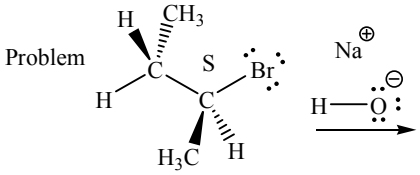
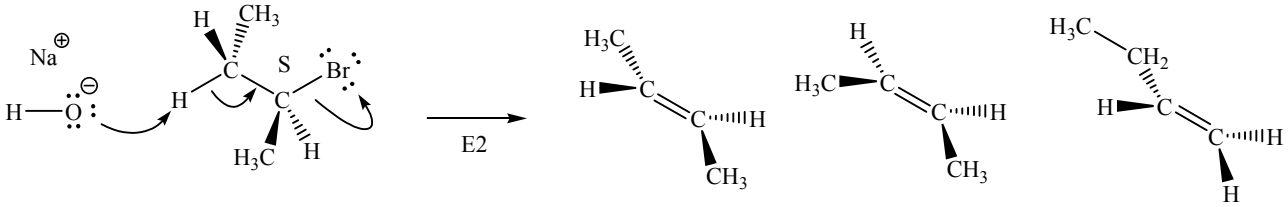
Electrophile (Lewis Acid) = electron loving = any general electron pair acceptor (can also be an acidic proton = Bronsted acid)
Nucleophile (Lewis Base) = nucleus/positive loving = any general electron pair donor (can also be donated to an acidic proton = Bronsted base)
Free Radicals = one electron transfers, only limited examples are emphasized in our course (free radical substitution at sp^3 C-H, anti-Markovnikov free radical addition reactions to pi bonds and some reactions with metals),

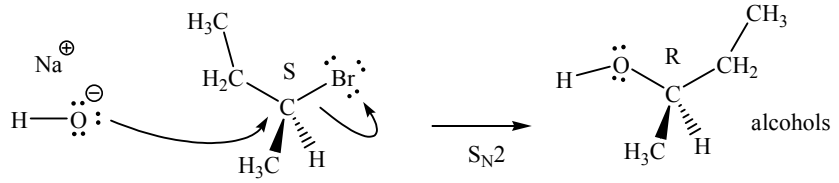
Problems - Supply the lone pairs, formal charge and the curved arrows to show how the electrons move for each step of a reaction mechanism. Be able to identify nucleophiles and electrophiles in each step of the reactions below. Our two free radical mechanisms (substitution at sp^3 C-H and anti-Markovnikov addition to pi bonds) are at the end. Check your mechanisms against the examples provided.

S_N2 and E2 Mechanisms (strong base/nucleophile competition reacting at a carbon or reacting at a proton)

1. Hydroxide (available as NaOH, KOH or LiOH)

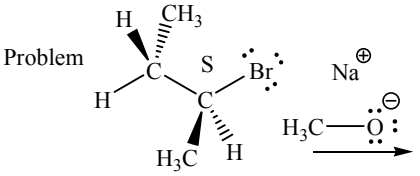


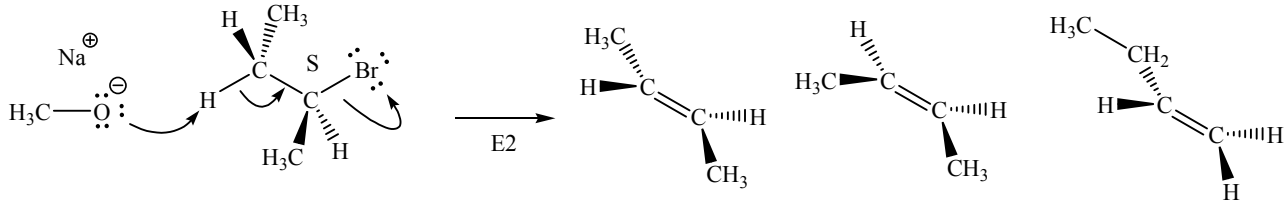


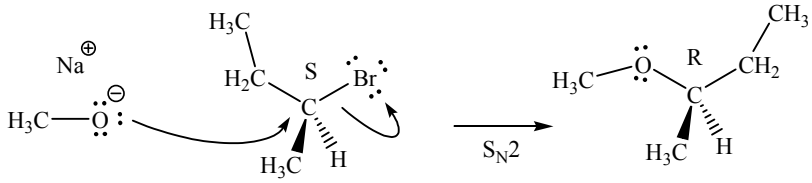


methyl RBr	= only S_N2
primary RBr	= S_N2 > E2
secondary RBr	= E2 > S_N2
tertiary RBr	= only E2

2. Alkoxide (make with ROH + NaH or make ROH + Na)

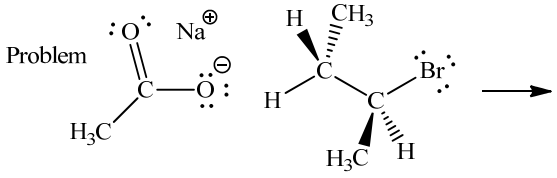


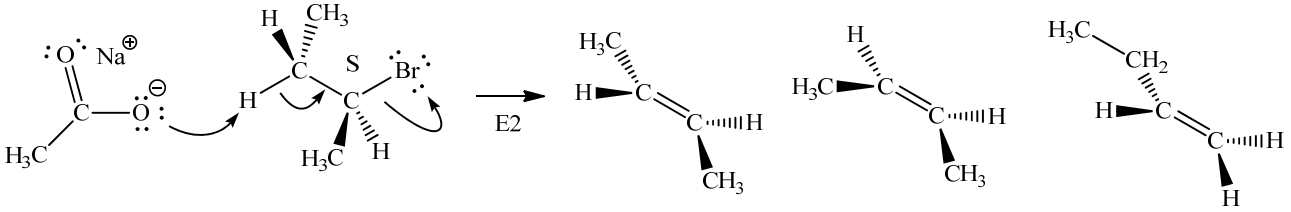


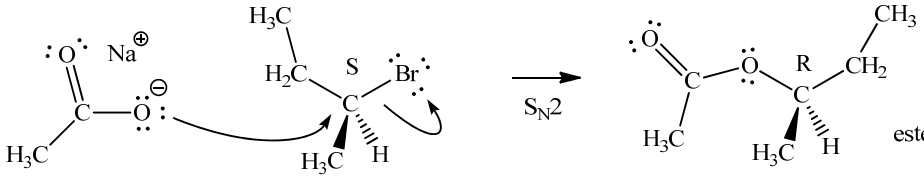


methyl RBr	= only S_N2
primary RBr	= S_N2 > E2
secondary RBr	= E2 > S_N2
tertiary RBr	= only E2

3. Carboxylates (make with RCO_2H + NaOH)

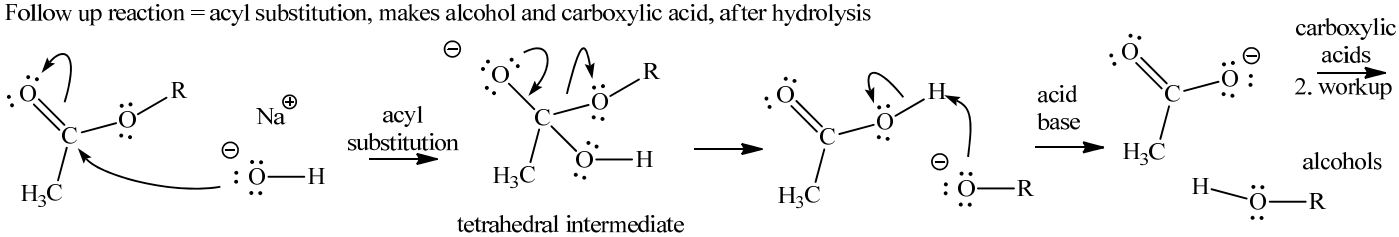




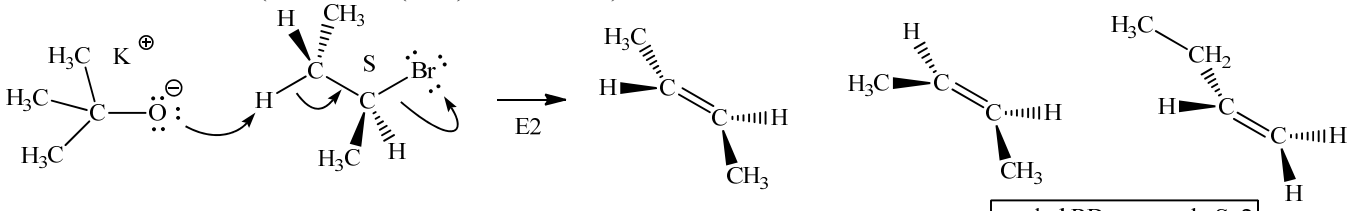


methyl RBr	= only S_N2
primary RBr	= S_N2 > E2
secondary RBr	= S_N2 > E2
tertiary RBr	= only E2

Follow up reaction = acyl substitution, makes alcohol and carboxylic acid, after hydrolysis

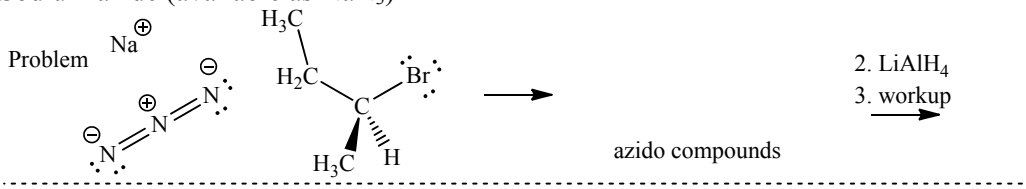


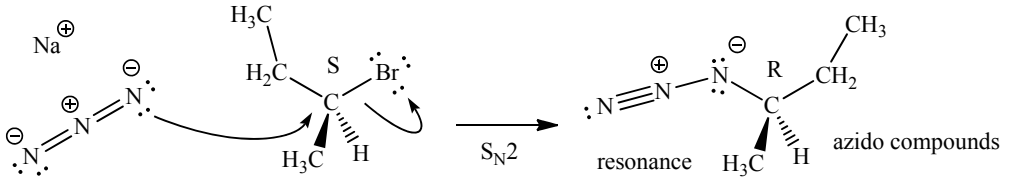
4. Potassium t-butoxide (make with $(CH_3)_3COH$ + KH)



methyl RBr	= only S_N2
primary RBr	= E2 > S_N2
secondary RBr	= only E2
tertiary RBr	= only E2

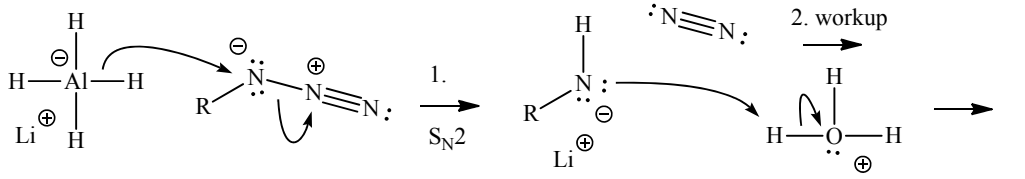
5. Sodium azide (available as NaN_3)





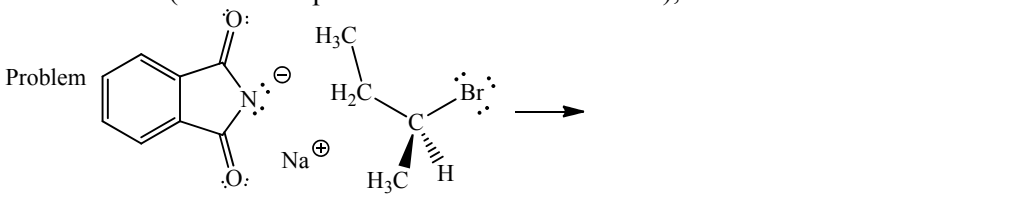
methyl RBr	= only S_N2
primary RBr	= mainly S_N2
secondary RBr	= mainly S_N2
tertiary RBr	= only E2

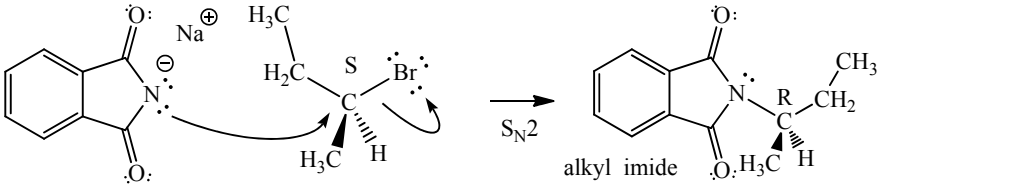
Follow up reaction = S_N2 reaction at nitrogen, followed by workup (protonates nitrogen)



Can also use the Gabriel amine synthesis (next).

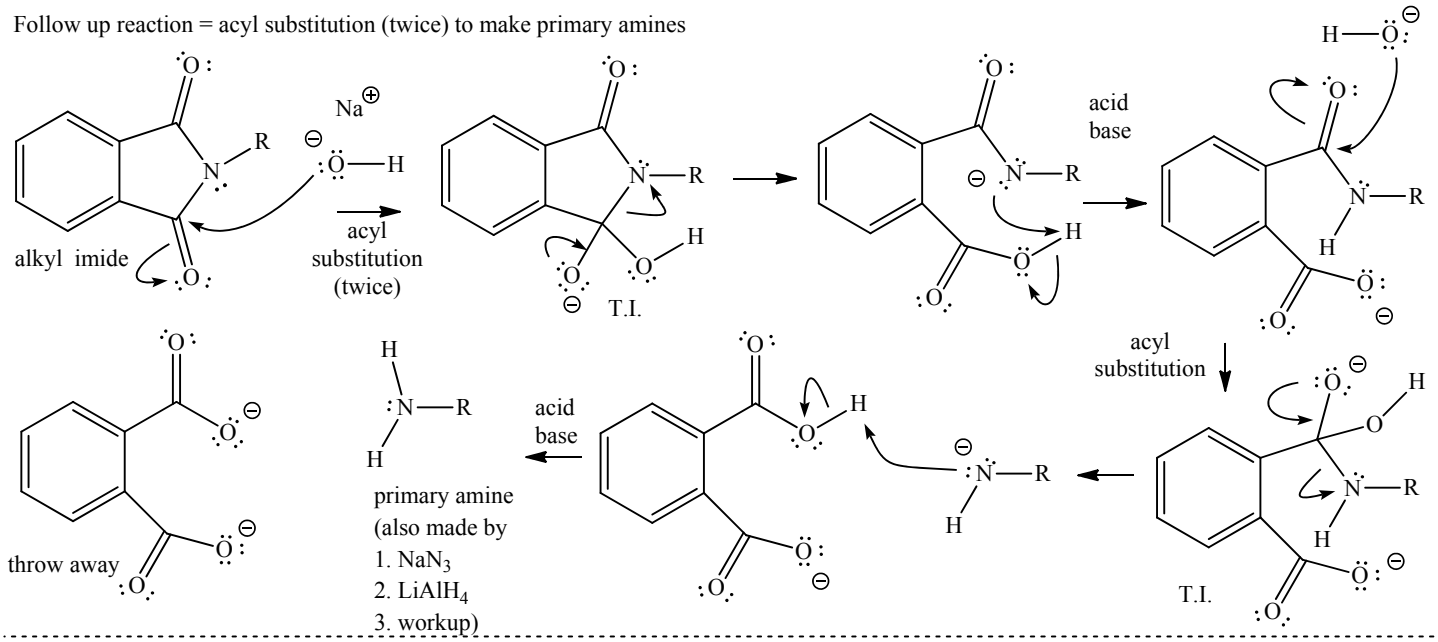
6. Phthalimidate (make from phthalimide + NaOH or KOH), Also called the Gabriel amine synthesis.



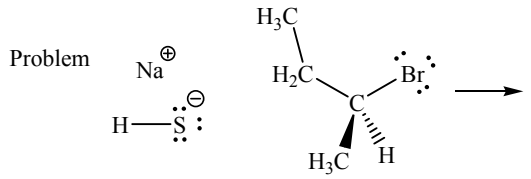


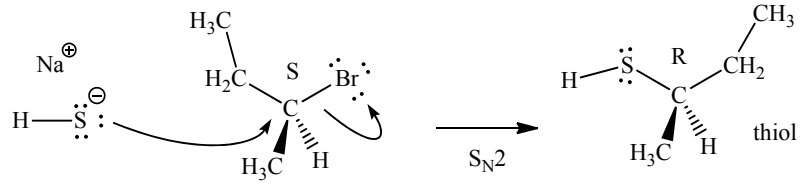
methyl RBr	= only S_N2
primary RBr	= mainly S_N2
secondary RBr	= mainly S_N2
tertiary RBr	= only E2

Follow up reaction = acyl substitution (twice) to make primary amines



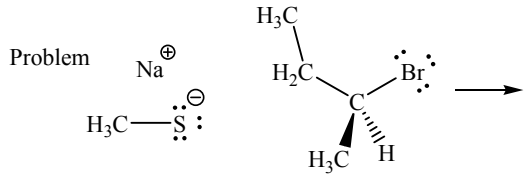
7. Sodium hydrogensulfide (available as NaSH)

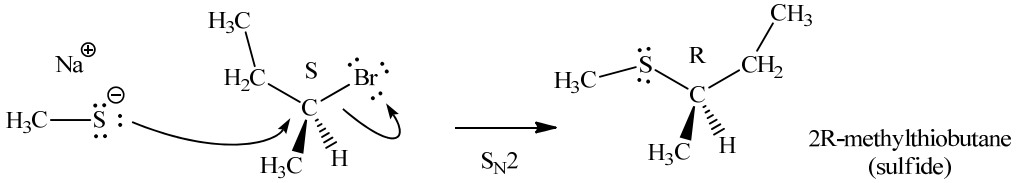




methyl RBr	= only S_N2
primary RBr	= mainly S_N2
secondary RBr	= mainly S_N2
tertiary RBr	= only E2

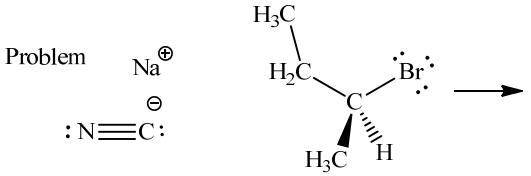
8. Sodium alkylsulfide (make from RSH + NaOH)

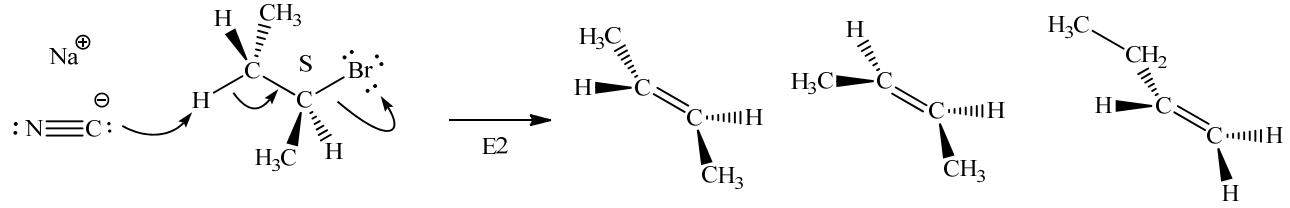


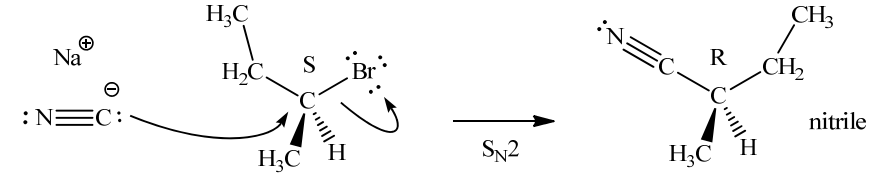


methyl RBr	= only S_N2
primary RBr	= mainly S_N2
secondary RBr	= mainly S_N2
tertiary RBr	= only E2

