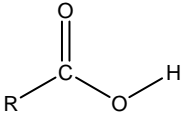
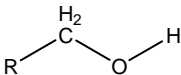
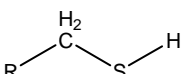
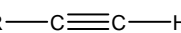
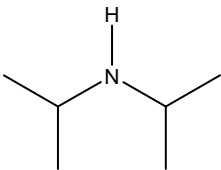
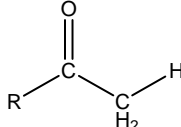


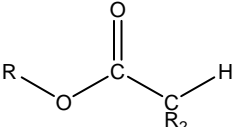
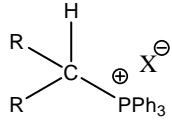
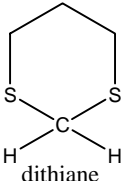
Reactions Study List Through Chem 315

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 are good nucleophiles, $S_{\text{N}}2 > E2$ 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 are OK nucleophiles, $S_{\text{N}}2 > E2$ at Me and 1° RX, and strong bases, $E2 > S_{\text{N}}2$ 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 are good nucleophiles, $S_{\text{N}}2 > E2$ at Me, 1° and 2° RX, and strong bases, $E2 > S_{\text{N}}2$ 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 are OK nucleophiles, $S_{\text{N}}2 > E2$ at Me and 1° RX, and strong bases, $E2 > S_{\text{N}}2$ 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 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>enolates are good nucleophiles, $S_{\text{N}}2 > E2$ at Me, 1° and 2° RX, and strong bases, $E2 > S_{\text{N}}2$ at 3°RX.</p>

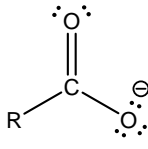
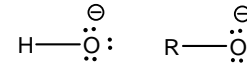
 <p>ketones / aldehydes</p>	<p>LDA = lithium diisopropylamide</p> $\xrightarrow{\text{Na}^{\oplus} \ominus \text{NR}_2}$ $K_{\text{eq}} = \frac{K_a(\text{ROCOCH}_3)}{K_a(\text{HNR}_2)}$ $K_{\text{eq}} = \frac{10^{-25}}{10^{-37}} = 10^{+12}$	<p>enolates are good nucleophiles, $S_N2 > E2$ at Me, 1° and 2° RX, and strong bases, $E2 > S_N2$ at 3° RX.</p>
 <p>Wittig salt = ylid</p>	<p>n-butyl lithium</p> $\xrightarrow{\text{Li}^{\oplus} \ominus \text{n-Bu}}$ $K_{\text{eq}} = \frac{K_a(\text{HCR}_2\text{PPh}_3)}{K_a(\text{H-C}_4\text{H}_9)}$ $K_{\text{eq}} = \frac{10^{-33}}{10^{-50}} = 10^{+17}$	<p>n-butyl lithium removes proton from Wittig salt and makes a good nucleophile at ketones and aldehydes, forming alkenes.</p>
 <p>dithiane</p>	<p>n-butyl lithium</p> $\xrightarrow{\text{Li}^{\oplus} \ominus \text{n-Bu}}$ $K_{\text{eq}} = \frac{K_a(\text{dithiane})}{K_a(\text{H-C}_4\text{H}_9)}$ $K_{\text{eq}} = \frac{10^{-33}}{10^{-50}} = 10^{+17}$	<p>n-butyl lithium removes proton from dithiane and makes a good nucleophile at RX compounds. Can react once or twice in S_N2 reactions. Sulfur acetal forms carbonyl group after hydrolysis. Makes aldehydes and ketones.</p>

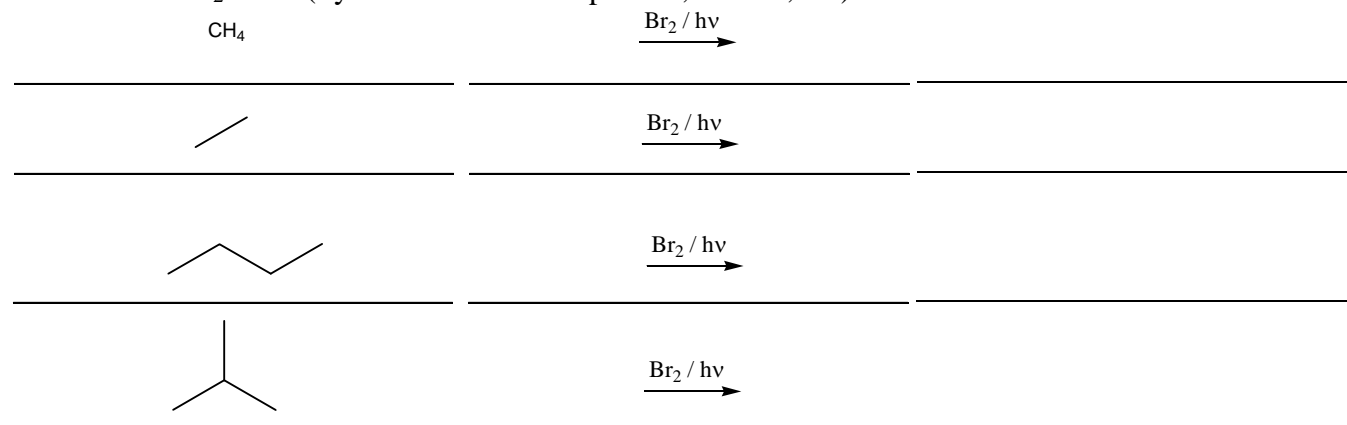
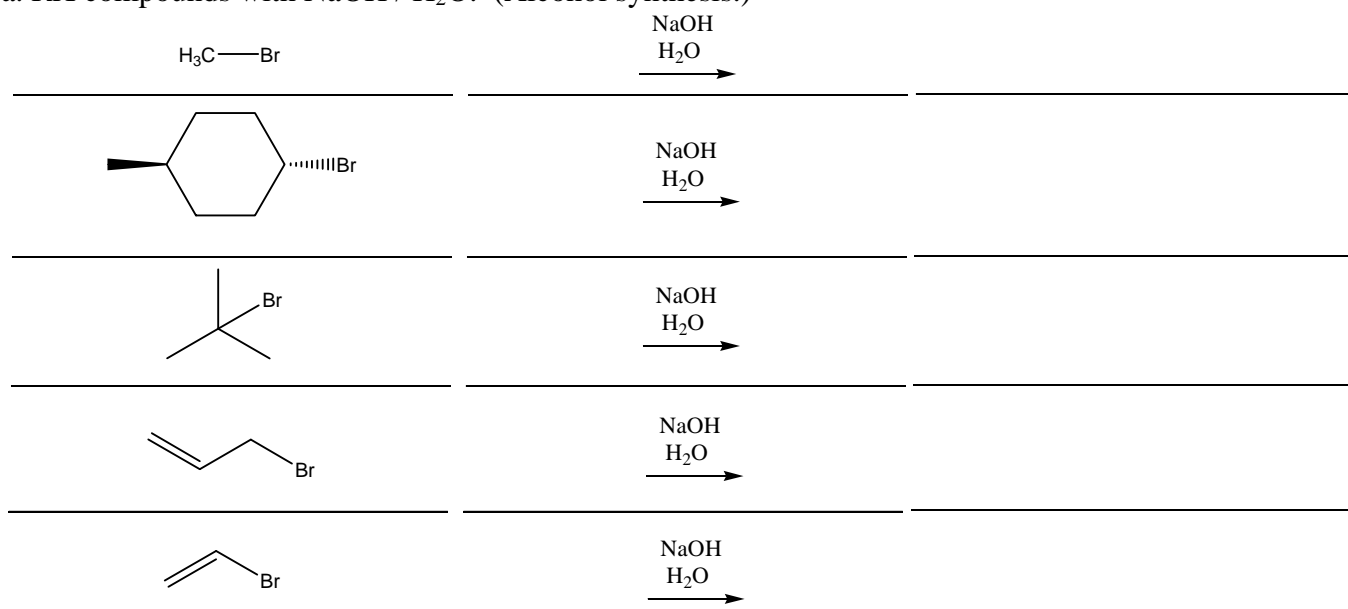
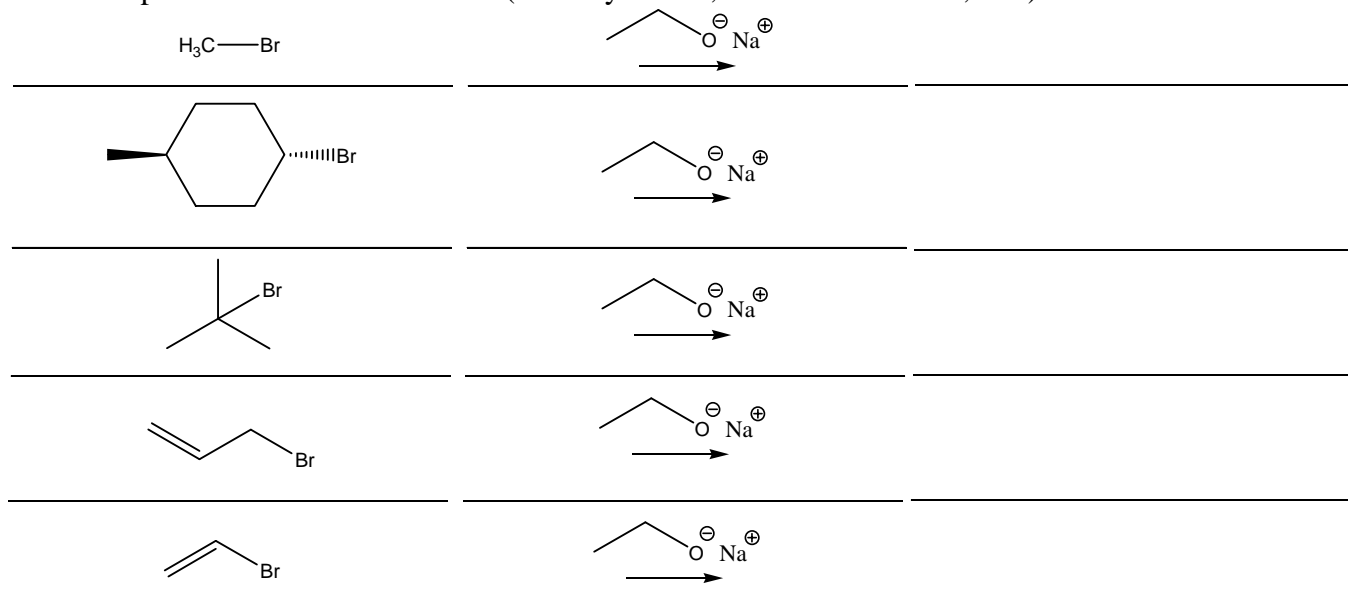
S_N2 versus $E2$ reactions at 2° RX.

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° 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 $E2 > S_N2$.

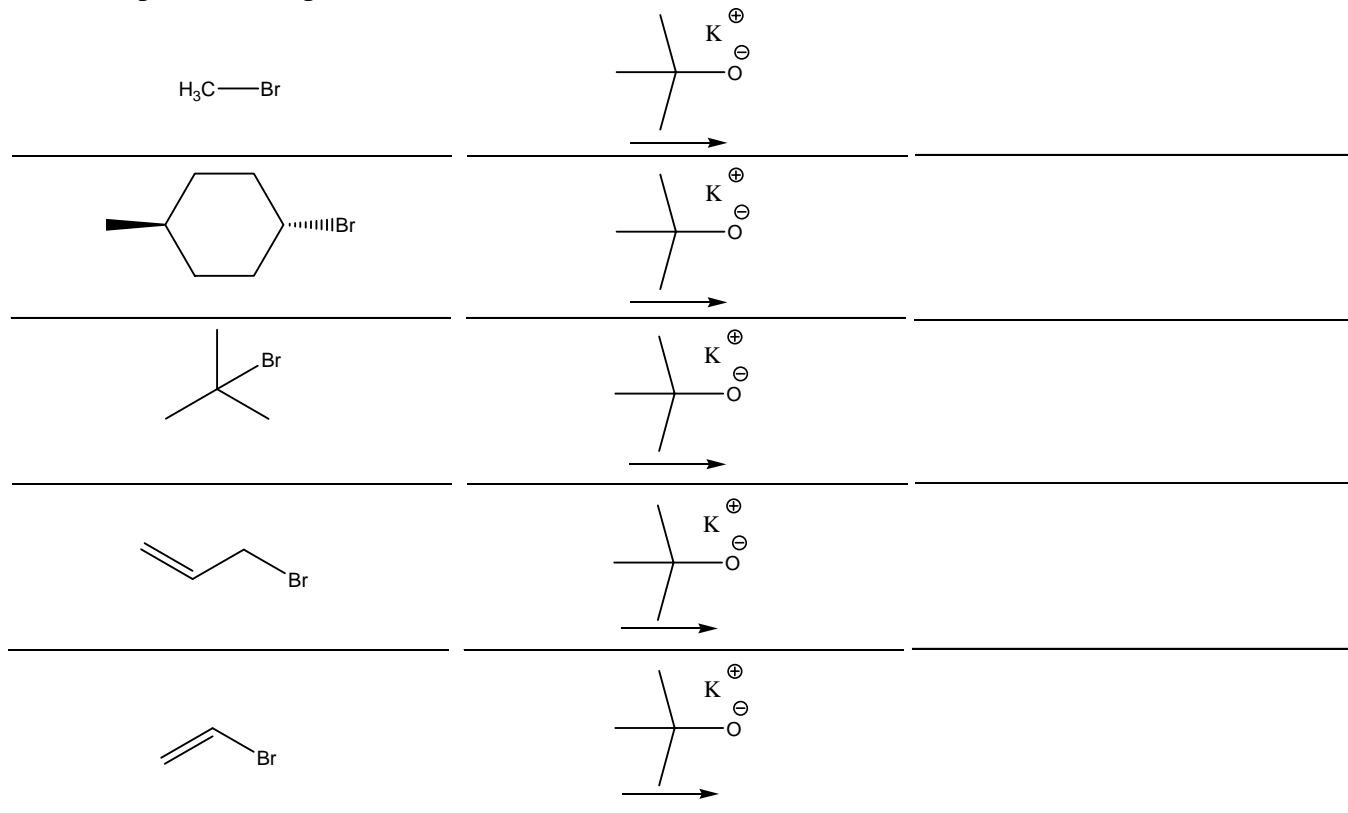
Similar looking base/nucleophiles (used in our course) that react differently with 2° RX structures. (They all react by S_N2 at methyl and 1° RX and they all react by $E2$ at 3° RX.)

