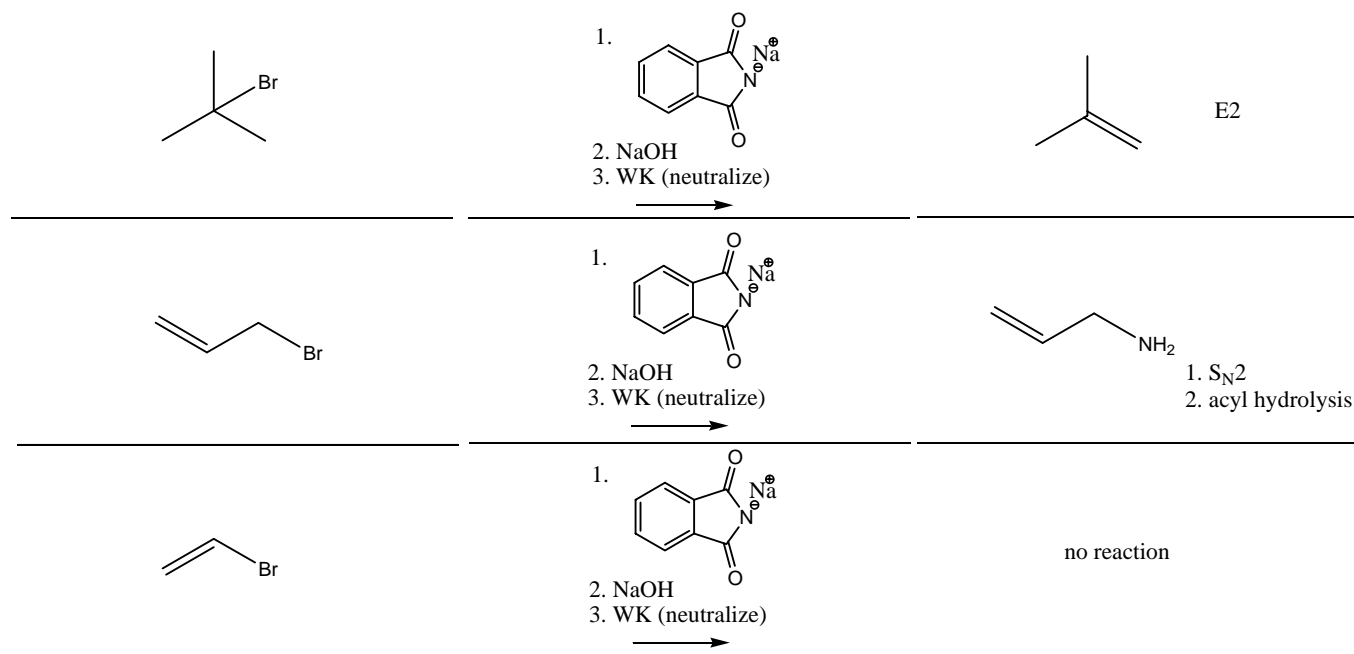
RX compounds with terminal acetylides (need to make). Alkyne synthesis at methyl and primary RX.



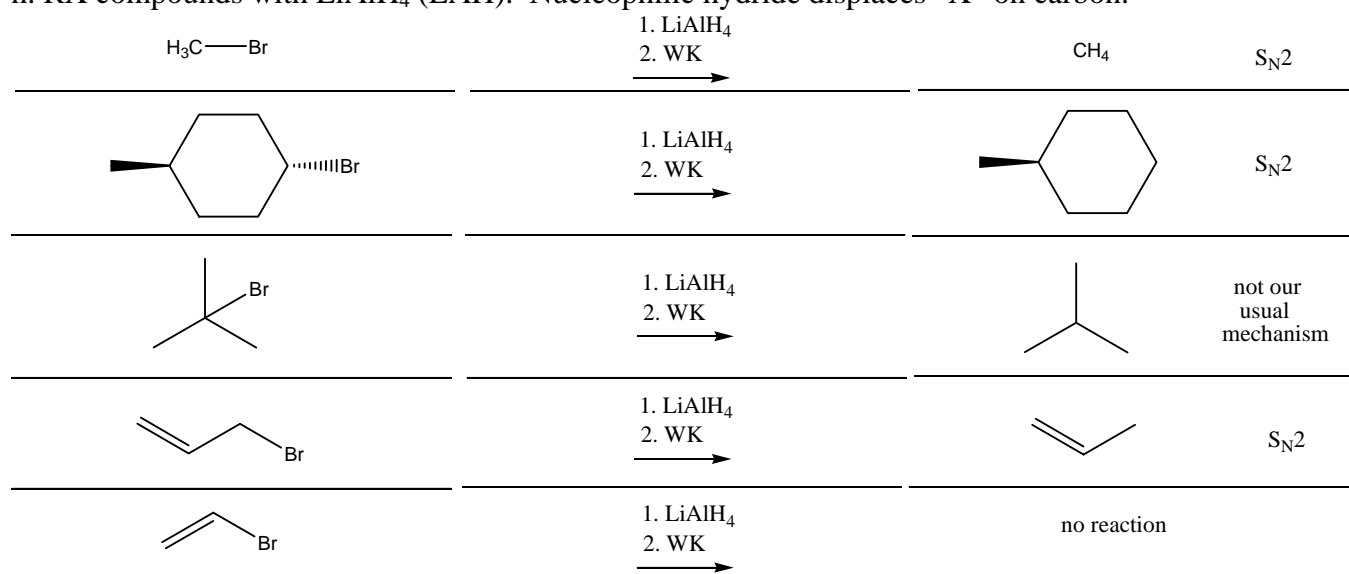
g.

RX compounds with conjugate base of phthalimide (need to make).  $1^\circ \text{RNH}_2$  synthesis, after hydrolysis.



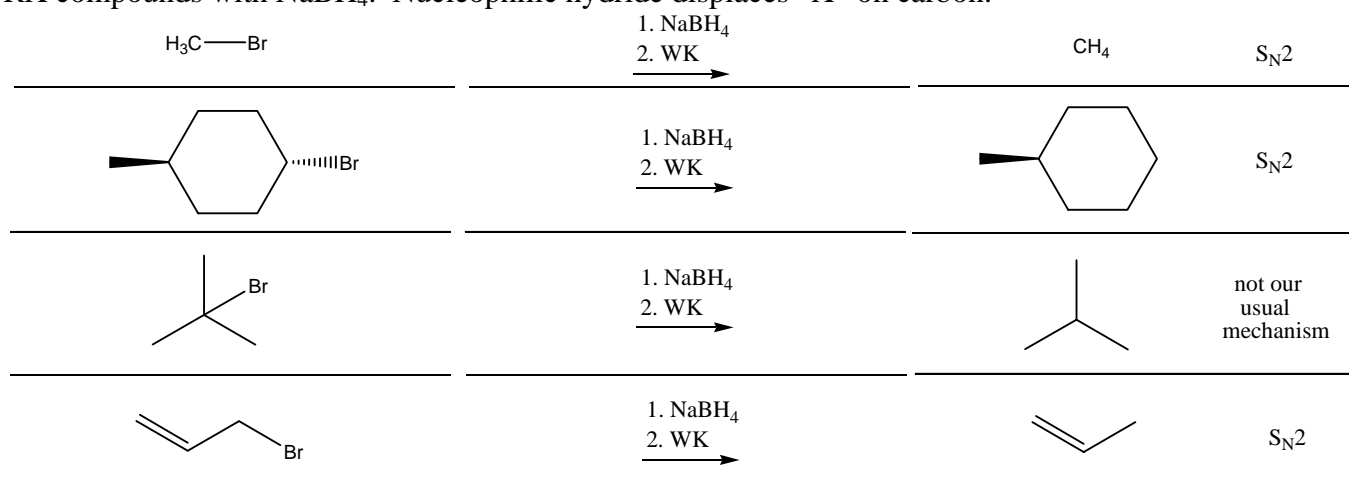


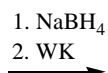
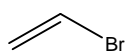
h. RX compounds with LiAlH<sub>4</sub> (LAH). Nucleophilic hydride displaces "X" on carbon.



i.

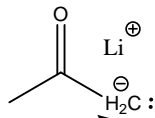
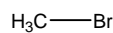
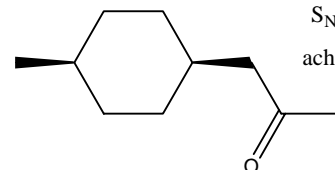
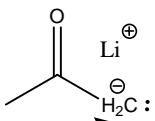
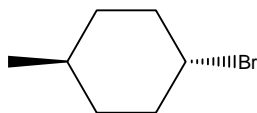
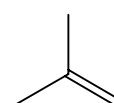
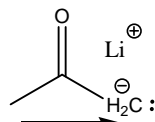
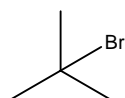
RX compounds with NaBH<sub>4</sub>. Nucleophilic hydride displaces "X" on carbon.



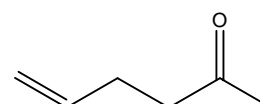
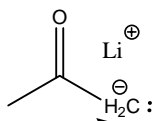
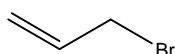
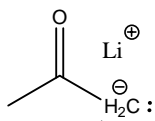
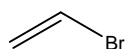


no reaction

j. RX compounds with enolates (need to make with LDA/-78°C). Alkylation of carbonyl compounds.

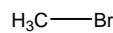
S<sub>N</sub>2S<sub>N</sub>2  
achiral

E2

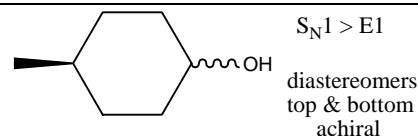
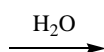
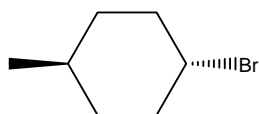
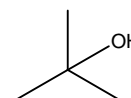
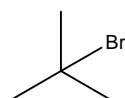
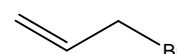
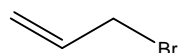
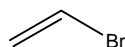
S<sub>N</sub>2

no reaction

k. RX compounds with water. Alcohol synthesis (rearrangements are possible).

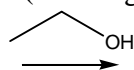
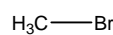


no reaction

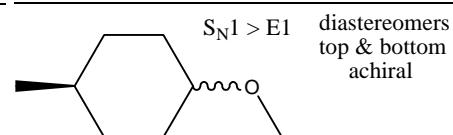
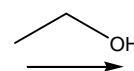
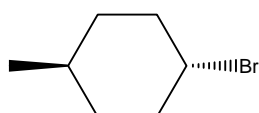
S<sub>N</sub>1 > E1  
diastereomers  
top & bottom  
achiralS<sub>N</sub>1 > E1  
top = bottomS<sub>N</sub>1

no reaction

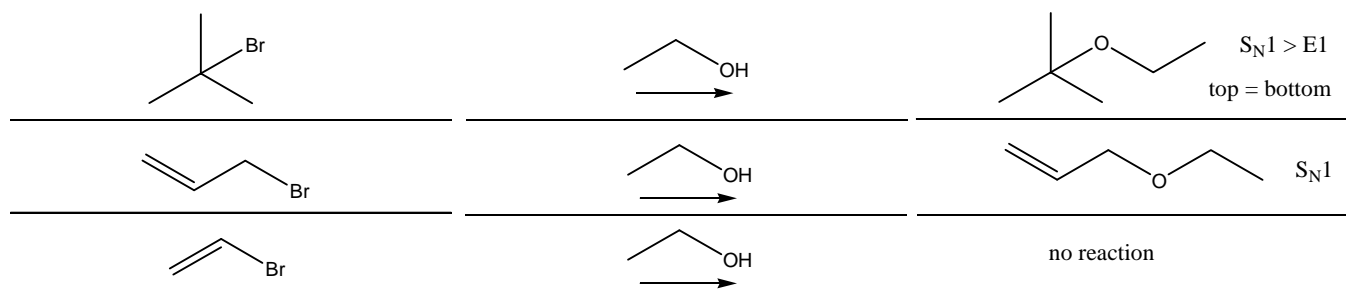
l. RX compounds with alcohols. Ether synthesis (rearrangements are possible).



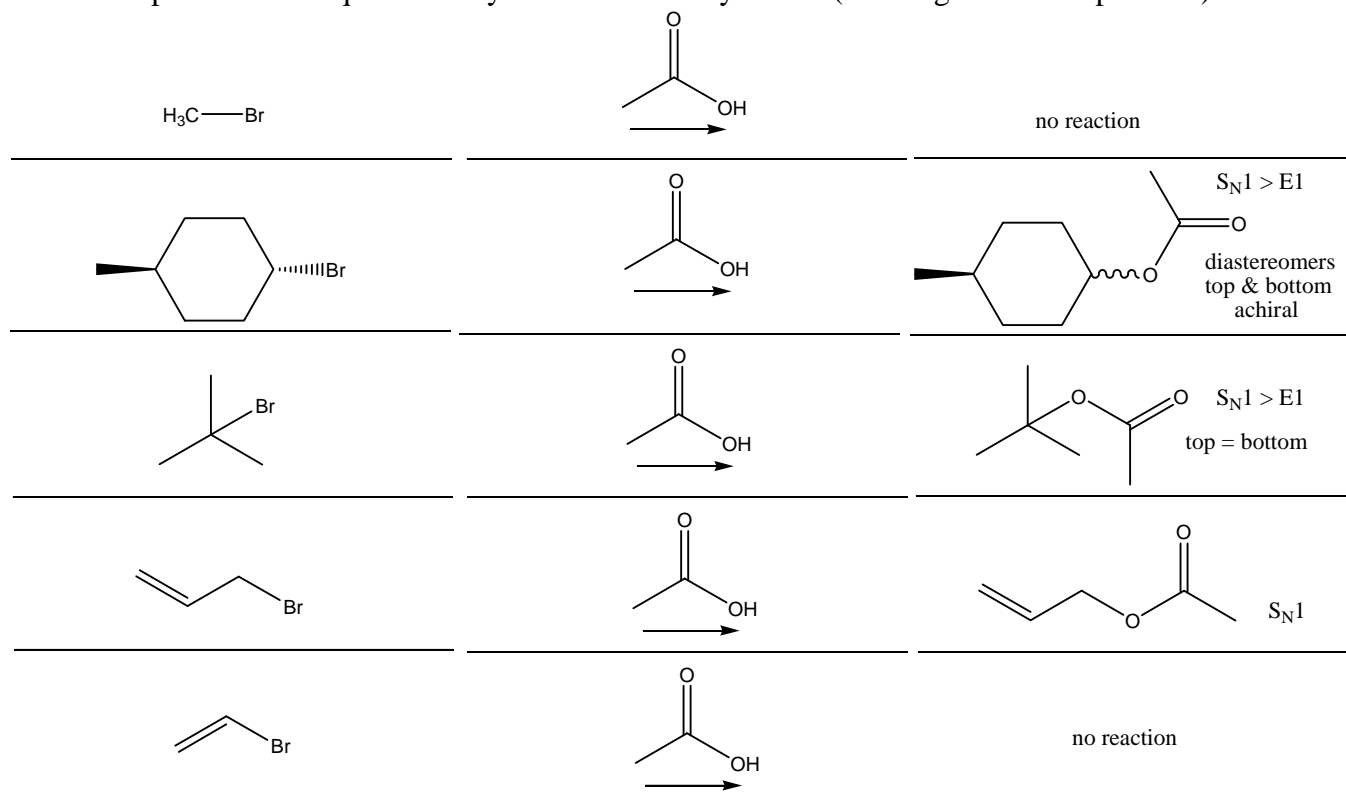
no reaction

S<sub>N</sub>1 > E1  
diastereomers  
top & bottom  
achiral

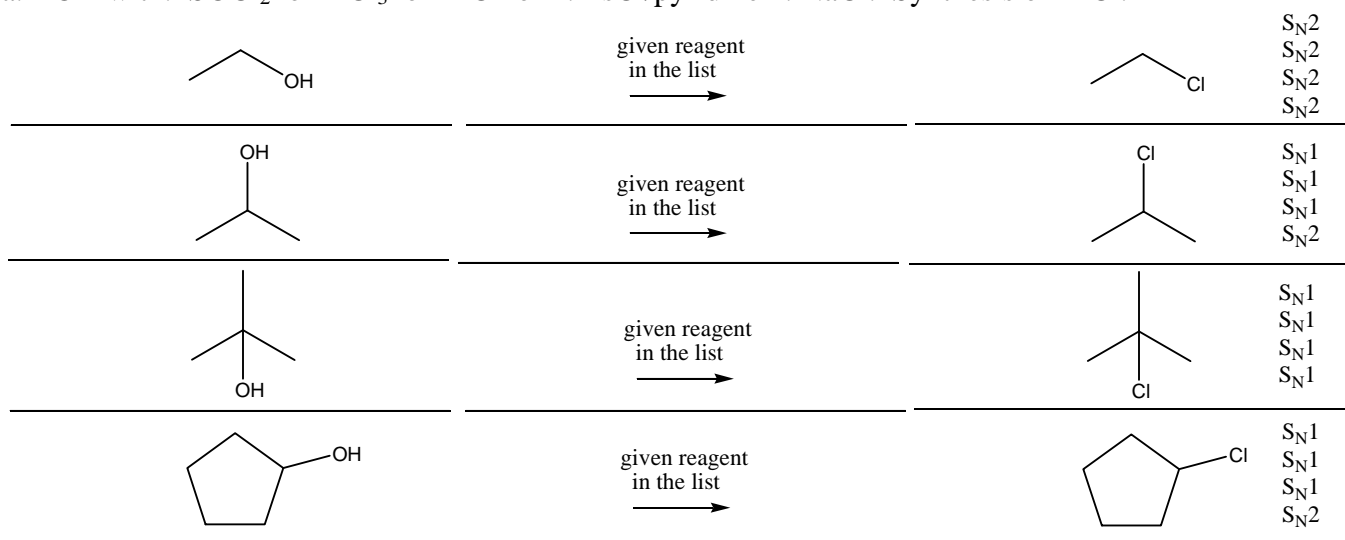


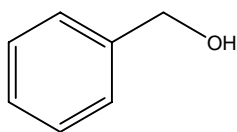


m. RX compounds with liquid carboxylic acids. Ester synthesis (rearrangements are possible).

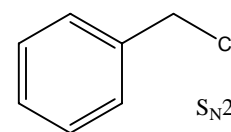


2. a. ROH with:  $SOCl_2$  or  $PCl_3$  or  $HCl$  or 1.  $TsCl$ /pyridine 2.  $NaCl$ . Synthesis of R-Cl.



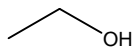


given reagent  
in the list  
→

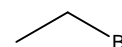


$S_N2$  or  $S_N1$

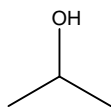
b. ROH with:  $PBr_3$  or  $HBr$  or 1.  $TsCl$ /pyridine 2.  $NaBr$ . Synthesis of R-Br.



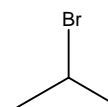
given reagent  
in the list  
→



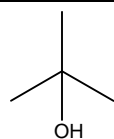
$S_N2$   
 $S_N2$   
 $S_N2$



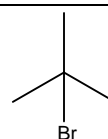
given reagent  
in the list  
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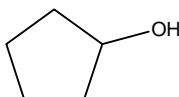
$S_N1$   
 $S_N1$   
 $S_N2$



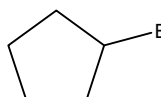
given reagent  
in the list  
→



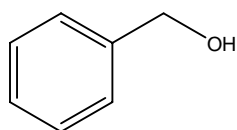
$S_N1$   
 $S_N1$   
 $S_N1$



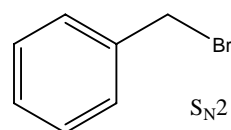
given reagent  
in the list  
→



$S_N1$   
 $S_N1$   
 $S_N2$

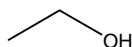


given reagent  
in the list  
→

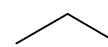


$S_N2$  or  $S_N1$

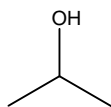
c. ROH with:  $PI_3$  or  $HI$  or 1.  $TsCl$ /pyridine 2.  $NaI$ . Synthesis of R-I.



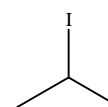
given reagent  
in the list  
→



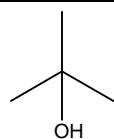
$S_N2$   
 $S_N2$   
 $S_N2$



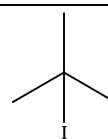
given reagent  
in the list  
→



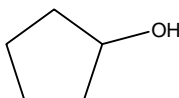
$S_N1$   
 $S_N1$   
 $S_N2$



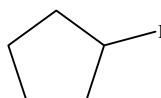
given reagent  
in the list  
→



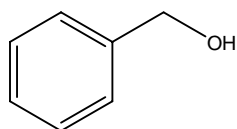
$S_N1$   
 $S_N1$   
 $S_N1$



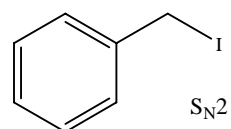
given reagent  
in the list  
→



$S_N1$   
 $S_N1$   
 $S_N2$

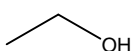


given reagent  
in the list  
→

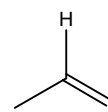


$S_N2$  or  $S_N1$

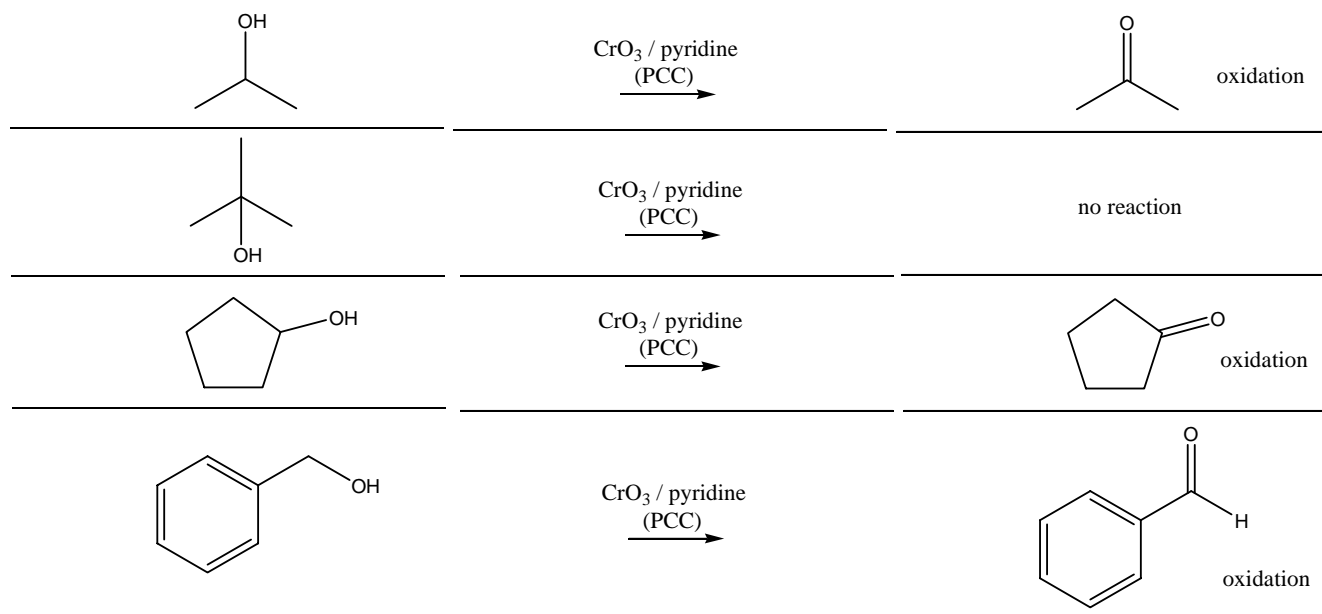
d. ROH with:  $CrO_3$  / pyridine (PCC). Synthesis of aldehydes or ketones.