9. Cyanide (available as NaCN)

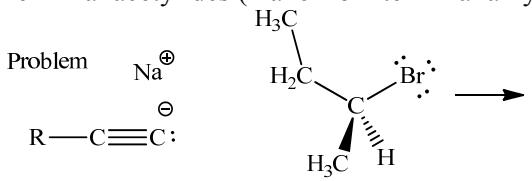


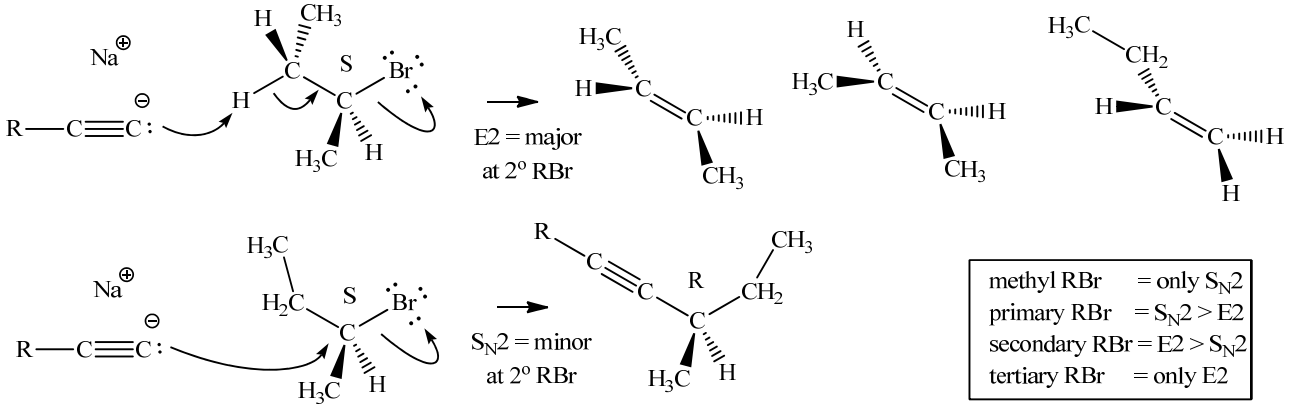




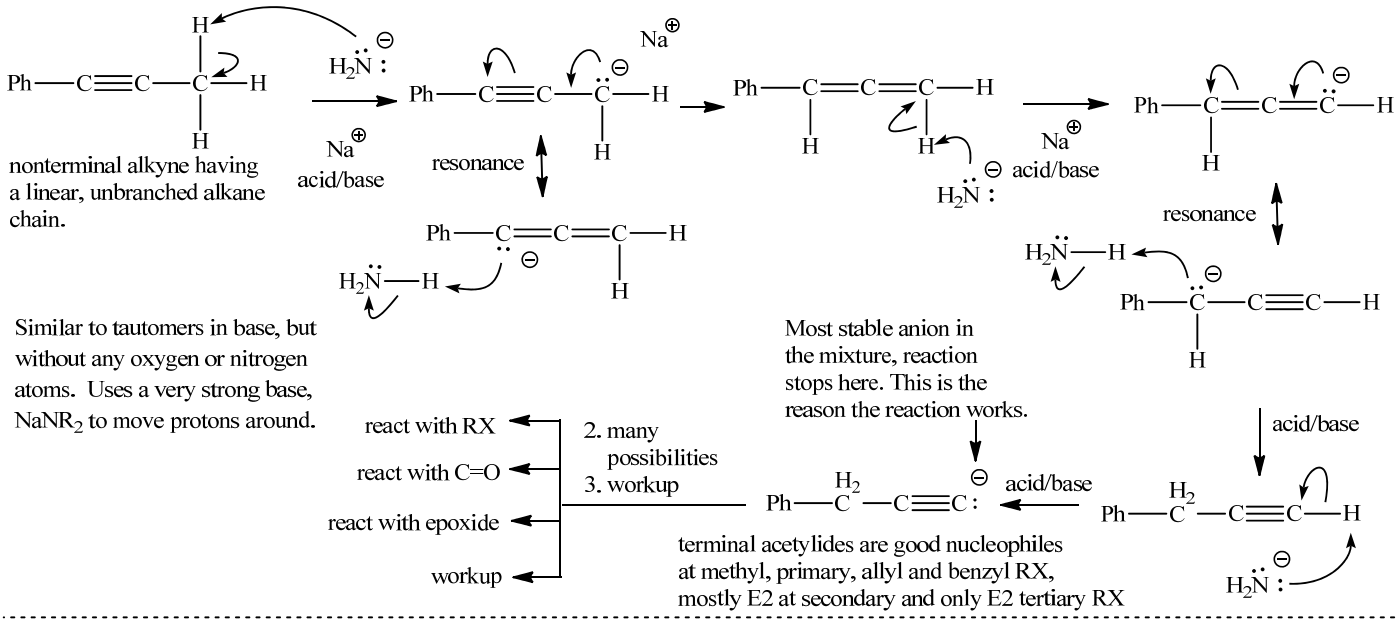
methyl RBr	= only S_N2
primary RBr	= S_N2 > E2
secondary RBr	= S_N2 > E2
tertiary RBr	= only E2

10. Terminal acetylides (make from terminal alkynes, RCCH + $NaNR_2$)

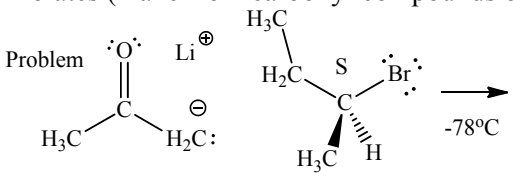


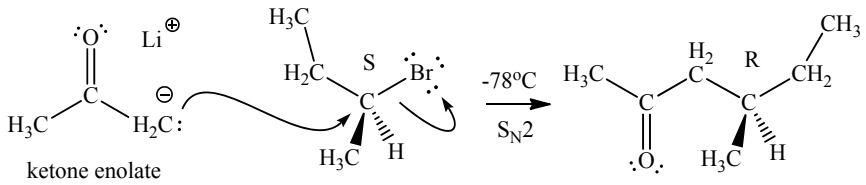


zipper reaction – moves an internal triple bond (CC) to the end position in unbranched chains where the negative charge is the most stable (in sp orbital).

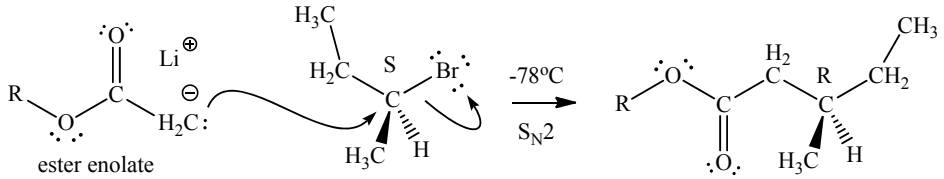


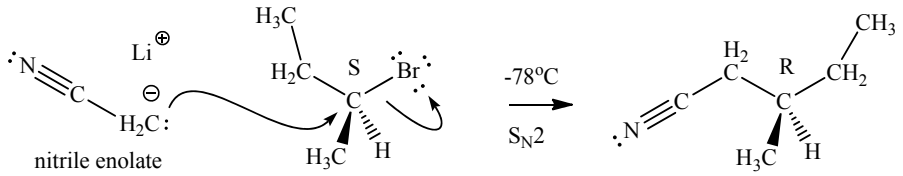
11. Enolates (make from carbonyl compounds or nitriles + LDA, -78°C to prevent side reactions)





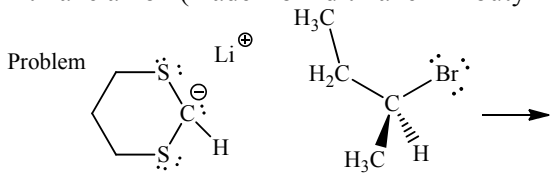
methyl RBr	= only S_N2
primary RBr	= mainly S_N2
secondary RBr	= mainly S_N2
tertiary RBr	= only E2

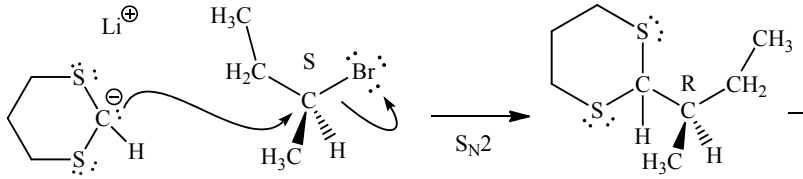




There are many variations of this reaction on the enolate component and on the electrophilic component.

12. Dithiane anion (made from dithiane + n-butyl lithium)

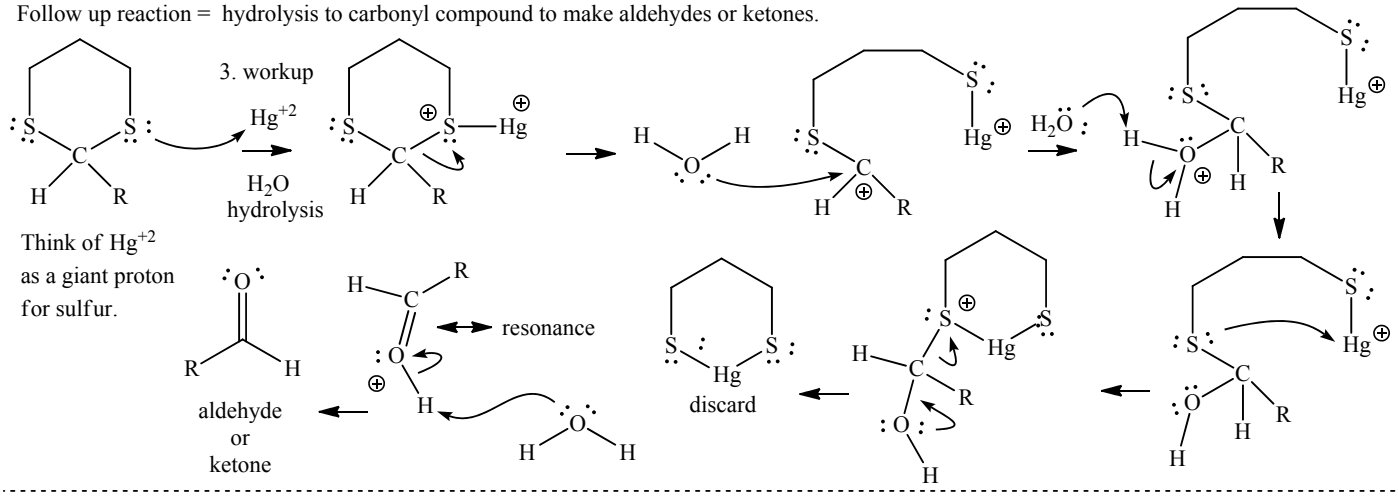




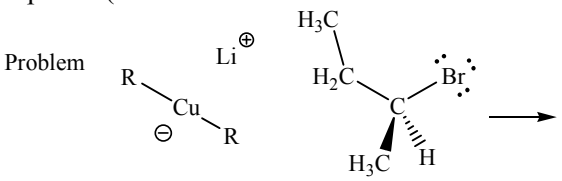
Can repeat one more time.

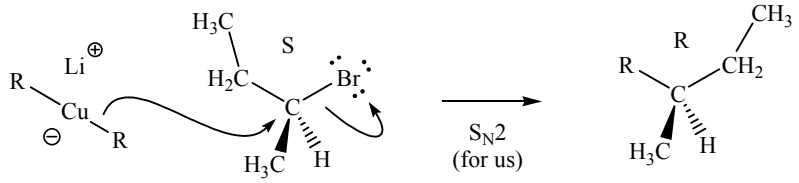
methyl RBr	= only S_N2
primary RBr	= mainly S_N2
secondary RBr	= mainly S_N2
tertiary RBr	= only E2

Follow up reaction = hydrolysis to carbonyl compound to make aldehydes or ketones.



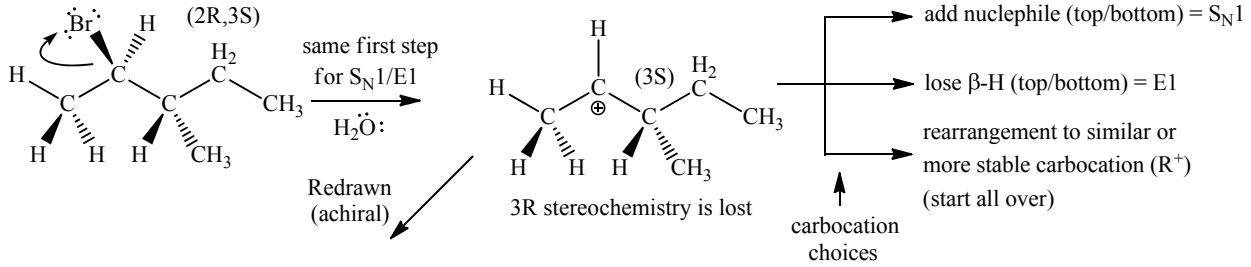
13. Cuprates (made from RBr/Li → RLi + CuBr → R_2Cu^{-} + R'Br → R-R')



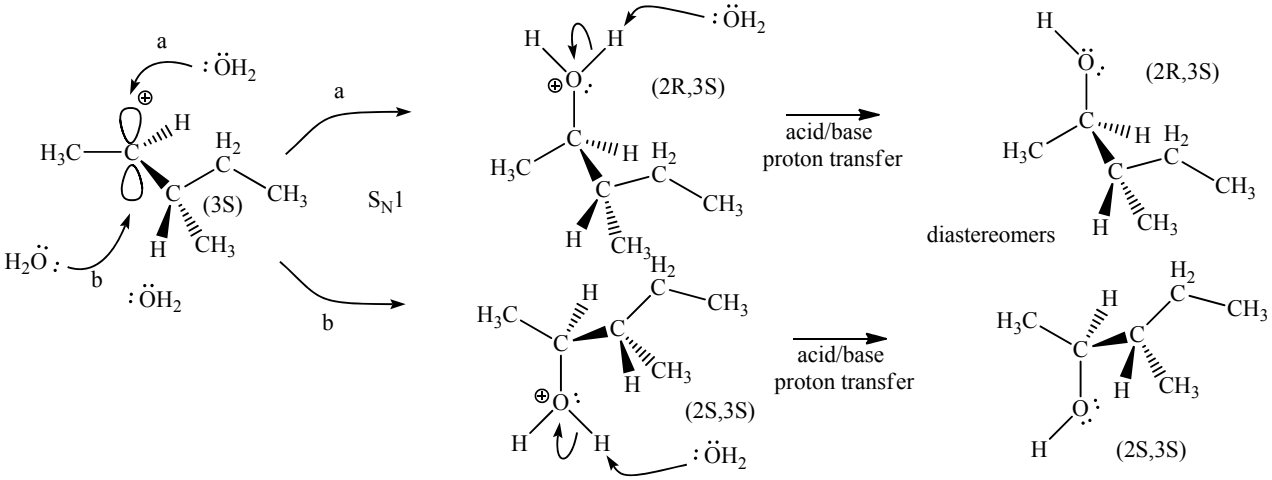


methyl RBr	= only S_N2
primary RBr	= mainly S_N2
secondary RBr	= mainly S_N2
tertiary RBr	= only E2

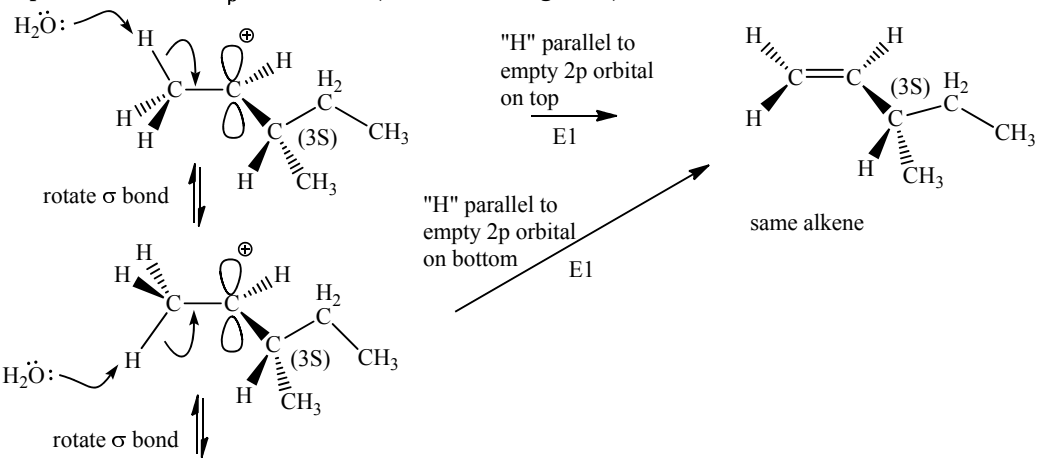
S_N1 / E1 possibilities –extra complications at C_β positions of 2^o RX, rearrangement to more stable 3^o R^+ considered



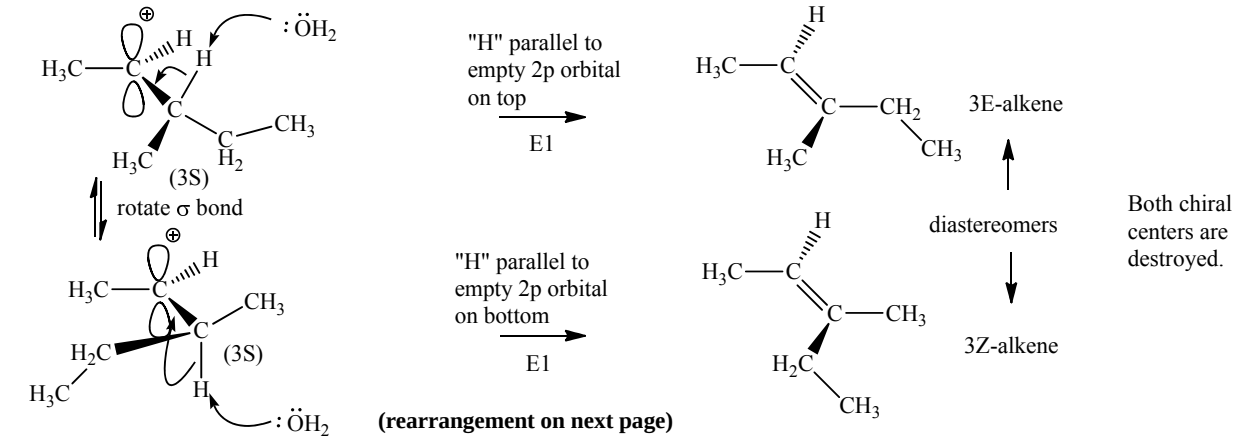
S_N1 product (a. add from top and b. add from bottom), (without rearrangement), usually S_N1 > E1 (in our course)



E1 product from left C_β carbon atom (without rearrangement)