2° RX structures

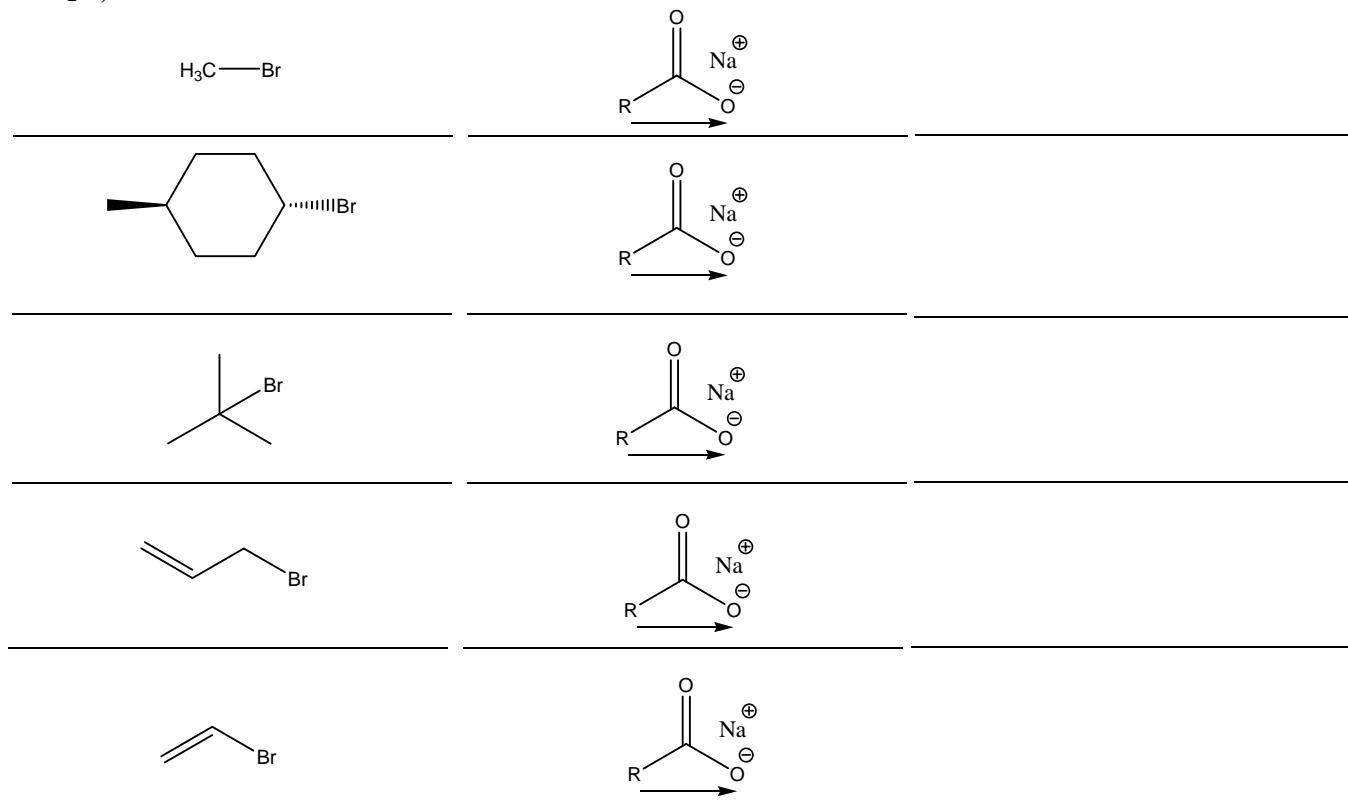
<p>Less basic, so $S_N2 > E2$.</p> $\text{:N}\equiv\text{C}^{\ominus}$ <p>cyanide pK_a of conjugate acid = 9</p>	<p>More basic, so $E2 > S_N2$.</p> $\text{R}-\text{C}\equiv\text{C}^{\ominus}$ <p>terminal acetylides pK_a of conjugate acid = 25</p>	<p>Less basic, so $S_N2 > E2$.</p>  <p>carboxylates pK_a of conjugate acid = 5</p>	<p>More basic, so $E2 > S_N2$.</p>  <p>hydroxide and alkoxides pK_a of conjugate acid = 16-19</p>
---	--	---	---

Alkanes with $\text{Br}_2 / h\nu$. (Synthesis of RX compounds, X = Br, Cl.)1. a. RX compounds with $\text{NaOH} / \text{H}_2\text{O}$. (Alcohol synthesis.)b. RX compounds with NaOR / ROH . (Ether synthesis, need to make RO^- , Na^+ .)

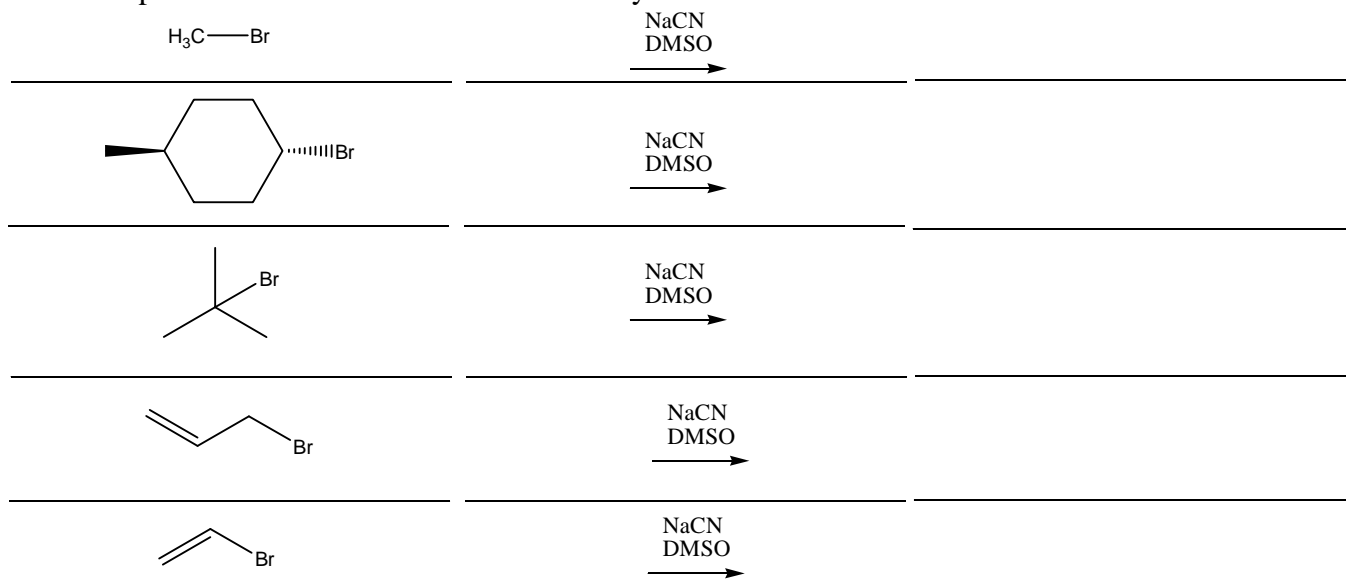
c. RX compounds with potassium t-butoxide (favors E2 > S_N2).



d. RX compounds with sodium carboxylates. Ester synthesis (can hydrolyze with base to ROH and RCO₂H).

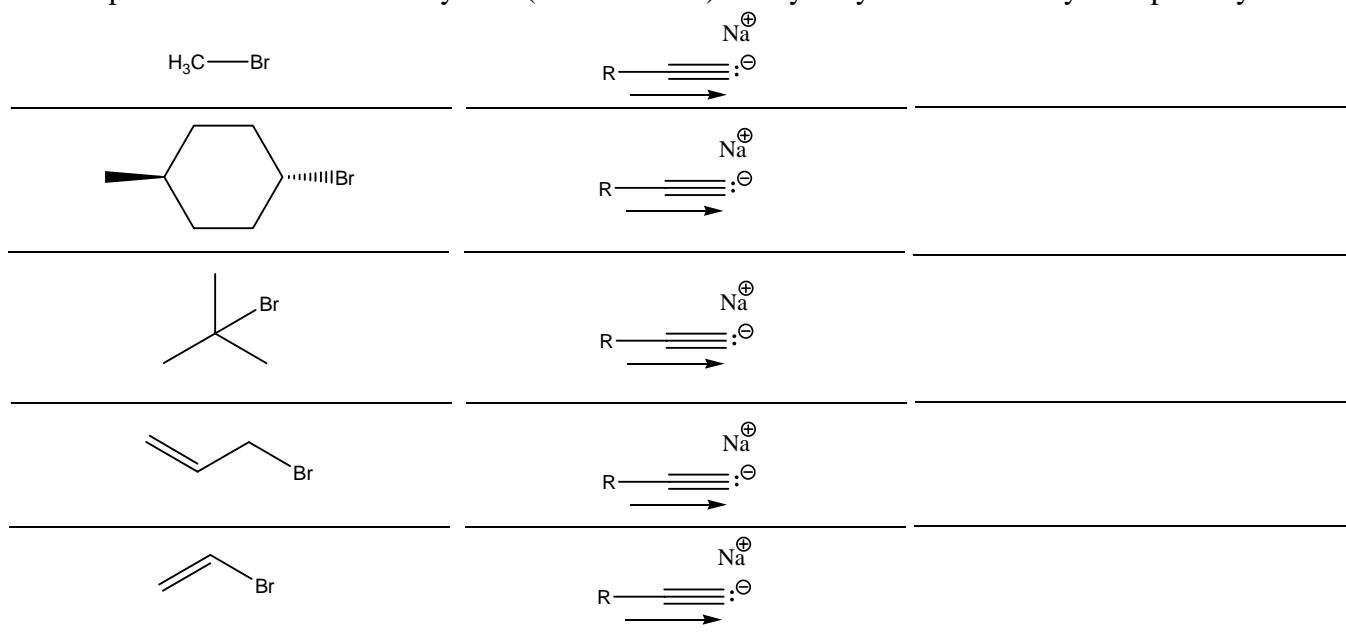


e. RX compounds with NaCN / DMSO. Nitrile synthesis.



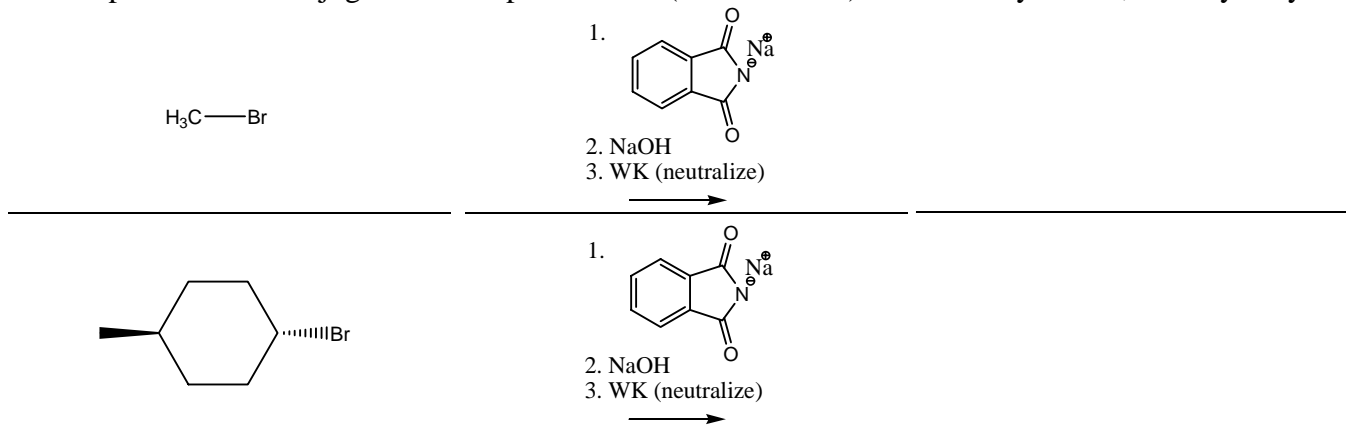
f.