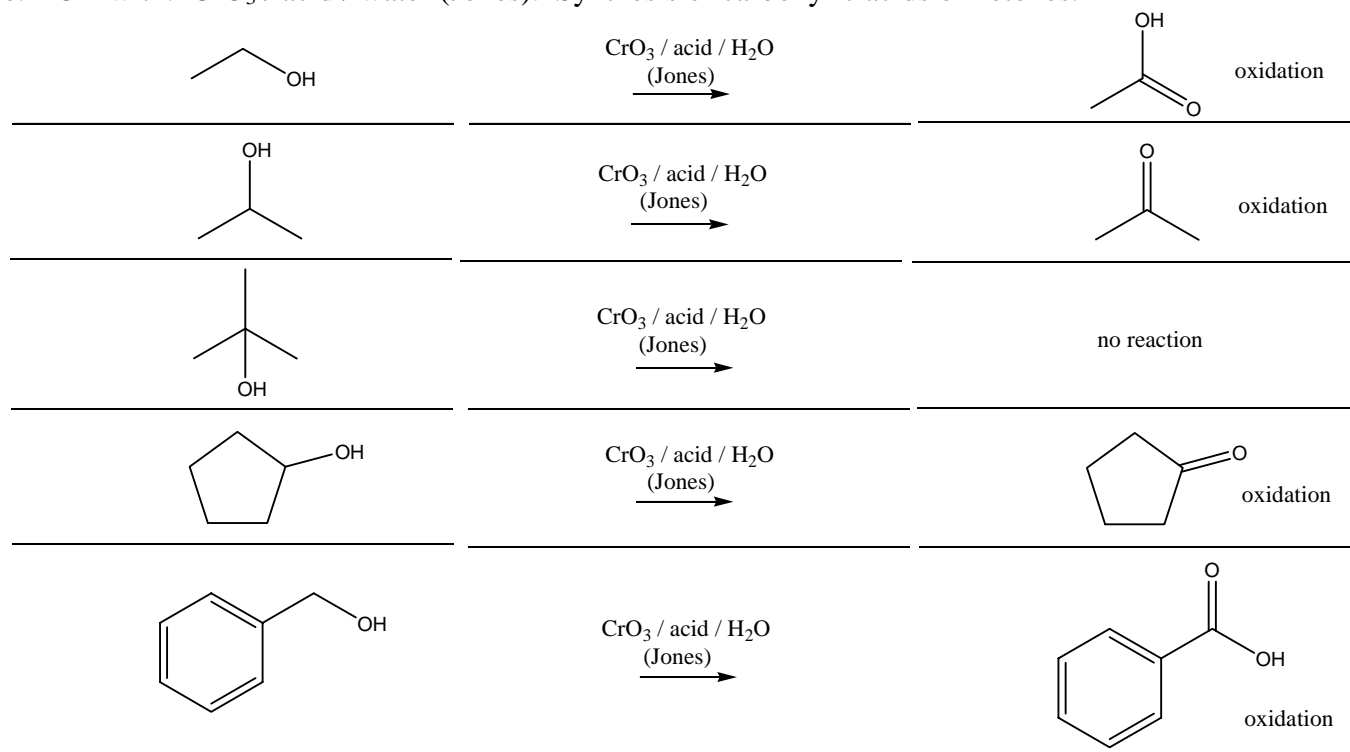
$CrO_3$  / pyridine  
(PCC)  
→



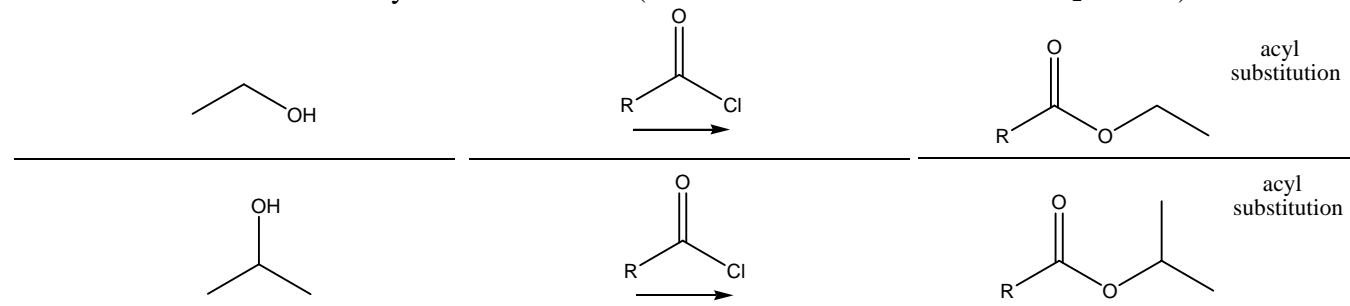
oxidation

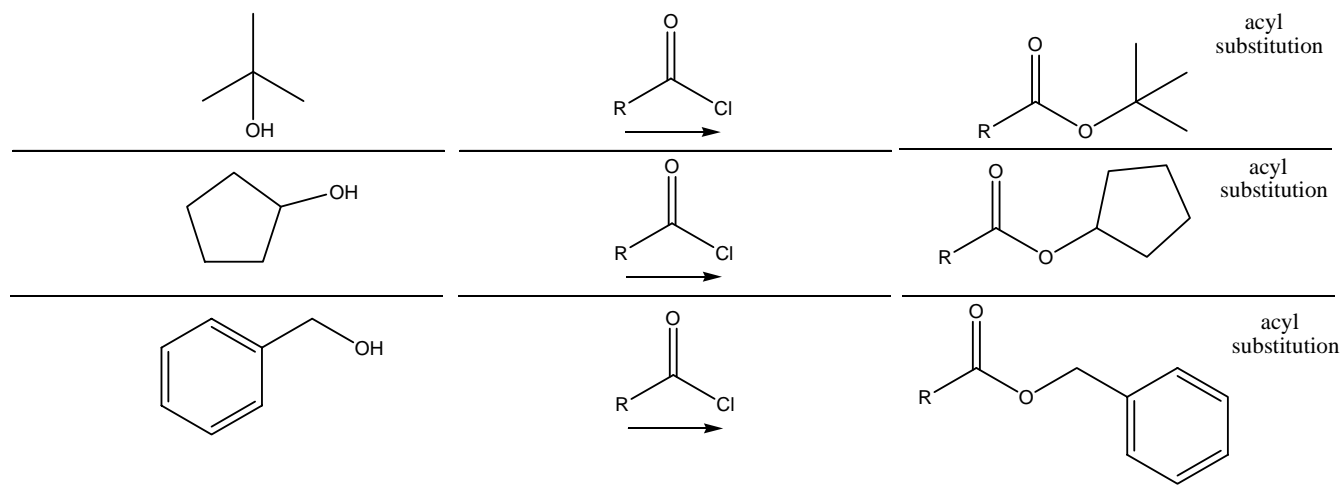


e. ROH with:  $\text{CrO}_3$  / acid / water (Jones). Synthesis of carboxylic acids or ketones.

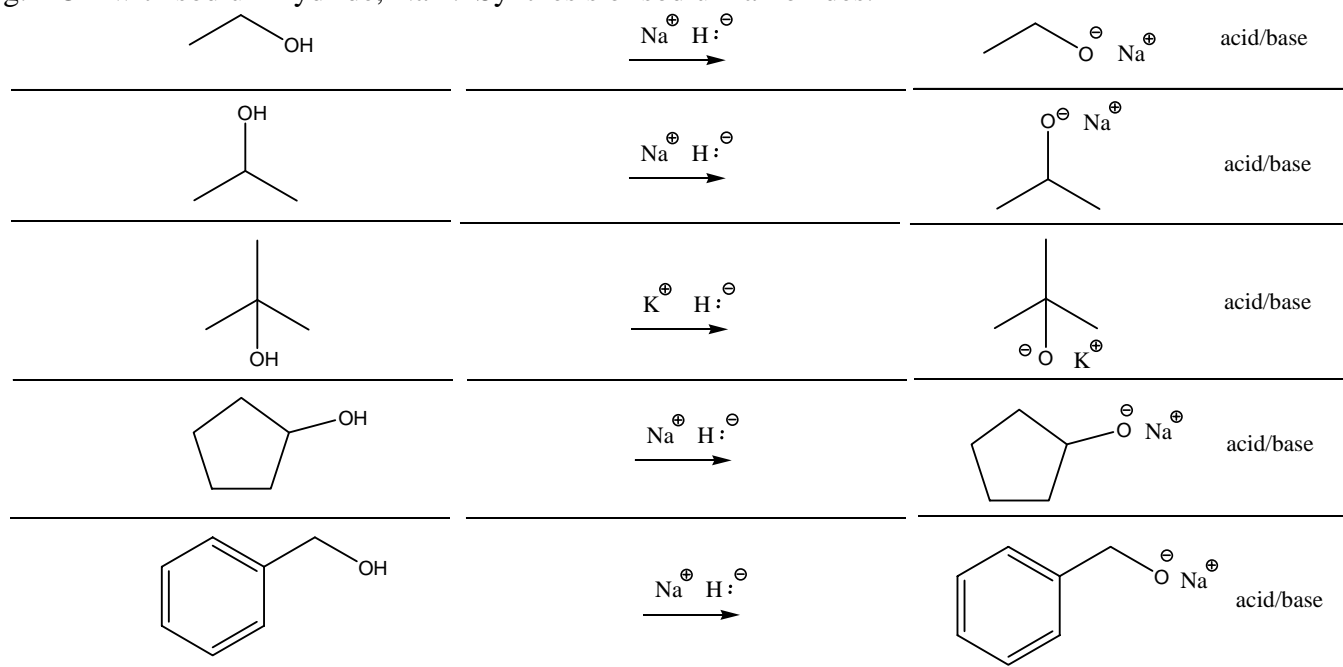


f. ROH with acid chlorides. Synthesis of esters. (Need to make  $\text{RCOCl}$  with  $\text{SOCl}_2$  + acid.)

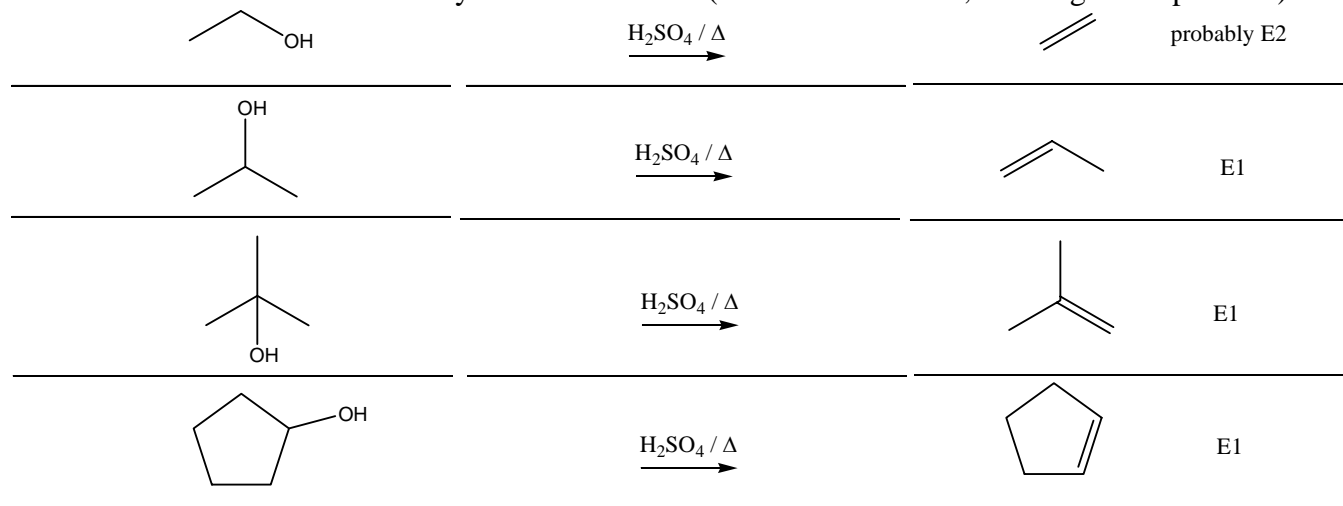




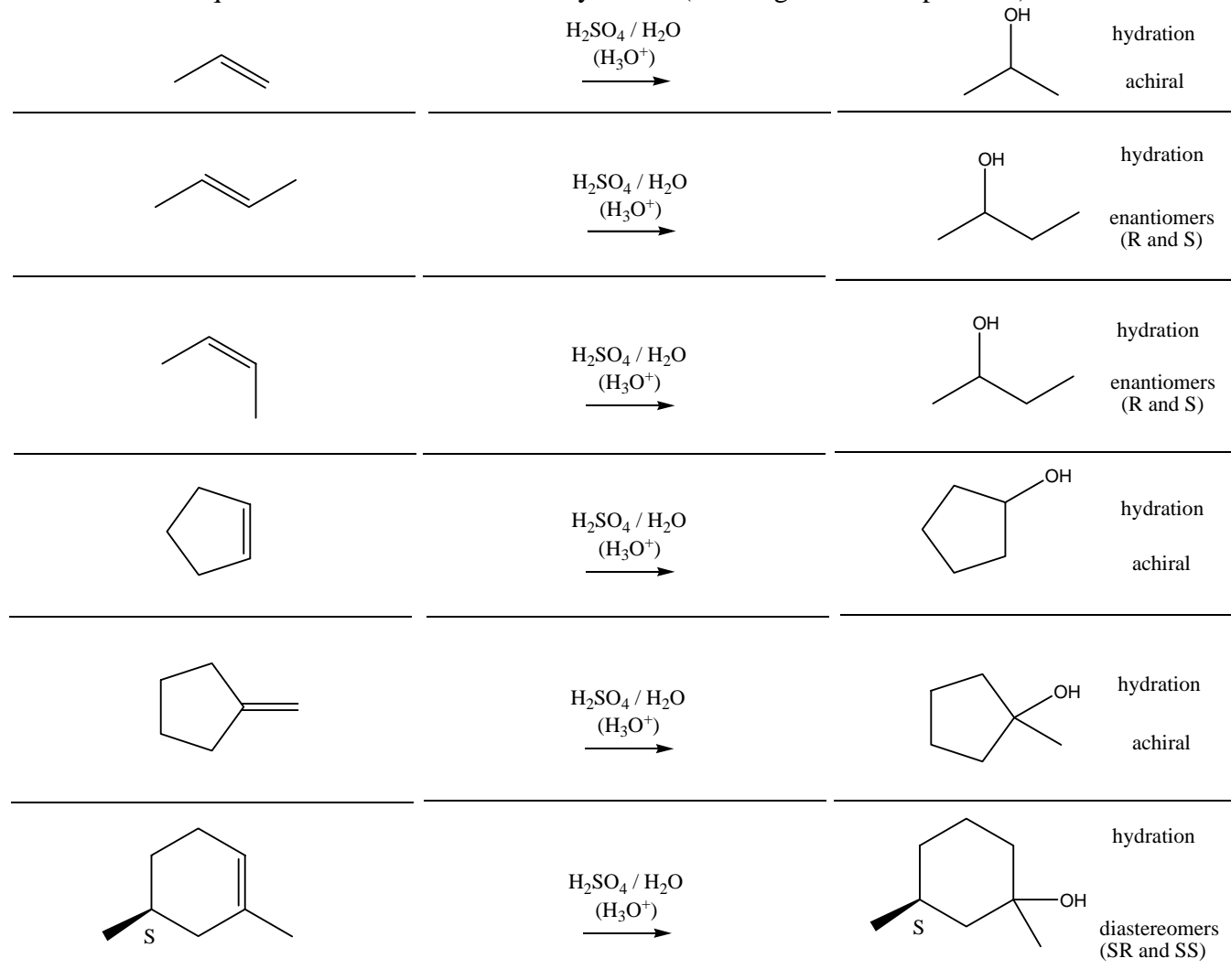
g. ROH with sodium hydride, NaH. Synthesis of sodium alkoxides.



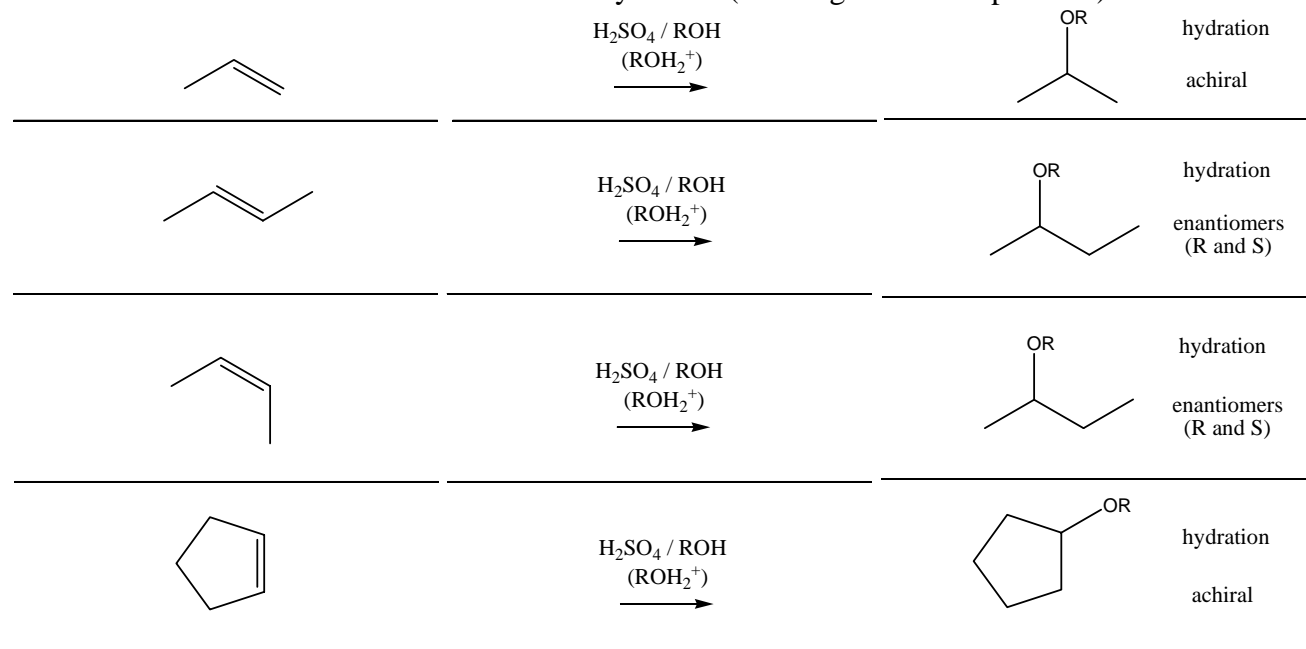
h. ROH with sulfuric acid / heat. Synthesis of alkenes (useful E1 reactions, rearrangement possible).

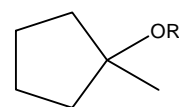
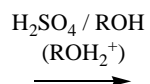
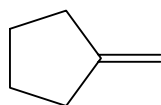


## 3. a. Alkenes with aqueous sulfuric acid. Alcohol synthesis (rearrangements are possible).

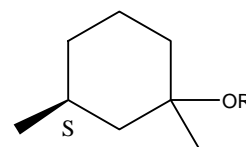
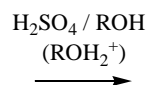
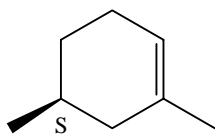


## b. Alkenes with alcohol + sulfuric acid. Ether synthesis (rearrangements are possible).



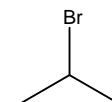
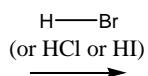
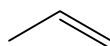


hydration  
achiral

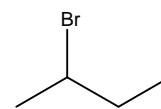
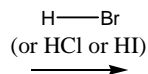
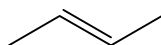


hydration  
diastereomers  
(SR and SS)

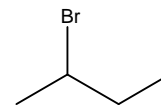
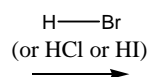
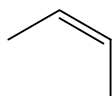
c. Alkenes with HX acid (HCl, HBr, HI). Synthesis of RX compounds.



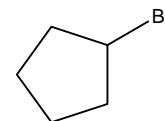
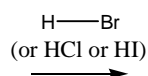
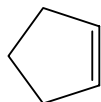
addition  
achiral



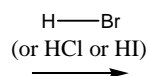
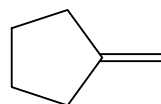
addition  
enantiomers  
(R and S)



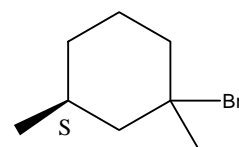
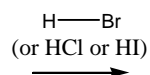
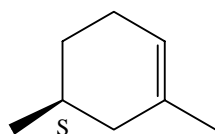
addition  
enantiomers  
(R and S)



addition  
achiral

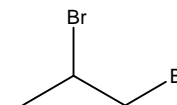
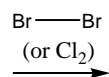
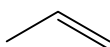


addition  
achiral

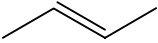
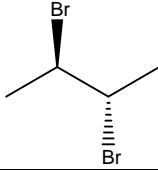
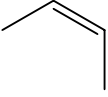
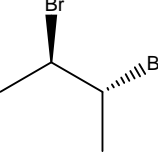

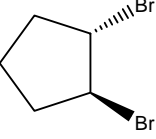
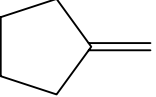
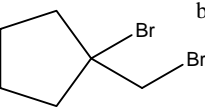
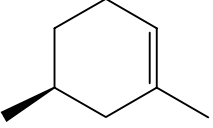
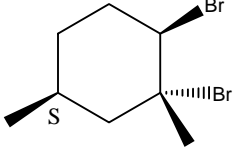


addition  
diastereomers  
(SR and SS)

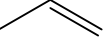
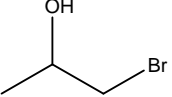
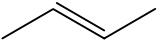
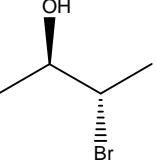
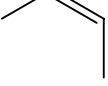
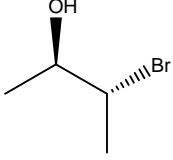

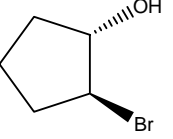
d. Alkenes with Br<sub>2</sub> or Cl<sub>2</sub>. Synthesis of vicinal dihalide (anti addition).