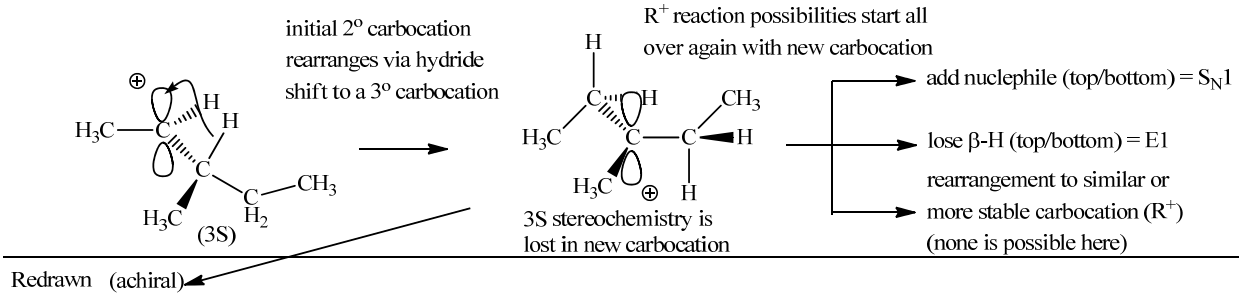


E1 product from right C_β carbon atom (without rearrangement)



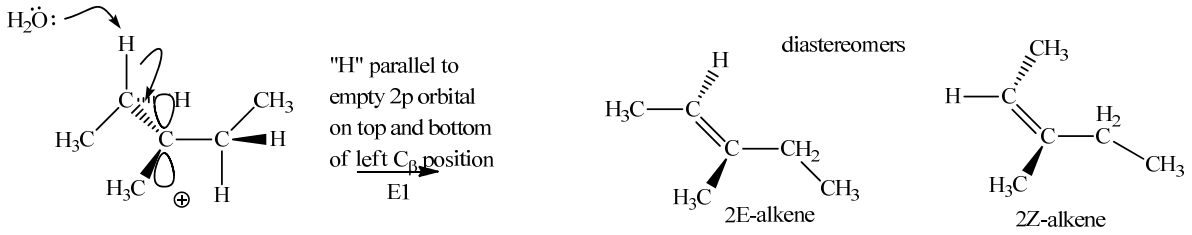
(rearrangement on next page)

After rearrangement to 3° carbocation (R^+)

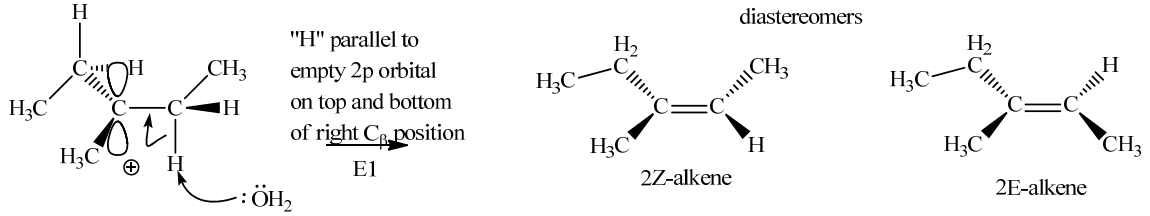


Redrawn (achiral)

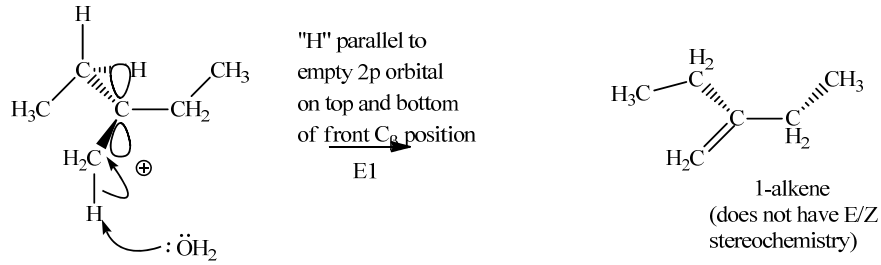
E1 products from left C_β carbon atom (top and bottom, after rearrangement)



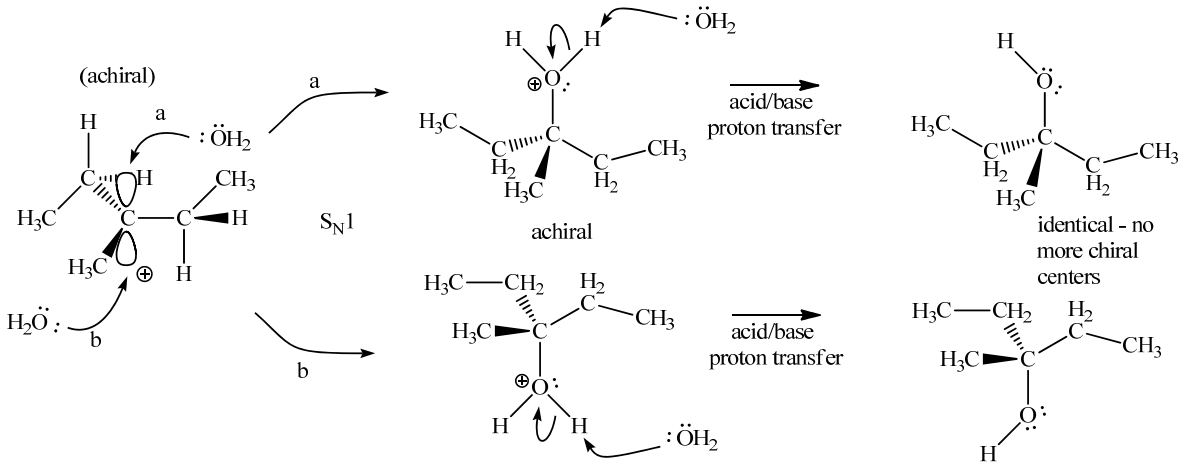
E1 product from right C_β carbon atom (top and bottom, after rearrangement)



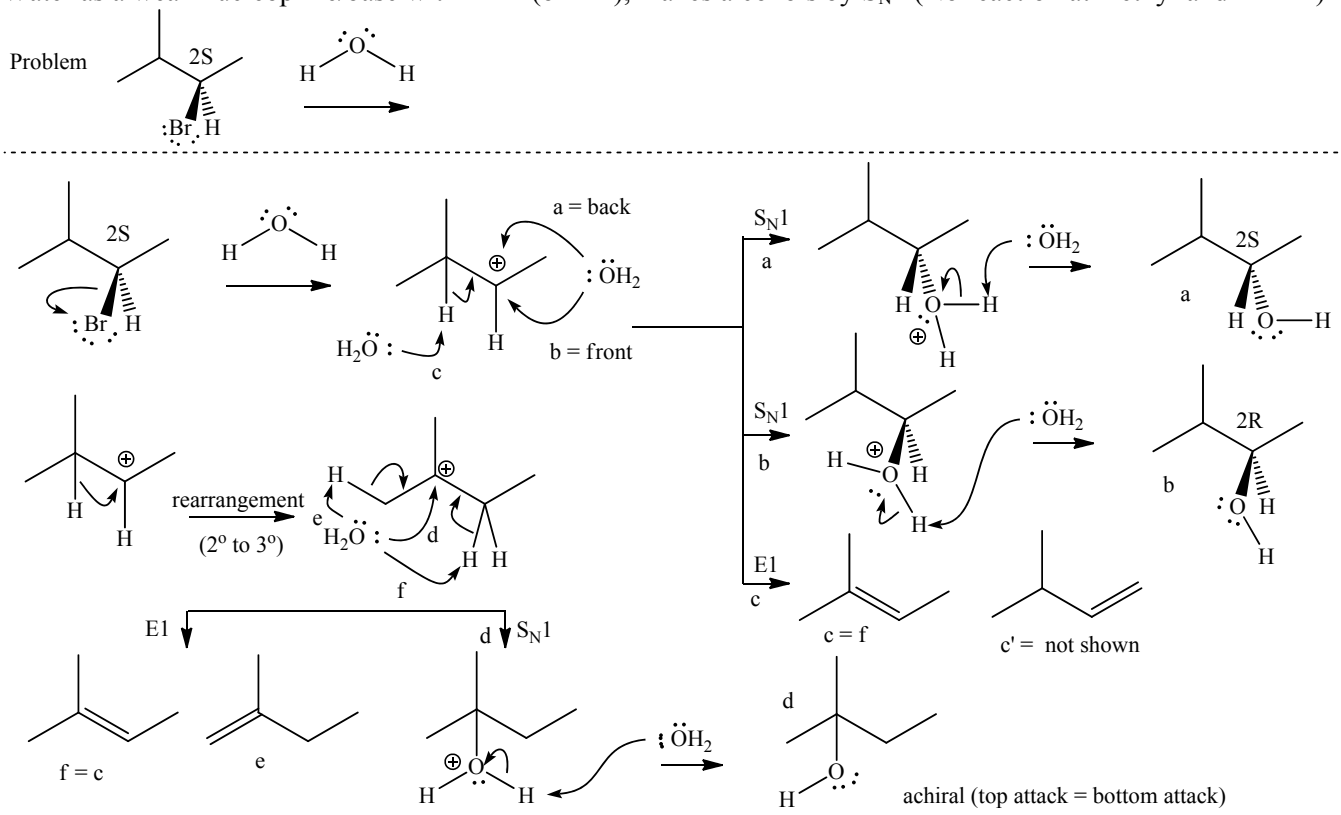
E1 product from methyl C_β carbon atom (top and bottom, after rearrangement, only one product from the methyl)



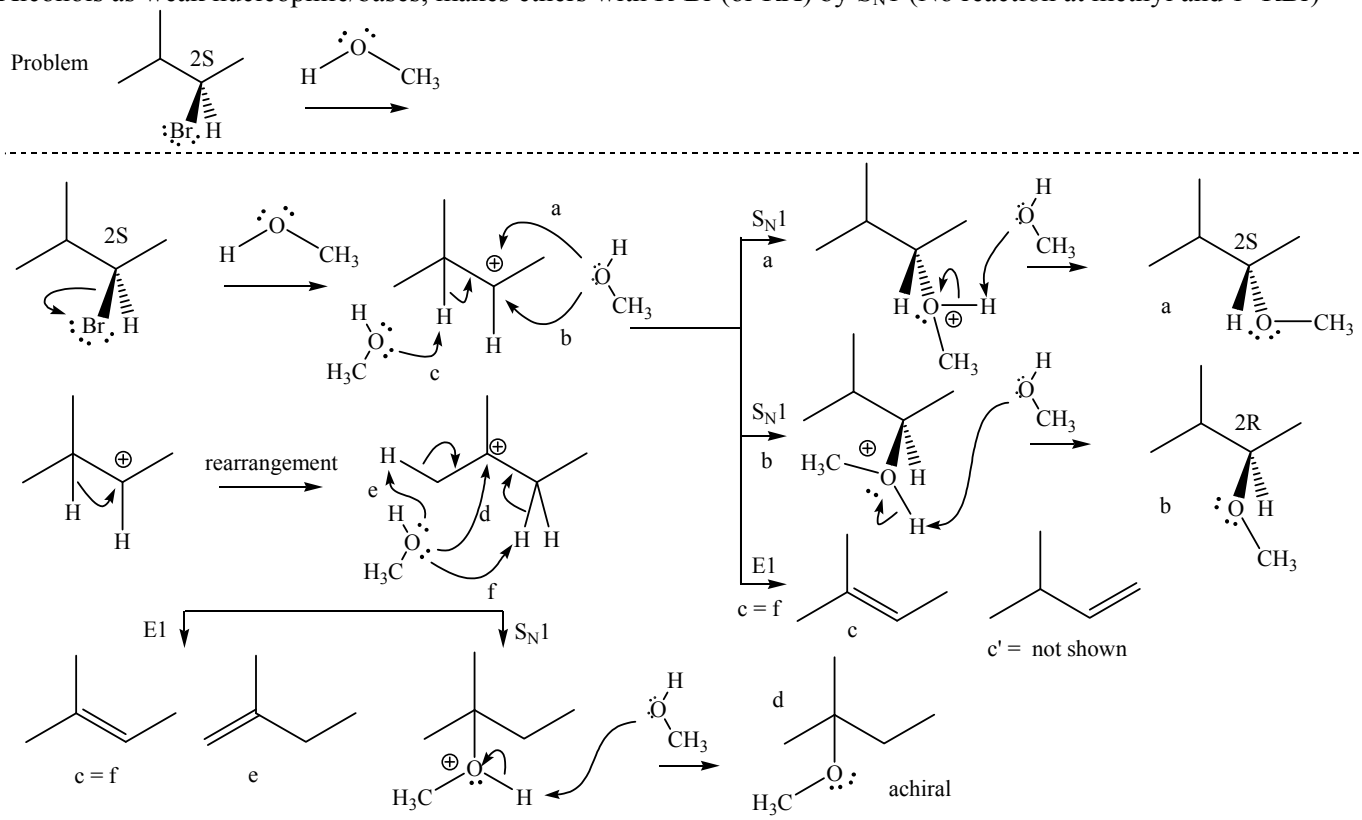
S_N1 product (a. add from top and b. add from bottom = identical in this example, after rearrangement)



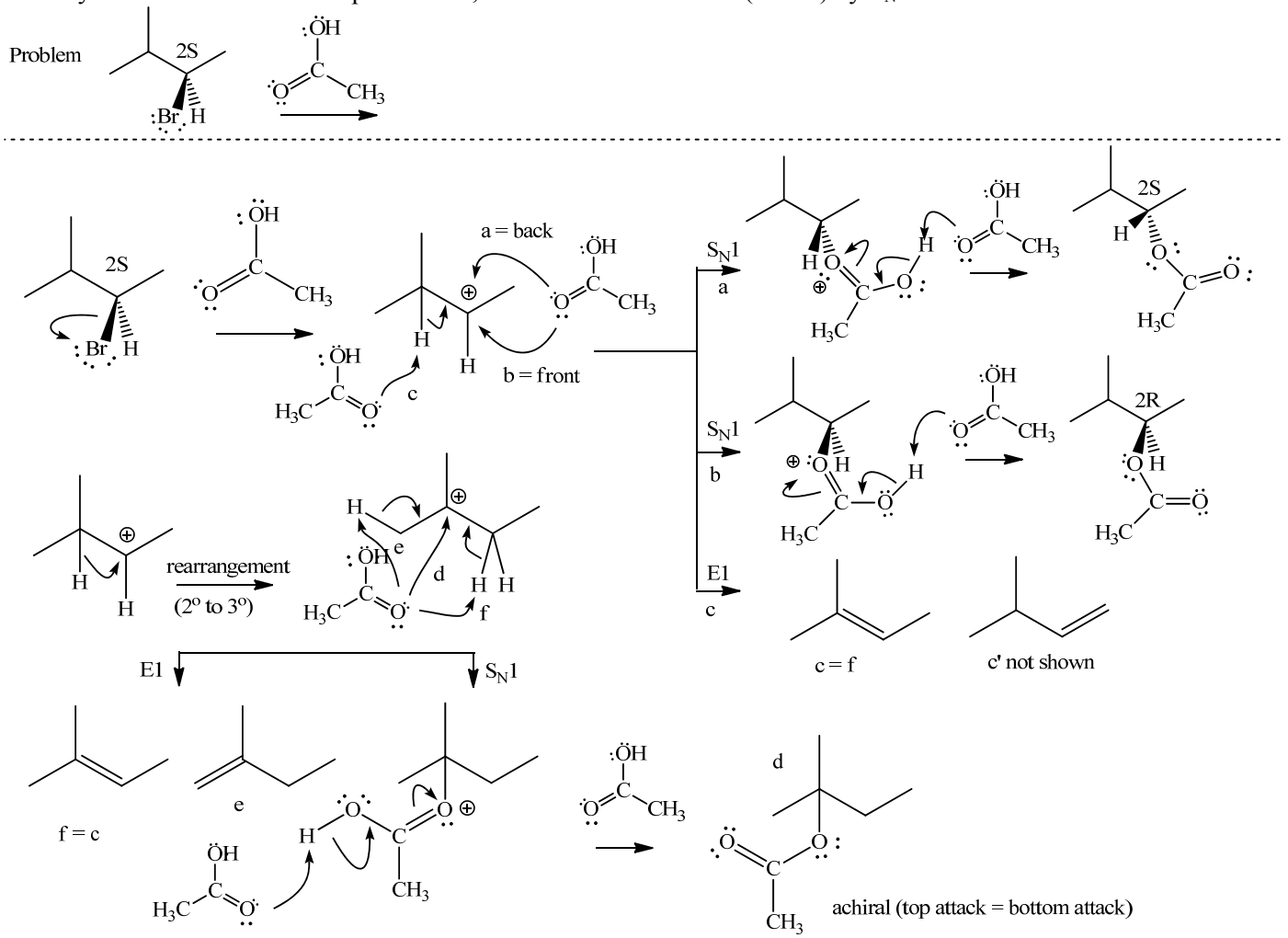
1. Water as a weak nucleophile/base with R-Br (or RX), makes alcohols by S_N1 (No reaction at methyl and 1° RBr)



2. Alcohols as weak nucleophile/bases, makes ethers with R-Br (or RX) by S_N1 (No reaction at methyl and 1° RBr)

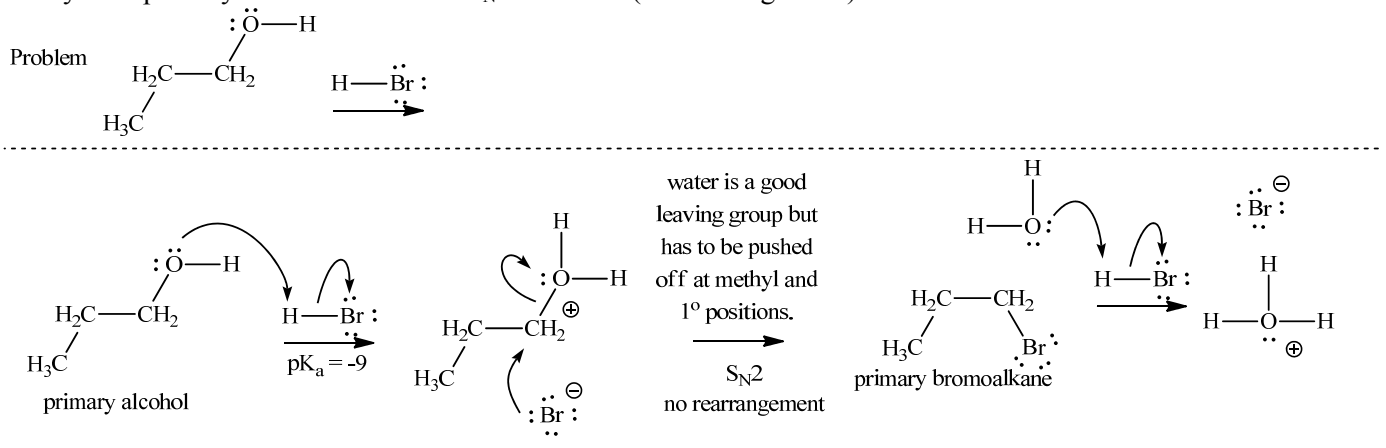


3. Carboxylic acids as weak nucleophile/bases, makes esters with R-Br (or RX) by S_N1

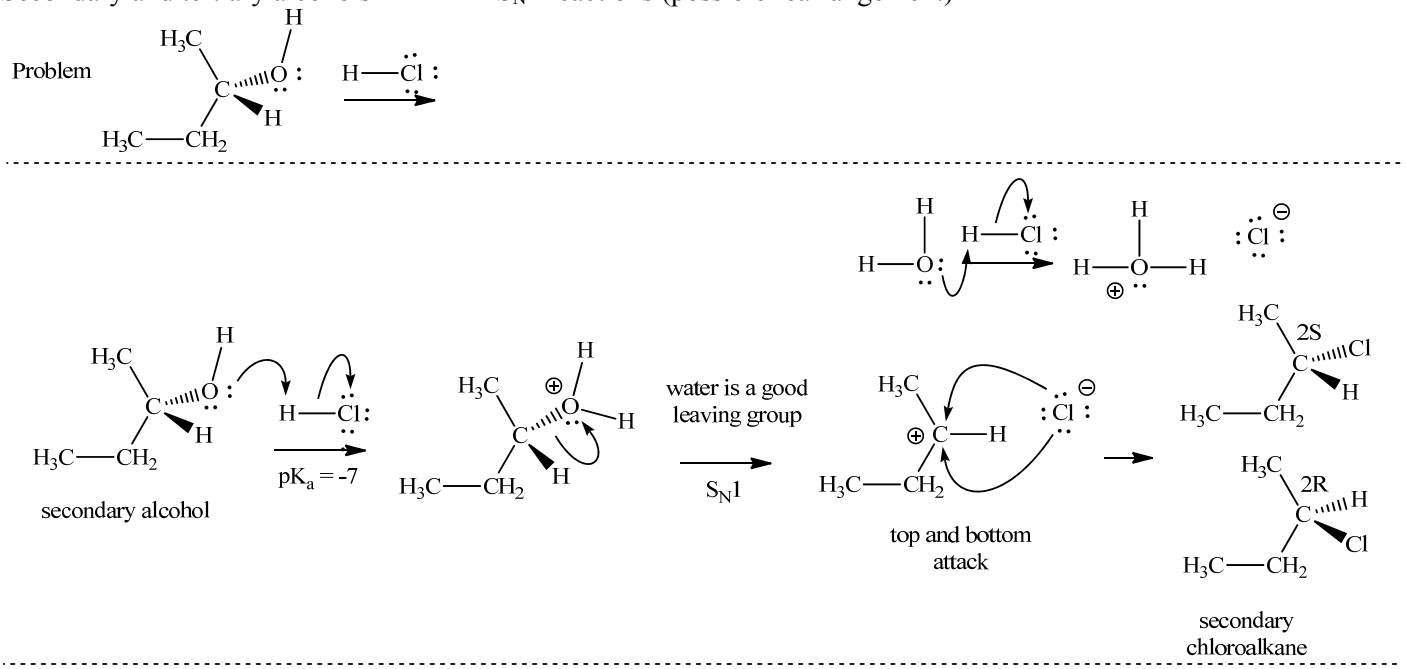


Alcohol reactions in strong acid (HCl, HBr, HI, H_2SO_4, TsOH are available): (HBr = S_N2 and S_N1), (H_2SO_4/Δ = E1) in our course.