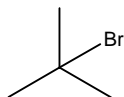
RX compounds with terminal acetylides (need to make). Alkyne synthesis at methyl and primary RX.



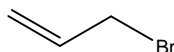
g.

RX compounds with conjugate base of phthalimide (need to make). 1°RNH_2 synthesis, after hydrolysis.

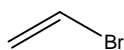




- 1.
2. NaOH
3. WK (neutralize)

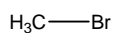


- 1.
2. NaOH
3. WK (neutralize)

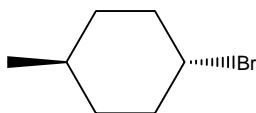


- 1.
2. NaOH
3. WK (neutralize)

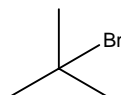
h. RX compounds with LiAlH_4 (LAH). Nucleophilic hydride displaces "X" on carbon.



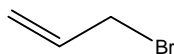
1. LiAlH_4
2. WK



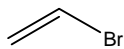
1. LiAlH_4
2. WK



1. LiAlH_4
2. WK



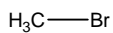
1. LiAlH_4
2. WK



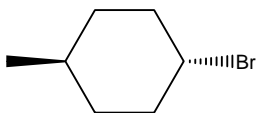
1. LiAlH_4
2. WK

i.

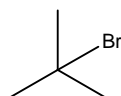
RX compounds with NaBH_4 . Nucleophilic hydride displaces "X" on carbon.



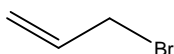
1. NaBH_4
2. WK



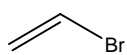
1. NaBH_4
2. WK



1. NaBH_4
2. WK

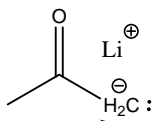
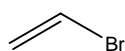
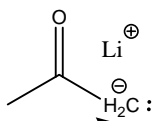
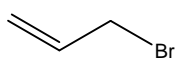
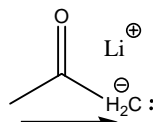
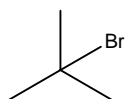
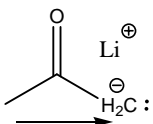
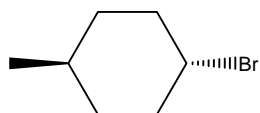
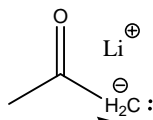
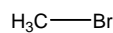


1. NaBH_4
2. WK

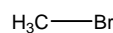


1. NaBH₄
2. WK

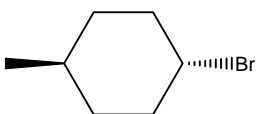
j. RX compounds with enolates (need to make with LDA/-78°C). Alkylation of carbonyl compounds.



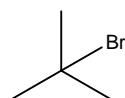
k. RX compounds with water. Alcohol synthesis (rearrangements are possible).



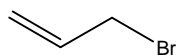
H₂O



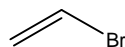
H₂O



H₂O

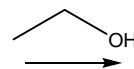
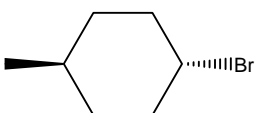
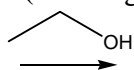
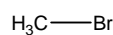


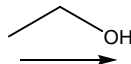
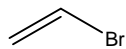
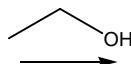
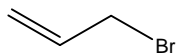
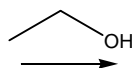
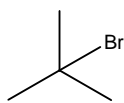
H₂O



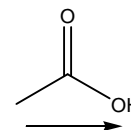
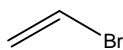
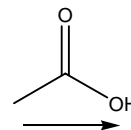
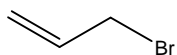
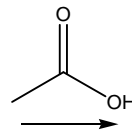
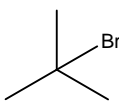
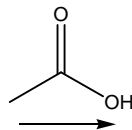
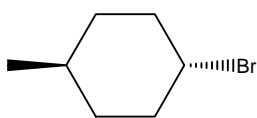
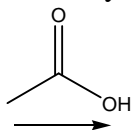
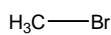
H₂O

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

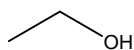




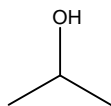
m. RX compounds with liquid carboxylic acids. Ester synthesis (rearrangements are possible).



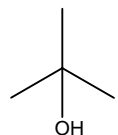
2. a. ROH with: SOCl_2 or PCl_3 or HCl or 1. TsCl /pyridine 2. NaCl . Synthesis of R-Cl.



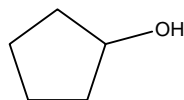
given reagent
in the list
→



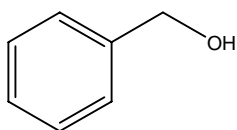
given reagent
in the list
→



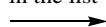
given reagent
in the list
→



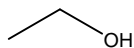
given reagent
in the list
→



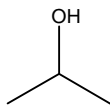
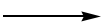
given reagent
in the list



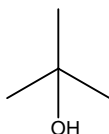
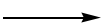
b. ROH with: PBr_3 or HBr or 1. TsCl/pyridine 2. NaBr . Synthesis of R-Br.



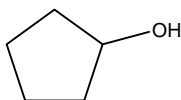
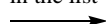
given reagent
in the list



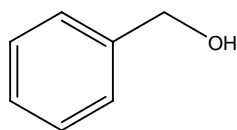
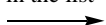
given reagent
in the list



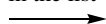
given reagent
in the list



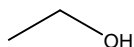
given reagent
in the list



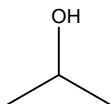
given reagent
in the list



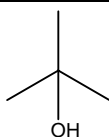
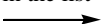
c. ROH with: PI_3 or HI or 1. TsCl/pyridine 2. NaI . Synthesis of R-I.



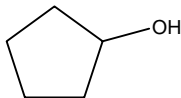
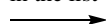
given reagent
in the list



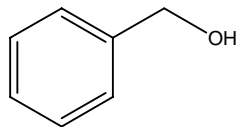
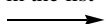
given reagent
in the list



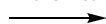
given reagent
in the list



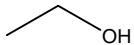
given reagent
in the list



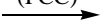
given reagent
in the list

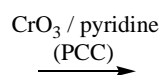
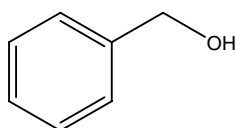
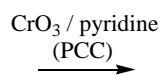
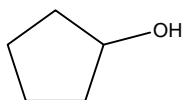
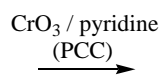
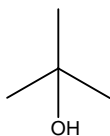
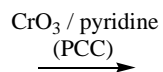
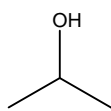


d. ROH with: CrO_3 / pyridine (PCC). Synthesis of aldehydes or ketones.

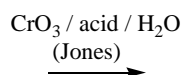
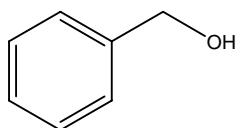
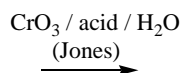
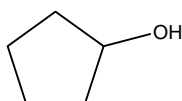
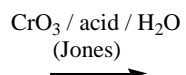
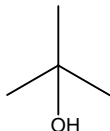
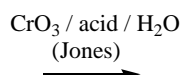
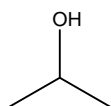
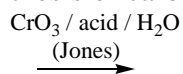
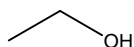


CrO_3 / pyridine
(PCC)

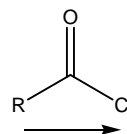
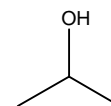
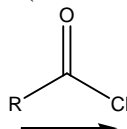
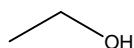


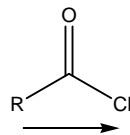
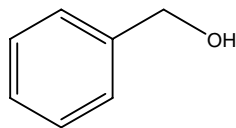
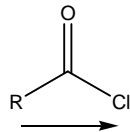
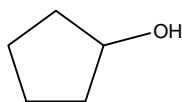
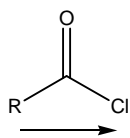
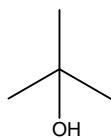


e. ROH with: CrO_3 / acid / water (Jones). Synthesis of carboxylic acids or ketones.

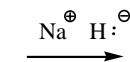
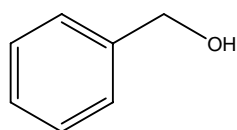
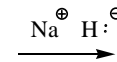
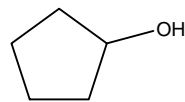
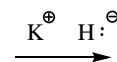
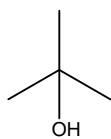
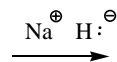
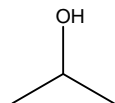
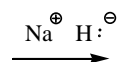
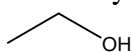


f. ROH with acid chlorides. Synthesis of esters. (Need to make RCOCl with SOCl_2 + acid.)

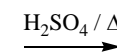
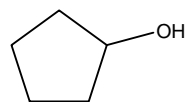
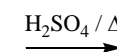
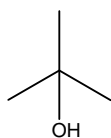
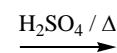
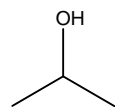
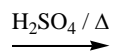
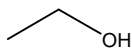




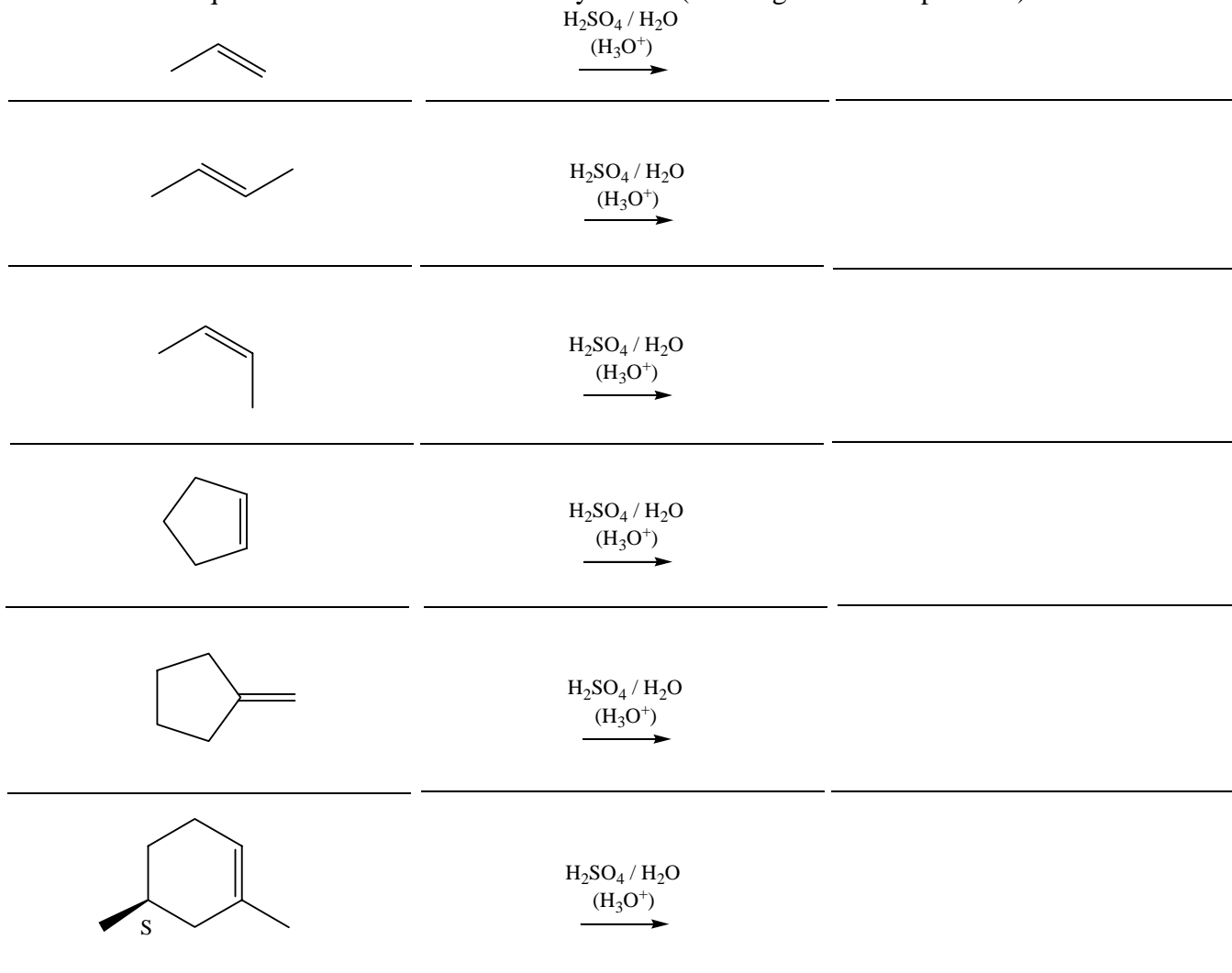
g. ROH with sodium hydride, NaH. Synthesis of sodium alkoxides.