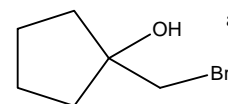
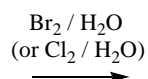
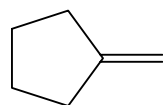


bromination  
enantiomers  
R and S

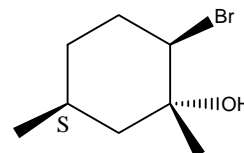
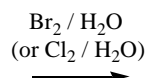
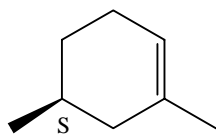
	$\xrightarrow{\text{Br}-\text{Br} \text{ (or Cl}_2\text{)}} \longrightarrow$		bromination meso, RS
	$\xrightarrow{\text{Br}-\text{Br} \text{ (or Cl}_2\text{)}} \longrightarrow$		bromination enantiomers RR and SS
	$\xrightarrow{\text{Br}-\text{Br} \text{ (or Cl}_2\text{)}} \longrightarrow$		bromination enantiomers RR and SS
	$\xrightarrow{\text{Br}-\text{Br} \text{ (or Cl}_2\text{)}} \longrightarrow$		bromination achiral
	$\xrightarrow{\text{Br}-\text{Br} \text{ (or Cl}_2\text{)}} \longrightarrow$		bromination diastereomers SRR and SSS

e. Alkenes with  $\text{Br}_2/\text{H}_2\text{O}$  or  $\text{Cl}_2/\text{H}_2\text{O}$ . Synthesis of bromohydrin or chlorohydrin (anti + Markovnikov addition).

	$\xrightarrow{\text{Br}_2 / \text{H}_2\text{O} \text{ (or Cl}_2 / \text{H}_2\text{O)}} \longrightarrow$		anti + Markovnikov addition enantiomers R and S
	$\xrightarrow{\text{Br}_2 / \text{H}_2\text{O} \text{ (or Cl}_2 / \text{H}_2\text{O)}} \longrightarrow$		anti + Markovnikov addition enantiomers RS and SR
	$\xrightarrow{\text{Br}_2 / \text{H}_2\text{O} \text{ (or Cl}_2 / \text{H}_2\text{O)}} \longrightarrow$		anti + Markovnikov addition enantiomers RR and SS
	$\xrightarrow{\text{Br}_2 / \text{H}_2\text{O} \text{ (or Cl}_2 / \text{H}_2\text{O)}} \longrightarrow$		anti + Markovnikov addition enantiomers RR and SS

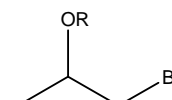
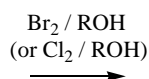
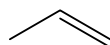


anti + Markovnikov  
addition  
  
achiral

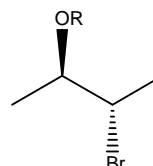
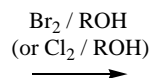
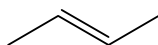


anti + Markovnikov  
addition  
  
diastereomers  
SRR and SSS

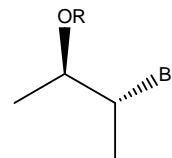
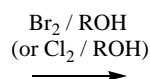
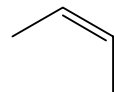
f. Alkenes with  $\text{Br}_2/\text{ROH}$  or  $\text{Cl}_2/\text{ROH}$ . Synthesis of bromo or chloro "ethers".



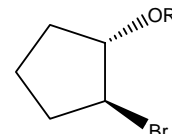
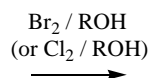
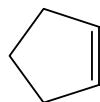
anti + Markovnikov  
addition  
  
enantiomers  
R and S



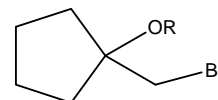
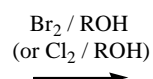
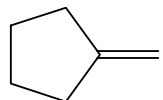
anti + Markovnikov  
addition  
  
enantiomers  
RS and SR



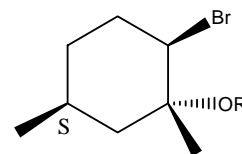
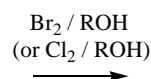
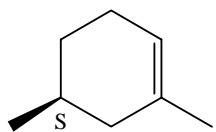
anti + Markovnikov  
addition  
  
enantiomers  
RR and SS



anti + Markovnikov  
addition  
  
enantiomers  
RR and SS

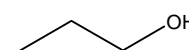
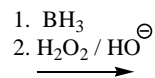
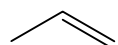


anti + Markovnikov  
addition  
  
achiral

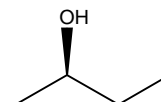
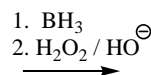
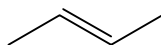


anti + Markovnikov  
addition  
  
diastereomers  
SRR and SSS

g. Alkenes with 1.  $\text{BH}_3$  2.  $\text{H}_2\text{O}_2/\text{HO}^-$ . Hydroboration/oxidation = anti-Markovnikov alcohols.

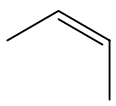
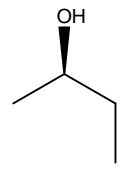
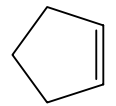
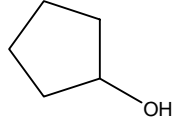
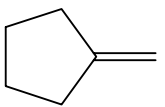
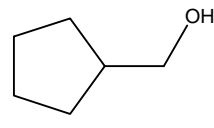
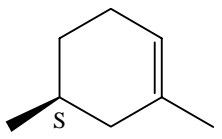
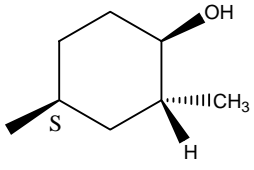


1. syn addition  
2. oxidation  
  
achiral

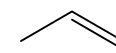
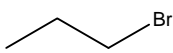
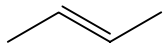
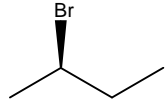
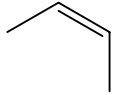
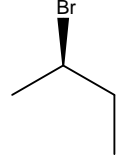
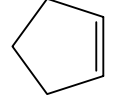
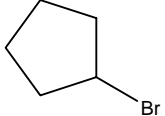
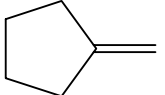
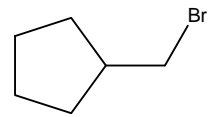


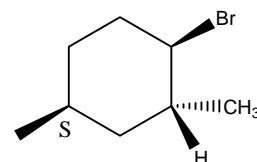
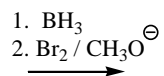
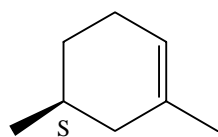
1. syn addition  
2. oxidation  
  
enantiomers  
R and S



	$\begin{array}{l} 1. \text{BH}_3 \\ 2. \text{H}_2\text{O}_2 / \text{HO}^\ominus \end{array} \longrightarrow$		<ol style="list-style-type: none"> <li>syn addition</li> <li>oxidation</li> </ol> <p>enantiomers R and S</p>
	$\begin{array}{l} 1. \text{BH}_3 \\ 2. \text{H}_2\text{O}_2 / \text{HO}^\ominus \end{array} \longrightarrow$		<ol style="list-style-type: none"> <li>syn addition</li> <li>oxidation</li> </ol> <p>achiral</p>
	$\begin{array}{l} 1. \text{BH}_3 \\ 2. \text{H}_2\text{O}_2 / \text{HO}^\ominus \end{array} \longrightarrow$		<ol style="list-style-type: none"> <li>syn addition</li> <li>oxidation</li> </ol> <p>achiral</p>
	$\begin{array}{l} 1. \text{BH}_3 \\ 2. \text{H}_2\text{O}_2 / \text{HO}^\ominus \end{array} \longrightarrow$		<ol style="list-style-type: none"> <li>syn addition</li> <li>oxidation</li> </ol> <p>diastereomers SRR and SSS</p>

### h. Alkenes with 1. $\text{BH}_3$ 2. $\text{Br}_2/\text{CH}_3\text{O}^\ominus$ . Hydroboration/bromination = anti-Markovnikov R-Br.

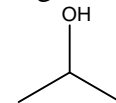
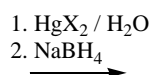
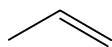
	$\begin{array}{l} 1. \text{BH}_3 \\ 2. \text{Br}_2 / \text{CH}_3\text{O}^\ominus \end{array} \longrightarrow$		<ol style="list-style-type: none"> <li>syn addition</li> <li>bromination</li> </ol> <p>achiral</p>
	$\begin{array}{l} 1. \text{BH}_3 \\ 2. \text{Br}_2 / \text{CH}_3\text{O}^\ominus \end{array} \longrightarrow$		<ol style="list-style-type: none"> <li>syn addition</li> <li>bromination</li> </ol> <p>enantiomers R and S</p>
	$\begin{array}{l} 1. \text{BH}_3 \\ 2. \text{Br}_2 / \text{CH}_3\text{O}^\ominus \end{array} \longrightarrow$		<ol style="list-style-type: none"> <li>syn addition</li> <li>bromination</li> </ol> <p>enantiomers R and S</p>
	$\begin{array}{l} 1. \text{BH}_3 \\ 2. \text{Br}_2 / \text{CH}_3\text{O}^\ominus \end{array} \longrightarrow$		<ol style="list-style-type: none"> <li>syn addition</li> <li>bromination</li> </ol> <p>achiral</p>
	$\begin{array}{l} 1. \text{BH}_3 \\ 2. \text{Br}_2 / \text{CH}_3\text{O}^\ominus \end{array} \longrightarrow$		<ol style="list-style-type: none"> <li>syn addition</li> <li>bromination</li> </ol> <p>achiral</p>



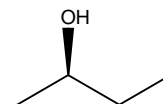
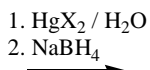
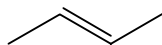
1. syn addition  
2. bromination

diastereomers  
SRR and SSS

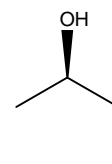
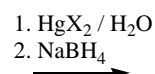
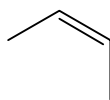
i. Alkenes with 1.  $\text{HgX}_2 / \text{H}_2\text{O}$  2.  $\text{NaBH}_4$ . Alcohol synthesis with minimal rearrangements (Markovnikov).



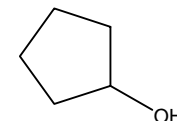
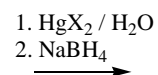
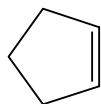
achiral



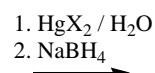
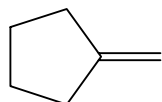
enantiomers  
R and S



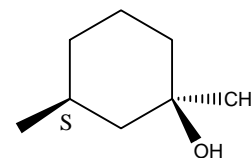
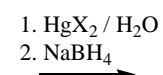
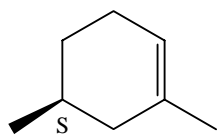
enantiomers  
R and S



achiral

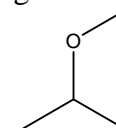
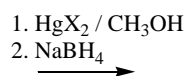
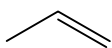


achiral

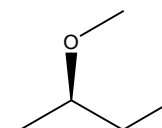
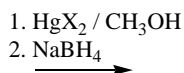
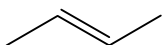


diastereomers  
SR and SS

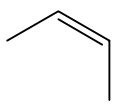
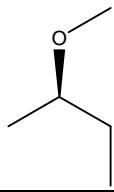
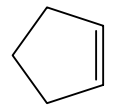
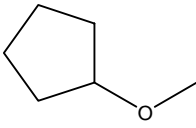
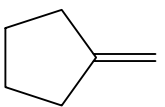
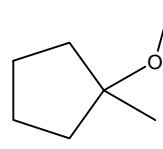
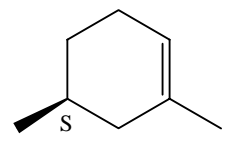
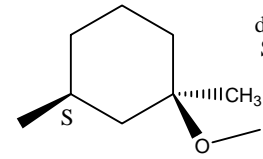
j. Alkenes with 1.  $\text{HgX}_2 / \text{ROH}$  2.  $\text{NaBH}_4$ . Ether synthesis with minimal rearrangements (Markovnikov).



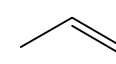
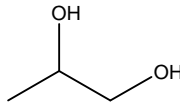
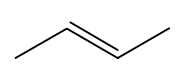
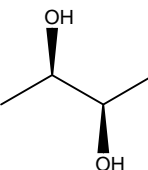
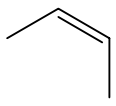
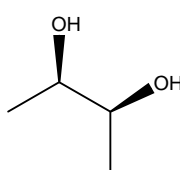
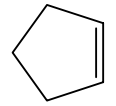
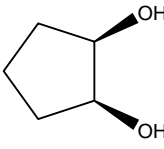
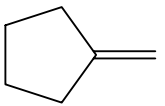
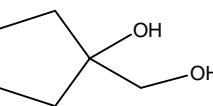
achiral

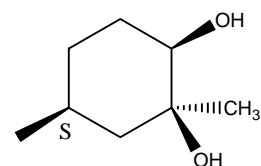
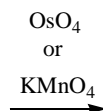
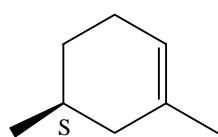


enantiomers  
R and S

	1. $\text{HgX}_2 / \text{CH}_3\text{OH}$ 2. $\text{NaBH}_4$ $\longrightarrow$		enantiomers R and S
	1. $\text{HgX}_2 / \text{CH}_3\text{OH}$ 2. $\text{NaBH}_4$ $\longrightarrow$		achiral
	1. $\text{HgX}_2 / \text{CH}_3\text{OH}$ 2. $\text{NaBH}_4$ $\longrightarrow$		achiral
	1. $\text{HgX}_2 / \text{CH}_3\text{OH}$ 2. $\text{NaBH}_4$ $\longrightarrow$		diastereomers SR and SS

k. Alkenes with  $\text{OsO}_4$  or  $\text{KMnO}_4$ . "Syn" synthesis of vicinal diols.

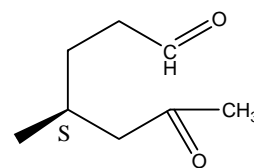
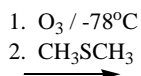
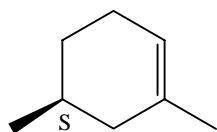
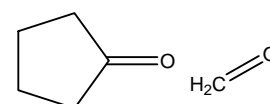
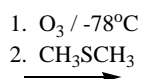
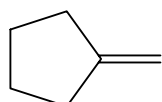
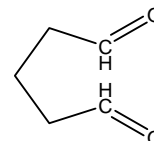
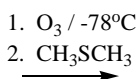
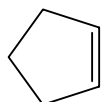
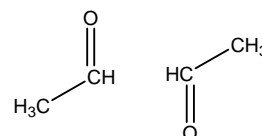
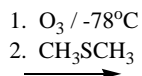
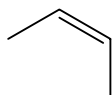
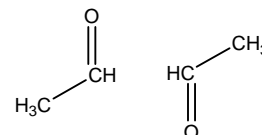
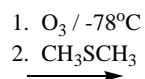
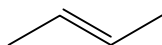
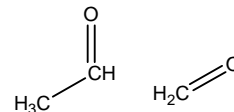
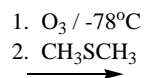
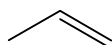
	$\text{OsO}_4$ or $\text{KMnO}_4$ $\longrightarrow$		syn addition enantiomers R and S
	$\text{OsO}_4$ or $\text{KMnO}_4$ $\longrightarrow$		syn addition enantiomers RR and SS
	$\text{OsO}_4$ or $\text{KMnO}_4$ $\longrightarrow$		syn addition meso RS and SR
	$\text{OsO}_4$ or $\text{KMnO}_4$ $\longrightarrow$		syn addition meso RS and SR
	$\text{OsO}_4$ or $\text{KMnO}_4$ $\longrightarrow$		syn addition achiral



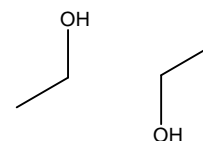
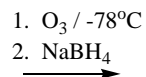
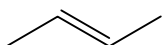
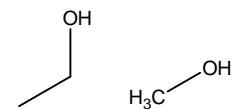
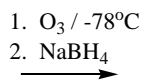
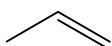
syn addition

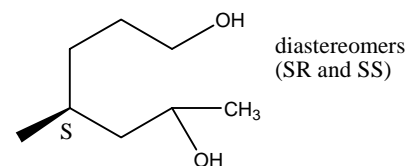
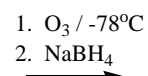
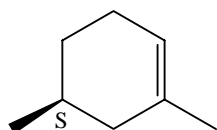
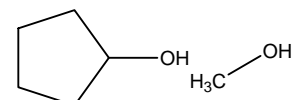
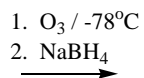
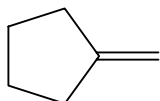
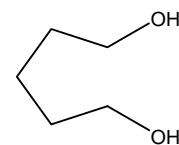
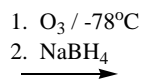
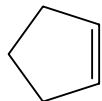
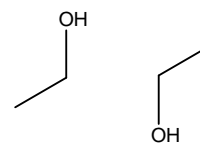
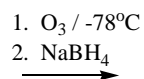
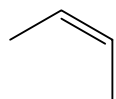
diastereomers  
SSR and SRS

l. Alkenes with 1.  $\text{O}_3 / -78^\circ\text{C}$  2.  $\text{CH}_3\text{SCH}_3$  or  $\text{Zn}$ . Synthesis of aldehydes or ketones.

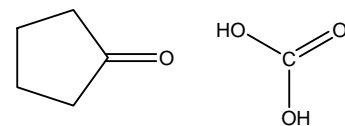
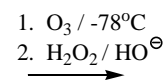
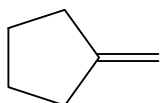
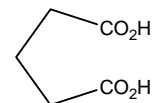
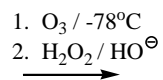
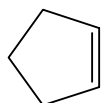
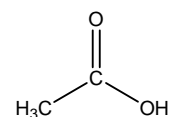
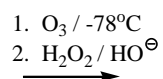
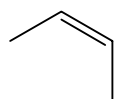
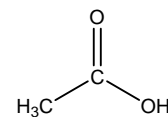
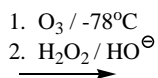
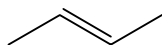
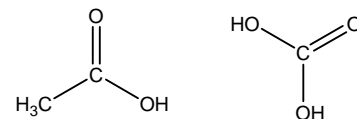
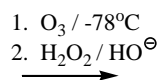
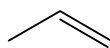


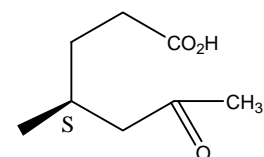
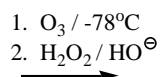
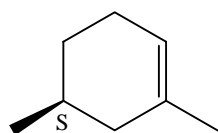
m. Alkenes with 1.  $\text{O}_3 / -78^\circ\text{C}$  2.  $\text{NaBH}_4$ . Synthesis of alcohols.



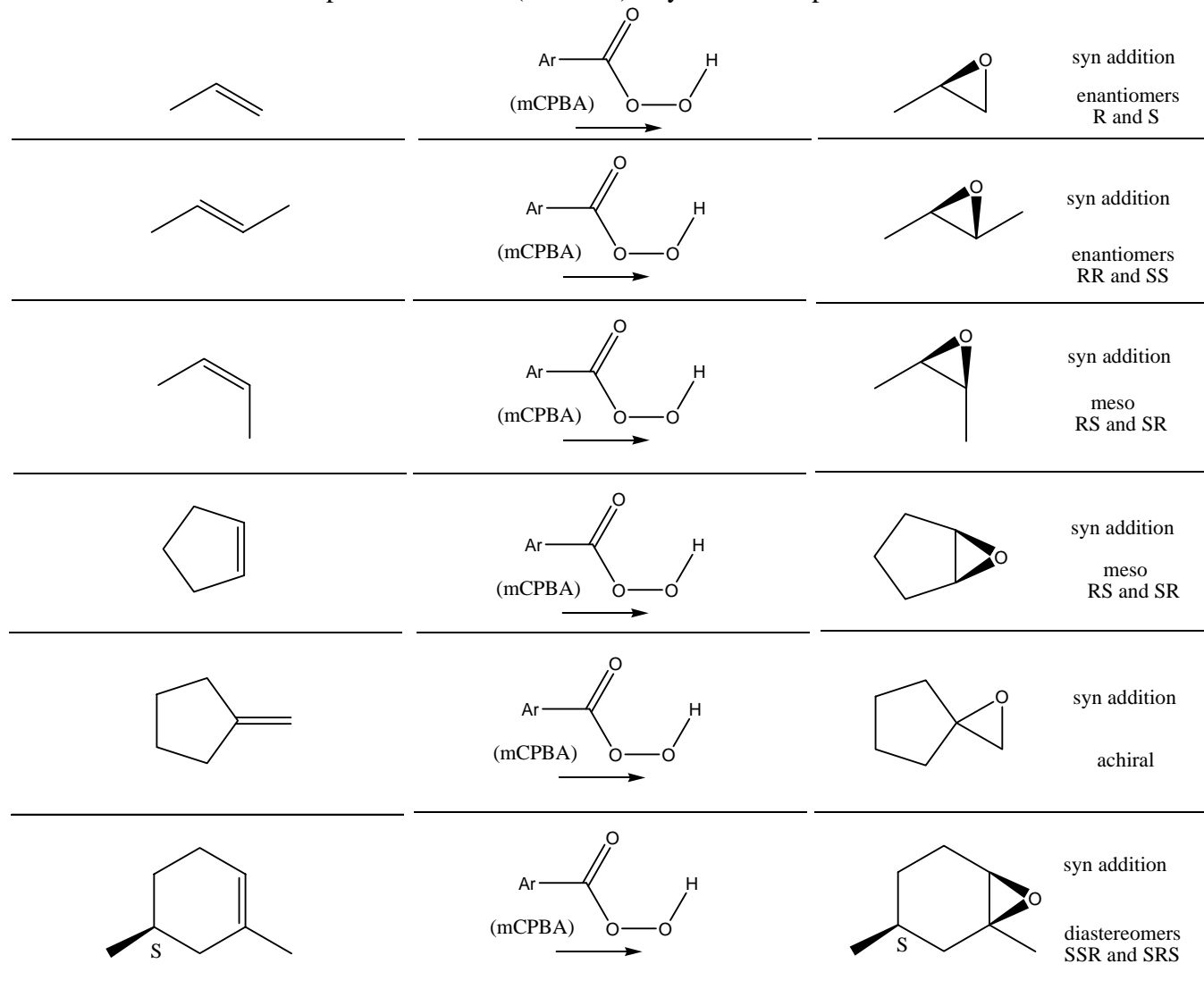


n. Alkenes with 1.  $O_3 / -78^\circ C$  2.  $H_2O_2 / HO^\ominus$ . Synthesis of carboxylic acids or ketones.