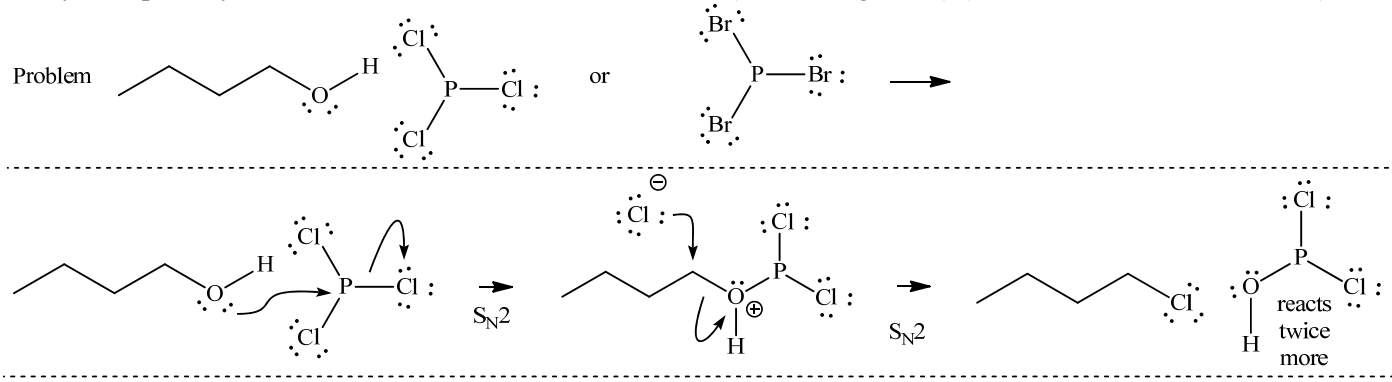
1. Methyl and primary alcohols + HBr → S_N2 reactions (no rearrangement)



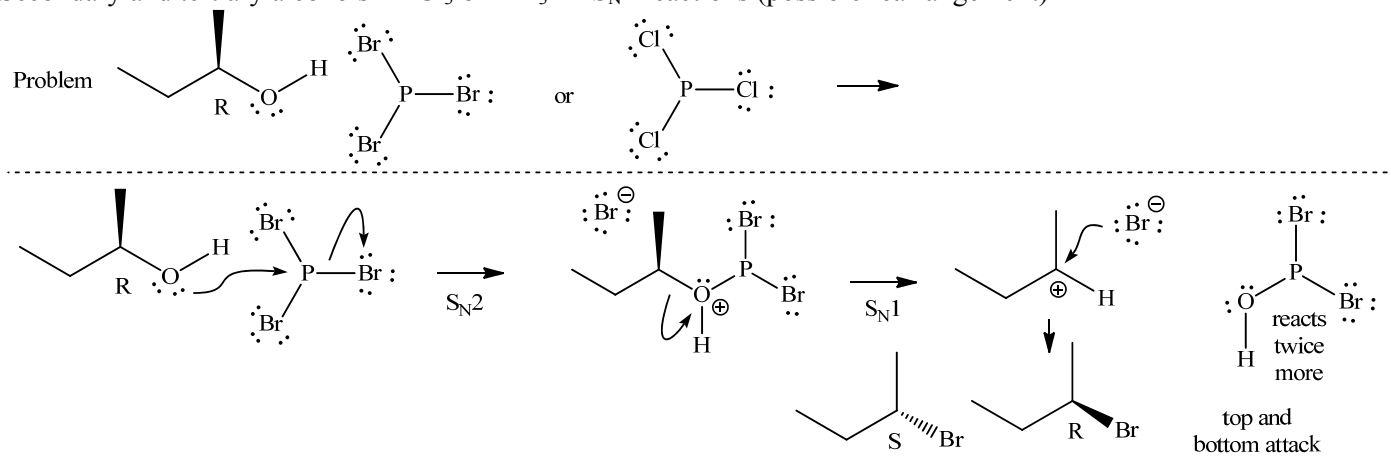
2. Secondary and tertiary alcohols + HBr → S_N1 reactions (possible rearrangement)



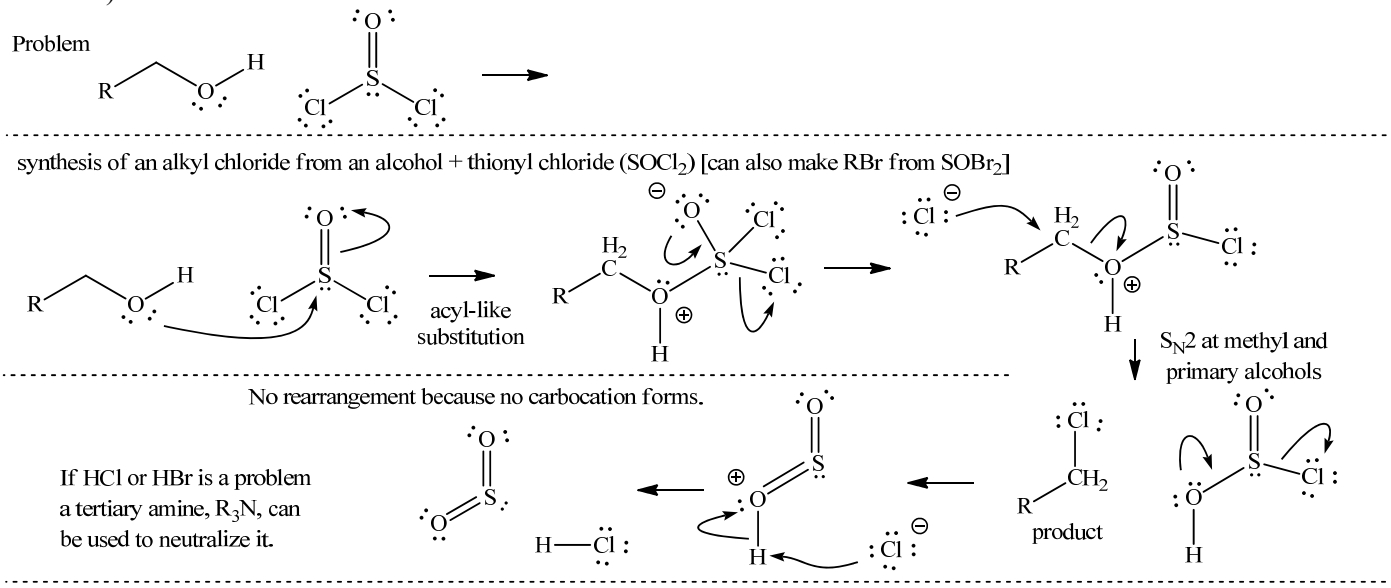
3. Methyl and primary alcohols + PCl_3 or PBr_3 → S_N2 reactions (no rearrangement) (PX_3 Lewis acids are available)



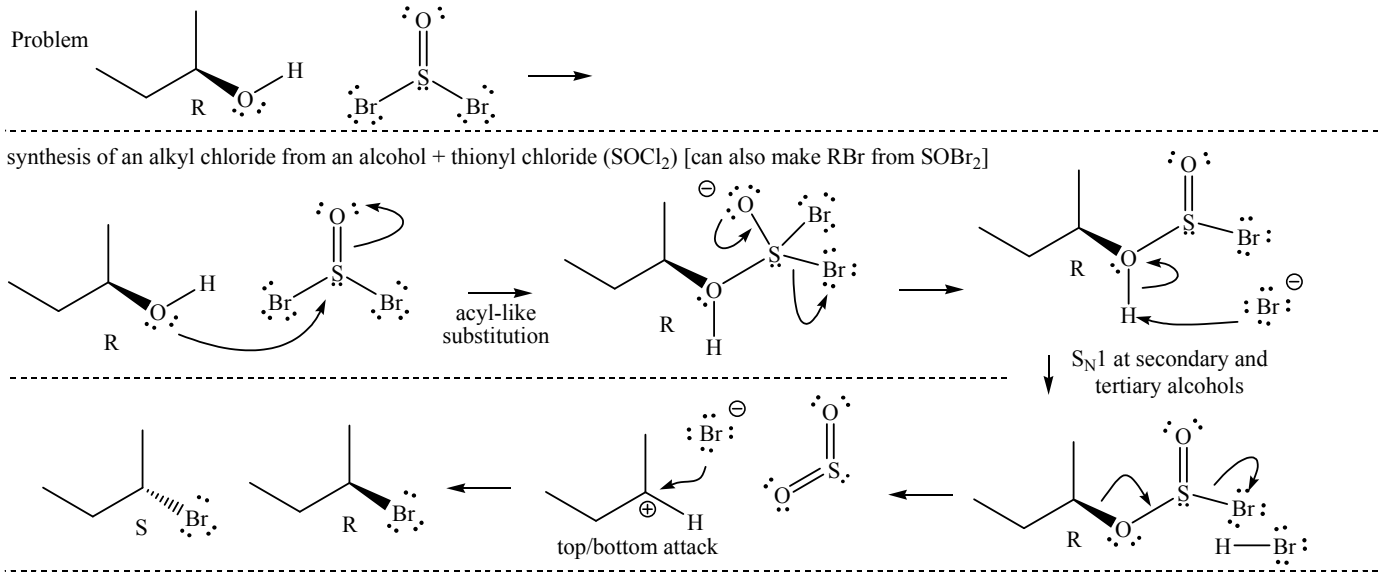
4. Secondary and tertiary alcohols + PCl_3 or PBr_3 → S_N1 reactions (possible rearrangement)



5. Methyl and primary alcohols + $SOCl_2$ or $SOBr_2$ → S_N2 reactions (no rearrangement) (SOX_2 Lewis acids are available)

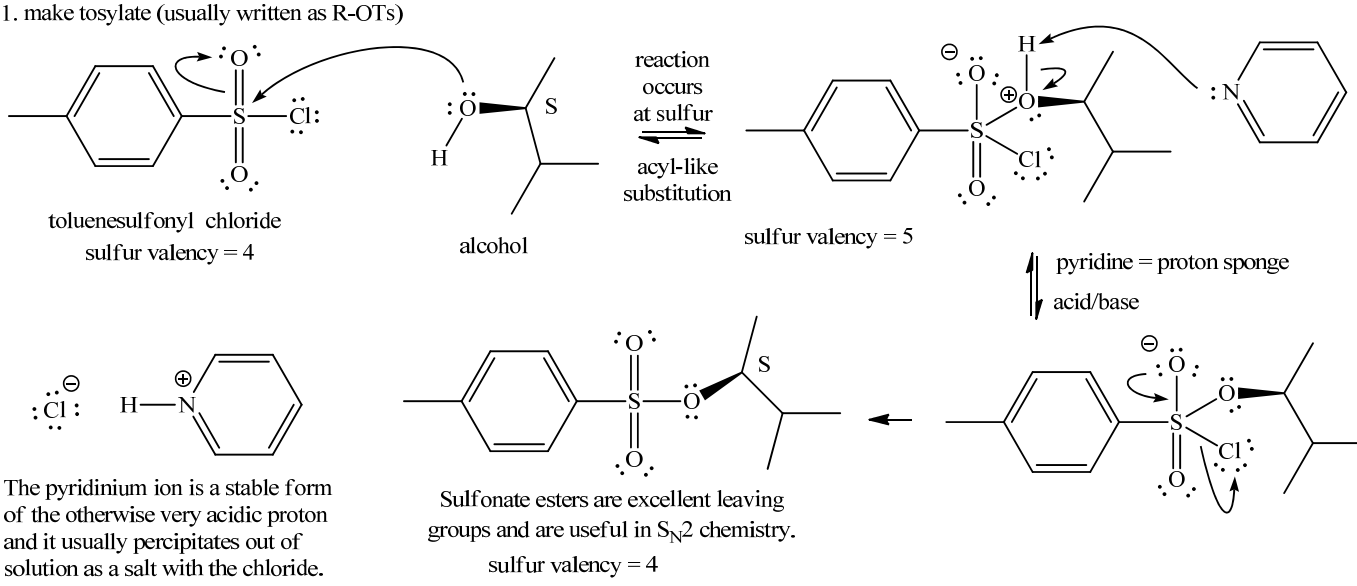


6. Secondary and tertiary alcohols + $SOCl_2$ or $SOBr_2$ → S_N1 reactions (possible rearrangement)

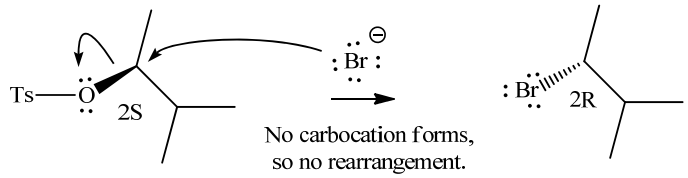


7. How to avoid rearrangement at secondary ROH → RBr (two steps, a. TsCl/pyridine b. NaBr = S_N2)

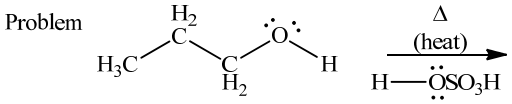
1. make tosylate (usually written as R-OTs)