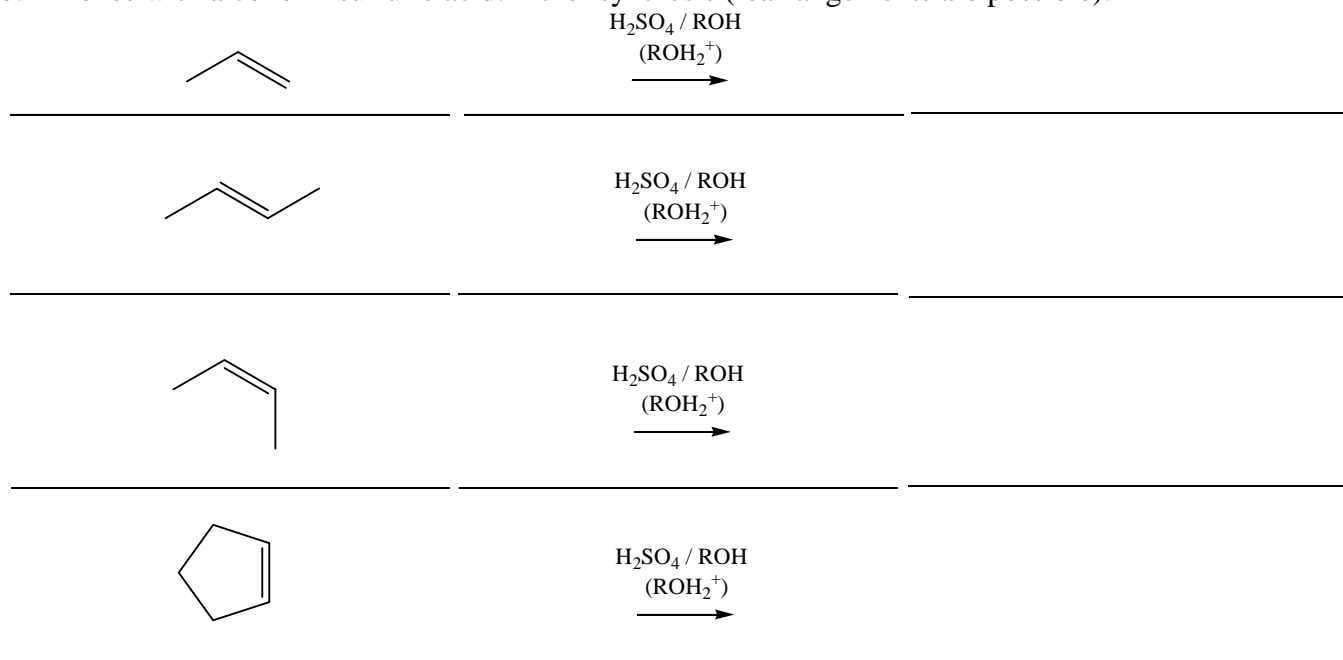
h. ROH with sulfuric acid / heat. Synthesis of alkenes (useful E1 reactions, rearrangement possible).

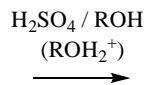
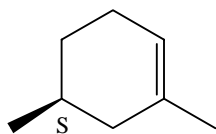
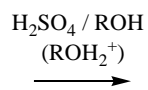
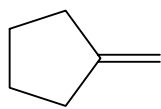


3. a. Alkenes with aqueous sulfuric acid. Alcohol synthesis (rearrangements are possible).

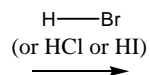
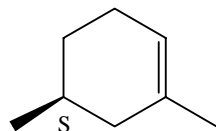
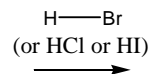
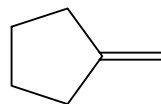
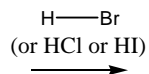
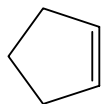
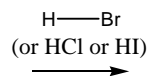
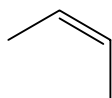
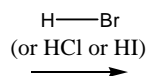
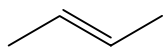
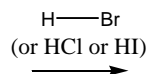
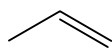
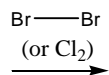
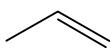


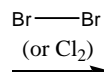
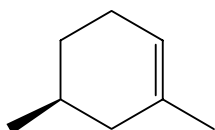
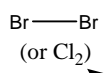
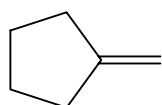
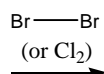
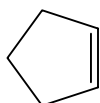
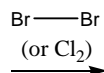
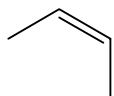
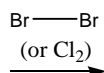
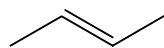
b. Alkenes with alcohol + sulfuric acid. Ether synthesis (rearrangements are possible).



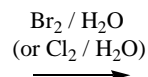
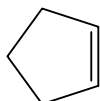
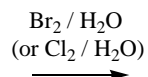
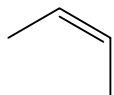
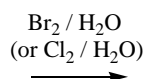
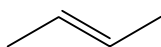
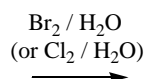
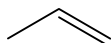


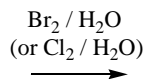
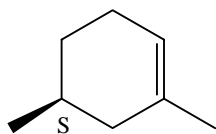
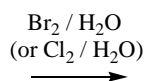
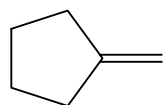
c. Alkenes with HX acid (HCl, HBr, HI). Synthesis of RX compounds.

d. Alkenes with Br₂ or Cl₂. Synthesis of vicinal dihalide (anti addition).

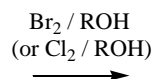
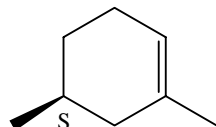
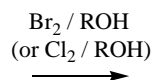
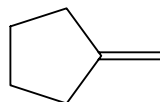
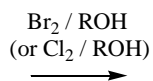
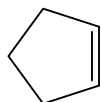
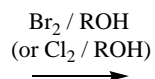
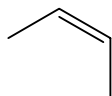
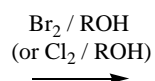
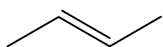
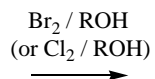
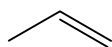


e. Alkenes with $\text{Br}_2/\text{H}_2\text{O}$ or $\text{Cl}_2/\text{H}_2\text{O}$. Synthesis of bromohydrin or chlorohydrin (anti + Markovnikov addition).

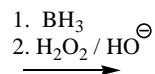
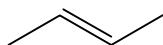
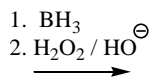
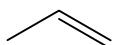


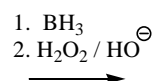
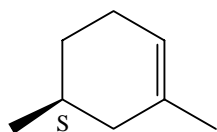
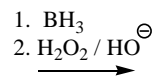
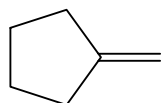
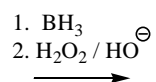
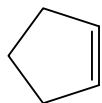
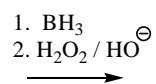
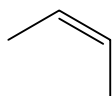


f. Alkenes with Br_2/ROH or Cl_2/ROH . Synthesis of bromo or chloro “ethers”.

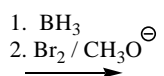
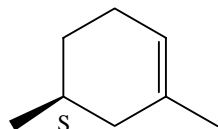
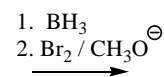
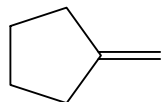
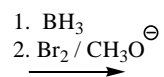
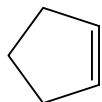
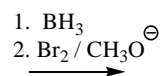
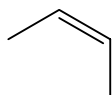
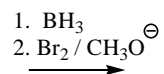
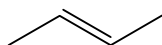
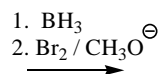
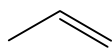


g. Alkenes with 1. BH_3 2. $\text{H}_2\text{O}_2/\text{HO}^-$. Hydroboration/oxidation = anti-Markovnikov alcohols.

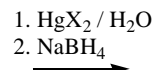
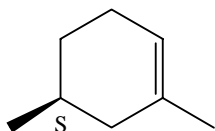
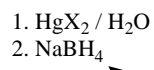
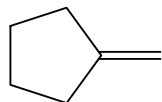
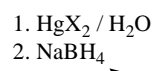
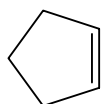
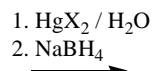
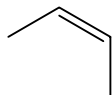
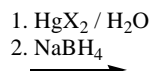
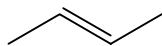
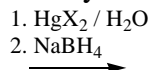
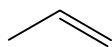




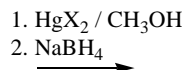
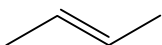
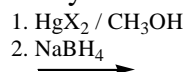
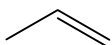
h. Alkenes with 1. BH_3 2. $\text{Br}_2/\text{CH}_3\text{O}^\ominus$. Hydroboration/bromination = anti-Markovnikov R-Br.

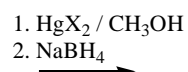
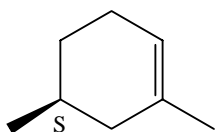
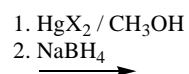
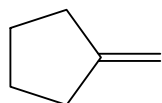
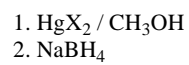
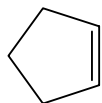
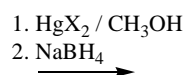
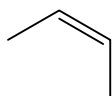


i. Alkenes with 1. $\text{HgX}_2 / \text{H}_2\text{O}$ 2. NaBH_4 . Alcohol synthesis with minimal rearrangements (Markovnikov).

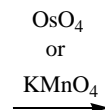
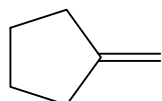
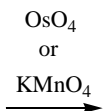
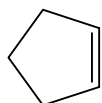
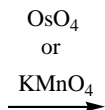
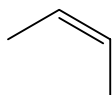
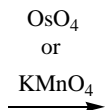
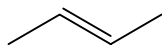
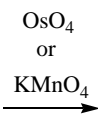
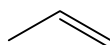


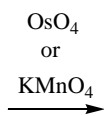
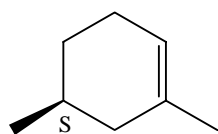
j. Alkenes with 1. $\text{HgX}_2 / \text{ROH}$ 2. NaBH_4 . Ether synthesis with minimal rearrangements (Markovnikov).



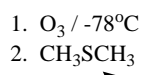
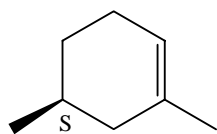
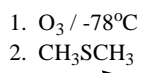
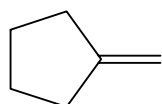
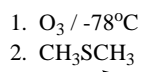
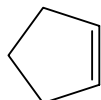
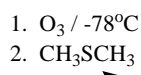
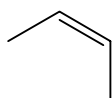
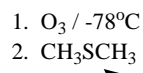
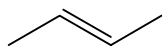
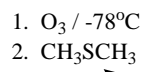
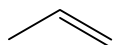


k. Alkenes with OsO_4 or KMnO_4 . "Syn" synthesis of vicinal diols.

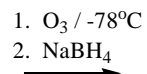
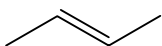
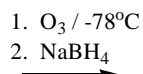
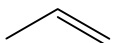


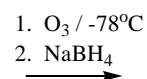
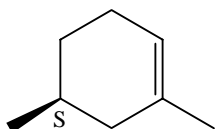
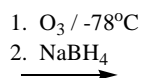
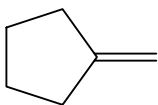
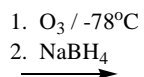
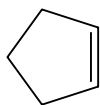
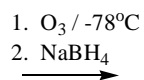
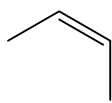


l. Alkenes with 1. $\text{O}_3 / -78^\circ\text{C}$ 2. CH_3SCH_3 or Zn. Synthesis of aldehydes or ketones.

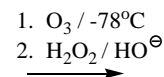
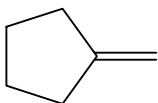
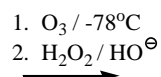
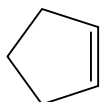
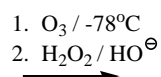
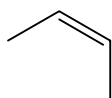
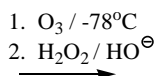
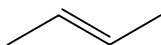
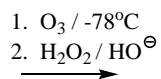
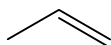


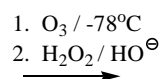
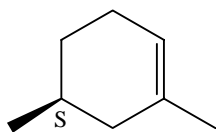
m. Alkenes with 1. $\text{O}_3 / -78^\circ\text{C}$ 2. NaBH_4 . Synthesis of alcohols.



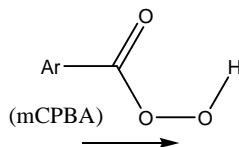
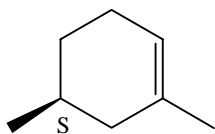
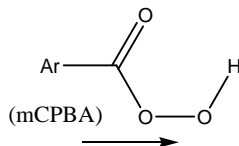
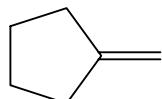
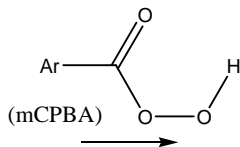
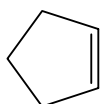
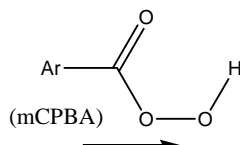
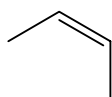
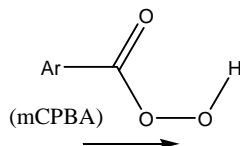
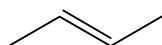
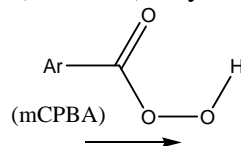
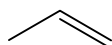


n. Alkenes with 1. $\text{O}_3 / -78^\circ\text{C}$ 2. $\text{H}_2\text{O}_2 / \text{HO}^-$. Synthesis of carboxylic acids or ketones.