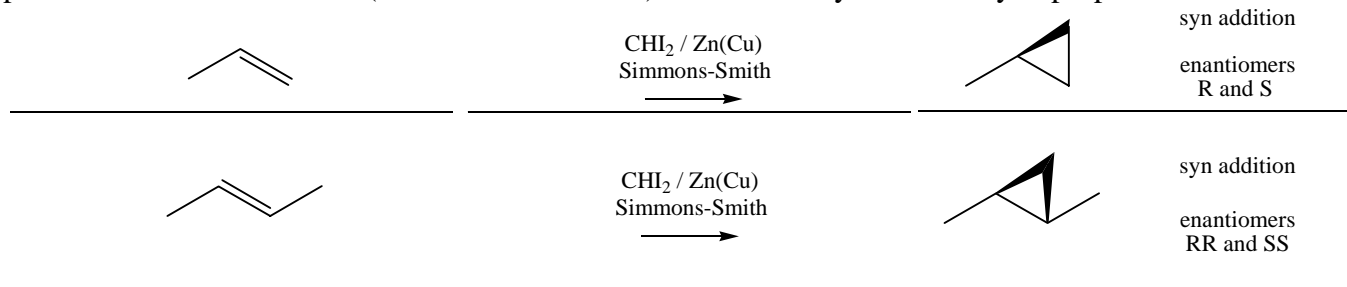


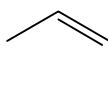

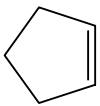
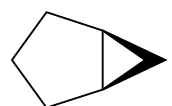
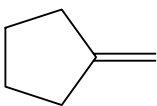

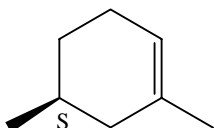
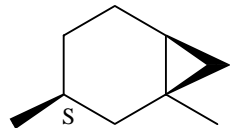


o. Alkenes with meta chloroperbenzoic acid (mCPBA). Synthesis of epoxides.

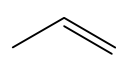
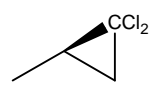
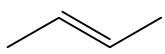
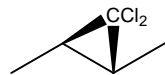
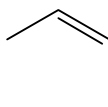
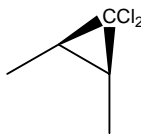
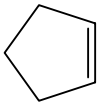
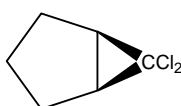
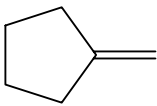
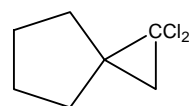


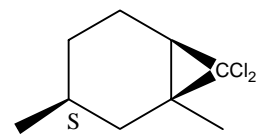
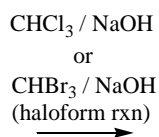
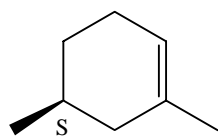
p. Alkenes with  $\text{CH}_2\text{I}_2 / \text{Zn}$  (Simmons-Smith Rxn). Carbenoid synthesis of cyclopropanes.



	$\text{CHI}_2 / \text{Zn}(\text{Cu})$ Simmons-Smith $\longrightarrow$		syn addition meso RS and SR
	$\text{CHI}_2 / \text{Zn}(\text{Cu})$ Simmons-Smith $\longrightarrow$		syn addition meso RS and SR
	$\text{CHI}_2 / \text{Zn}(\text{Cu})$ Simmons-Smith $\longrightarrow$		syn addition achiral
	$\text{CHI}_2 / \text{Zn}(\text{Cu})$ Simmons-Smith $\longrightarrow$		syn addition diastereomers SSR and SRS

q. Alkenes with  $\text{CHCl}_3 / \text{RO}^-$  or  $\text{CHBr}_3 / \text{RO}^-$ . Carbene synthesis of dihalocyclopropanes.

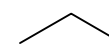
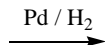
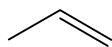
	$\text{CHCl}_3 / \text{NaOH}$ or $\text{CHBr}_3 / \text{NaOH}$ $\longrightarrow$		syn addition enantiomers R and S
	$\text{CHCl}_3 / \text{NaOH}$ or $\text{CHBr}_3 / \text{NaOH}$ $\longrightarrow$		syn addition enantiomers RR and SS
	$\text{CHCl}_3 / \text{NaOH}$ or $\text{CHBr}_3 / \text{NaOH}$ $\longrightarrow$		syn addition meso RS and SR
	$\text{CHCl}_3 / \text{NaOH}$ or $\text{CHBr}_3 / \text{NaOH}$ $\longrightarrow$		syn addition meso RS and SR
	$\text{CHCl}_3 / \text{NaOH}$ or $\text{CHBr}_3 / \text{NaOH}$ $\longrightarrow$		syn addition achiral



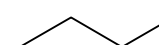
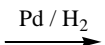
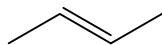
syn addition  
diastereomers  
SSR and SRS

r.

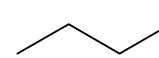
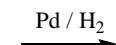
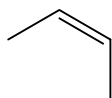
Alkenes with Pd / H<sub>2</sub>. Synthesis of "alkane" from "alkene" (hydrogenation).



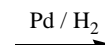
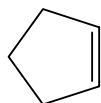
syn addition  
achiral



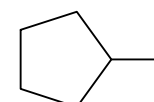
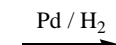
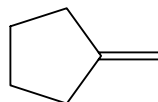
syn addition  
achiral



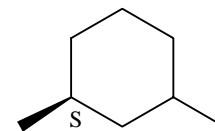
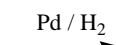
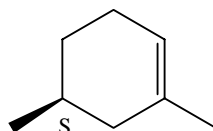
syn addition  
achiral



syn addition  
achiral

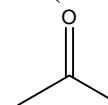
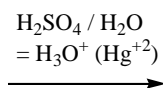


syn addition  
achiral

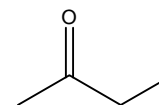
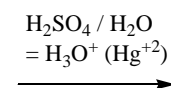


syn addition  
diastereomers  
SR and SS

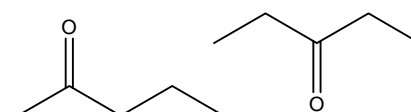
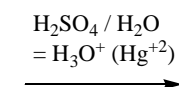
4. a. Alkynes with aqueous sulfuric acid (plus some Hg<sup>+2</sup> catalyst). Synthesis via enols (Markovnikov addition).



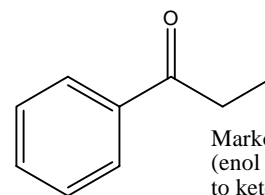
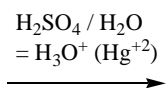
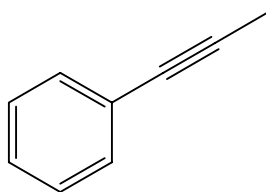
Markovnikov addition  
(enol tautomerization  
to keto)



Markovnikov addition  
(enol tautomerization  
to keto)

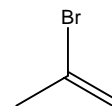
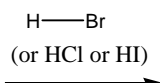




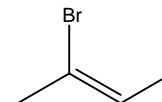
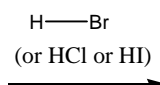


Markovnikov addition  
(enol tautomerization to keto)

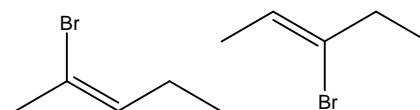
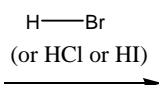
b. HX addition to alkynes. Markovnikov addition.



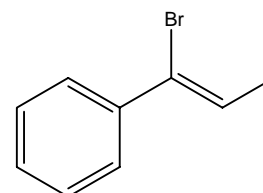
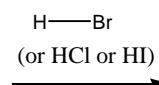
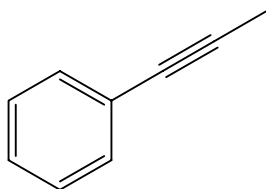
Markovnikov addition



Markovnikov addition

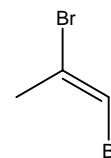
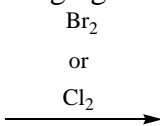


Markovnikov addition

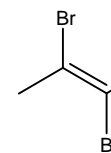
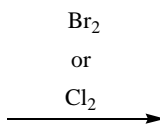


Markovnikov addition

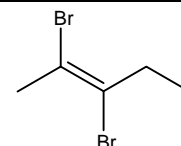
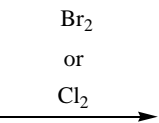
c. Bromination (or chlorination) of alkynes. Bridging bromonium ion.



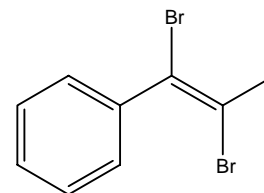
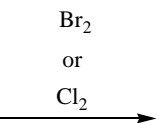
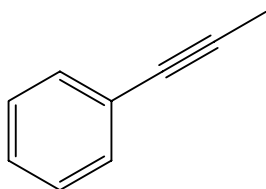
anti addition



anti addition

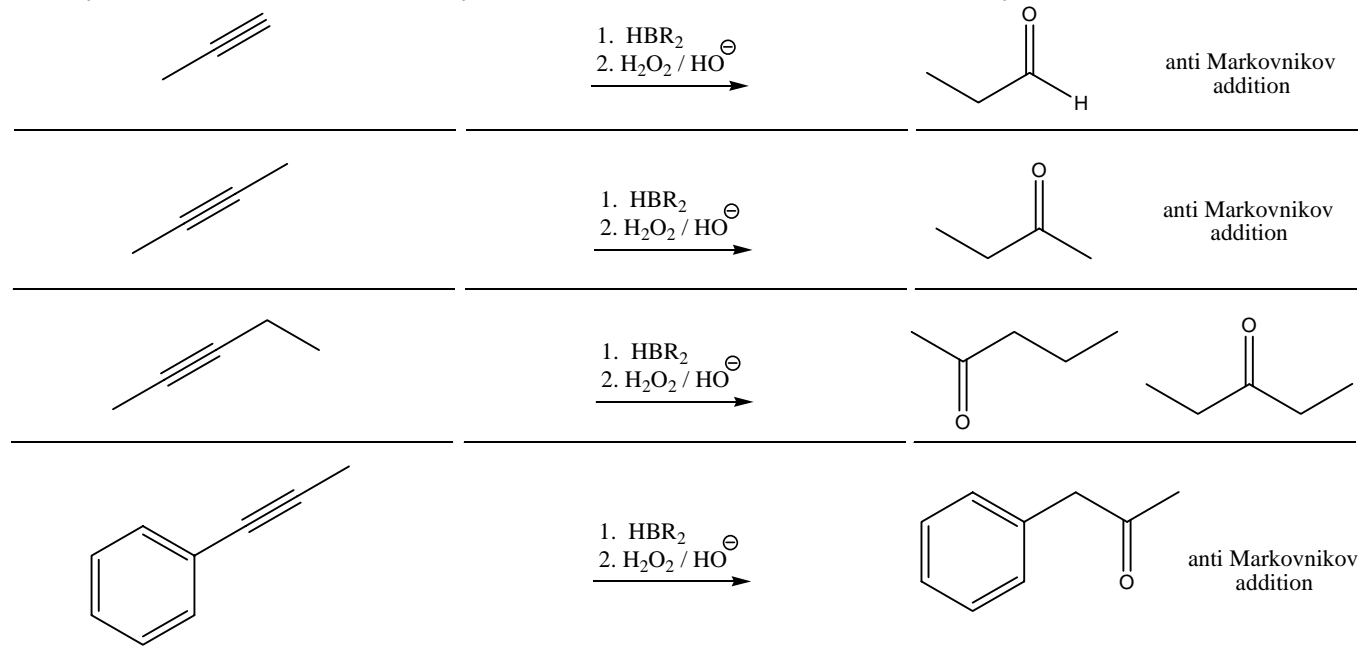


anti addition

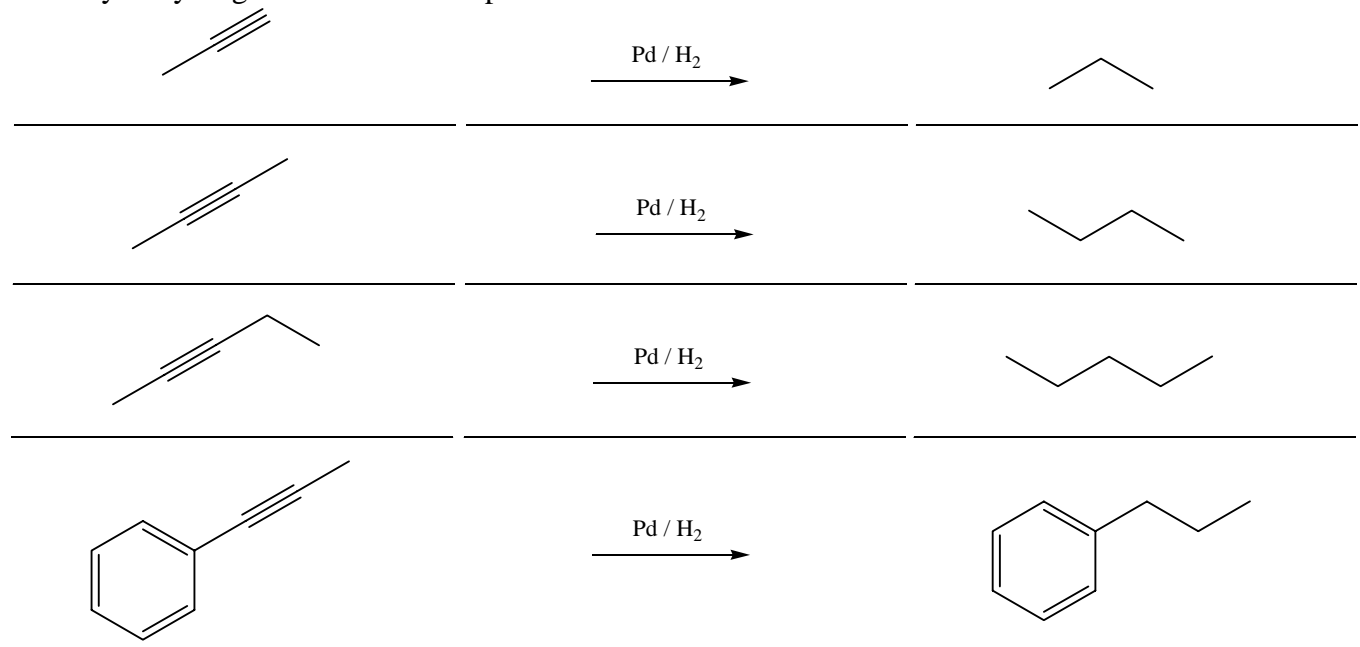


anti addition

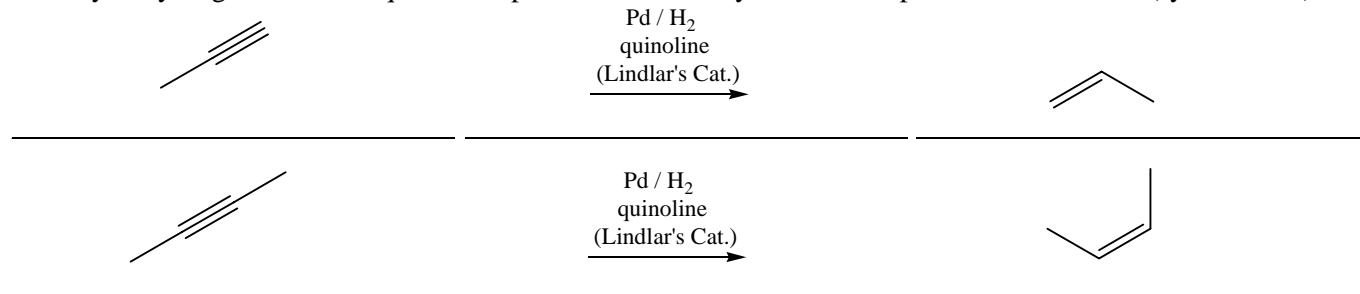
d. 1. Hydroboration 2. oxidation of alkynes (anti-Markovnikov addition makes aldehydes or ketones via enolate).

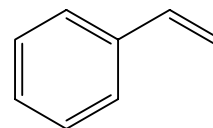
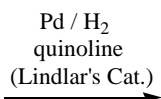
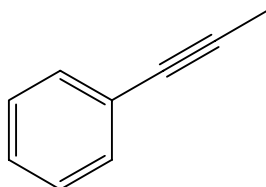
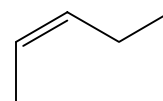
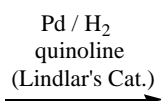


e. Catalytic hydrogenation reduces triple bond to "alkane".

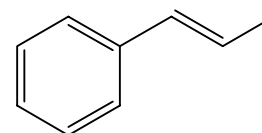
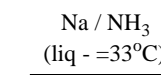
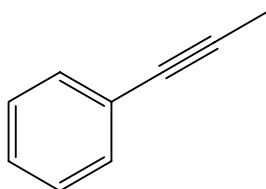
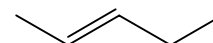
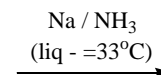
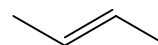
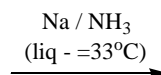
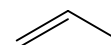
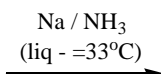


f. Catalytic hydrogenation with quinoline "poison" of Pd catalyst reduces triple bond to Z alkene (syn addition).

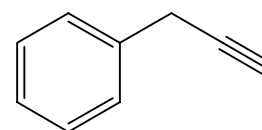
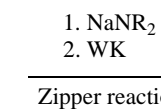
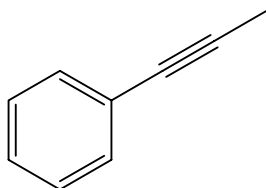
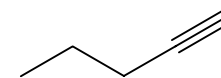
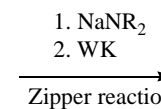
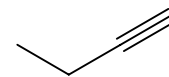
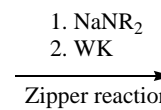
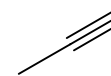
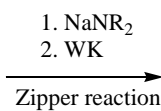




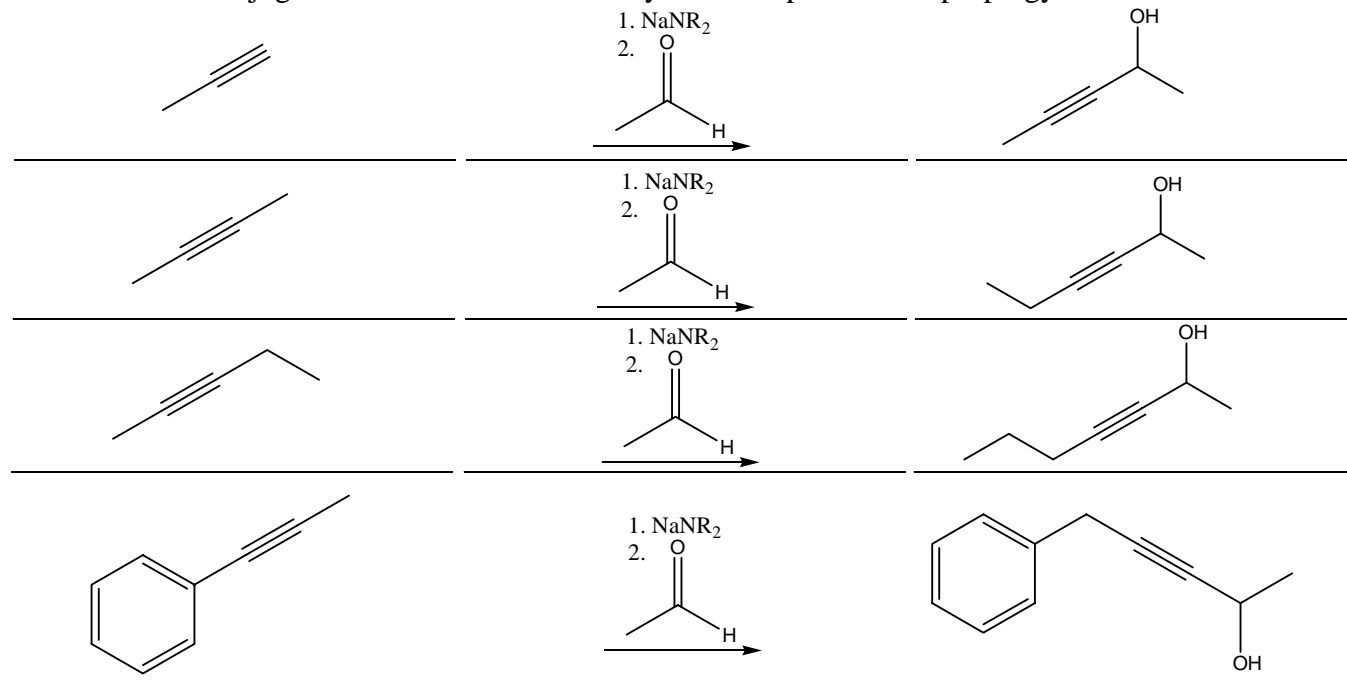
g. Sodium metal + liquid ammonia reduction of triple bond to E alkenes.



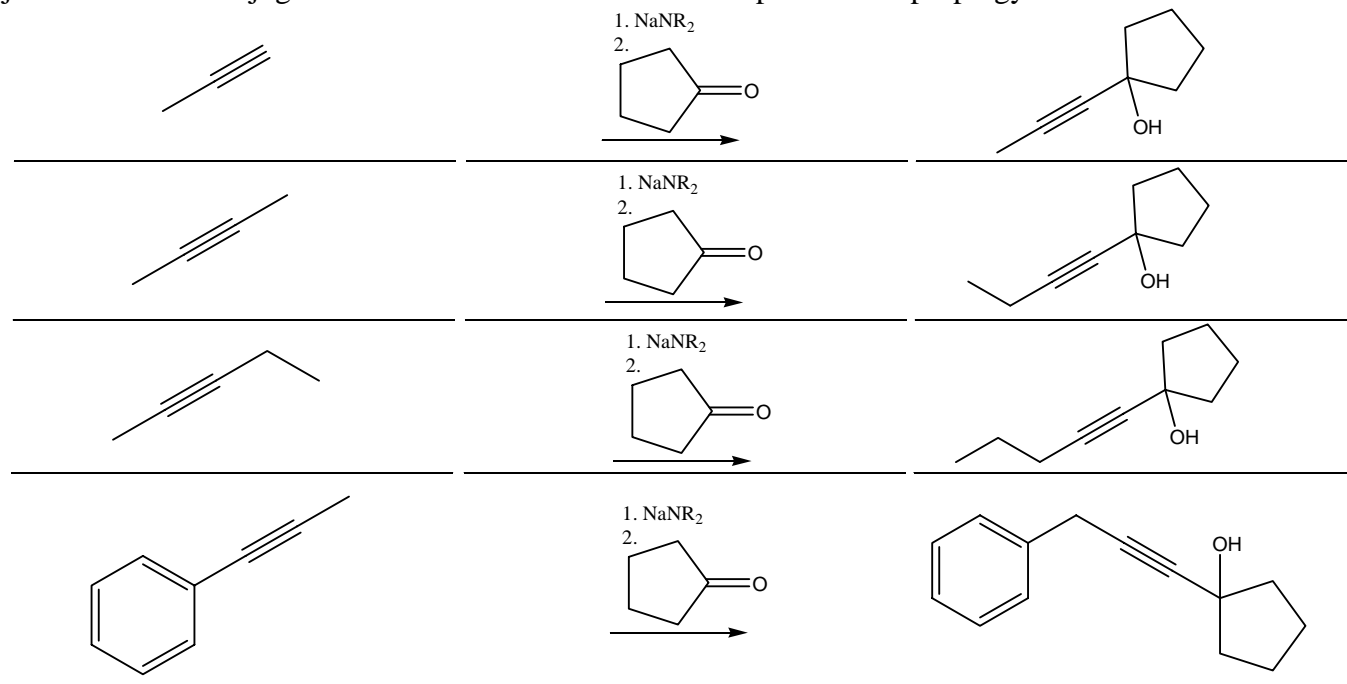
h. Zipper reaction moves triple bond to terminal position where it can be removed to form sp carbanion nucleophile.