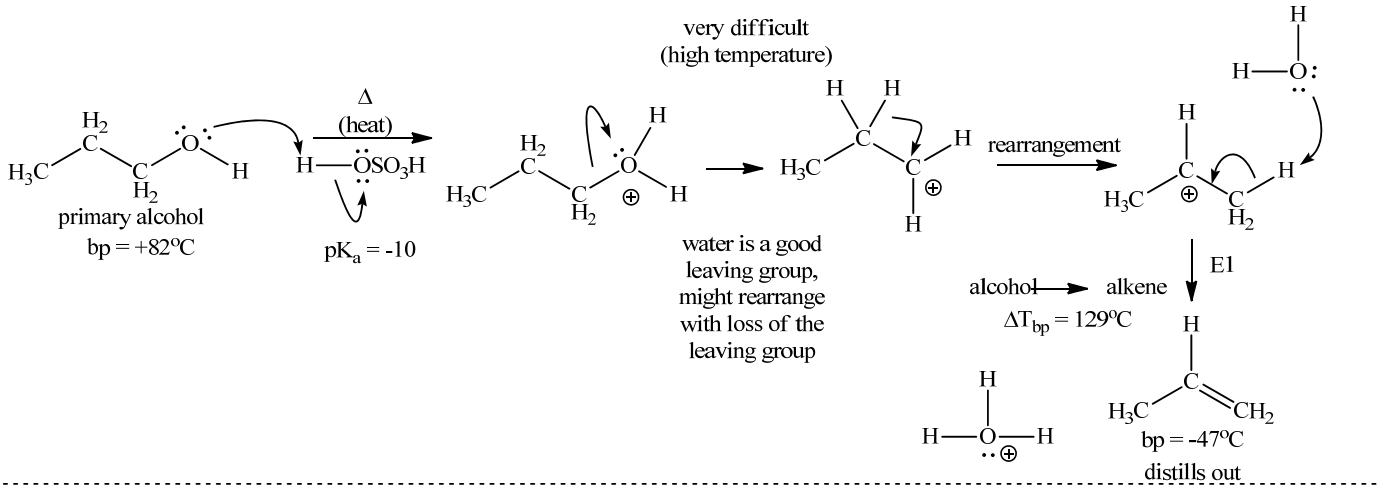


2. React tosylate with good nucleophile (bromide for us). Undergoes S_N2 without rearrangement.

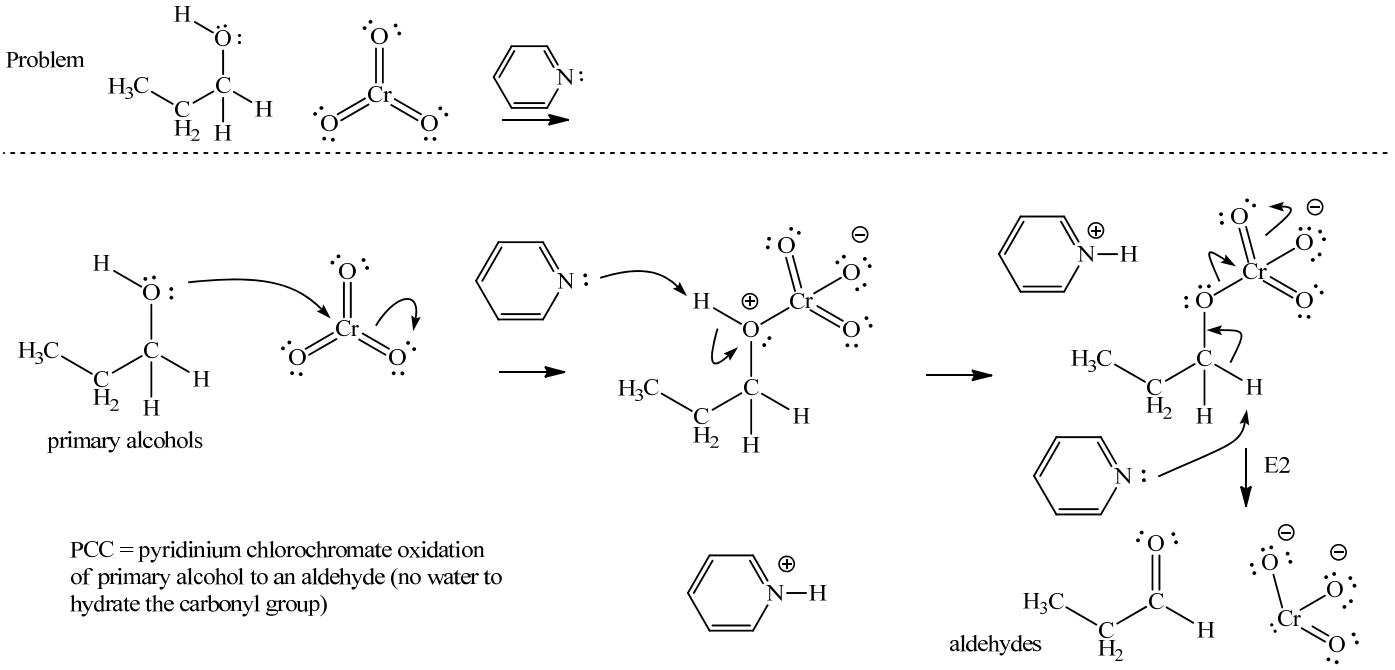


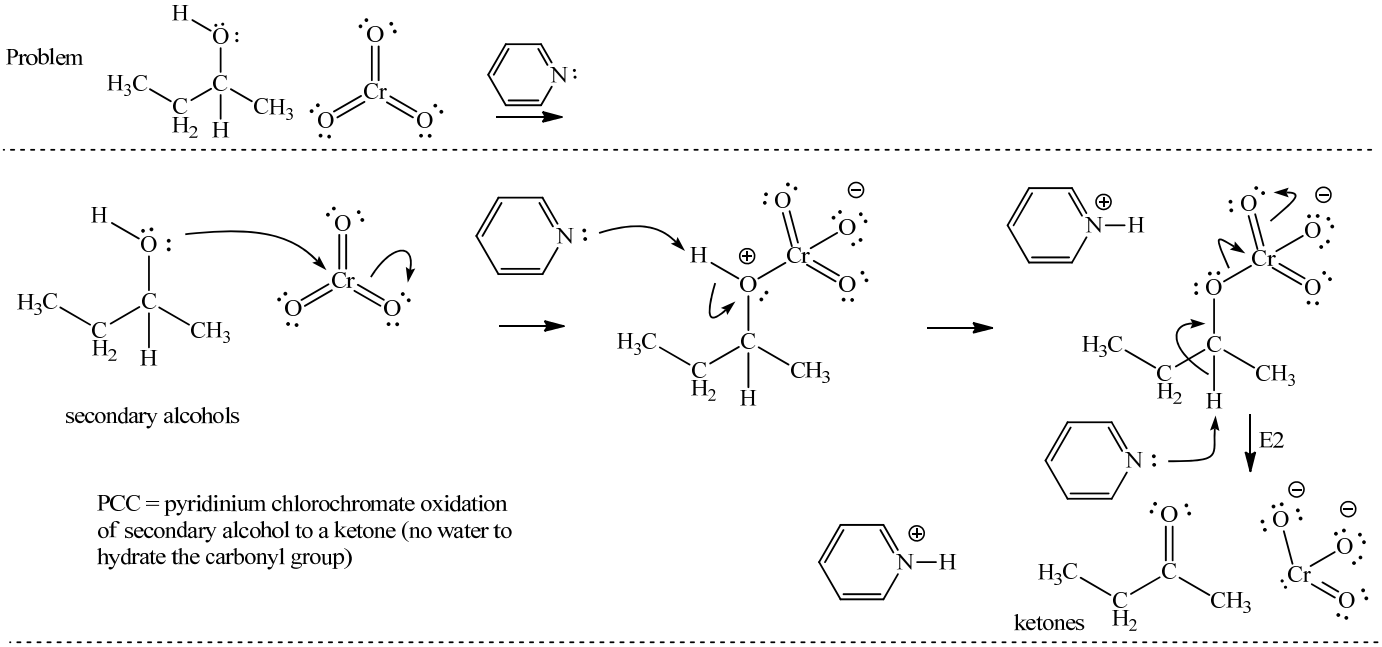
8. Alcohols + H_2SO_4/Δ = E1 (alkene products, possible rearrangements)



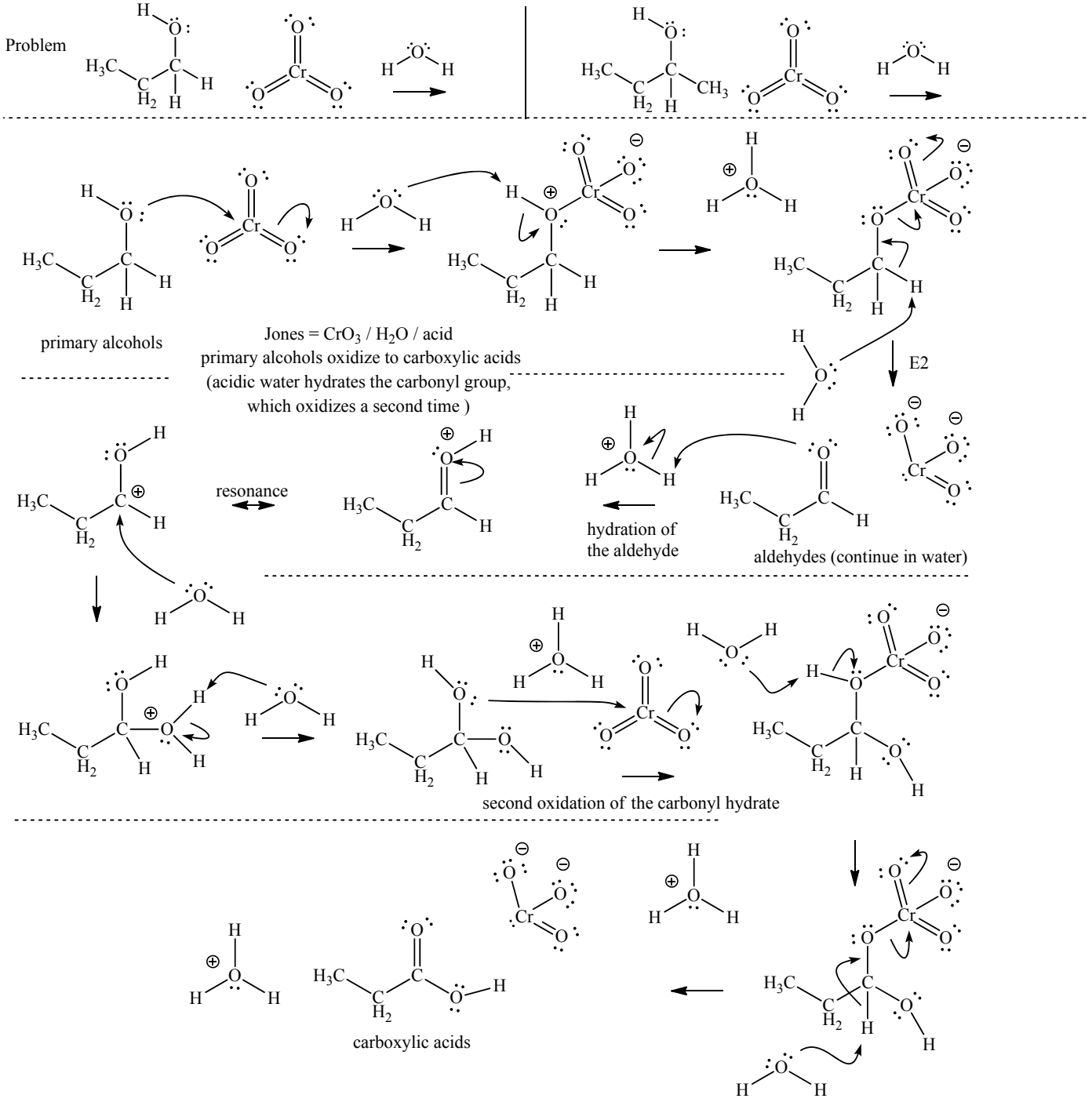


9. Alcohols + CrO_3/C_5H_6N (PCC) (oxidizes primary ROH to aldehyde and secondary ROH to ketone)

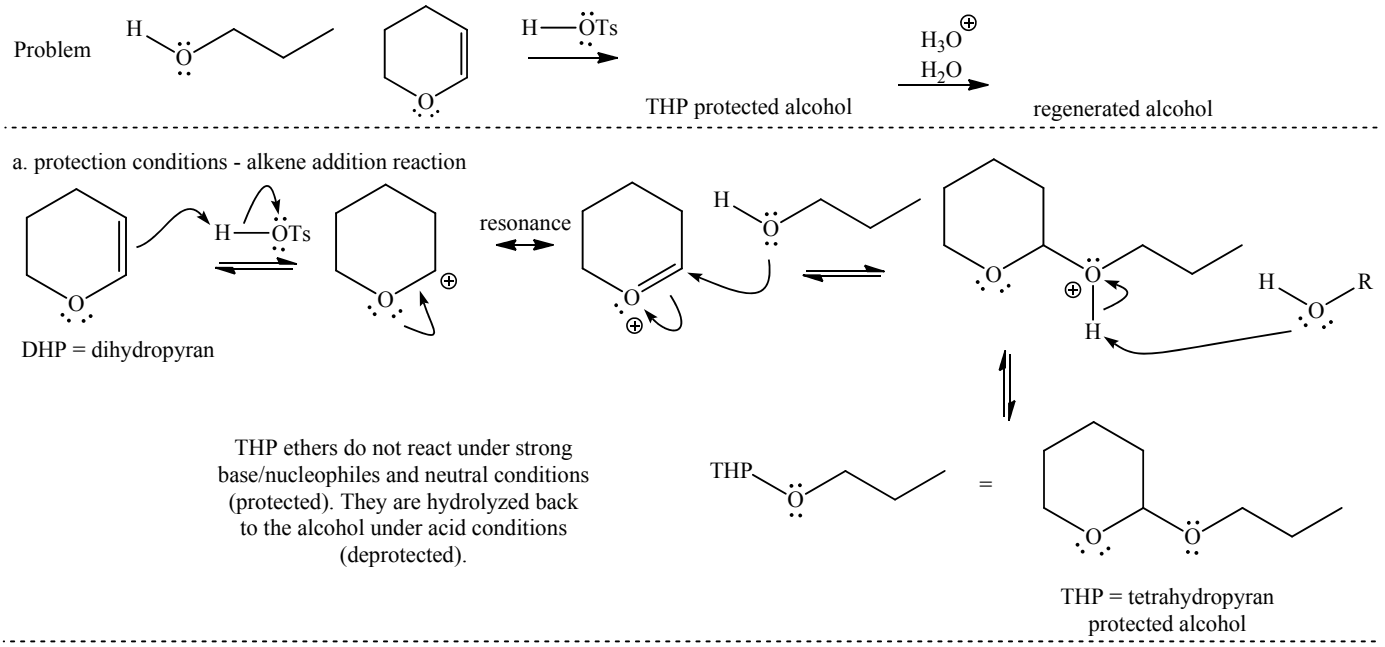


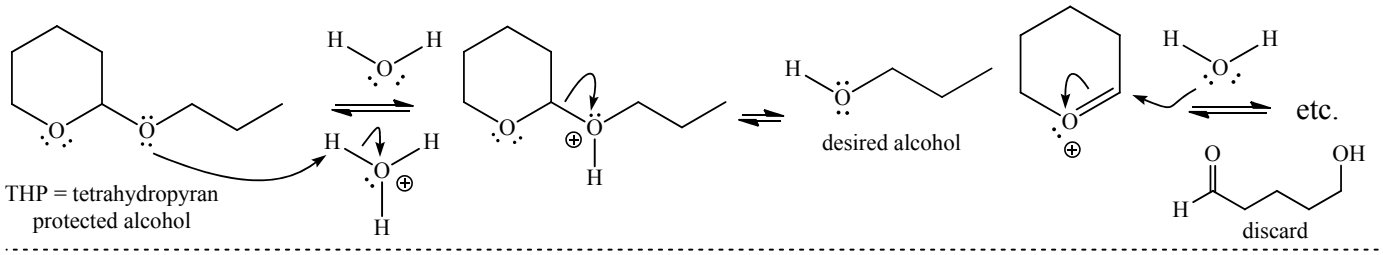


10. Alcohols + CrO_3/H_2O (Jones) (oxidizes primary ROH to carboxylic acid and secondary ROH to ketone)



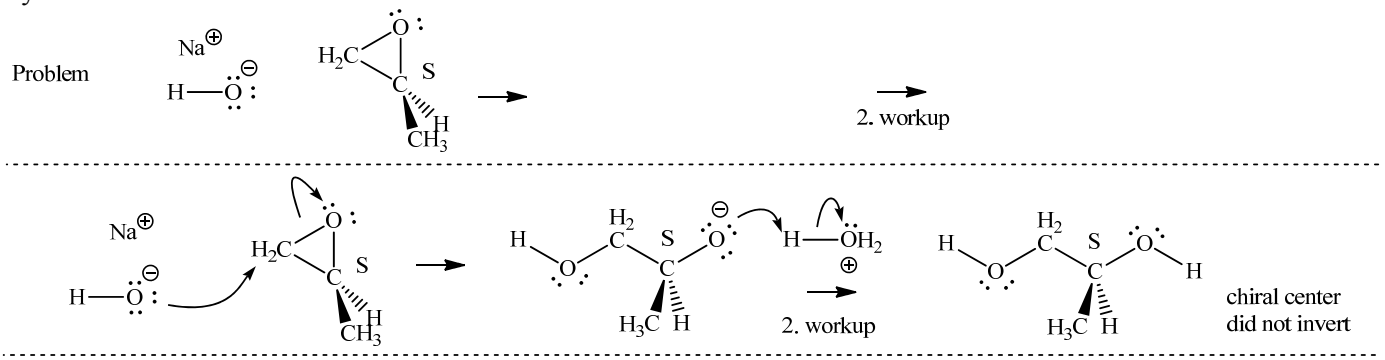
11. THP protection of alcohols, ROH + DHP (TsOH cat.) → THP ether, which can be deprotected with H_2SO_4/H_2O



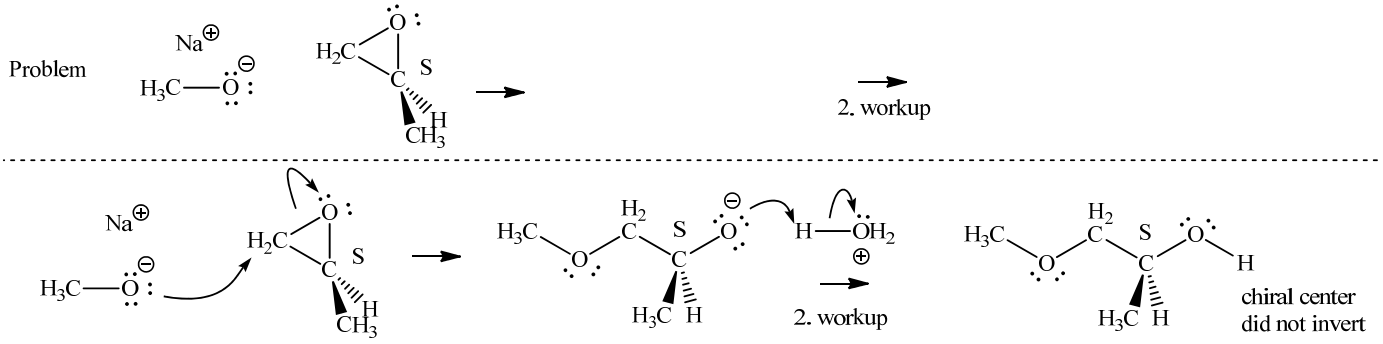


Epoxides in Strong Base/Nucleophile mixtures: backside attack at least hindered carbon.

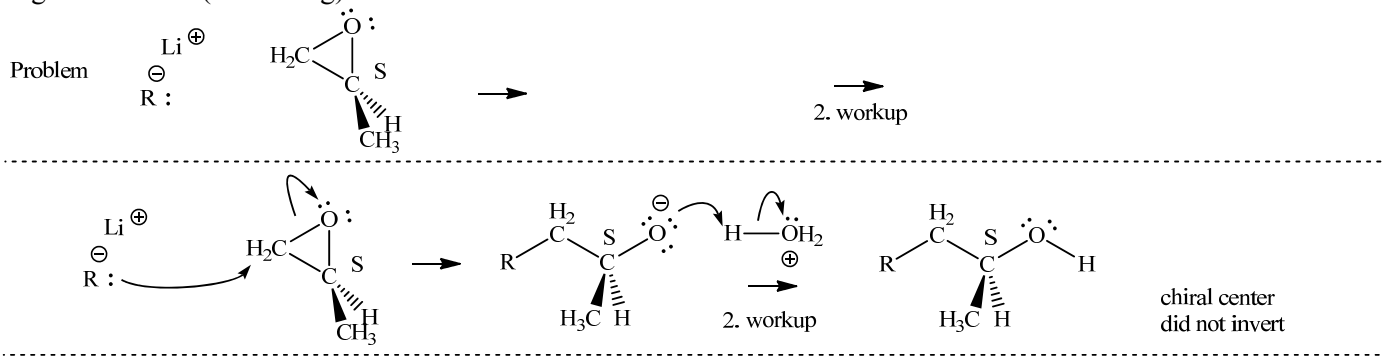
1. Hydroxide



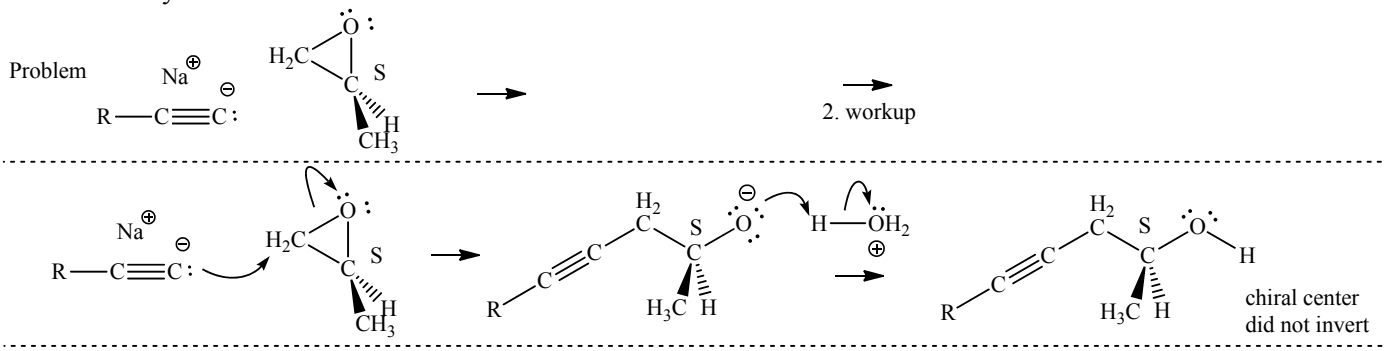
2. Alkoxides



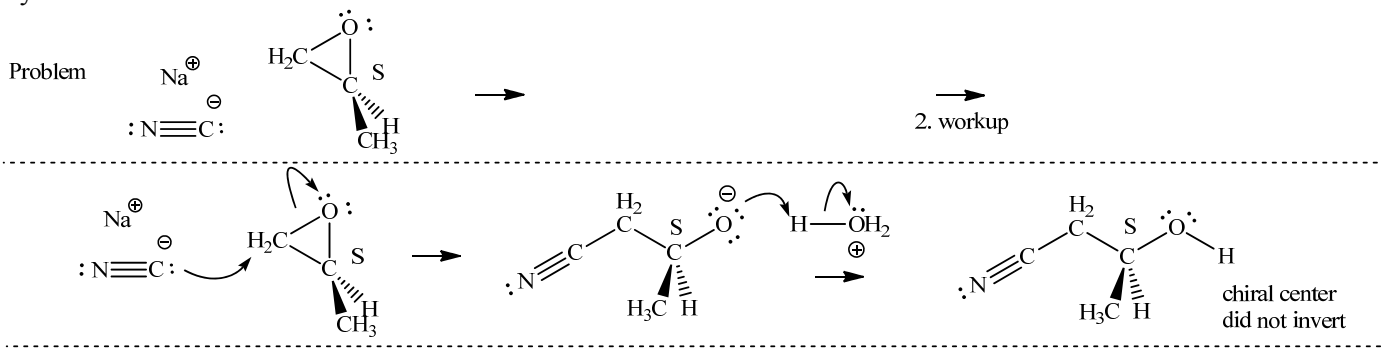
3. Organometallics (Li and Mg)