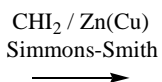
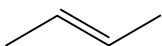
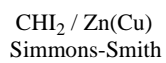
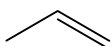


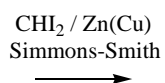
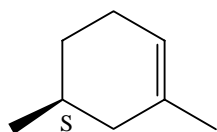
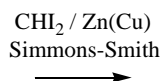
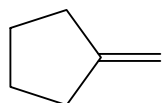
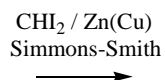
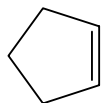
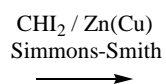
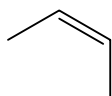


o. Alkenes with meta chloroperbenzoic acid (mCPBA). Synthesis of epoxides.

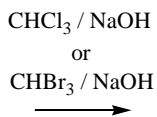
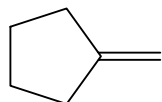
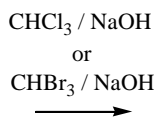
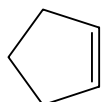
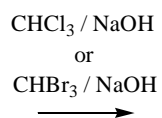
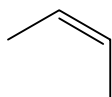
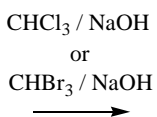
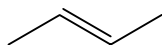
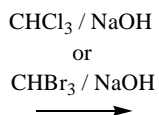
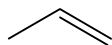


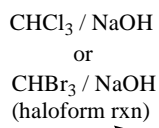
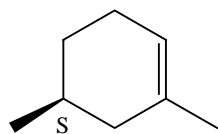
p. Alkenes with $\text{CH}_2\text{I}_2 / \text{Zn}$ (Simmons-Smith Rxn). Carbenoid synthesis of cyclopropanes.



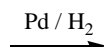
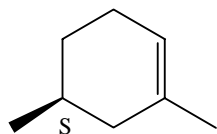
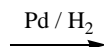
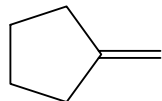
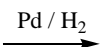
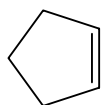
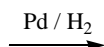
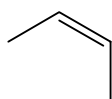
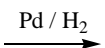
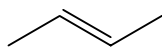
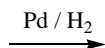
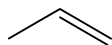
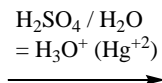
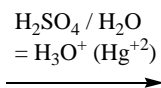
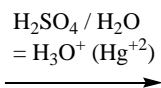


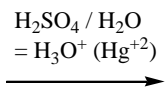
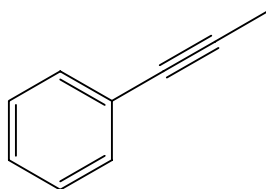
q. Alkenes with $\text{CHCl}_3 / \text{RO}^-$ or $\text{CHBr}_3 / \text{RO}^-$. Carbene synthesis of dihalocyclopanes.



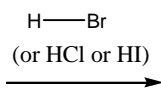
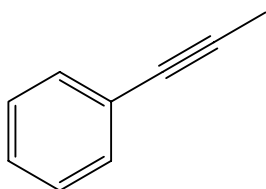
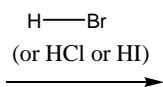
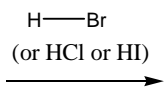
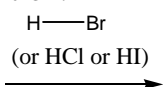


r.

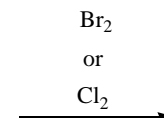
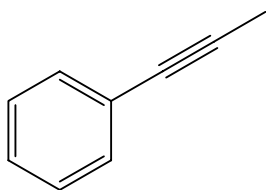
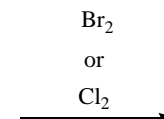
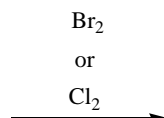
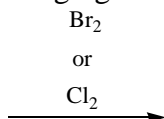
Alkenes with Pd / H₂. Synthesis of “alkane” from “alkene” (hydrogenation).4. a. Alkynes with aqueous sulfuric acid (plus some Hg⁺² catalyst). Synthesis via enols (Markovnikov addition).



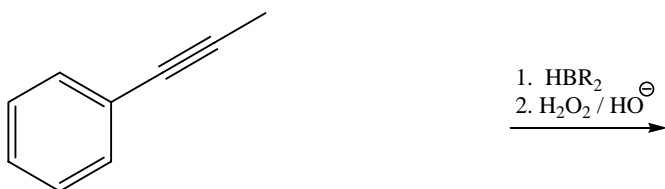
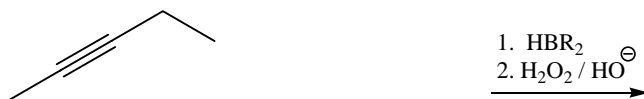
b. HX addition to alkynes. Markovnikov addition.



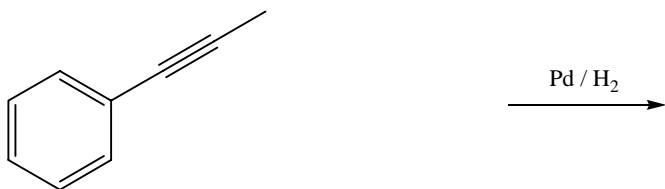
c. Bromination (or chlorination) of alkynes. Bridging bromonium ion.



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

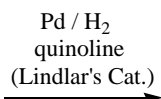
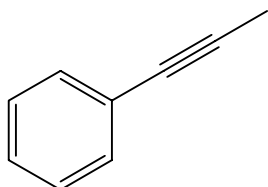
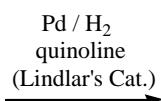


e. Catalytic hydrogenation reduces triple bond to “alkane”.

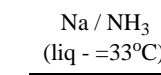
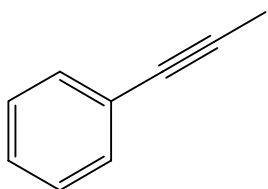
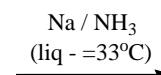
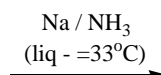
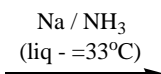


f. Catalytic hydrogenation with quinoline “poison” of Pd catalyst reduces triple bond to Z alkene (syn addition).

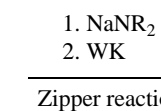
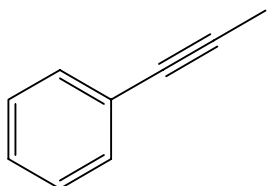
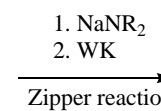
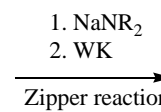
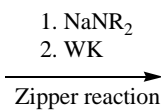




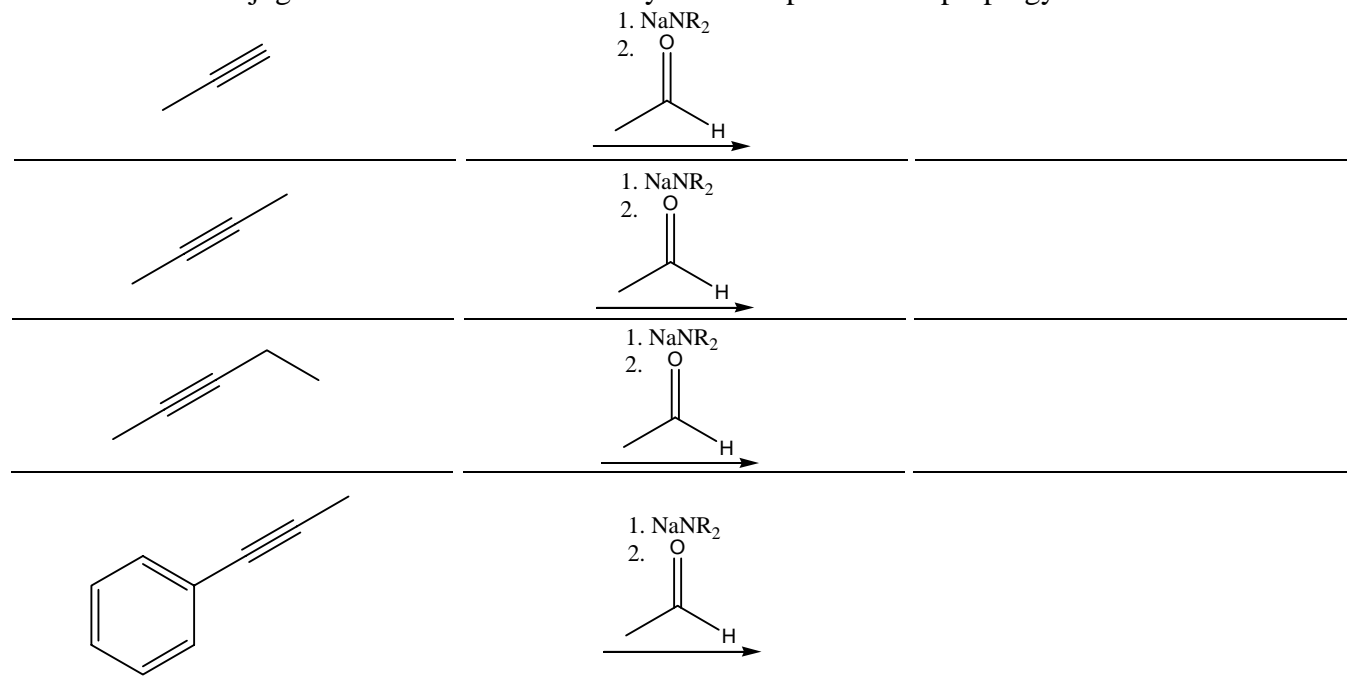
g. Sodium metal + liquid ammonia reduction of triple bond to E alkenes.



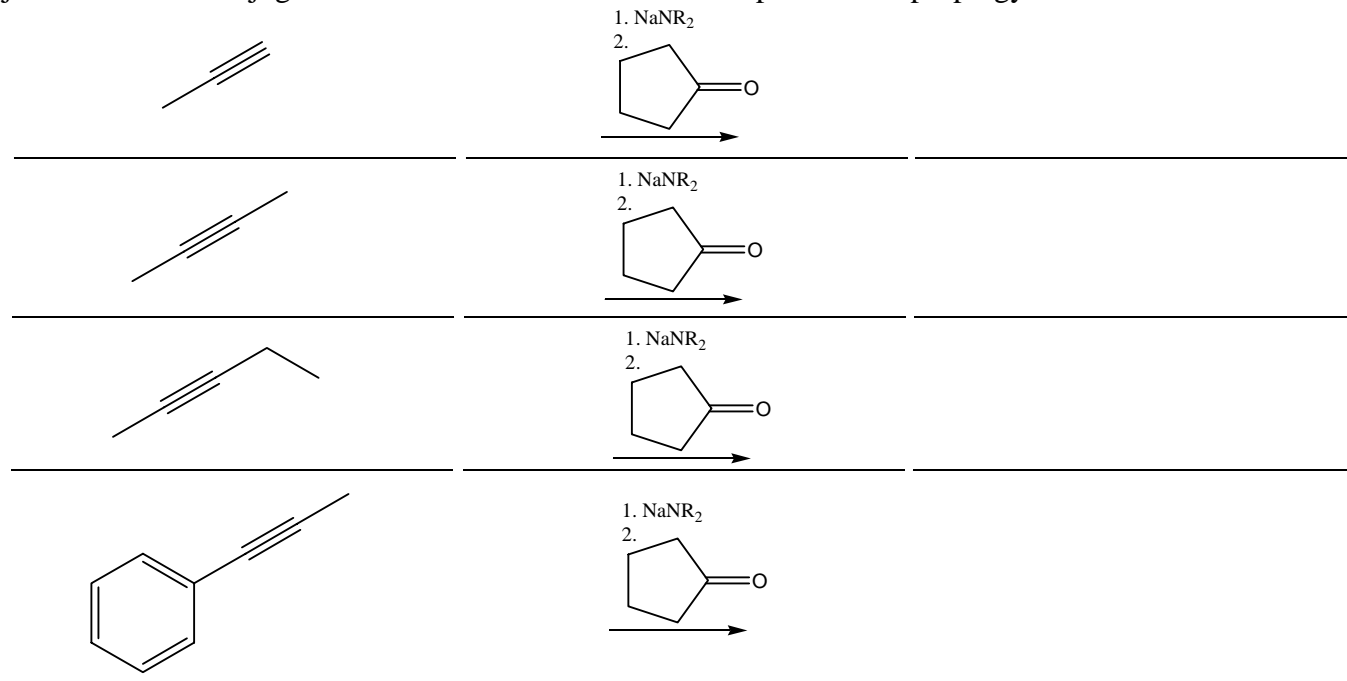
h. Zipper reaction moves triple bond to terminal position where it can be removed to form sp carbanion nucleophile.