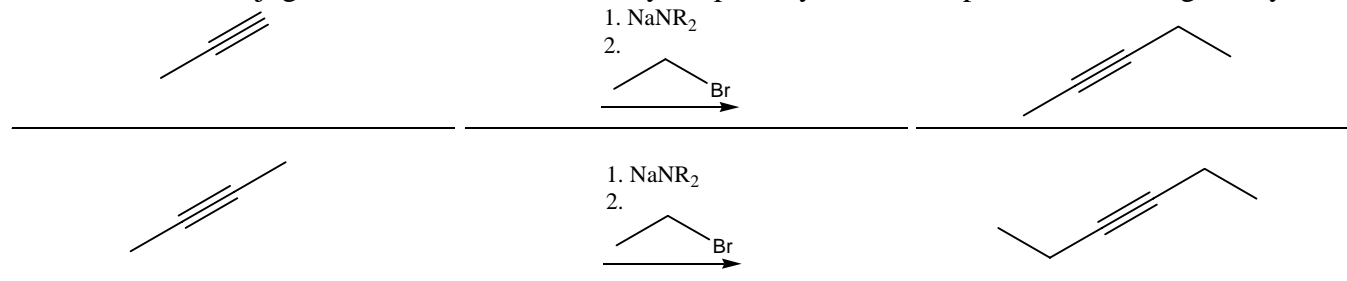
i. Formation of conjugate base + addition of aldehyde electrophile forms propargyl alcohol.

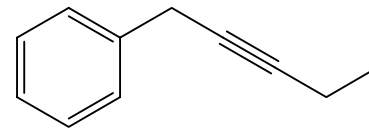
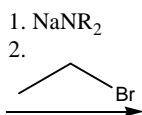
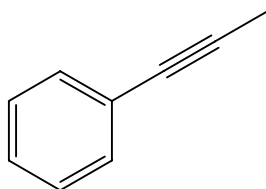
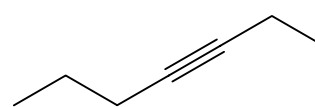
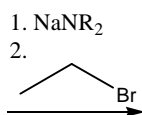


j. Formation of conjugate base + addition of ketone electrophile forms propargyl alcohol.

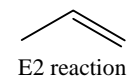
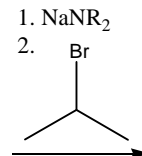
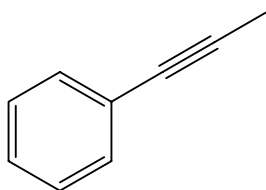
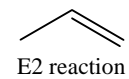
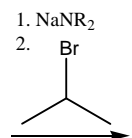
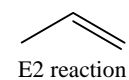
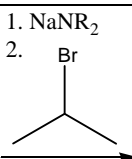
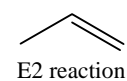
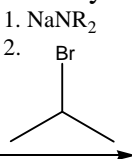
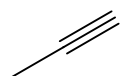


k. Formation of conjugate base + addition of methyl or primary RX electrophile forms a longer alkyne.



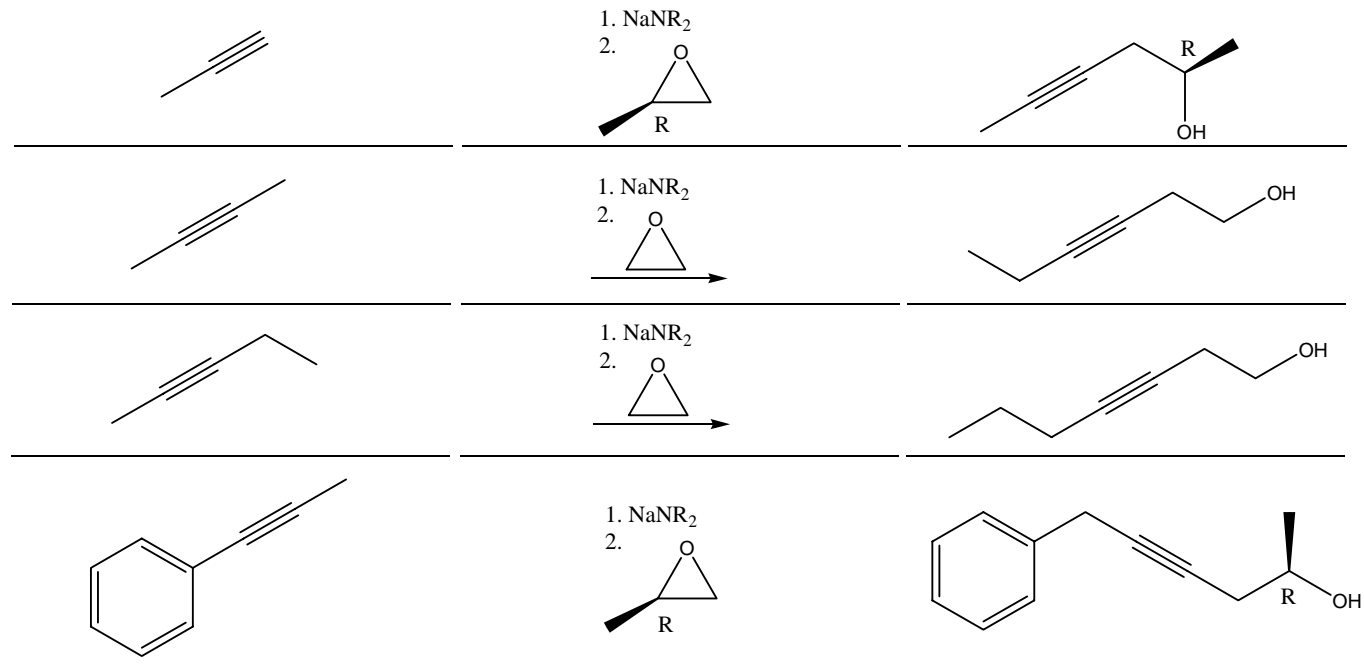


1. Formation of conjugate base + addition of secondary electrophile reacts in a nonproductive E2 reaction.

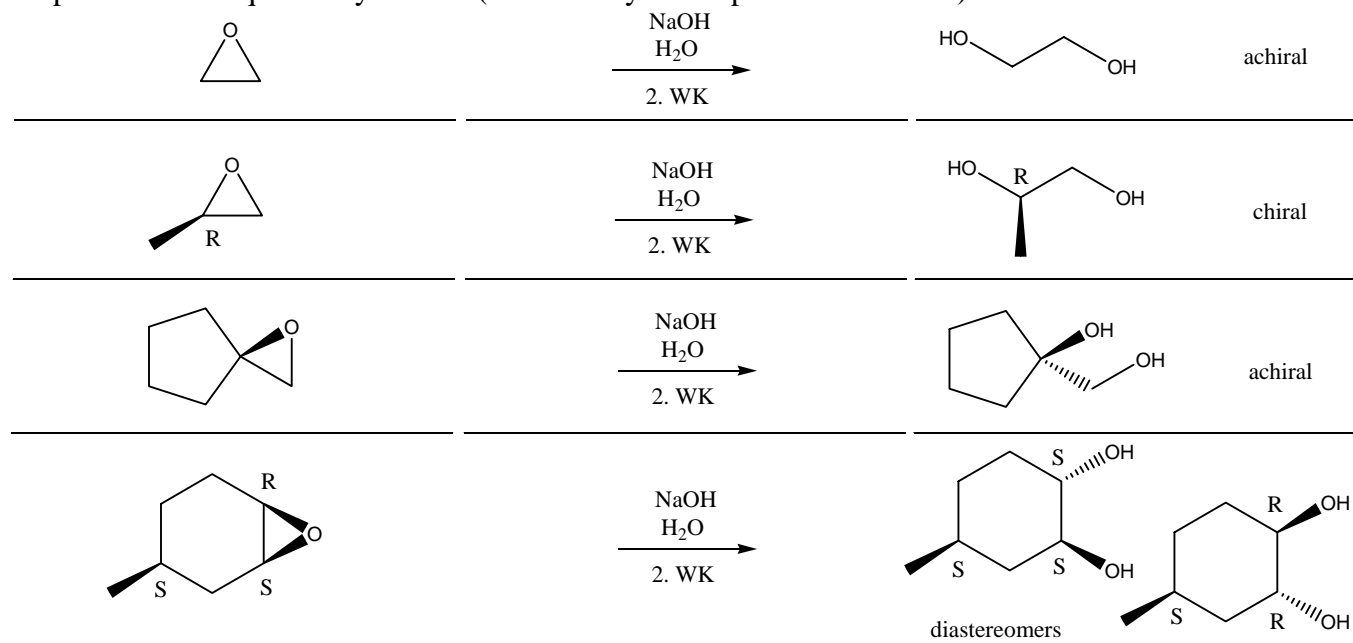


j. Formation of conjugate base + addition of epoxide electrophile forms an alkynyl alcohol via  $\text{S}_{\text{N}}2$


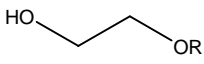
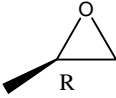
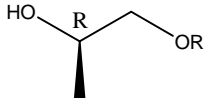
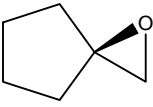
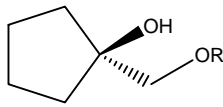
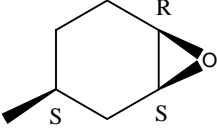
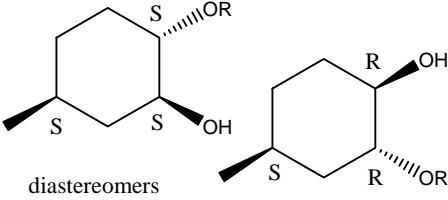
reaction.




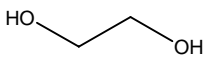
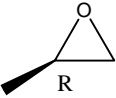
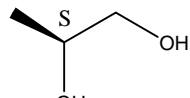
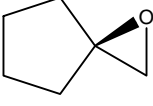
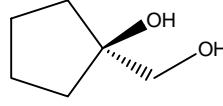
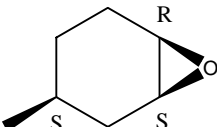
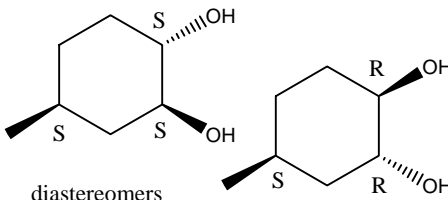
5. a. Epoxides with aqueous hydroxide (followed by workup = neutralization).




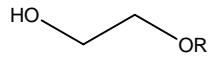
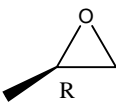
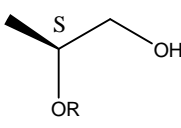
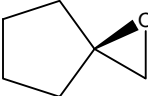

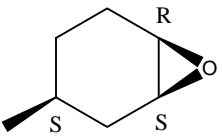
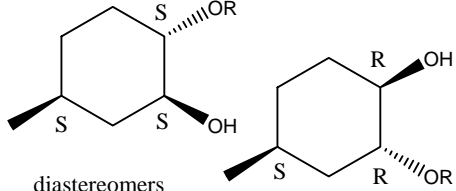

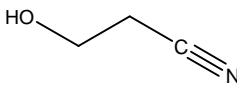
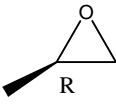
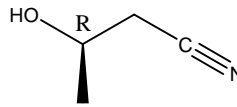
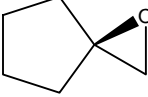
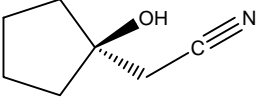
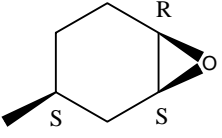
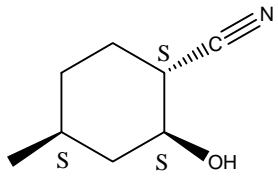
b. Epoxides with alcoholic alkoxide (followed by workup = neutralization).

	$\xrightarrow[2. \text{WK}]{\text{RO}^\ominus / \text{ROH}}$		achiral
	$\xrightarrow[2. \text{WK}]{\text{RO}^\ominus / \text{ROH}}$		chiral
	$\xrightarrow[2. \text{WK}]{\text{RO}^\ominus / \text{ROH}}$		achiral
	$\xrightarrow[2. \text{WK}]{\text{RO}^\ominus / \text{ROH}}$		diastereomers

## c. Epoxides with aqueous acid.

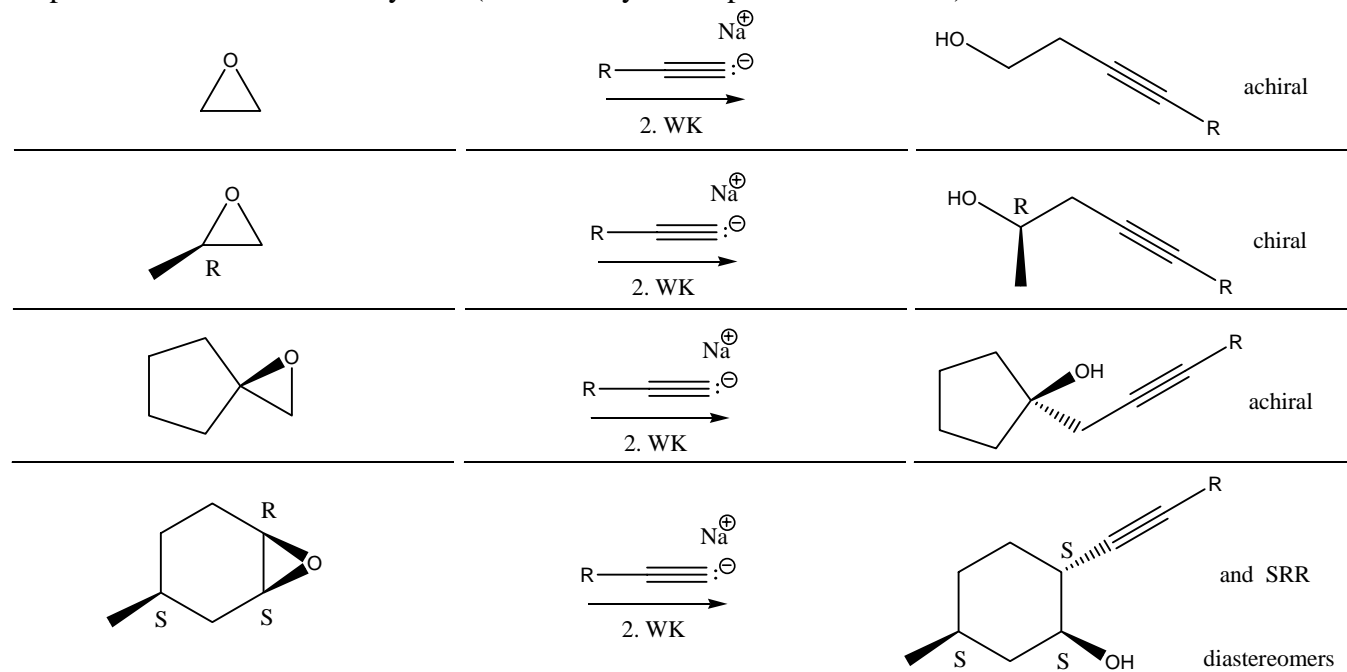
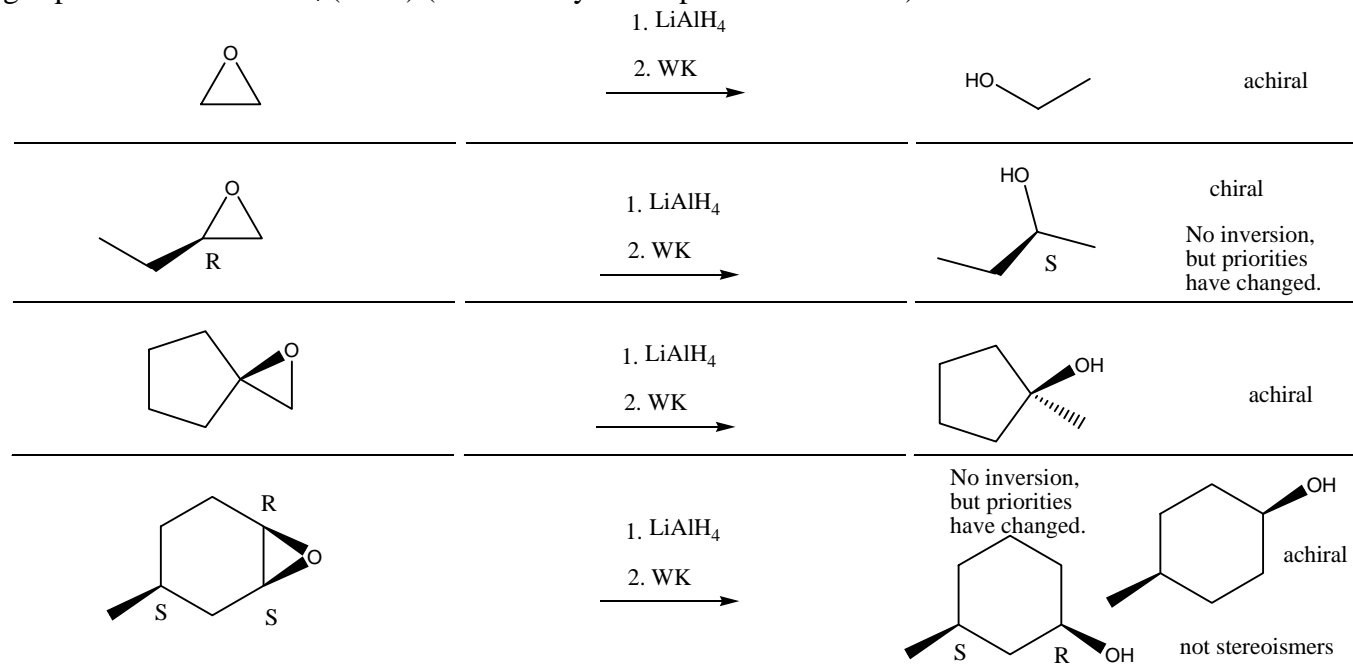
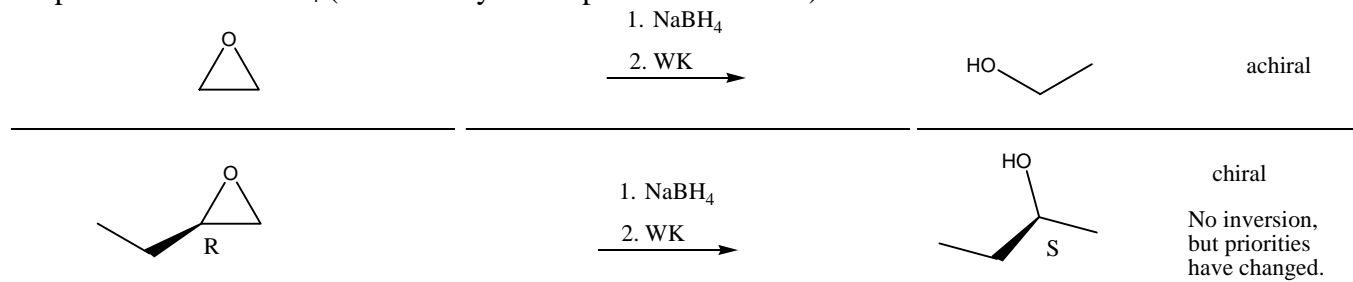
	$\xrightarrow[2. \text{WK}]{\text{H}_2\text{SO}_4 / \text{H}_2\text{O} (\text{H}_3\text{O}^+)}$		achiral
	$\xrightarrow[2. \text{WK}]{\text{H}_2\text{SO}_4 / \text{H}_2\text{O} (\text{H}_3\text{O}^+)}$		chiral (inversion)
	$\xrightarrow[2. \text{WK}]{\text{H}_2\text{SO}_4 / \text{H}_2\text{O} (\text{H}_3\text{O}^+)}$		achiral
	$\xrightarrow[2. \text{WK}]{\text{H}_2\text{SO}_4 / \text{H}_2\text{O} (\text{H}_3\text{O}^+)}$		diastereomers

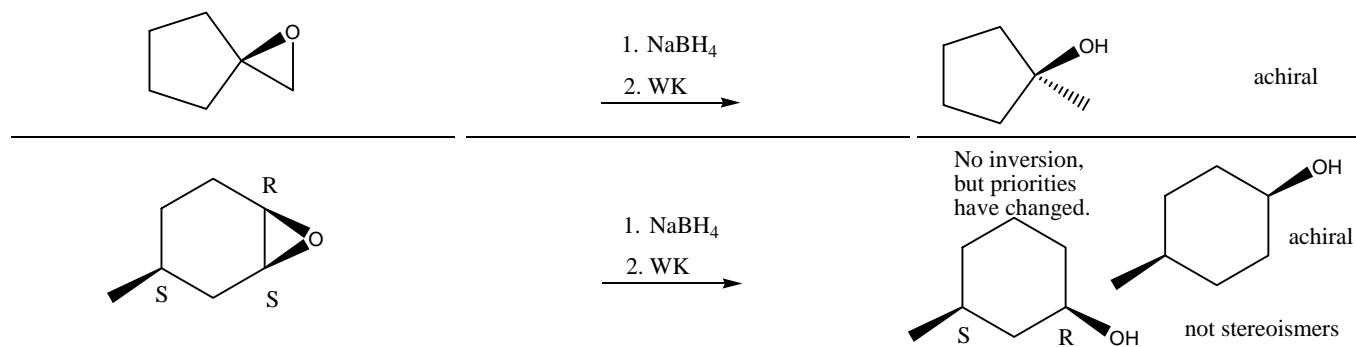
## d. Epoxides with alcoholic sulfuric acid.