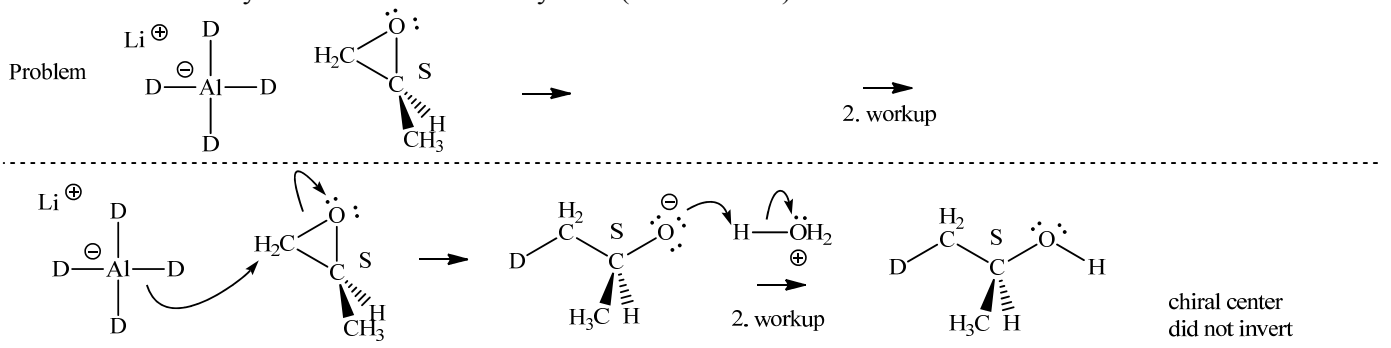
4. Terminal acetylides



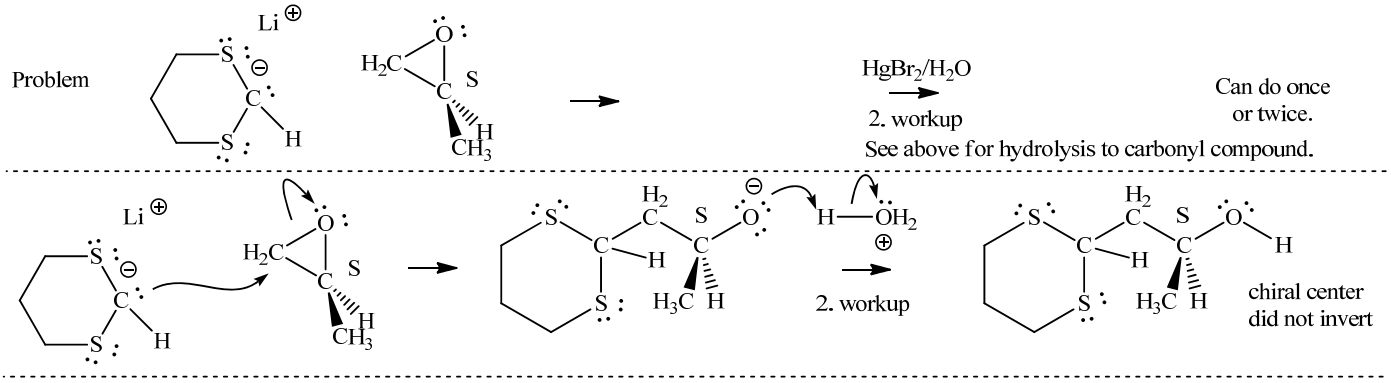
5. Cyanide



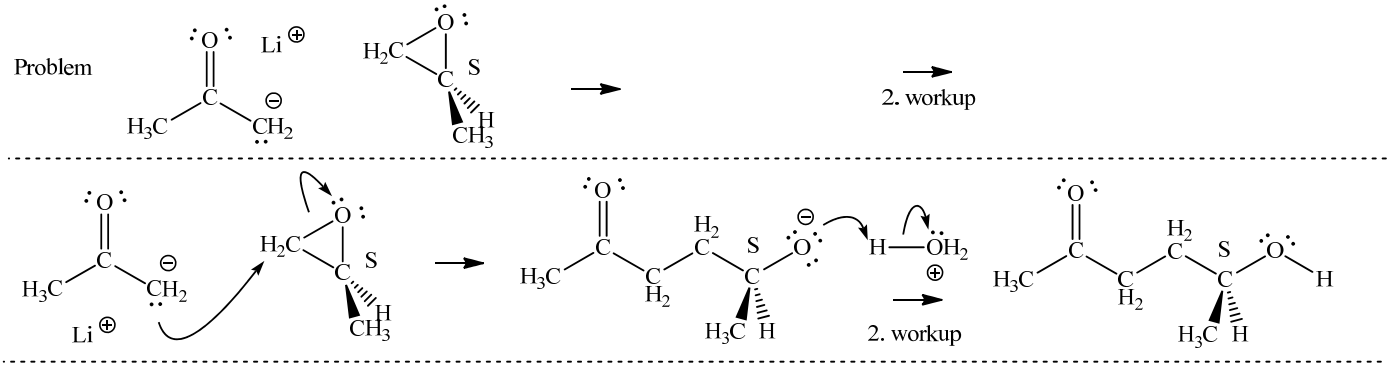
6. Lithium aluminum hydride and sodium borohydride (or deuterides)



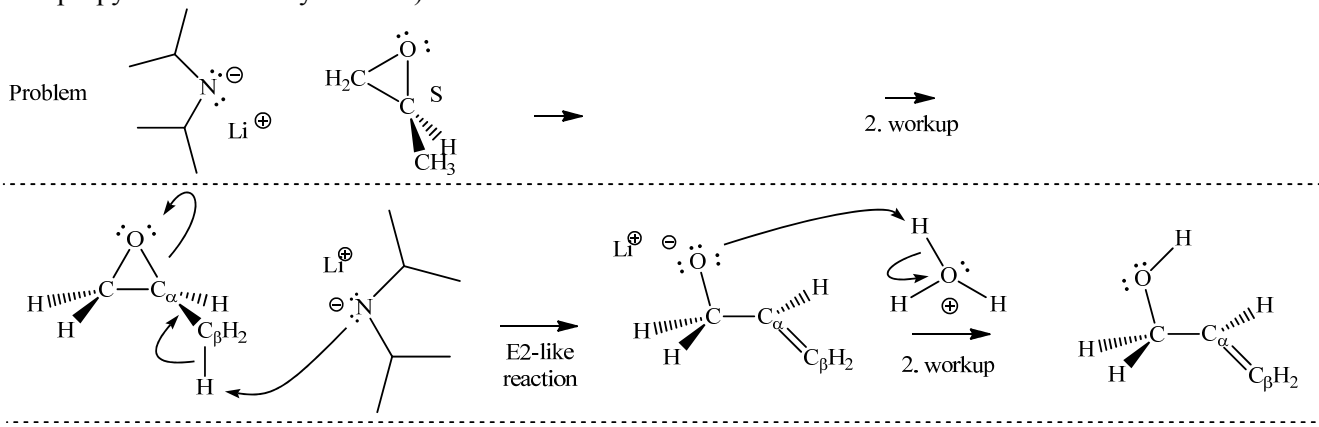
7. Dithiane anion



8. Enolates

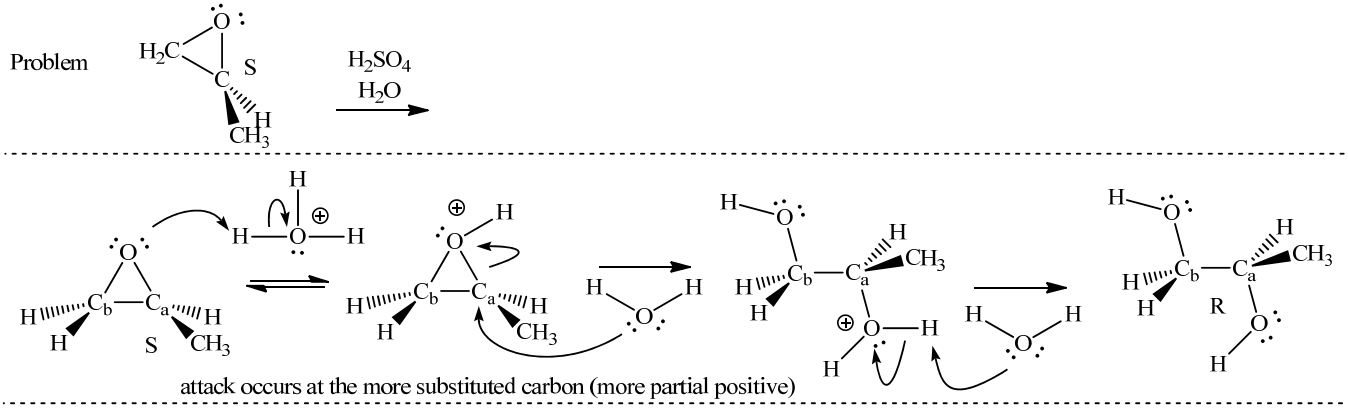


9. Reactions with LDA (lithium diisopropylamide = strong, bulky base removes a proton, made from diisopropylamine + n-butyl lithium)

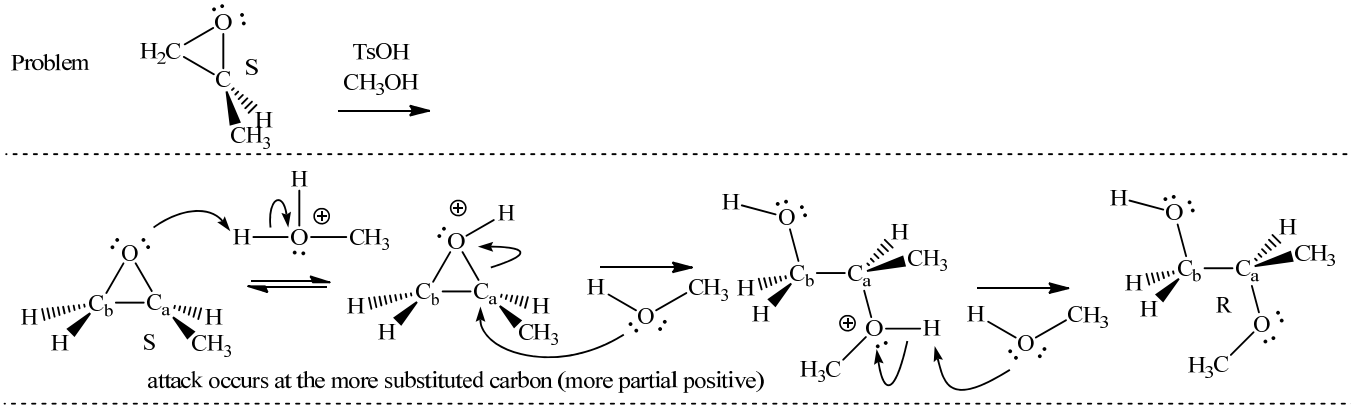


Epoxides in Strong Acid/Electrophile mixtures

1. Aqueous acid



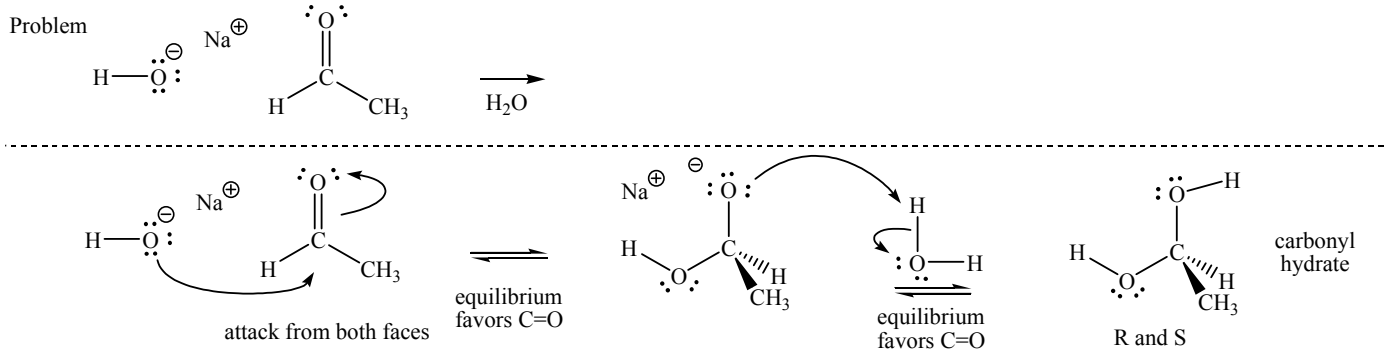
2. Alcohol + TsOH



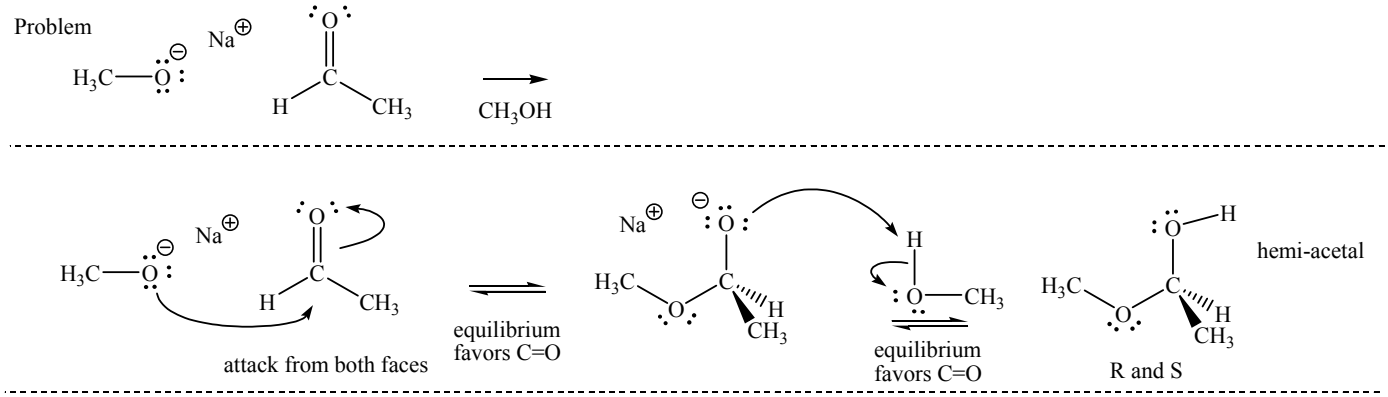
Carbonyl Groups in Strong Base/Nucleophile mixtures