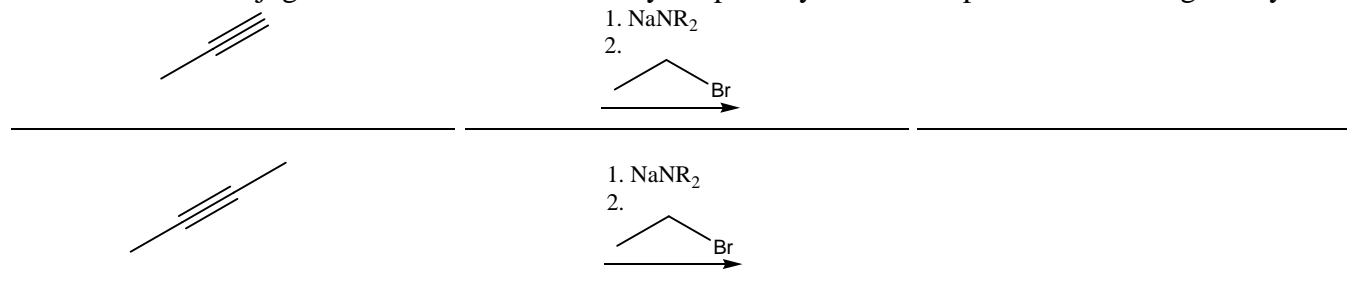
i. Formation of conjugate base + addition of aldehyde electrophile forms propargyl alcohol.

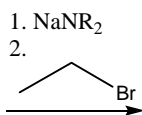
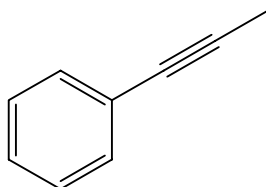
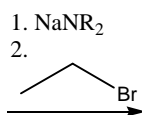


j. Formation of conjugate base + addition of ketone electrophile forms propargyl alcohol.

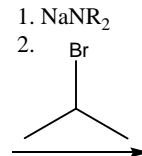
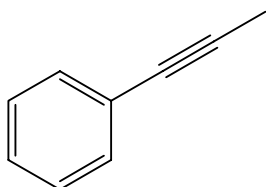
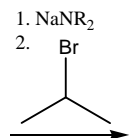
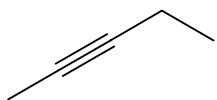
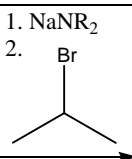
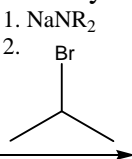


k. Formation of conjugate base + addition of methyl or primary RX electrophile forms a longer alkyne.



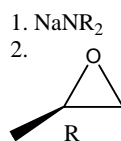
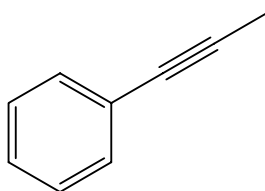
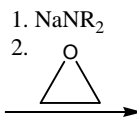
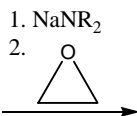
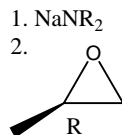


1. Formation of conjugate base + addition of secondary electrophile reacts in a nonproductive E2 reaction.

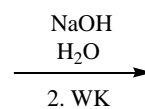
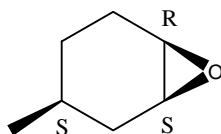
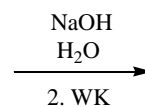
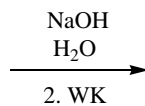
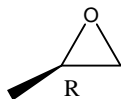
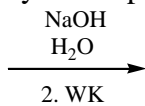


j. Formation of conjugate base + addition of epoxide electrophile forms an alkynyl alcohol via $\text{S}_{\text{N}}2$

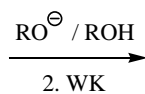
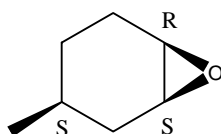
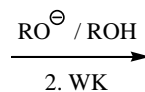
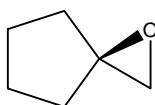
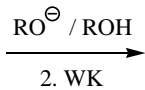
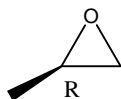
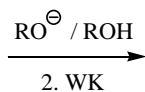
reaction.



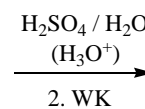
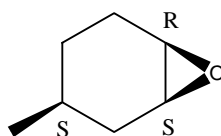
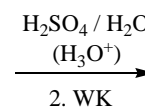
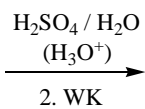
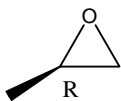
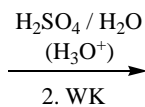
5. a. Epoxides with aqueous hydroxide (followed by workup = neutralization).



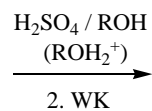
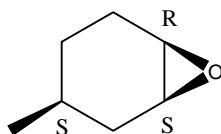
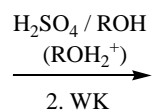
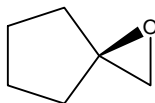
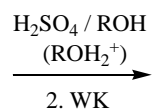
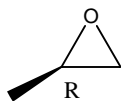
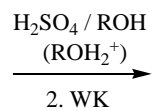
b. Epoxides with alcoholic alkoxide (followed by workup = neutralization).



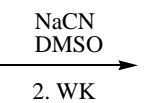
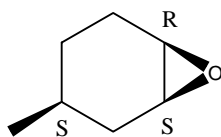
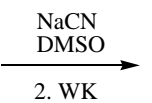
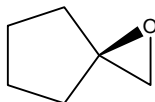
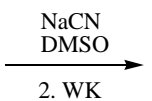
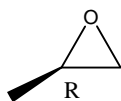
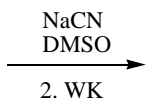
c. Epoxides with aqueous acid.



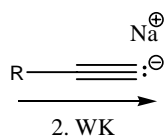
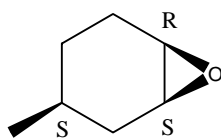
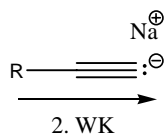
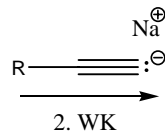
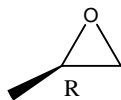
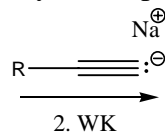
d. Epoxides with alcoholic sulfuric acid.



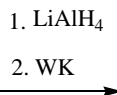
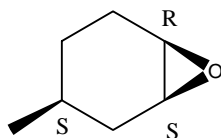
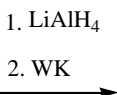
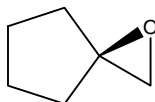
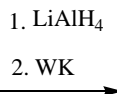
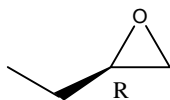
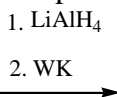
e. Epoxides with cyanide (followed by workup = neutralization)..



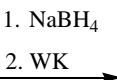
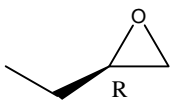
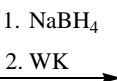
f. Epoxides with terminal acetylides (followed by workup = neutralization).

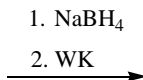
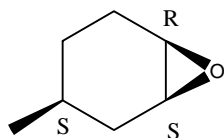
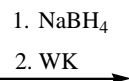
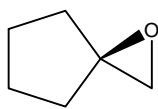


g. Epoxides with LiAlH₄ (LAH) (followed by workup = neutralization).

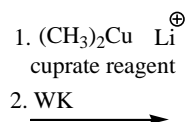
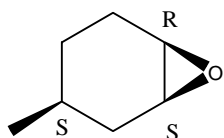
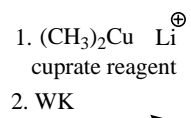
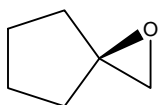
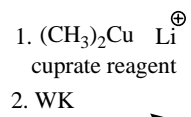
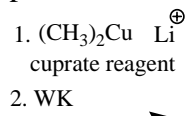


h. Epoxides with NaBH₄ (followed by workup = neutralization).

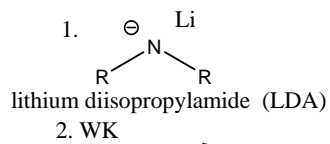
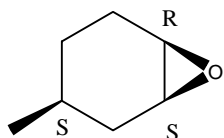
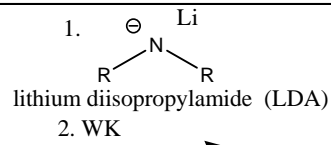
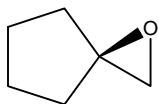
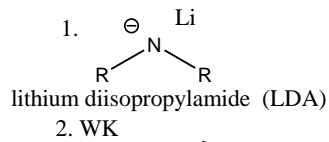
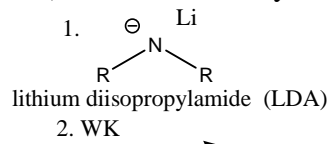
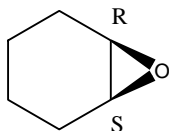




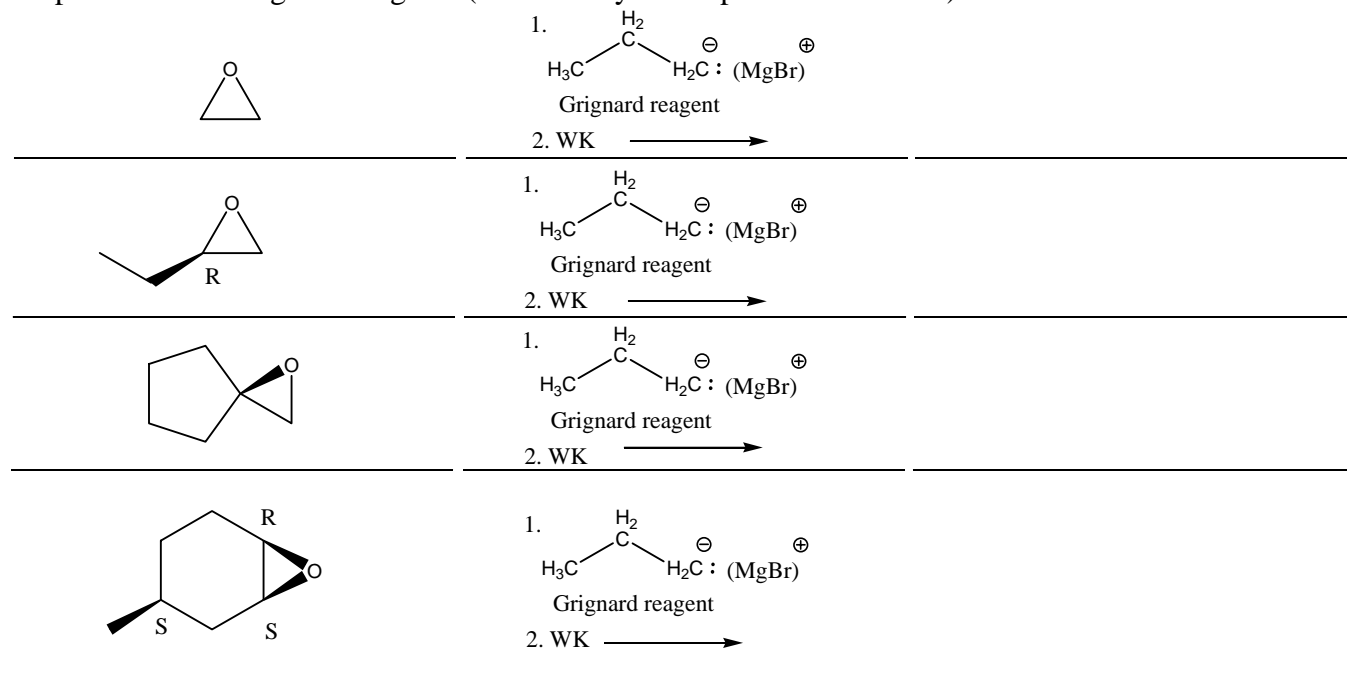
i. Epoxides with cuprates (followed by workup = neutralization).