	$\xrightarrow[2. \text{WK}]{\text{H}_2\text{SO}_4 / \text{ROH} \text{ (ROH}_2^+)}$		achiral
	$\xrightarrow[2. \text{WK}]{\text{H}_2\text{SO}_4 / \text{ROH} \text{ (ROH}_2^+)}$		chiral (inversion)
	$\xrightarrow[2. \text{WK}]{\text{H}_2\text{SO}_4 / \text{ROH} \text{ (ROH}_2^+)}$		achiral
	$\xrightarrow[2. \text{WK}]{\text{H}_2\text{SO}_4 / \text{ROH} \text{ (ROH}_2^+)}$		diastereomers
e. Epoxides with cyanide (followed by workup = neutralization)..			
	$\xrightarrow[2. \text{WK}]{\text{NaCN} \text{ DMSO}}$		achiral
	$\xrightarrow[2. \text{WK}]{\text{NaCN} \text{ DMSO}}$		chiral
	$\xrightarrow[2. \text{WK}]{\text{NaCN} \text{ DMSO}}$		achiral
	$\xrightarrow[2. \text{WK}]{\text{NaCN} \text{ DMSO}}$		and SRR diastereomers

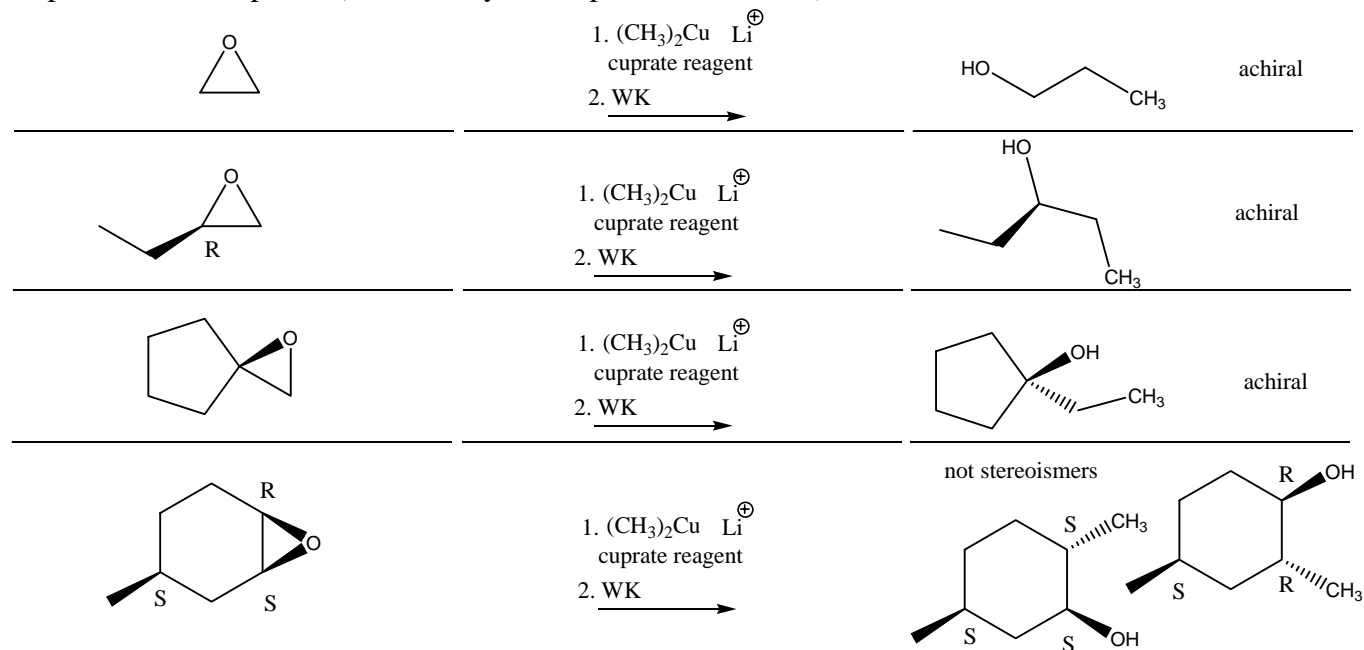


## f. Epoxides with terminal acetylides (followed by workup = neutralization).

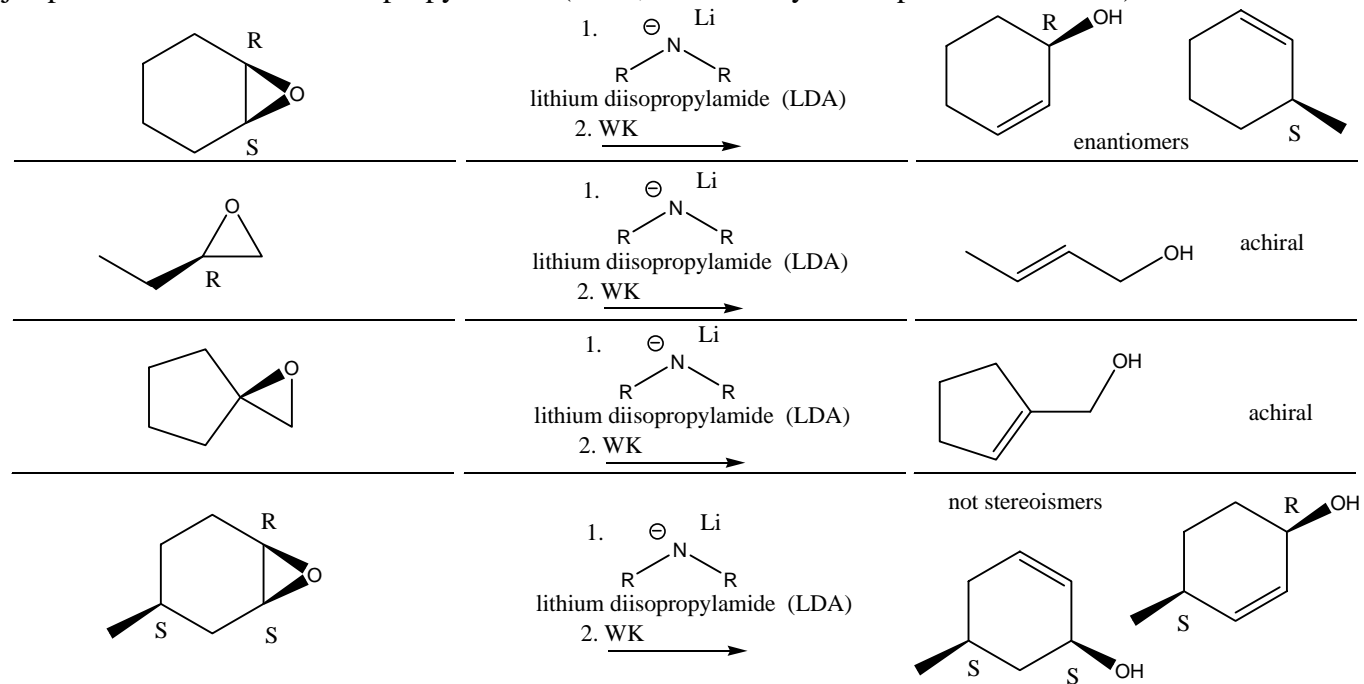
g. Epoxides with LiAlH<sub>4</sub> (LAH) (followed by workup = neutralization).h. Epoxides with NaBH<sub>4</sub> (followed by workup = neutralization).



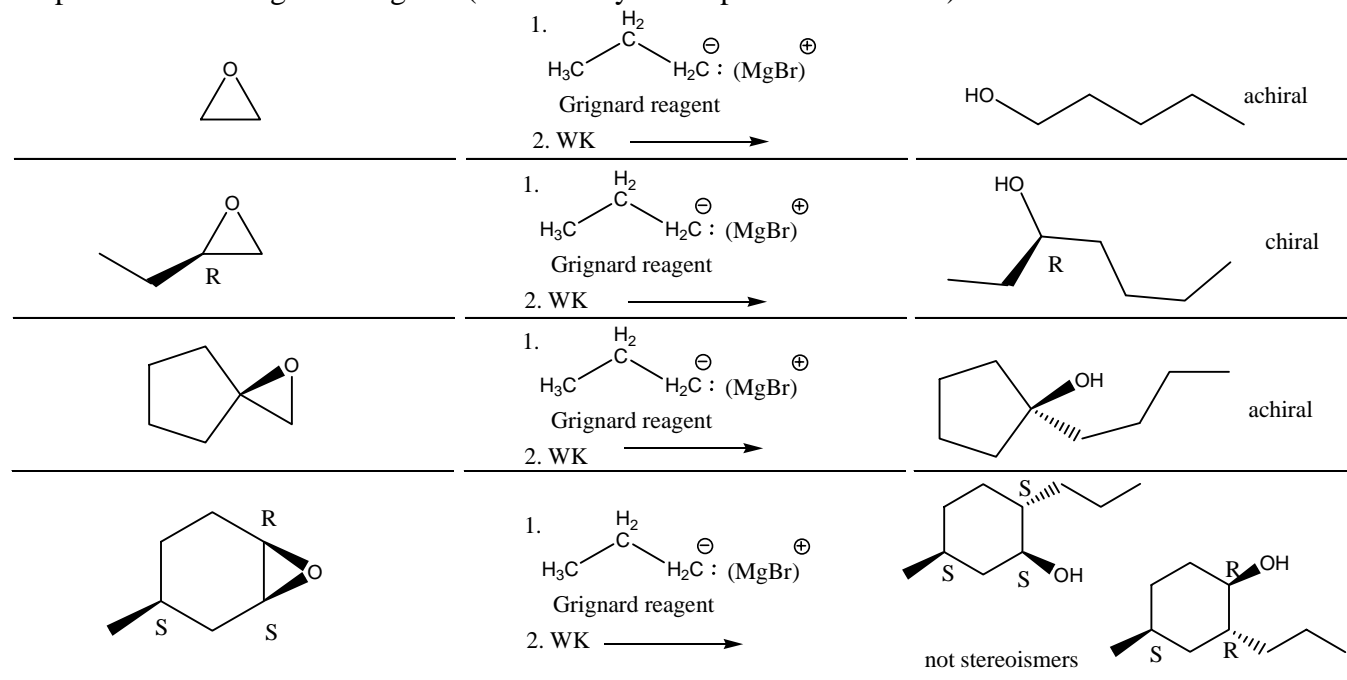
## i. Epoxides with cuprates (followed by workup = neutralization).



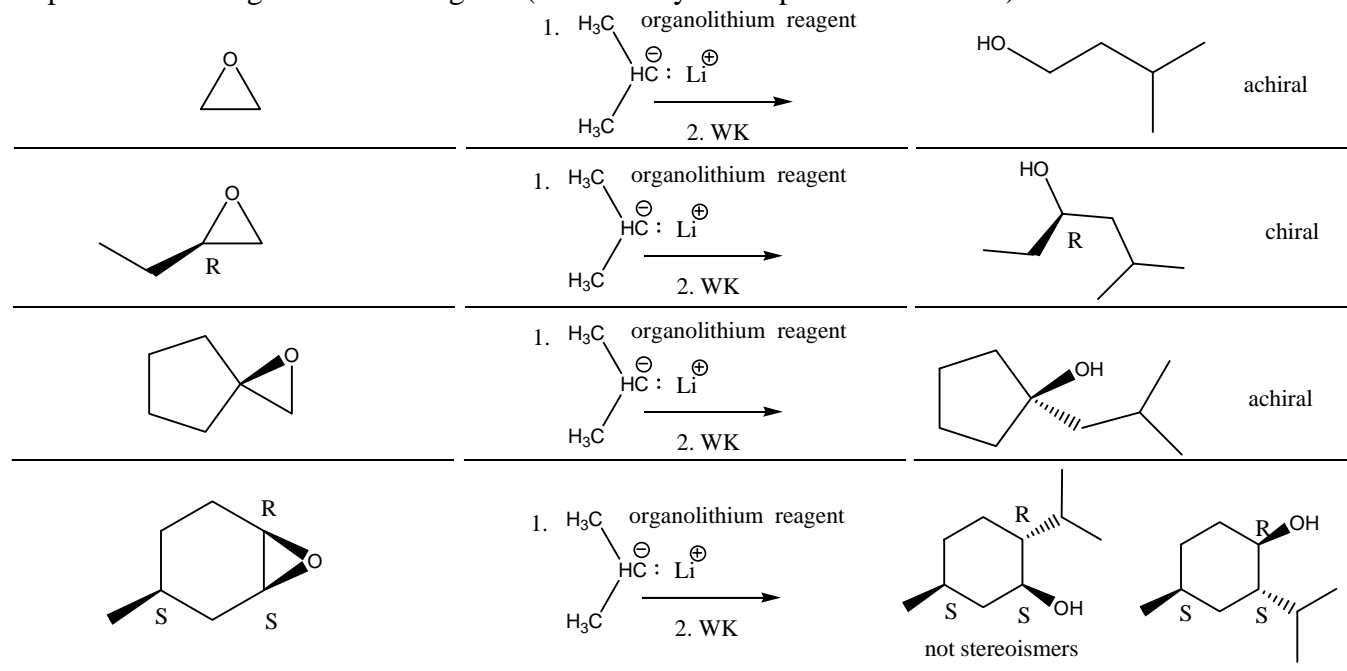
## j. Epoxides with lithium diisopropyl amide (LDA, followed by workup = neutralization).



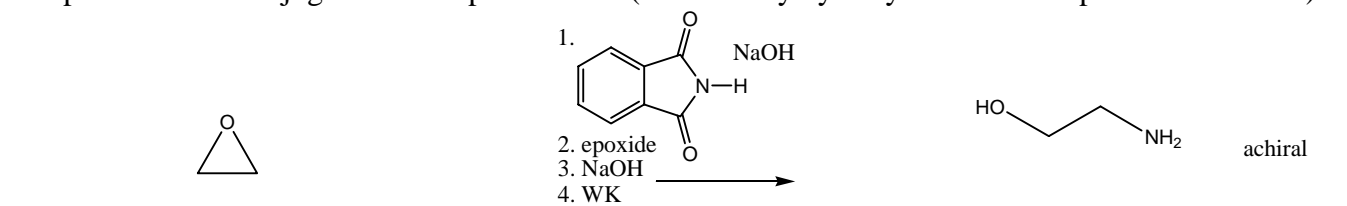
## k. Epoxides with Grignard reagents (followed by workup = neutralization).

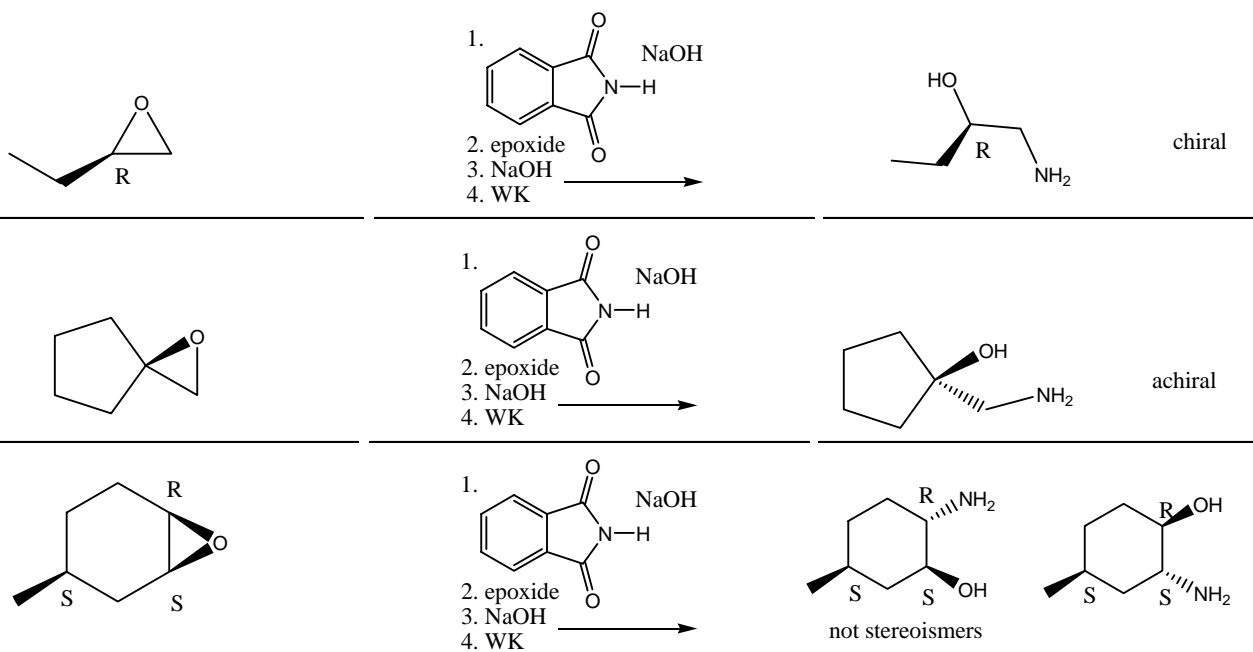


## l. Epoxides with organolithium reagents (followed by workup = neutralization).

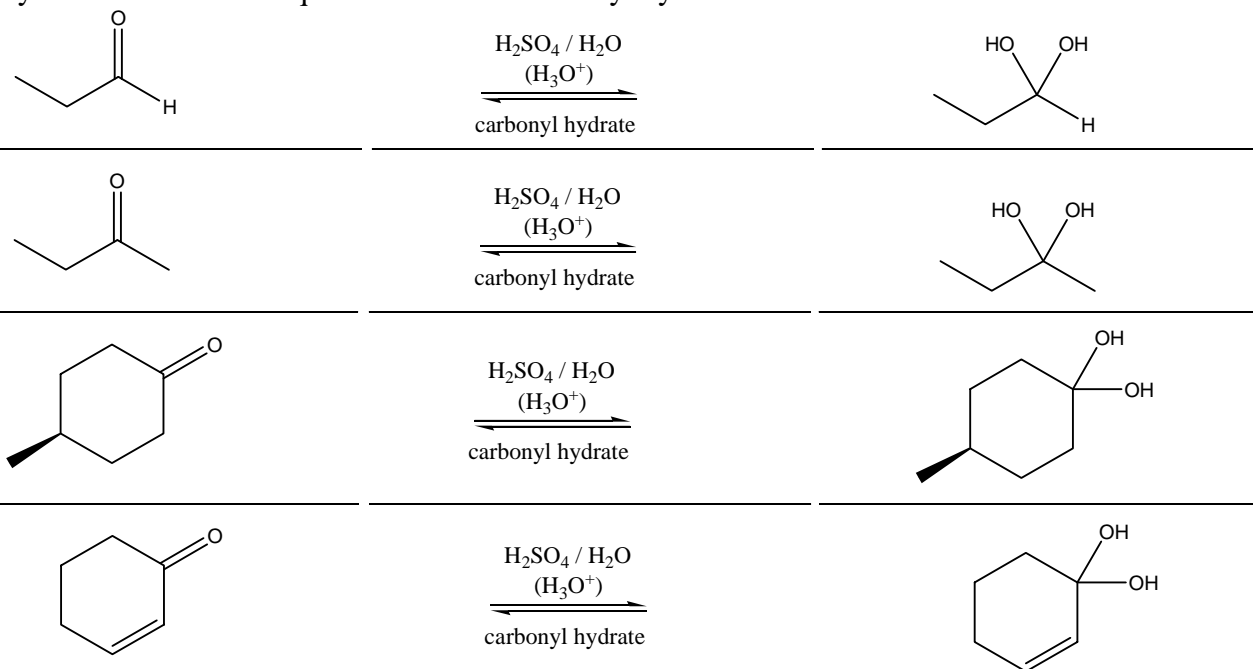


## m. Epoxides with conjugate base of phthalimide (followed by hydrolysis and workup = neutralization).

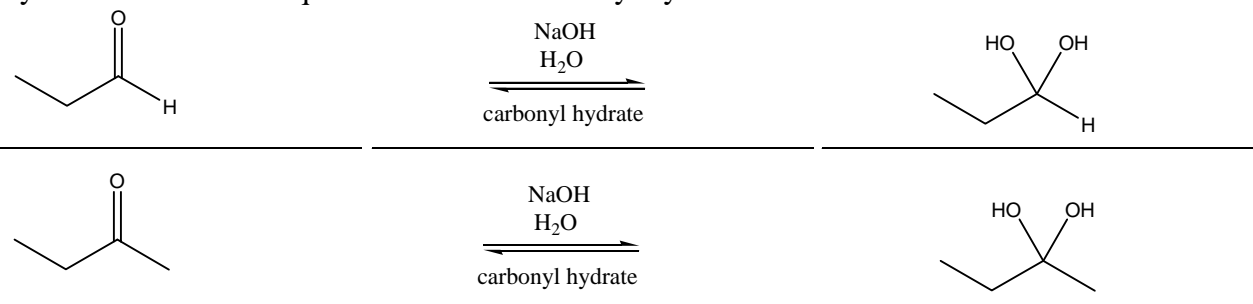


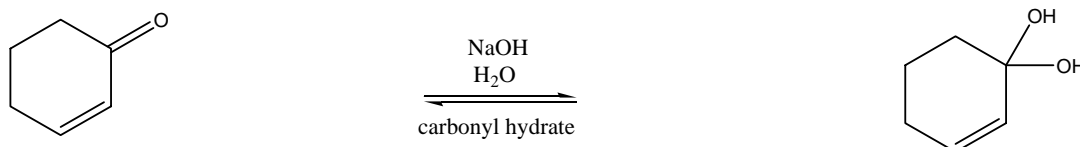
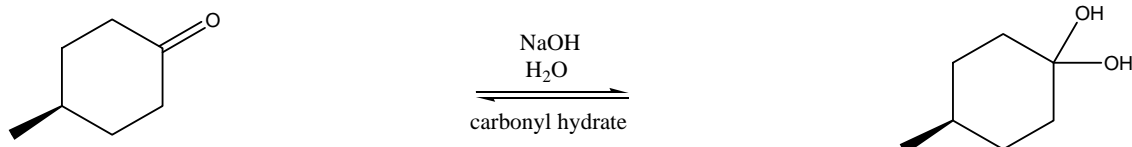


## 6. a. Aldehydes and ketones in aqueous acid form carbonyl hydrates.

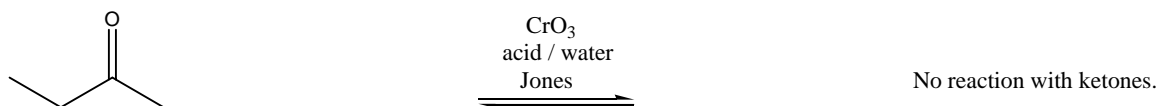
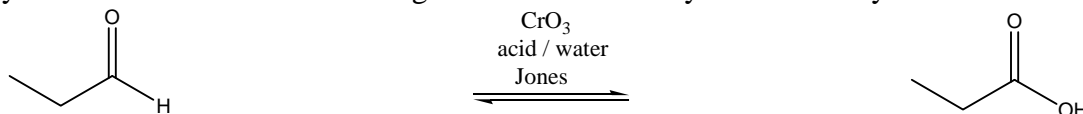


## b. Aldehydes and ketones in aqueous base form carbonyl hydrates.

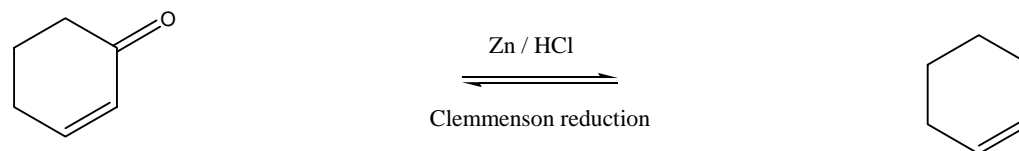
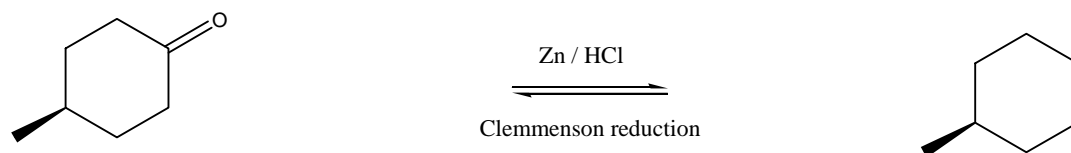
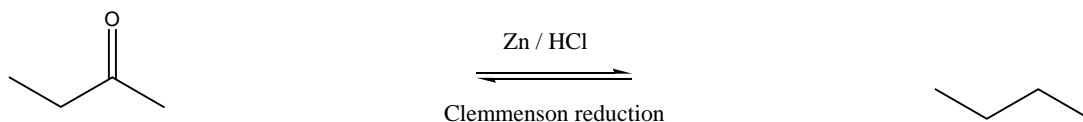
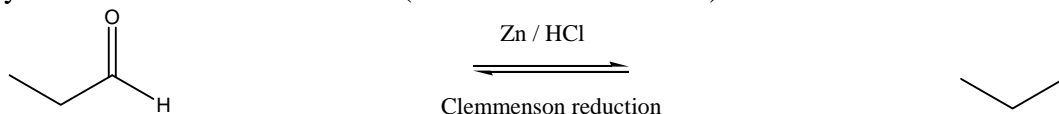




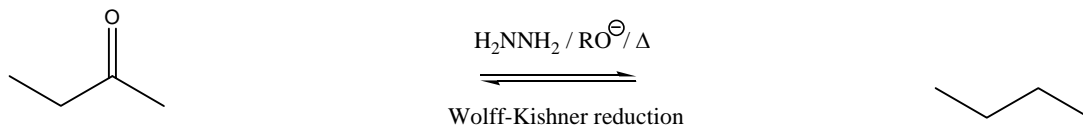
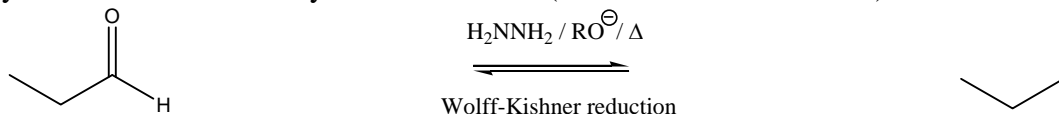
c. Aldehydes and ketones with Jones reagent. Converts aldehydes to carboxylic acids.