Aldehydes

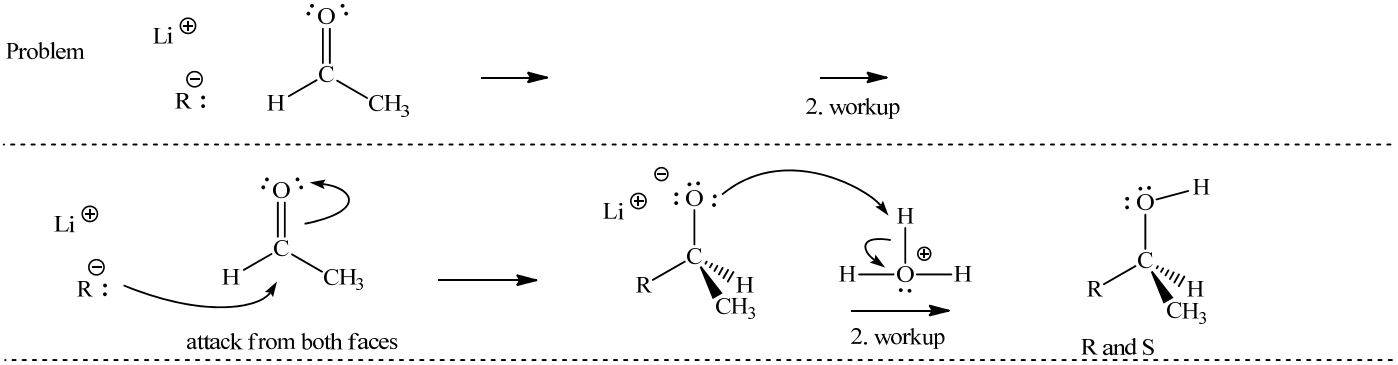
1. Hydroxide – hydration



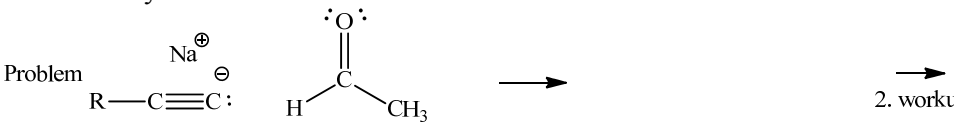
2. Alkoxide – hemi-acetal formation

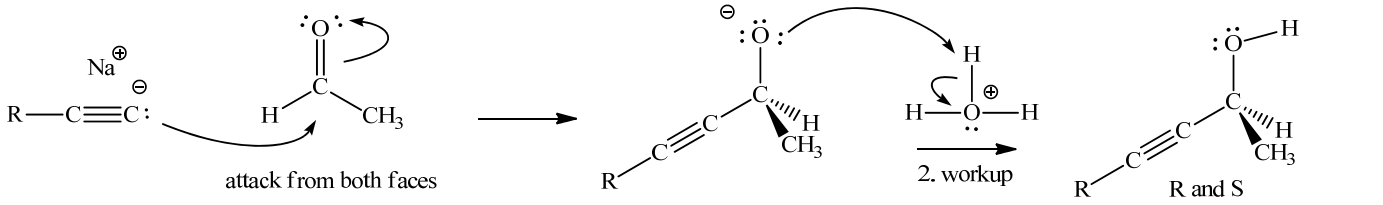


3. Organometallics (Li and Mg reagents)

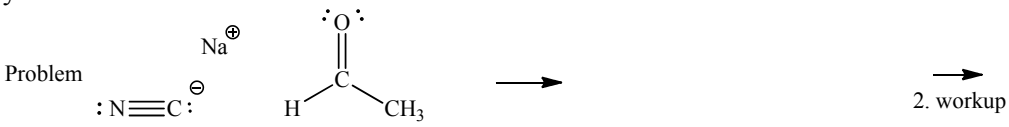


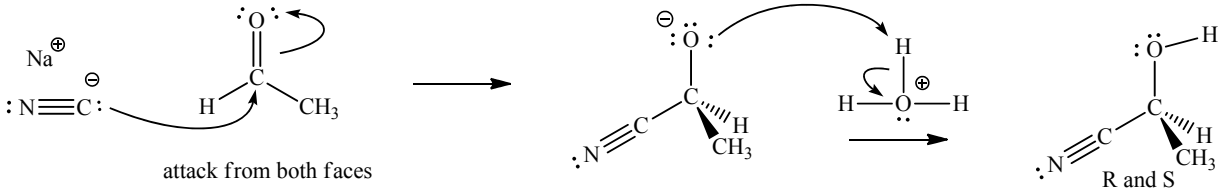
4. Terminal acetylides



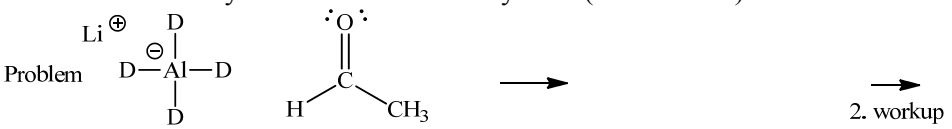


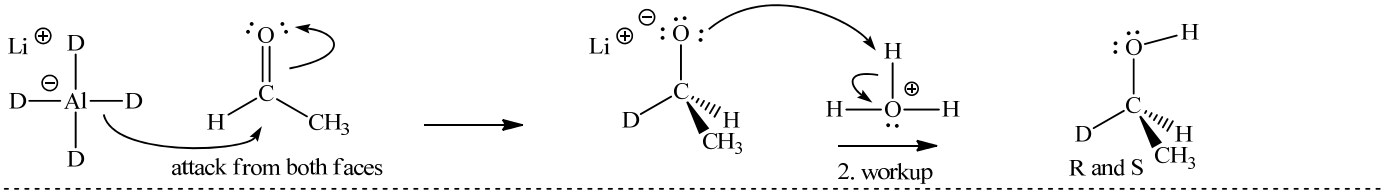
5. Cyanide



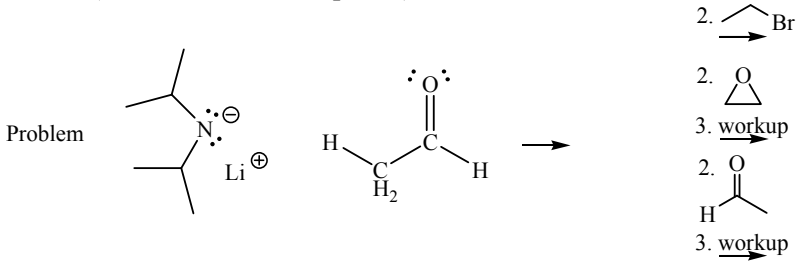


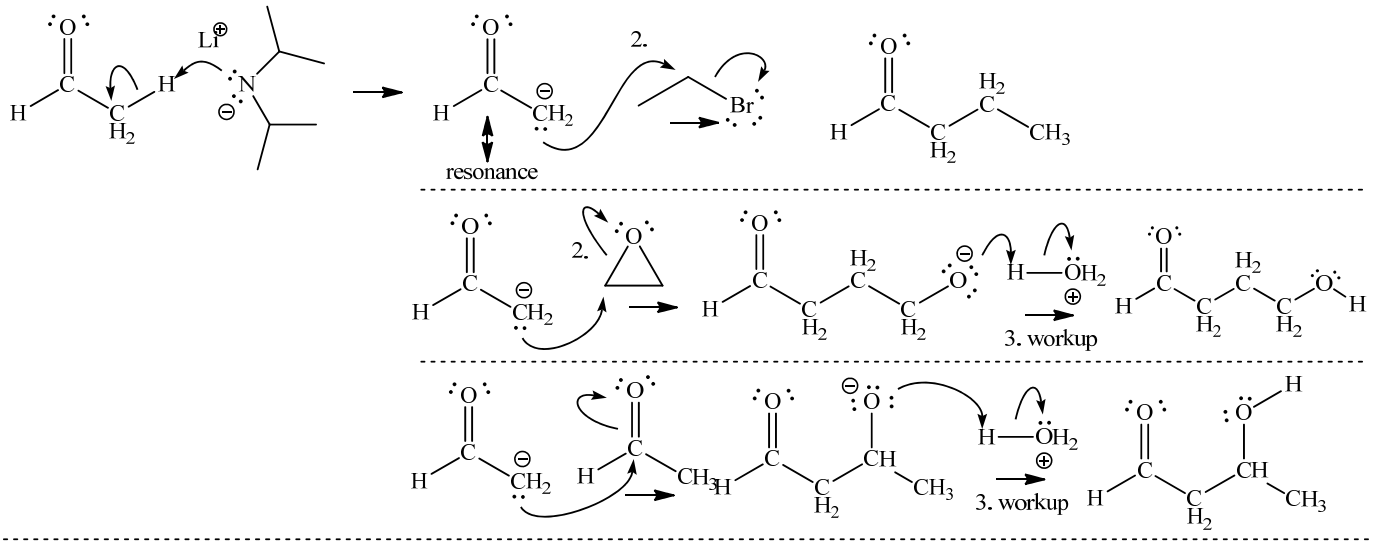
6. Lithium aluminum hydride or sodium borohydride (or deuteride)



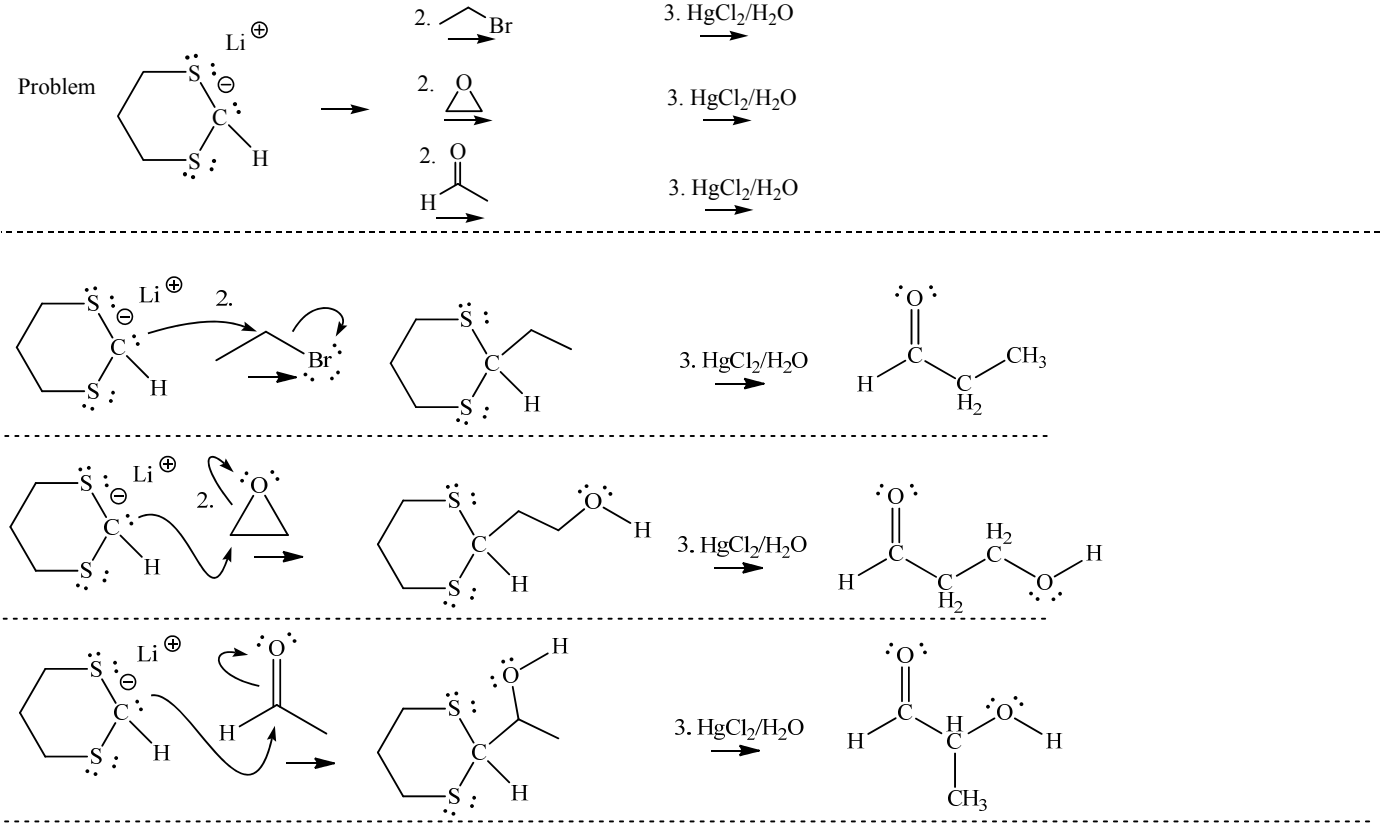


7. Enolates (with various electrophiles)

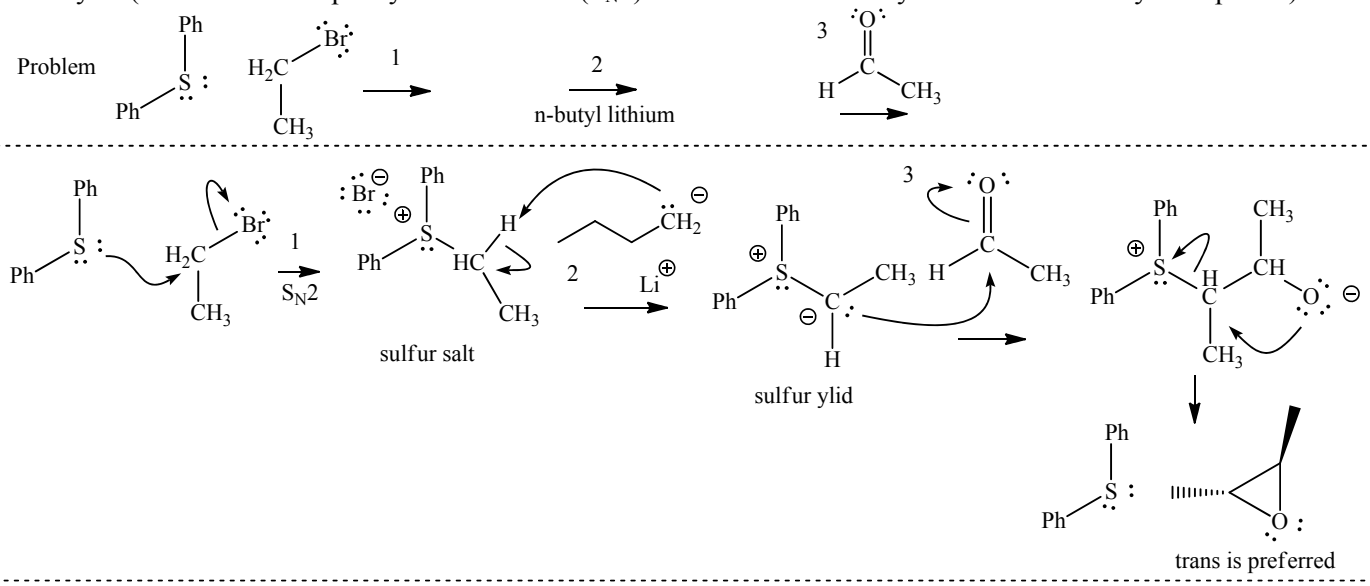




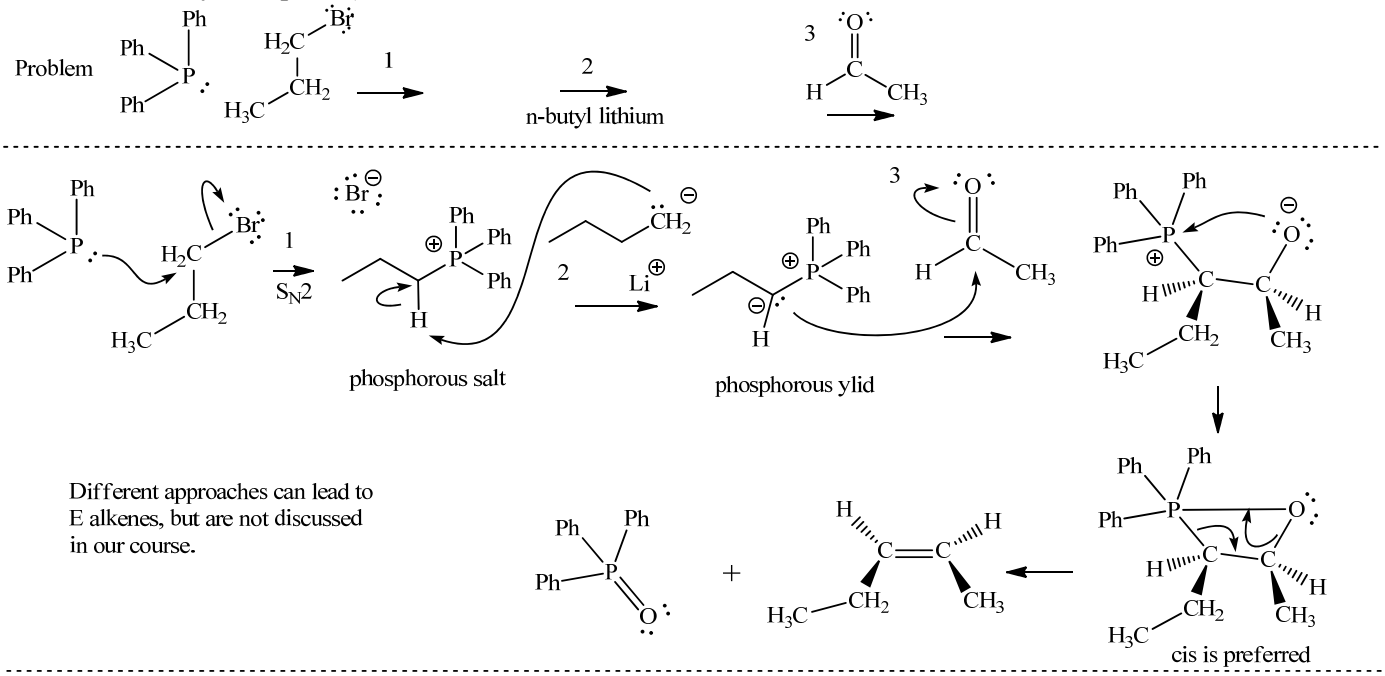
8. Dithiane anion - reacts with various electrophiles, can react once (make aldehydes) or twice (make ketones)



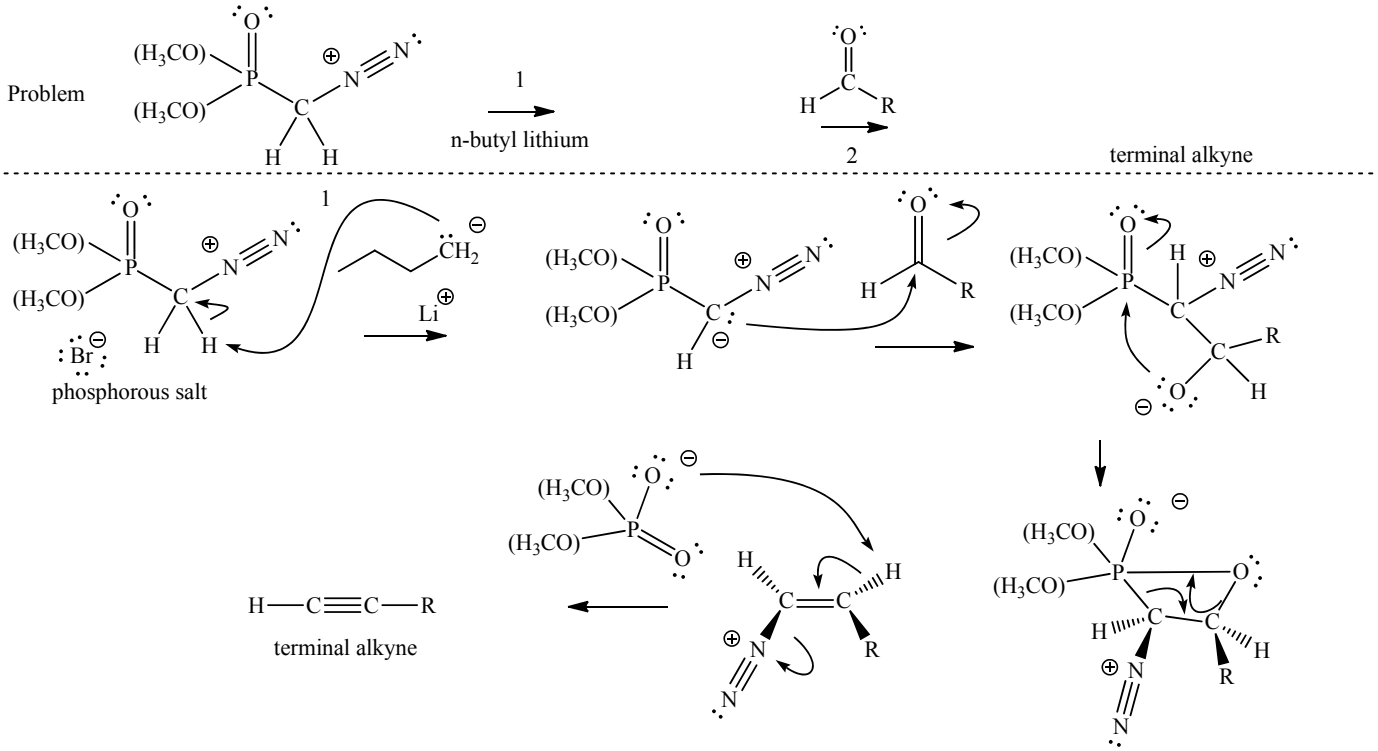
9. Sulfur ylid (make from a. diphenylsulfide + RBr (S_N2) b. sulfur salt + n-butyl lithium c. carbonyl compound)



10. Phosphorous ylid (Wittig reaction = make from a. triphenylphosphine + RBr (S_N2) b. phosphorous salt + n-butyl lithium c. carbonyl compound)

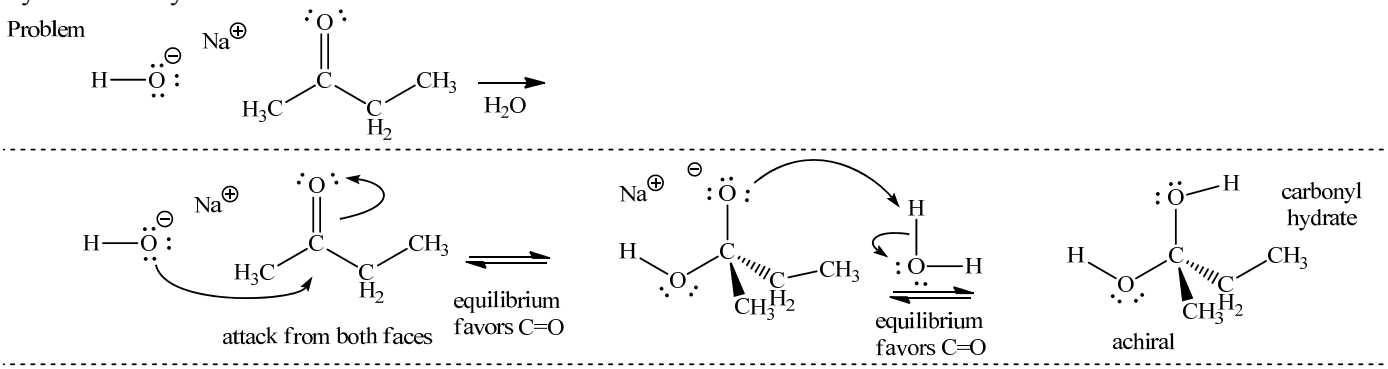


11. Wittig reaction that makes alkynes from aldehydes. (J.O.C., 1982, *47*, 1837-1845)

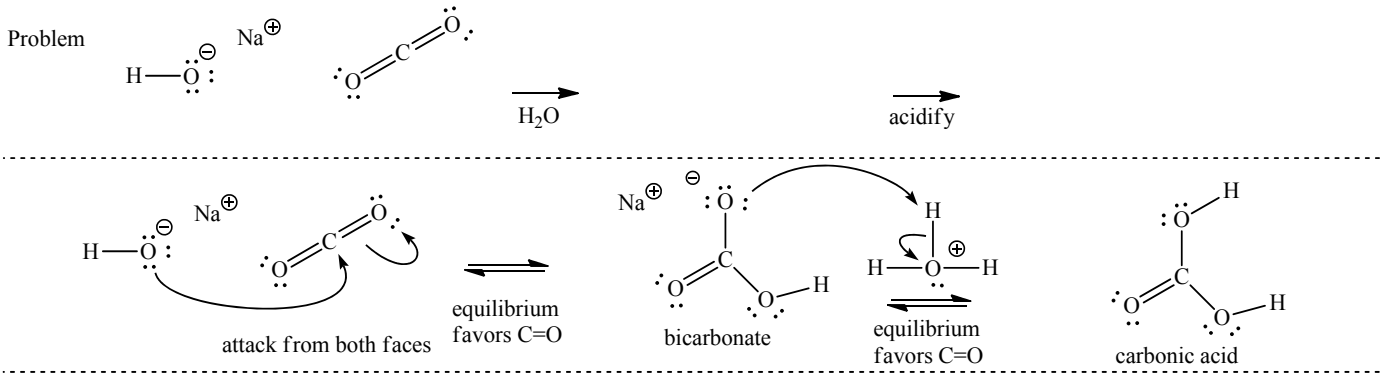


Ketones (and carbon dioxide)