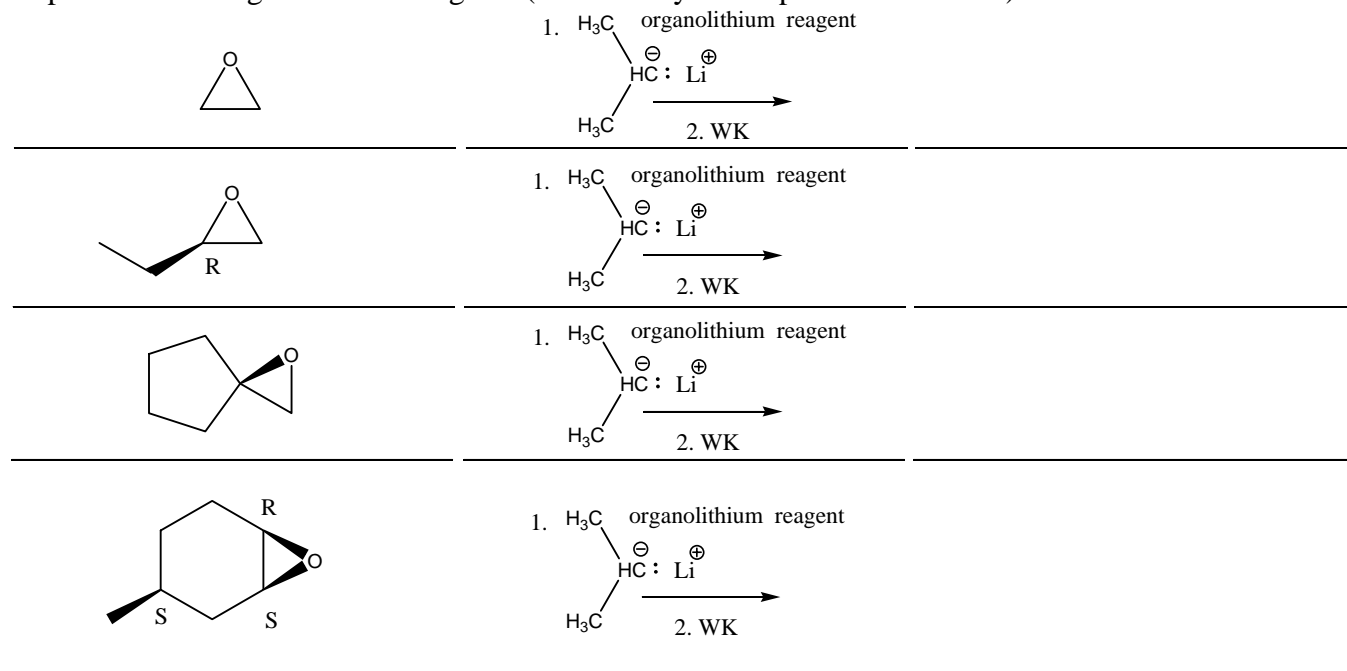
j. Epoxides with lithium diisopropyl amide (LDA, followed by workup = neutralization).



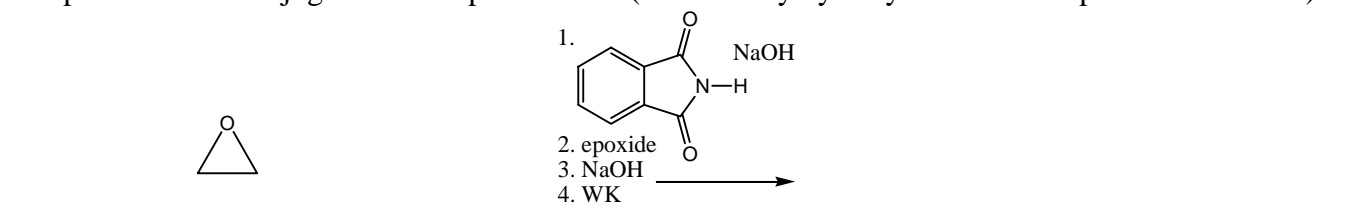
k. Epoxides with Grignard reagents (followed by workup = neutralization).

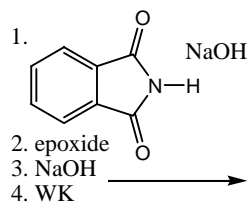
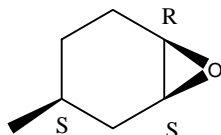
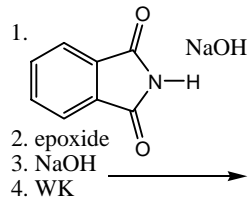
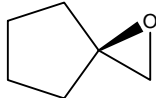
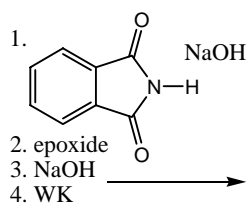


l. Epoxides with organolithium reagents (followed by workup = neutralization).

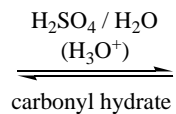
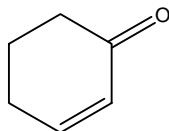
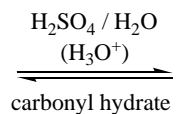
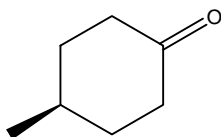
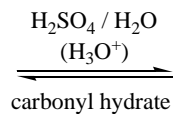
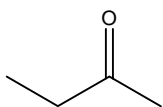
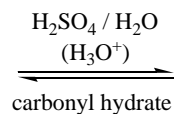
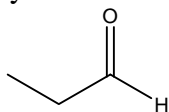


m. Epoxides with conjugate base of phthalimide (followed by hydrolysis and workup = neutralization).

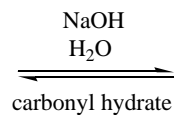
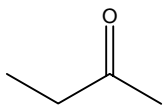
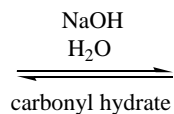
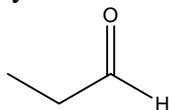




6. a. Aldehydes and ketones in aqueous acid form carbonyl hydrates.



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





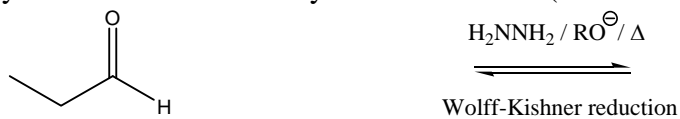
c. Aldehydes and ketones with Jones reagent. Converts aldehydes to carboxylic acids.

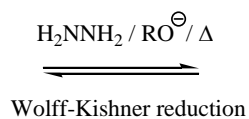
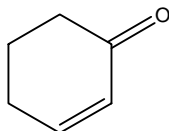
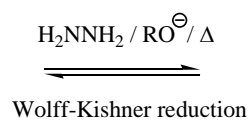
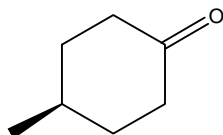
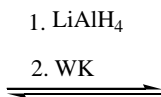
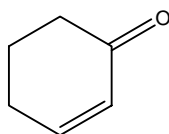
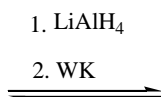
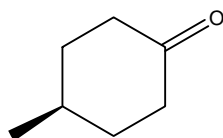
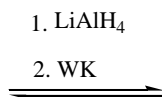
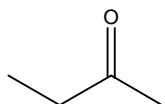
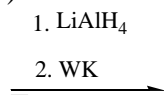
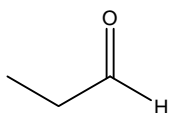
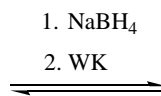
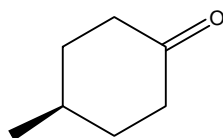
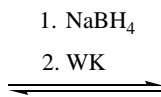
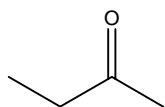
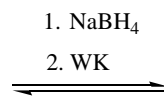
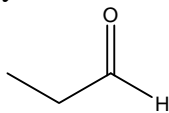


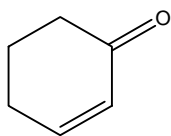
d. Aldehydes and ketones with Zn/HCl (Clemmenson reduction).



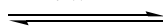
e. Aldehydes and ketones with hydrazine and base (Wolff-Kishner reduction).



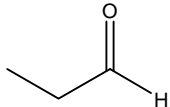
f. Aldehydes and ketones with LiAlH_4 (LAH).g. Aldehydes and ketones with NaBH_4 .



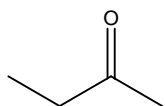
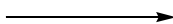
1. NaBH₄
2. WK



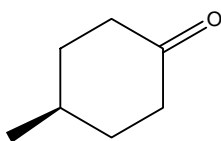
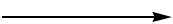
h. Aldehydes and ketones with cyanide, cyanohydrin synthesis or conjugate addition to alpha-beta unsaturated C=O.



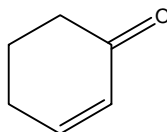
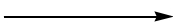
1. NaCN
2. acid addition



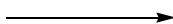
1. NaCN
2. acid addition



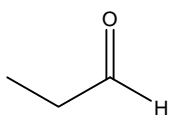
1. NaCN
2. acid addition



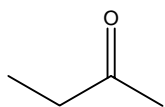
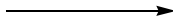
1. NaCN
2. acid addition



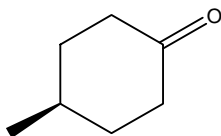
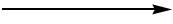
i. Aldehydes and ketones with terminal acetylides.



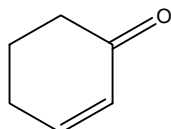
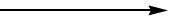
1. R—C≡C:[⊖]Na[⊕]
2. WK



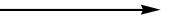
1. R—C≡C:[⊖]Na[⊕]
2. WK



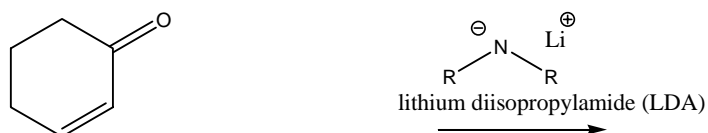
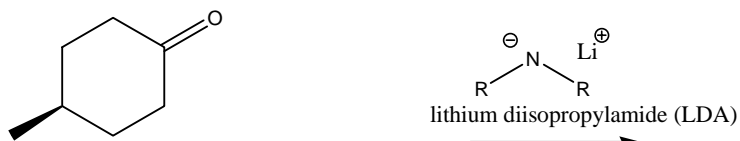
1. R—C≡C:[⊖]Na[⊕]
2. WK



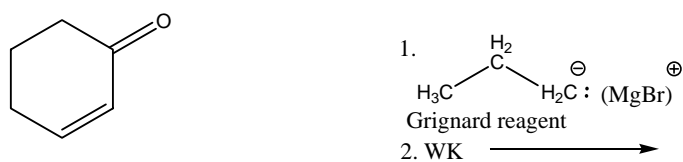
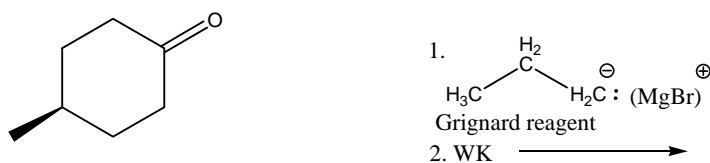
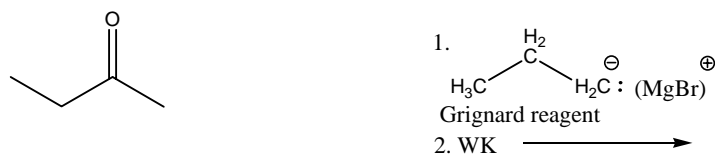
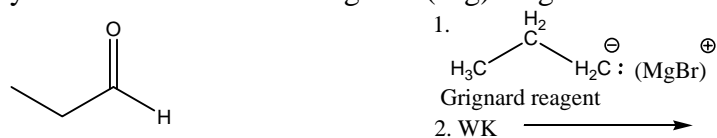
1. R—C≡C:[⊖]Na[⊕]
2. WK



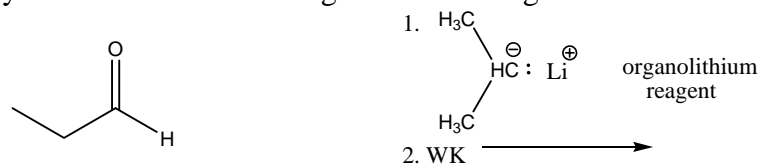
7. j. Aldehydes and ketones with LDA makes enolates (carbanion nucleophiles).

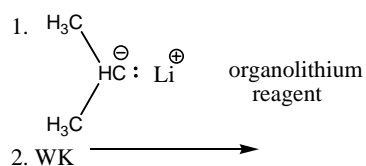
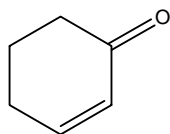
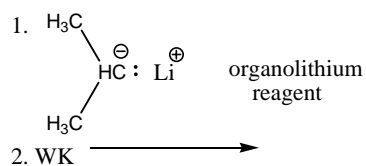
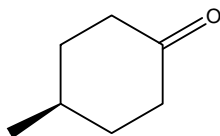
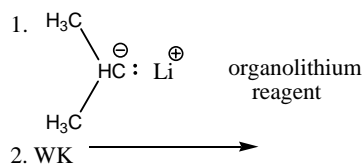
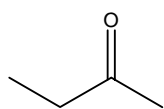


k. Aldehydes and ketones with Grignard (Mg) reagents.

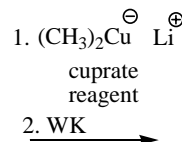
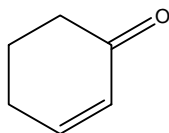
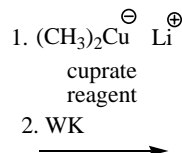
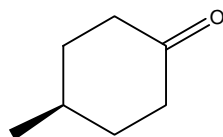
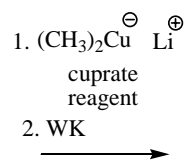
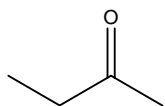
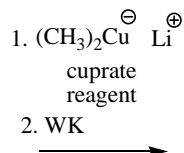
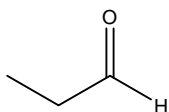


l. Aldehydes and ketones with organolithium reagents.