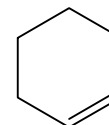
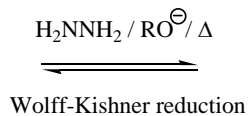
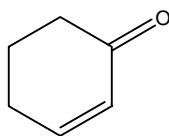
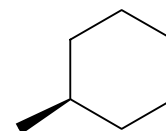
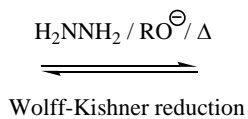
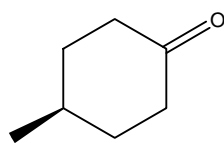
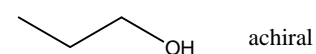
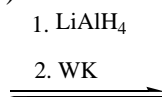
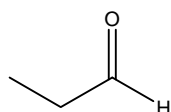


d. Aldehydes and ketones with Zn/HCl (Clemmenson reduction).

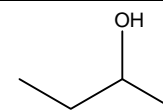
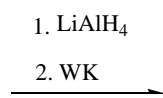
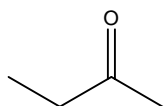


e. Aldehydes and ketones with hydrazine and base (Wolff-Kishner reduction).

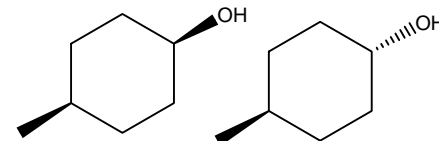
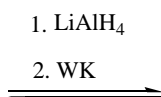
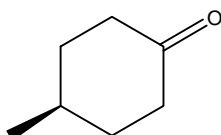


f. Aldehydes and ketones with  $\text{LiAlH}_4$  (LAH).

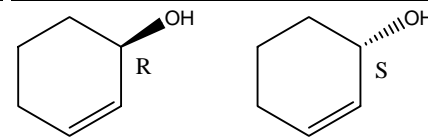
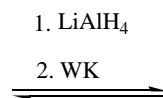
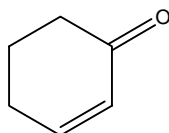
achiral



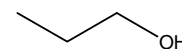
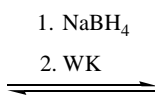
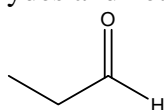
enantiomers (R and S)



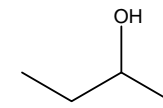
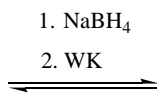
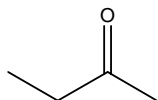
achiral diastereomers



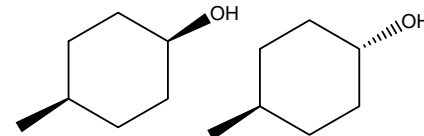
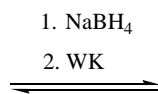
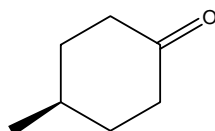
chiral enantiomers

g. Aldehydes and ketones with  $\text{NaBH}_4$ .

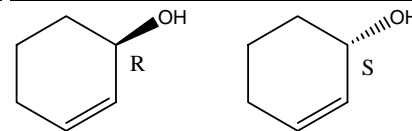
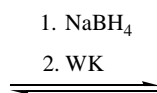
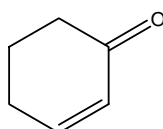
achiral



enantiomers (R and S)

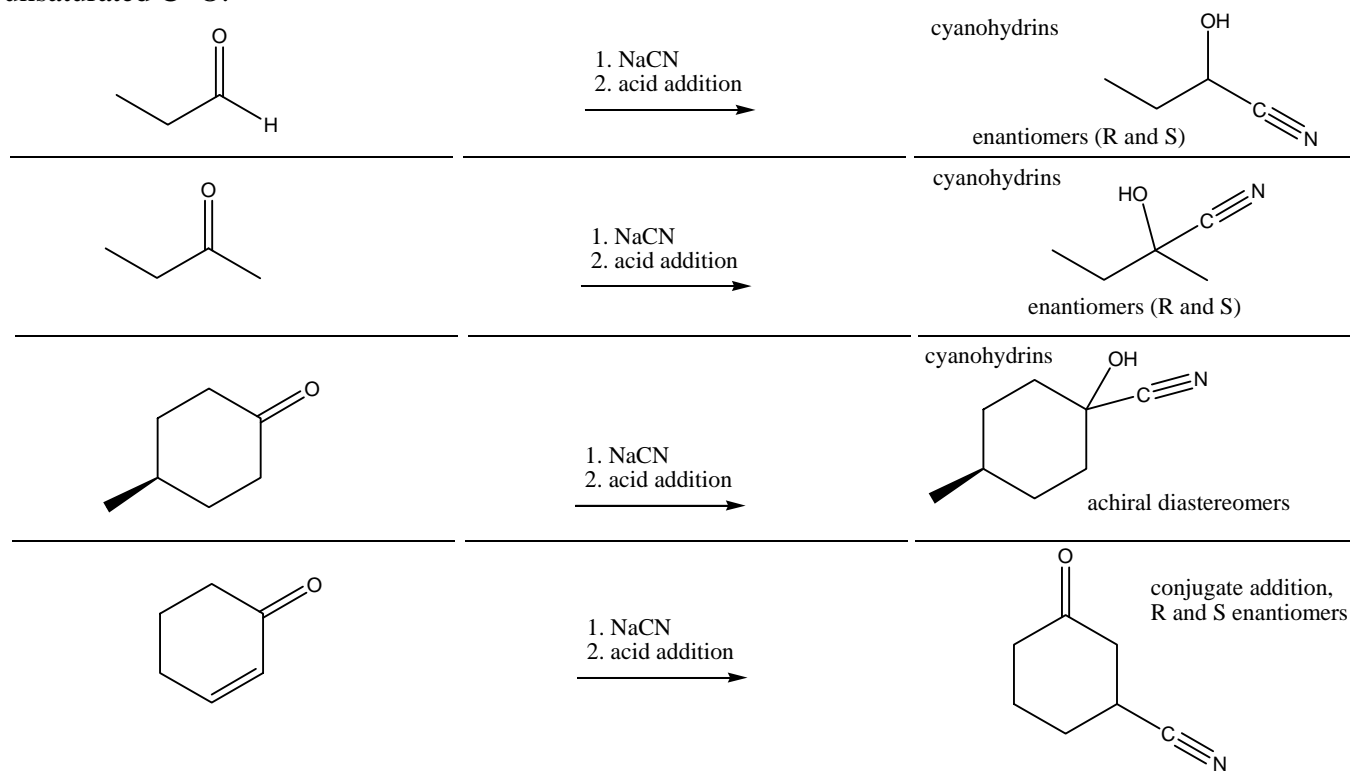


achiral diastereomers

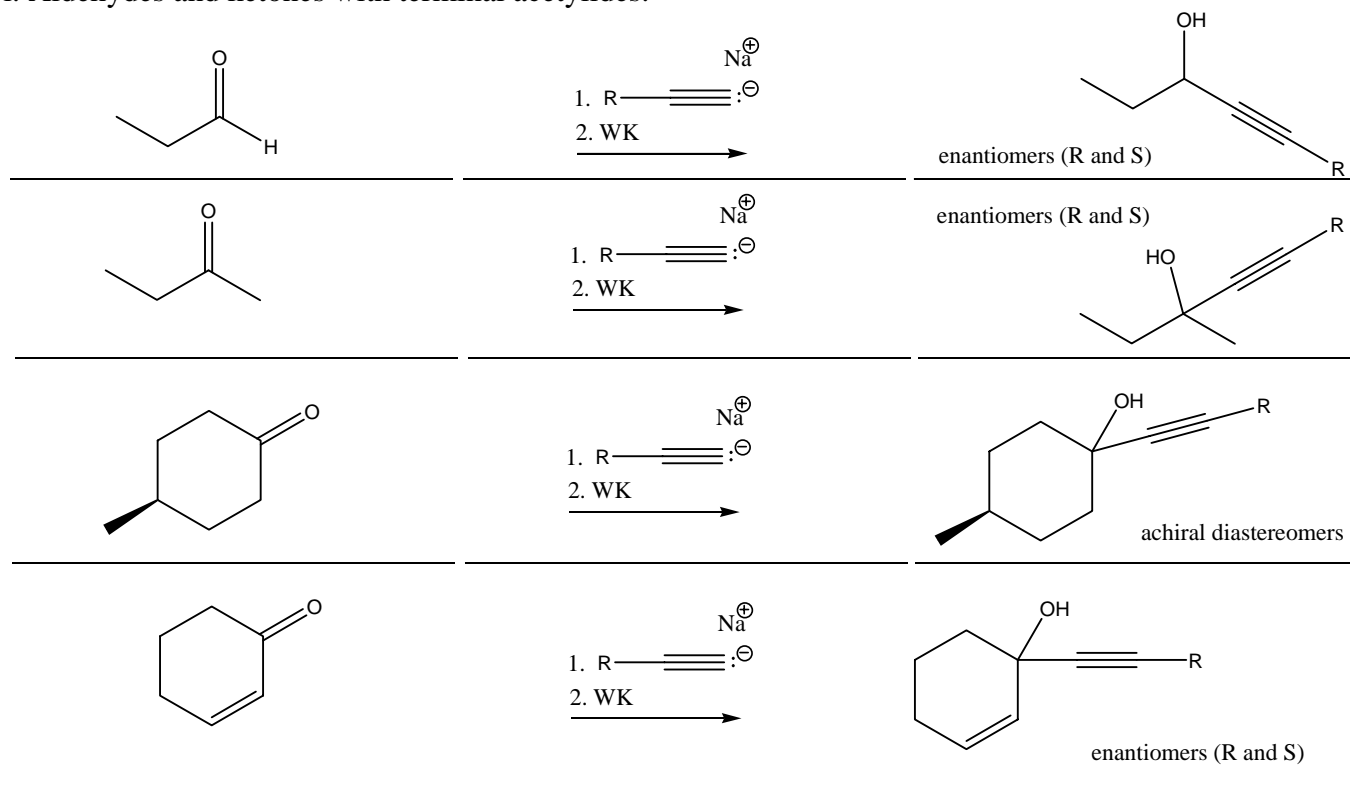


chiral enantiomers

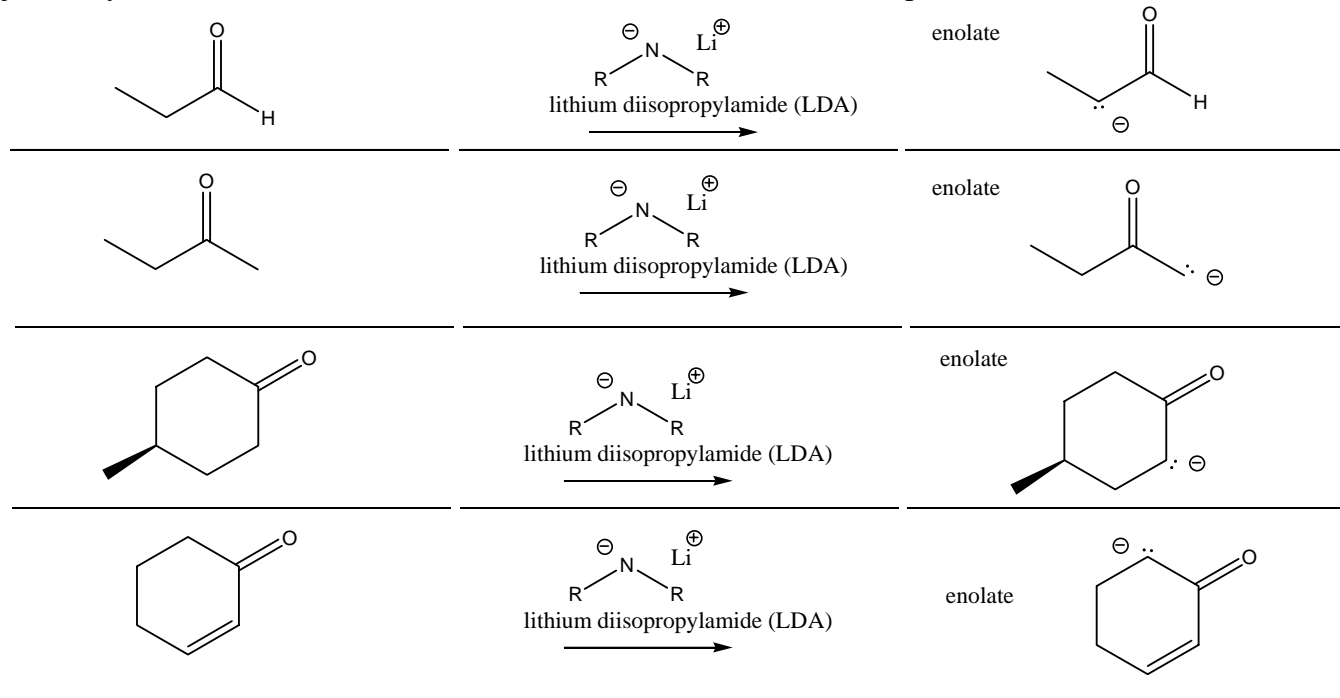
### h. Aldehydes and ketones with cyanide, cyanohydrin synthesis or conjugate addition to alpha-beta unsaturated C=O.



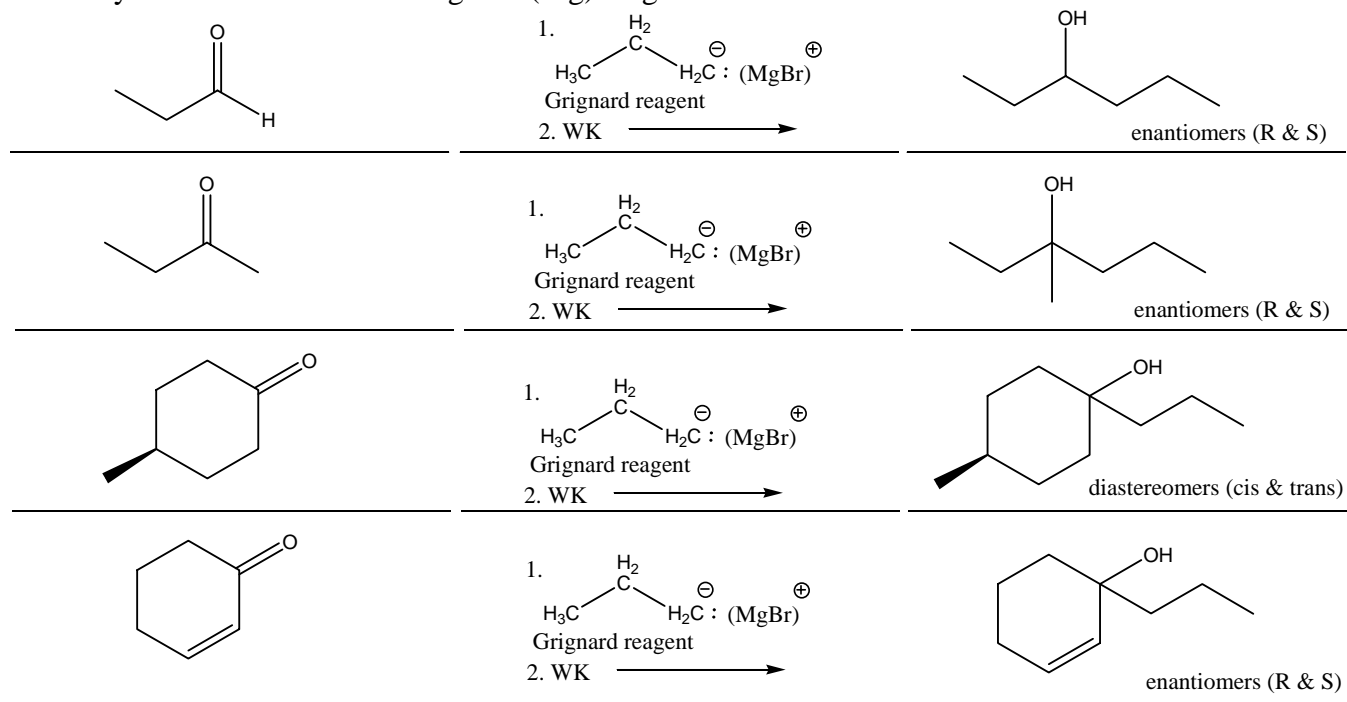
### i. Aldehydes and ketones with terminal acetylides.



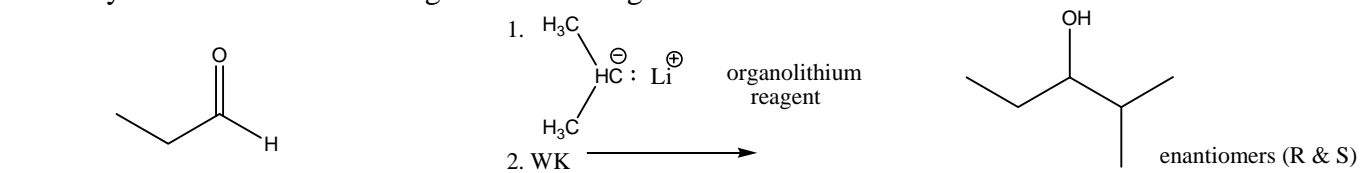
j. Aldehydes and ketones with LDA makes enolates (carbanion nucleophiles).



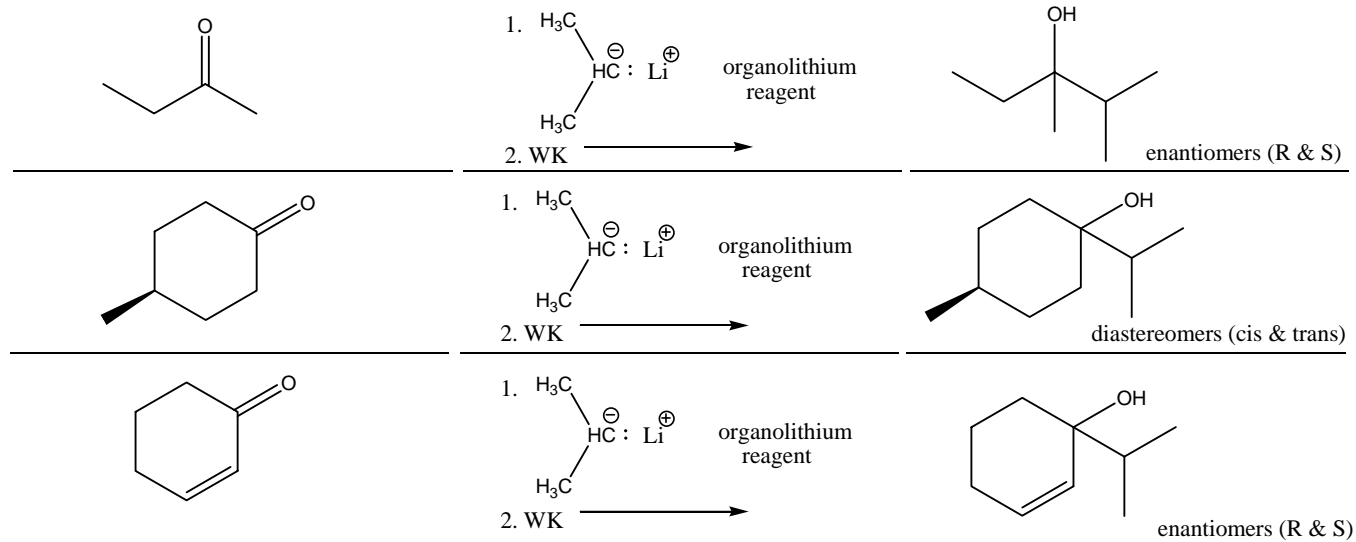
k. Aldehydes and ketones with Grignard (Mg) reagents.