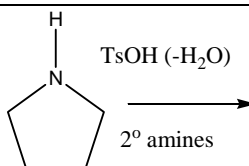
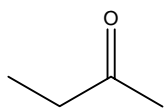
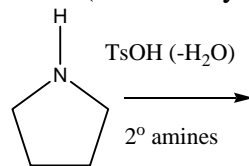
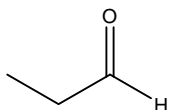


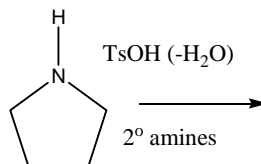
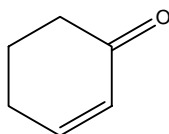
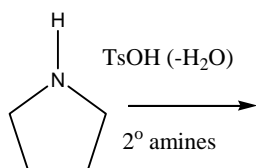
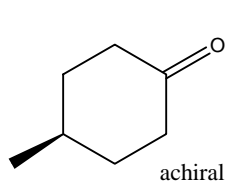


m. Aldehydes and ketones with cuprates.

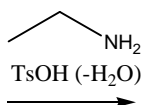
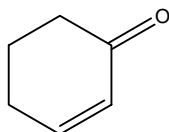
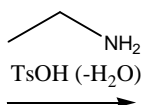
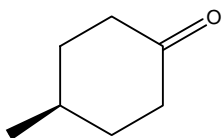
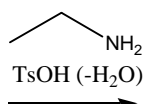
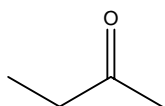
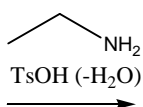
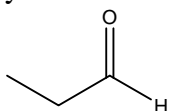


n. Aldehydes and ketones with secondary amines (enamine synthesis, alkylation, hydrolysis).

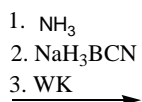
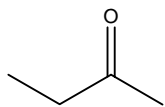
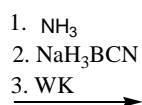
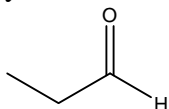




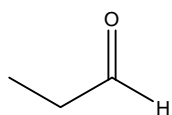
o. Aldehydes and ketones with primary amines (imine synthesis).



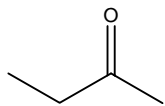
p. Aldehydes and ketones with ammonia + NaBH₃CN = primary amine synthesis.



q. Aldehydes and ketones primary amine + NaBH_3CN = secondary amine synthesis.

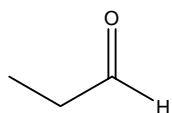


- 1.
2. NaBH_3CN
3. WK \longrightarrow

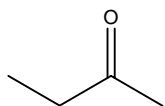


- 1.
2. NaBH_3CN
3. WK \longrightarrow

r. Aldehydes and ketones secondary amine + NaBH_3CN = tertiary amine synthesis.

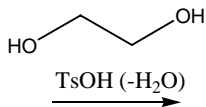
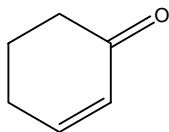
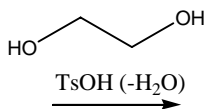
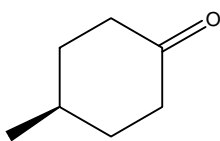
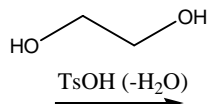
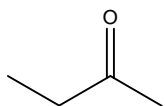
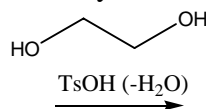
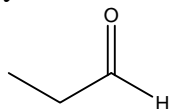


- 1.
2. NaBH_3CN
3. WK \longrightarrow

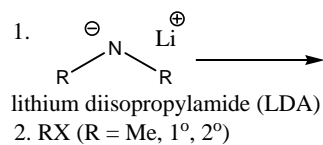
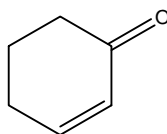
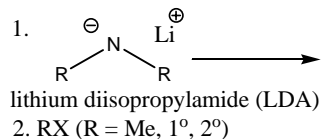
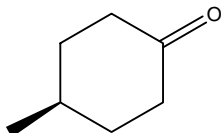
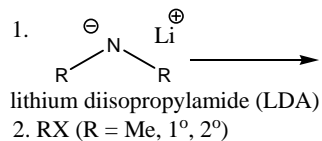
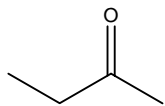
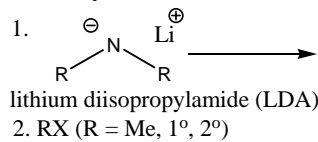
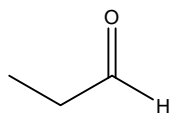


- 1.
2. NaBH_3CN
3. WK \longrightarrow

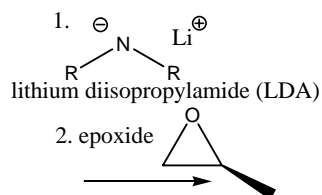
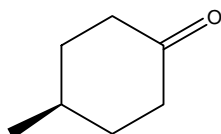
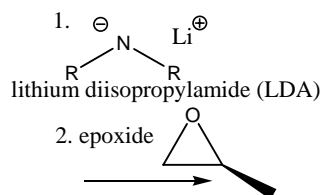
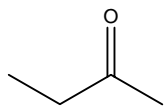
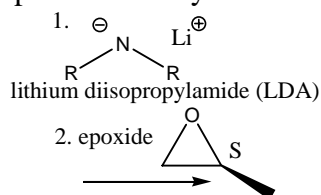
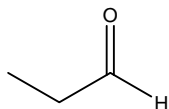
s. Aldehydes and ketones ethylene glycol, acid, dehydration: ketal and acetal synthesis = protection).



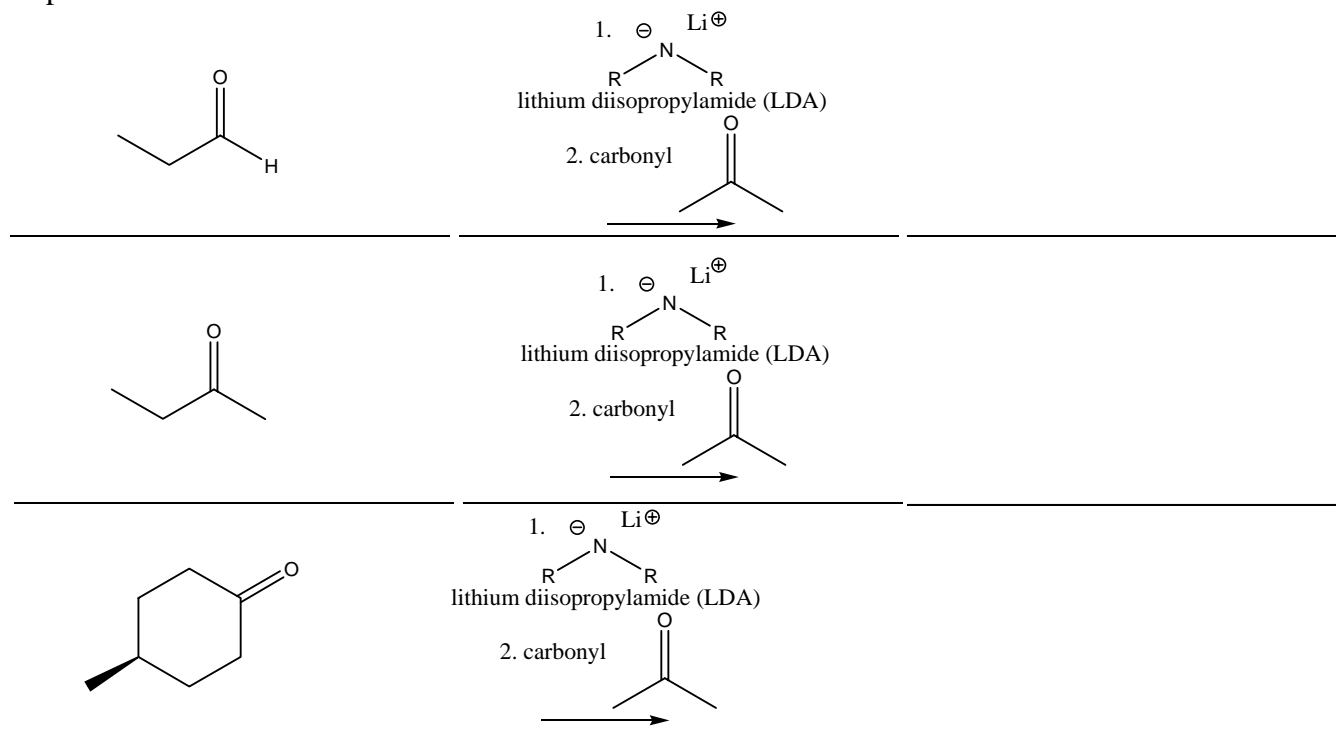
t. Aldehydes and ketones with 1. LDA 2. RX = alkylation of C=O.



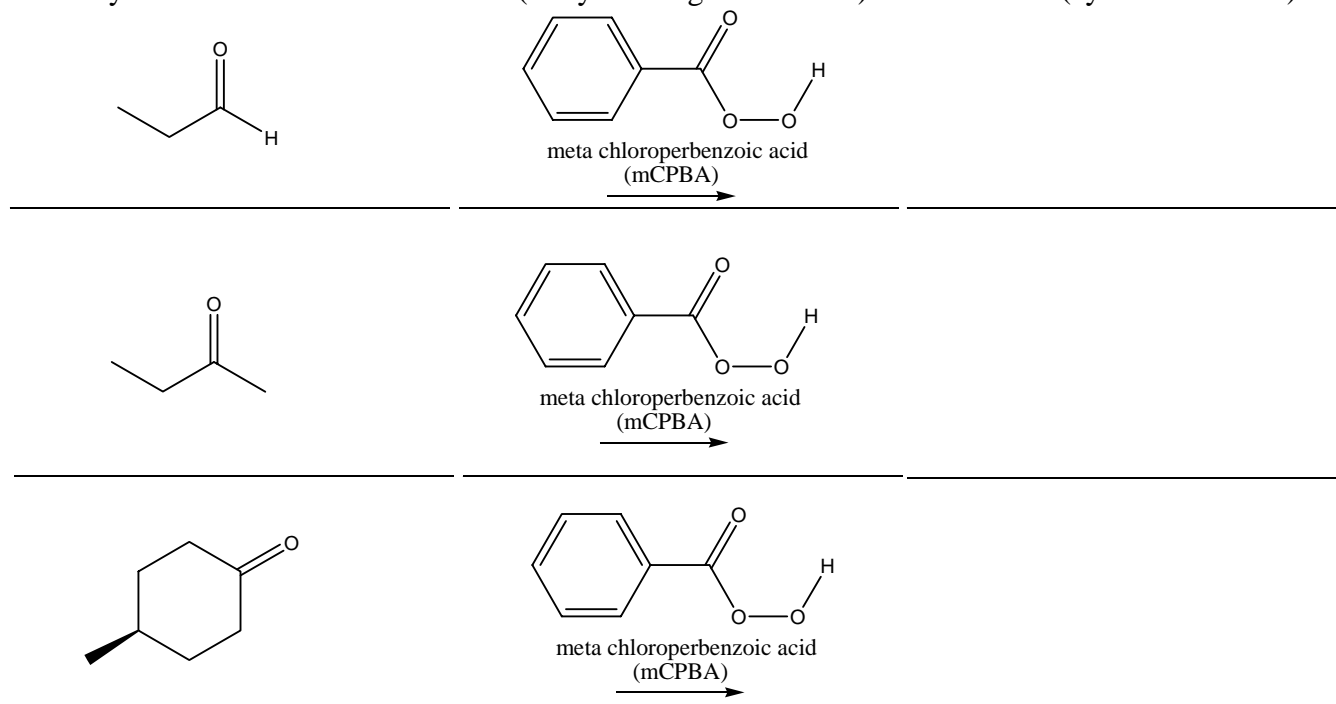
u. Aldehydes and ketones with 1. LDA 2. epoxide = alkylation of C=O.



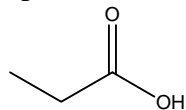
v. Aldehydes and ketones with 1. LDA 2. another C=O = addition to C=O. Forms a beta hydroxyl carbonyl, which can be dehydrated in acid or base (with heat) to an α,β -unsaturated carbonyl compound.



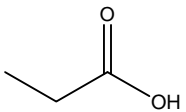
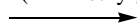
w. Aldehydes and ketones with mCPBA (Baeyer-Villiger oxidation) to form esters (cyclic = lactones).



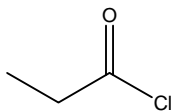
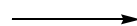
8. Show the products of the following miscellaneous reactions.



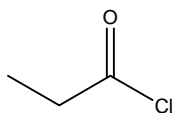
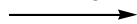
1. NaOH
2. RX (R = methyl, 1°, 2°)



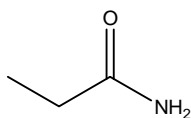
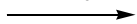
SOCl₂



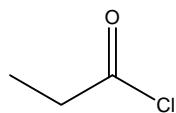
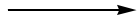
R—OH



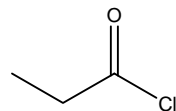
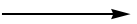
NH₃



SOCl₂



R—NH₂



R—NH—R