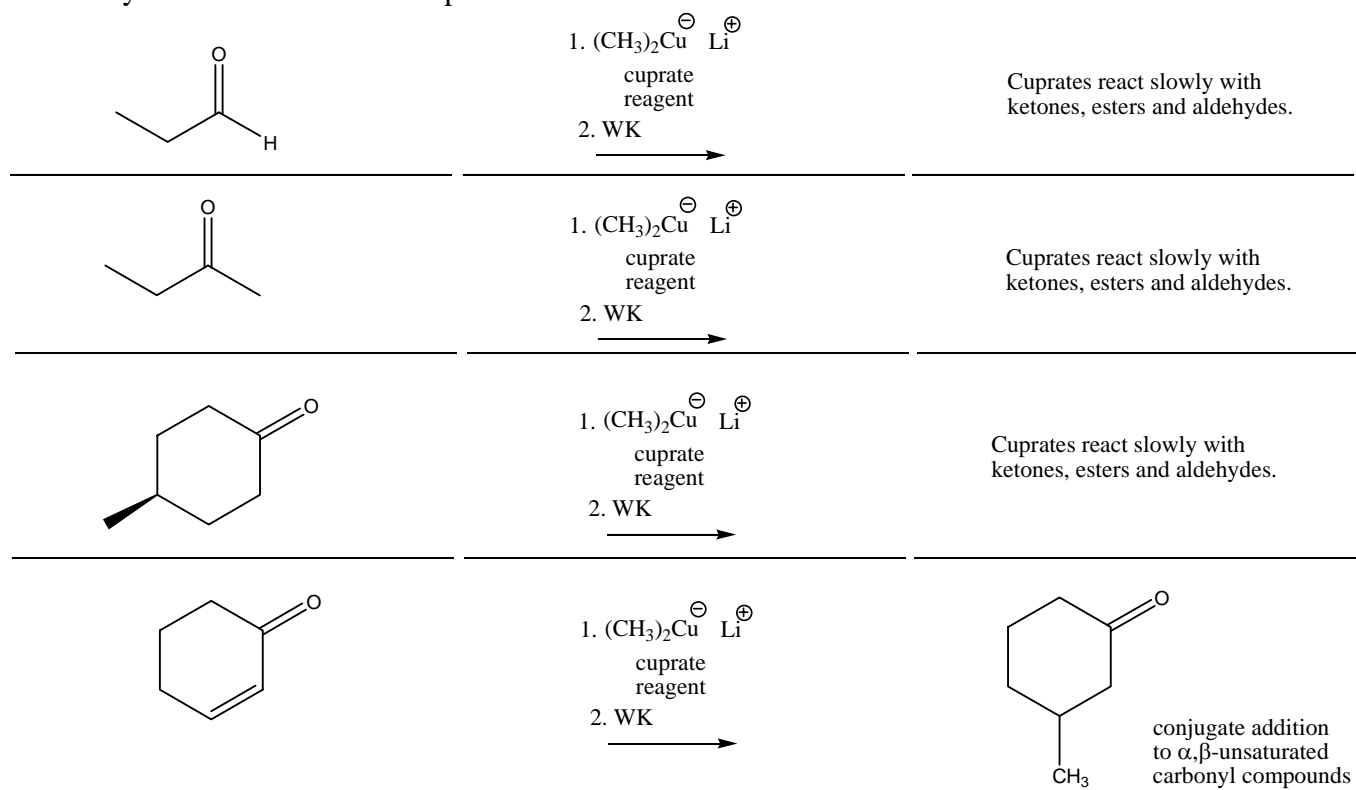
l. Aldehydes and ketones with organolithium reagents.



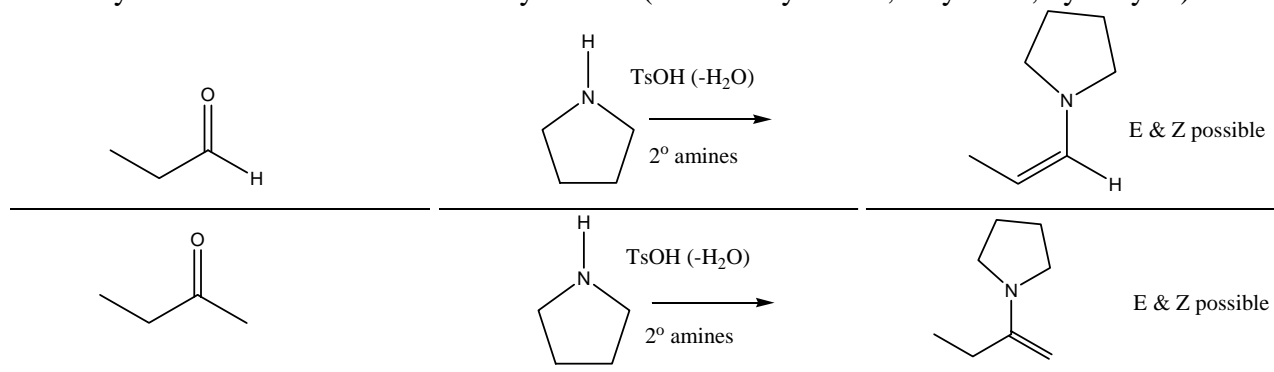


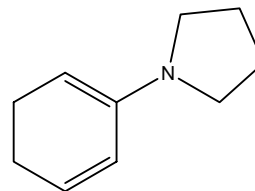
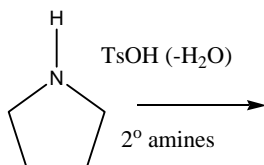
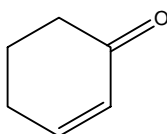
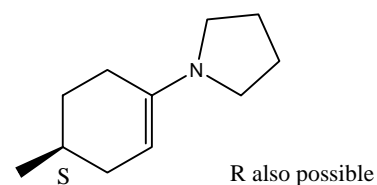
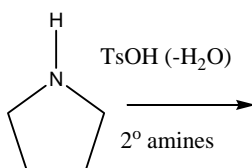
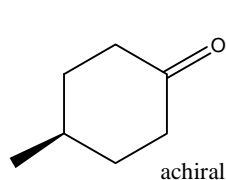


## m. Aldehydes and ketones with cuprates.

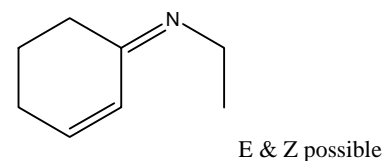
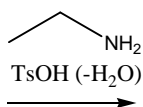
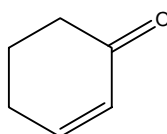
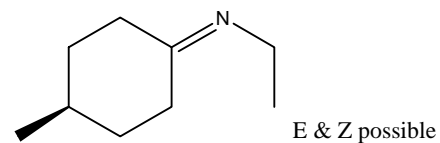
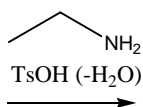
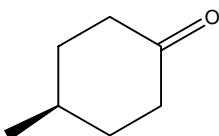
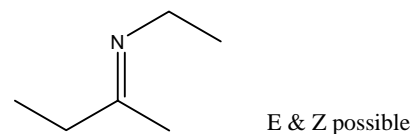
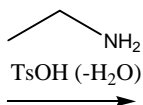
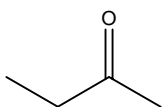
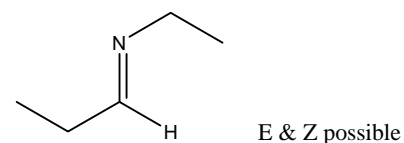
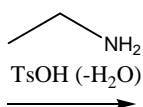
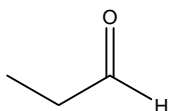
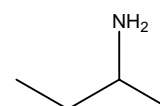
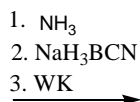
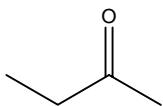
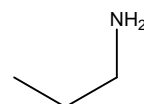
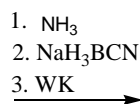
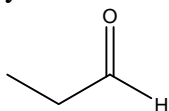


## n. Aldehydes and ketones with secondary amines (enamine synthesis, alkylation, hydrolysis).

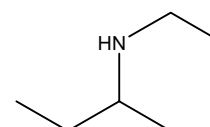
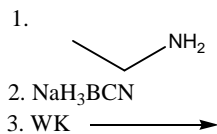
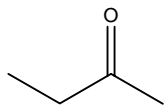
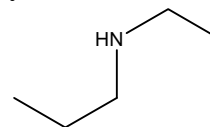
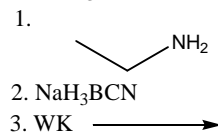
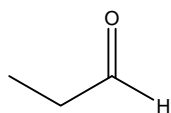




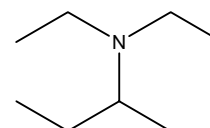
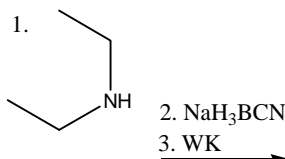
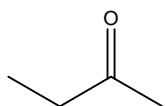
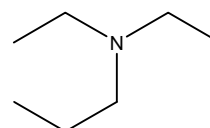
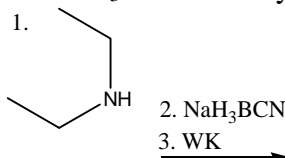
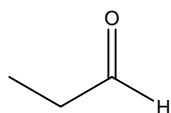
## o. Aldehydes and ketones with primary amines (imine synthesis).

p. Aldehydes and ketones with ammonia + NaBH<sub>3</sub>CN = primary amine synthesis.

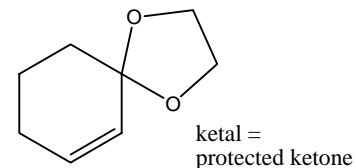
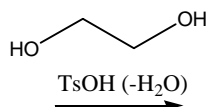
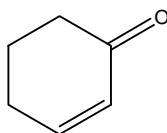
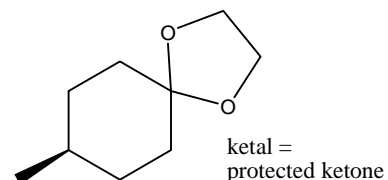
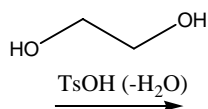
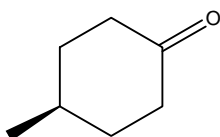
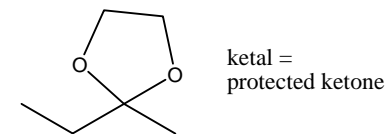
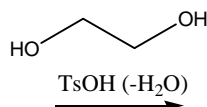
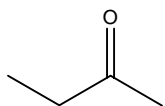
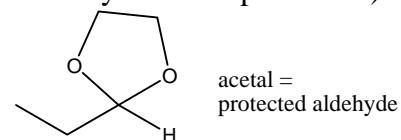
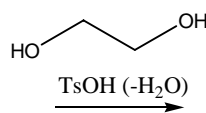
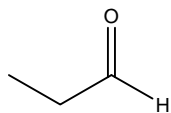
q. Aldehydes and ketones primary amine +  $\text{NaBH}_3\text{CN}$  = secondary amine synthesis.



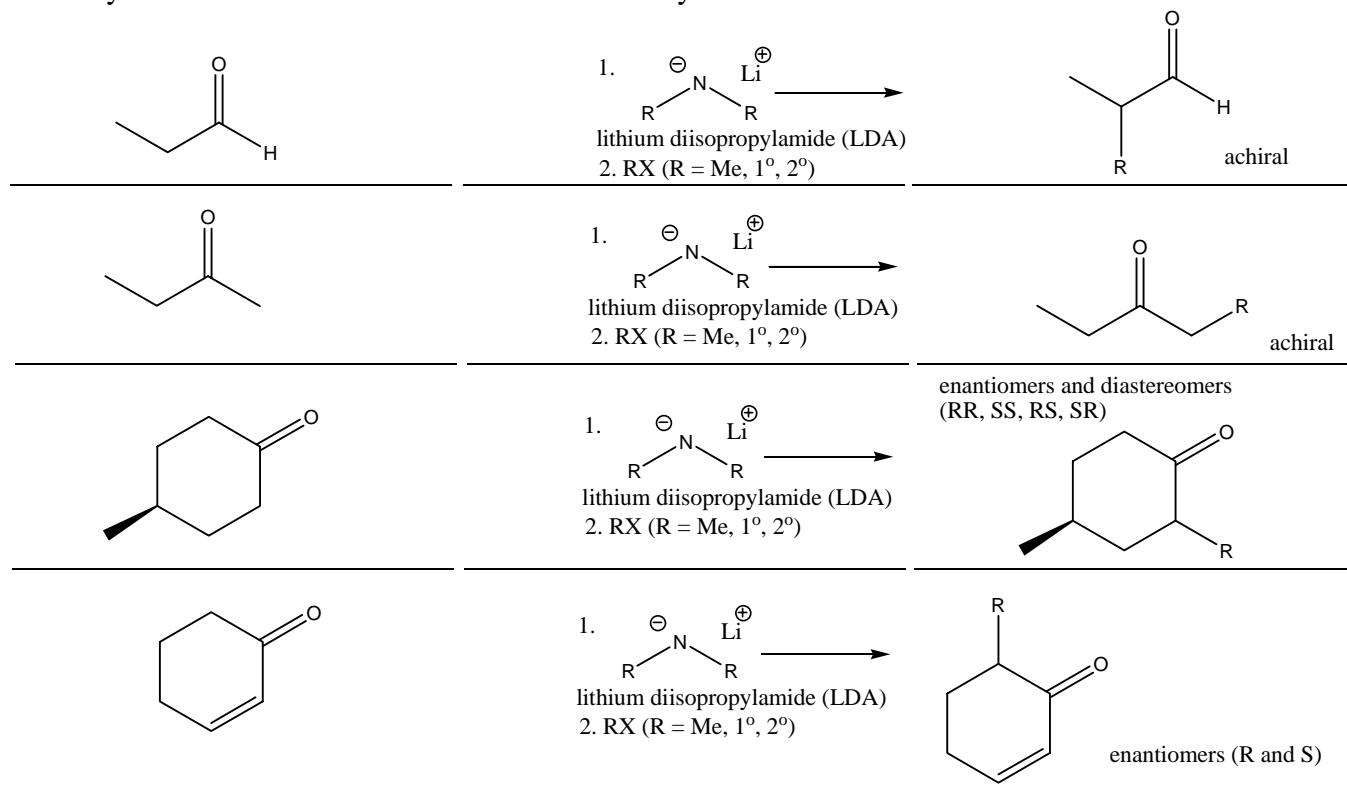
r. Aldehydes and ketones secondary amine +  $\text{NaBH}_3\text{CN}$  = tertiary amine synthesis.



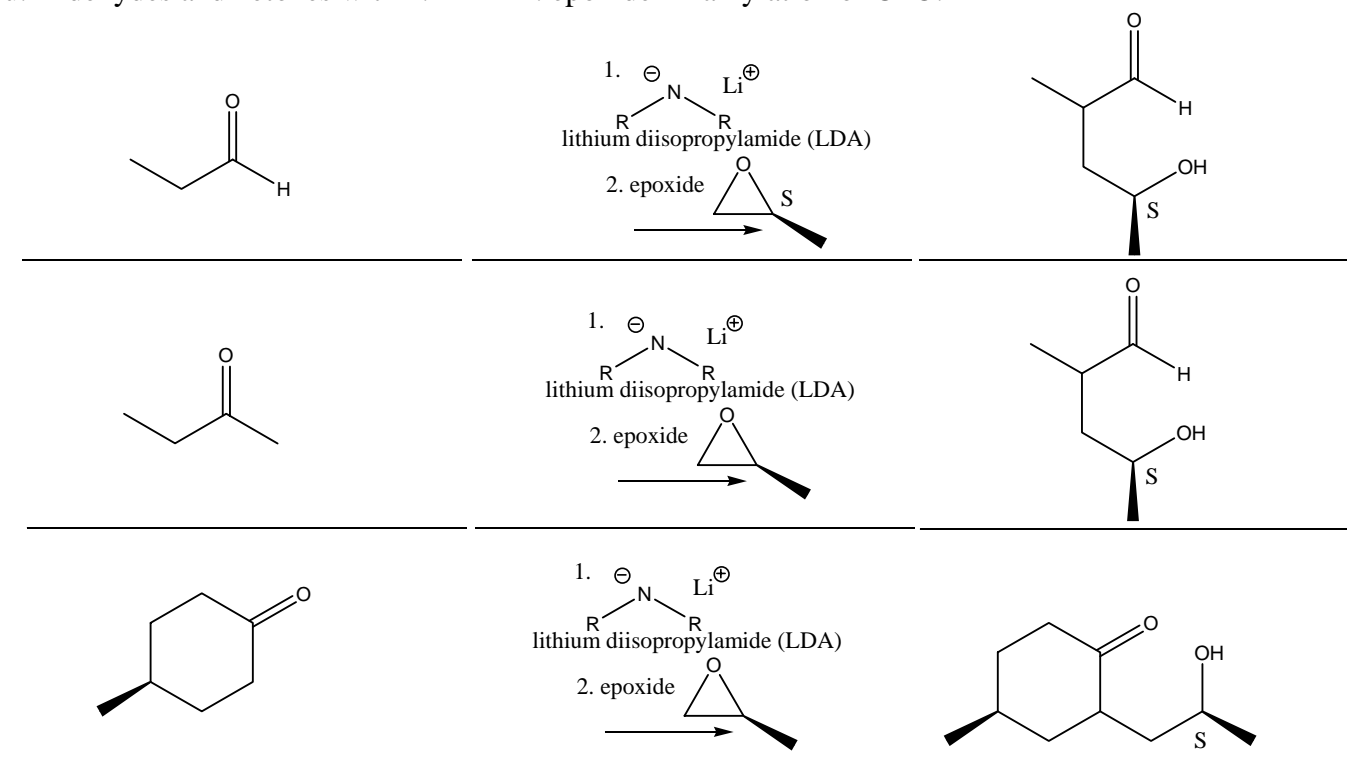
s. Aldehydes and ketones ethylene glycol, acid, dehydration: ketal and acetal synthesis = protection).



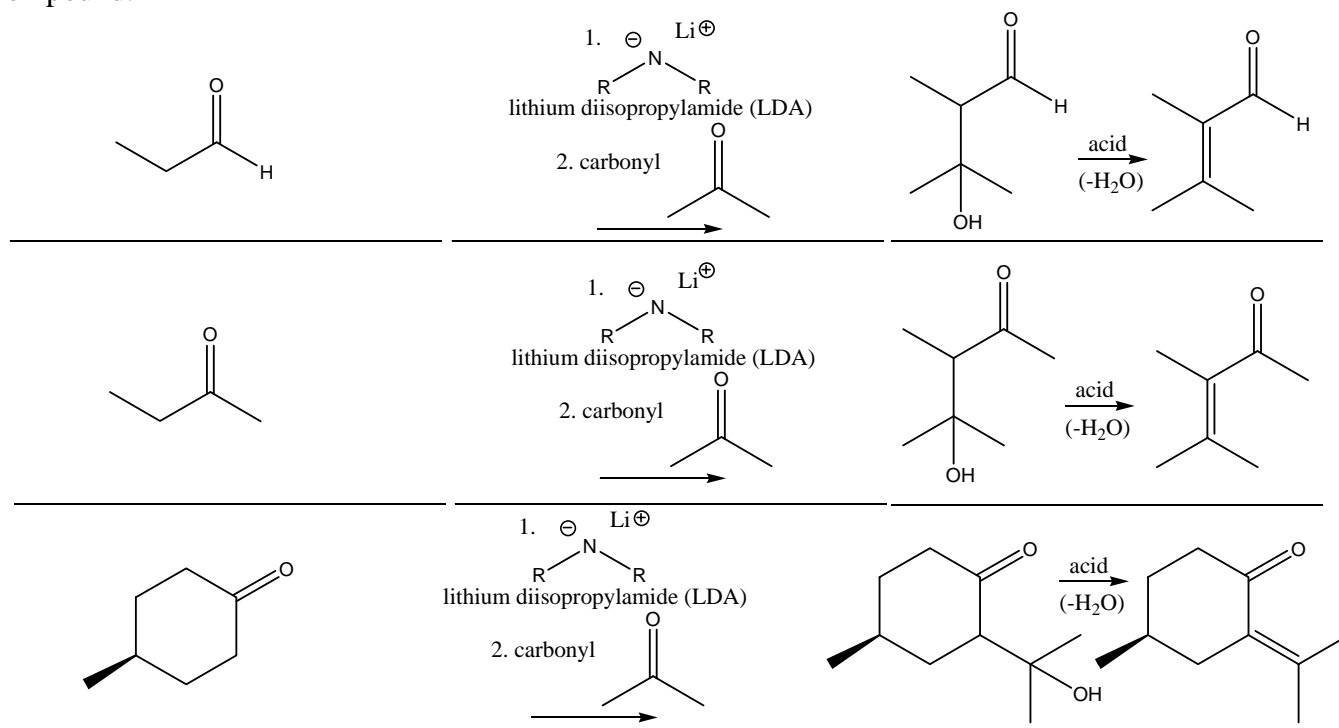
t. Aldehydes and ketones with 1. LDA 2. RX = alkylation of C=O.



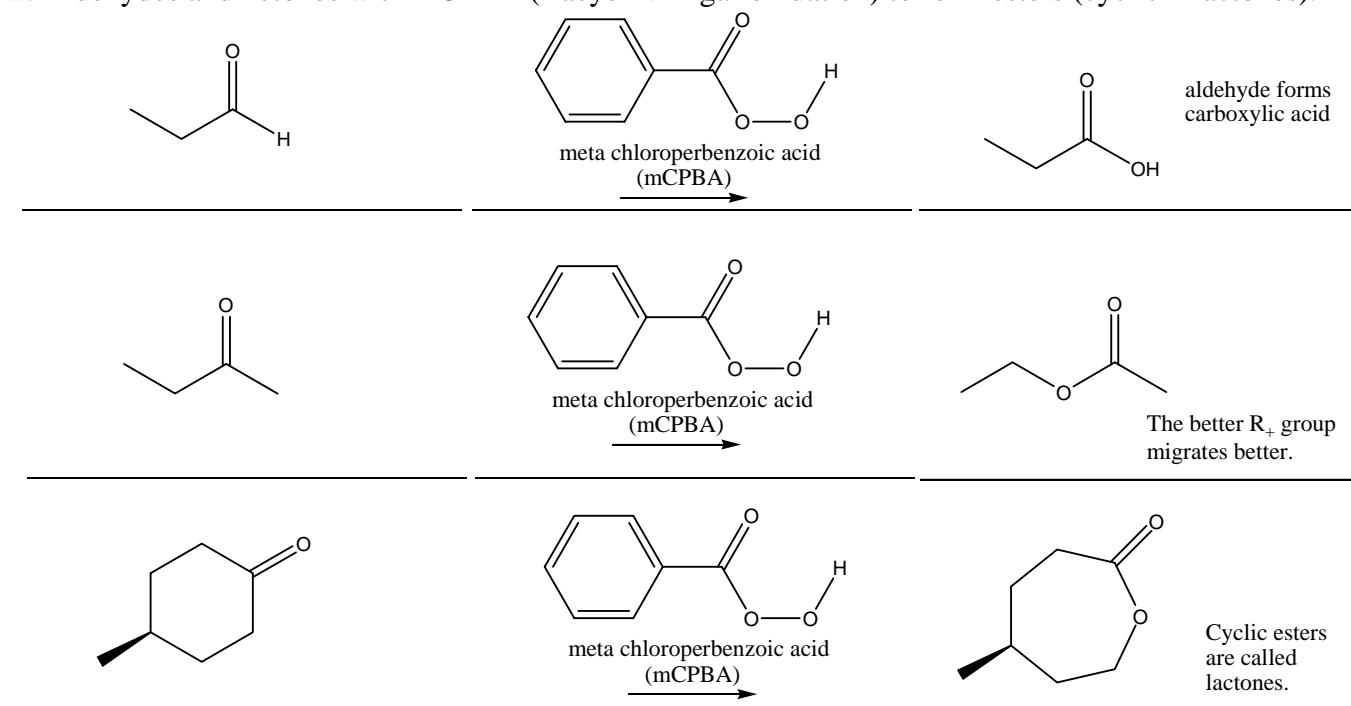
u. Aldehydes and ketones with 1. LDA 2. epoxide = alkylation of C=O.



v. Aldehydes and ketones with 1. LDA 2. another C=O = addition to C=O. Forms a beta hydroxyl carbonyl, which can be dehydrated in acid or base (with heat) to an  $\alpha,\beta$ -unsaturated carbonyl compound.



w. Aldehydes and ketones with mCPBA (Baeyer-Villiger oxidation) to form esters (cyclic = lactones).



7. Show the products of the following miscellaneous reactions.