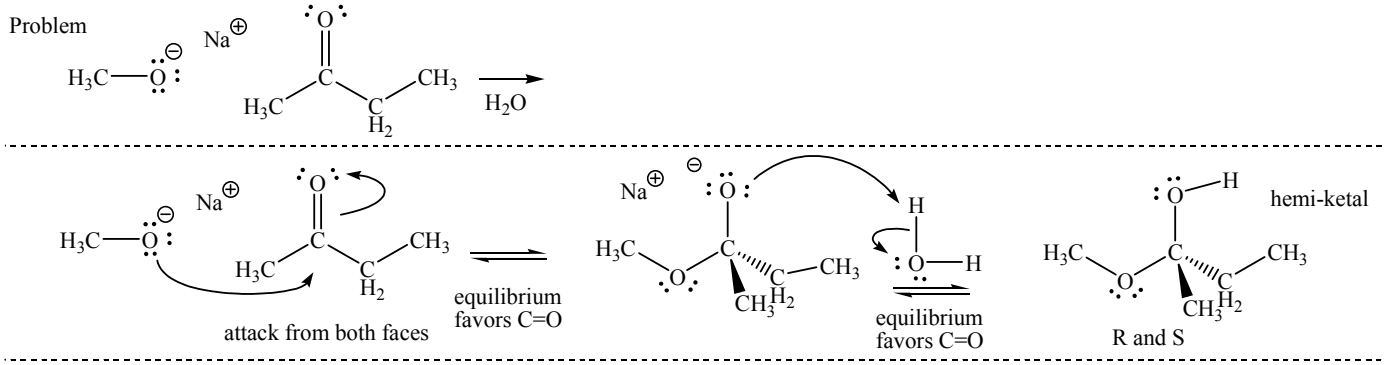
1. Hydroxide – hydration



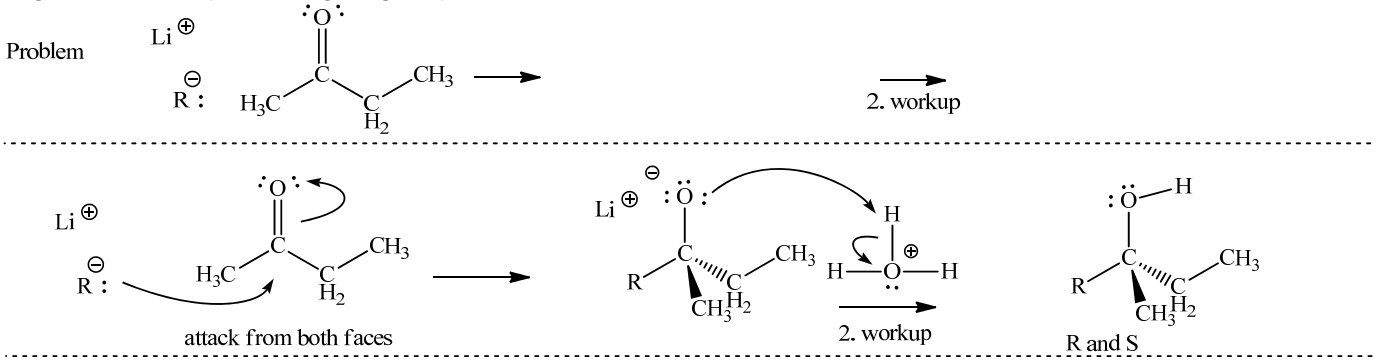
2. Hydroxide with carbon dioxide → makes bicarbonate → makes carbonic acid (an inorganic example)



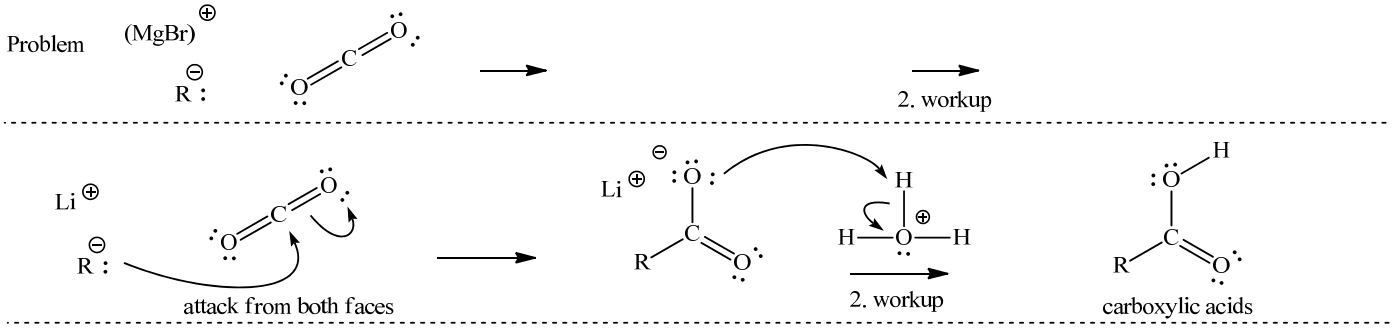
3. Alkoxide – makes hemi-ketal



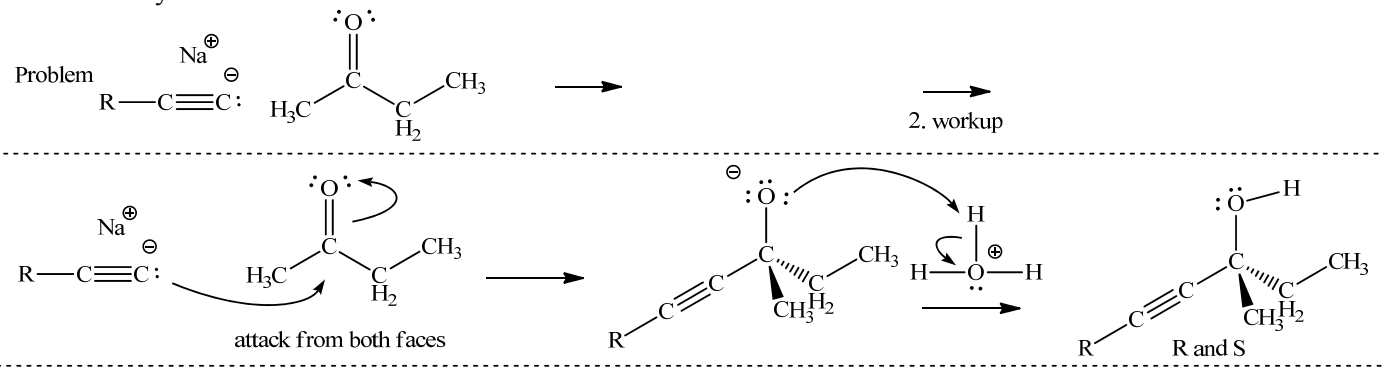
4. Organometallics (Li and Mg reagents)



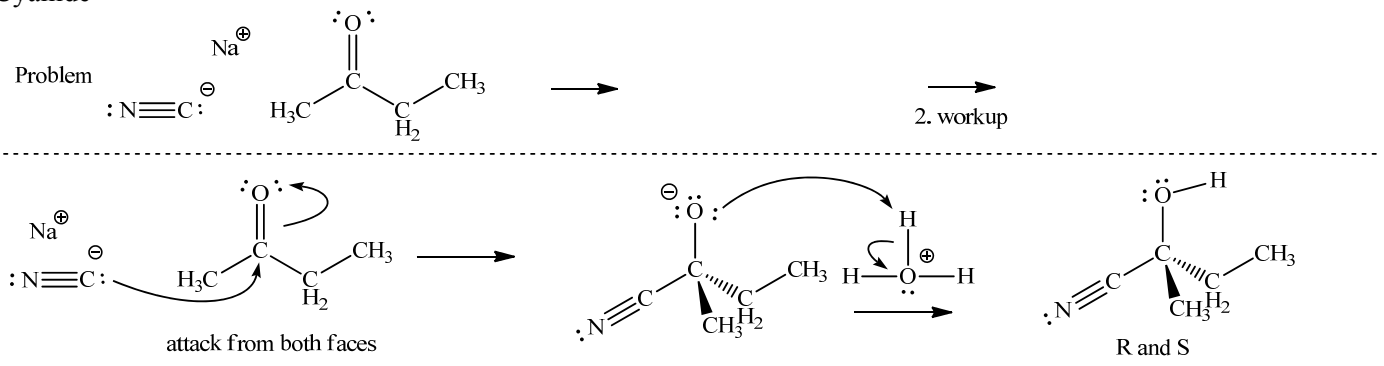
5. Organometallics (Li and Mg reagents) + CO_2 (special carbonyl) 2. workup



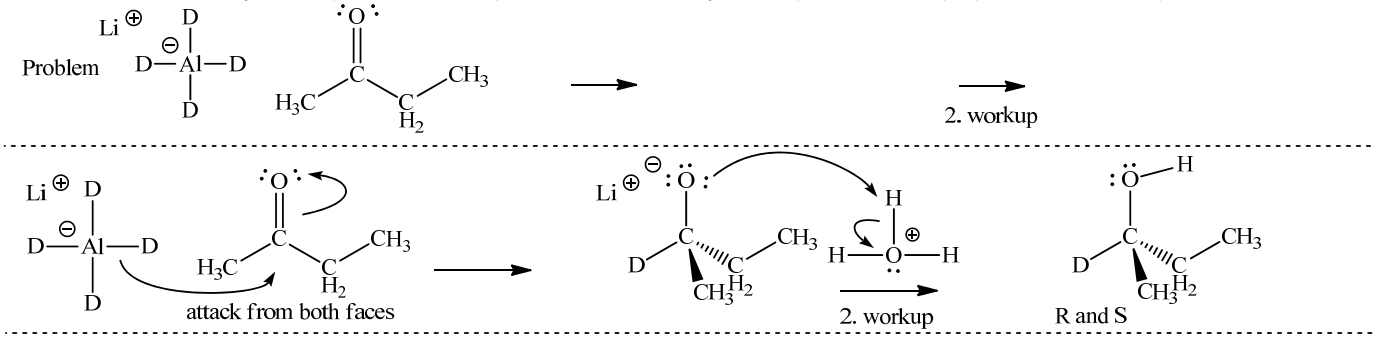
6. Terminal acetylides



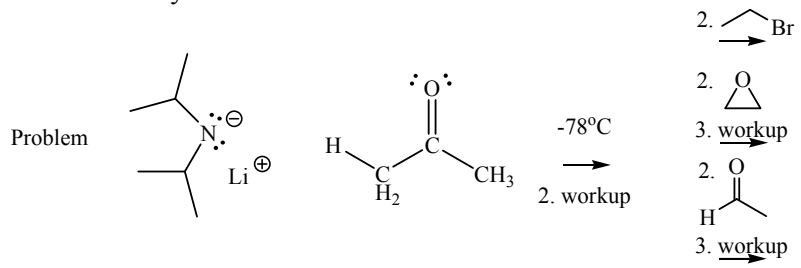
7. Cyanide

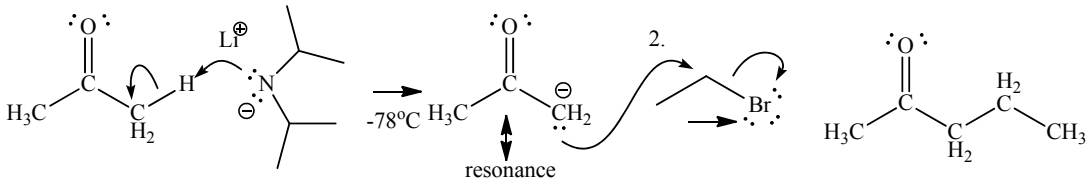


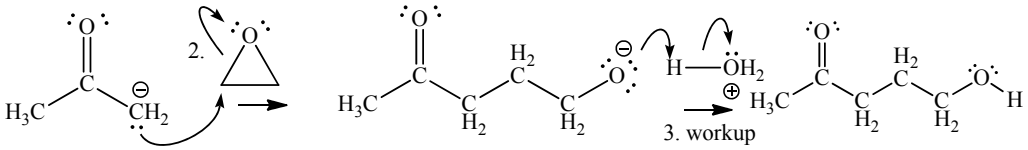
8. Lithium aluminum hydride (more reactive) or sodium borohydride (less reactive) (…or deuterides)

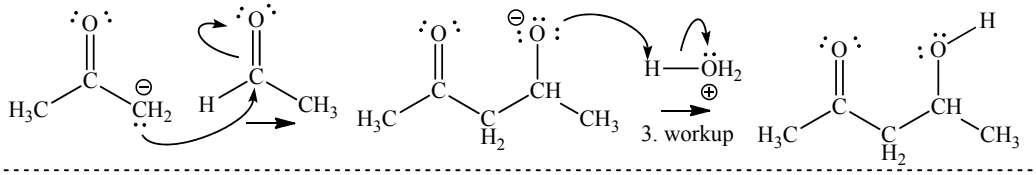


9. Enolates - many variations

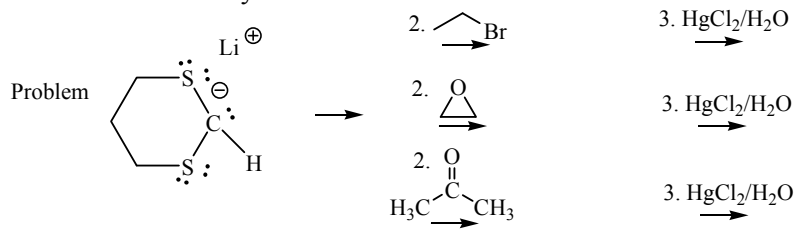


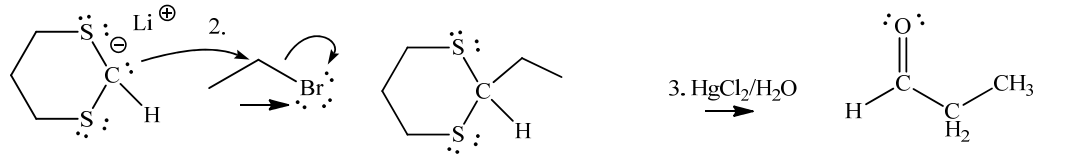


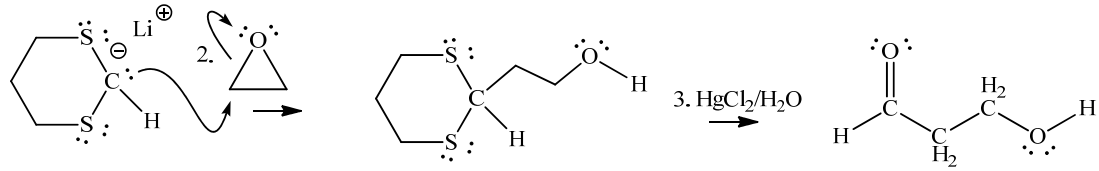


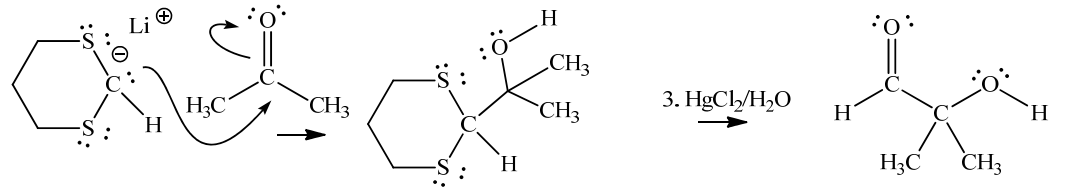


10. Dithiane anion – many variations

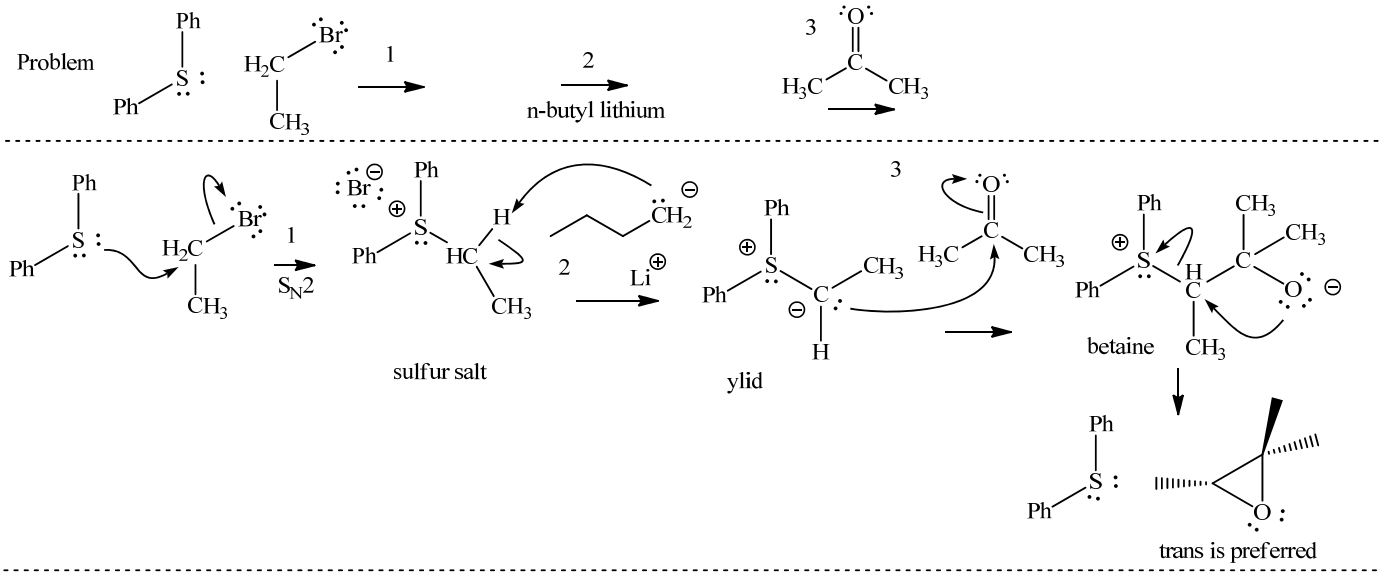




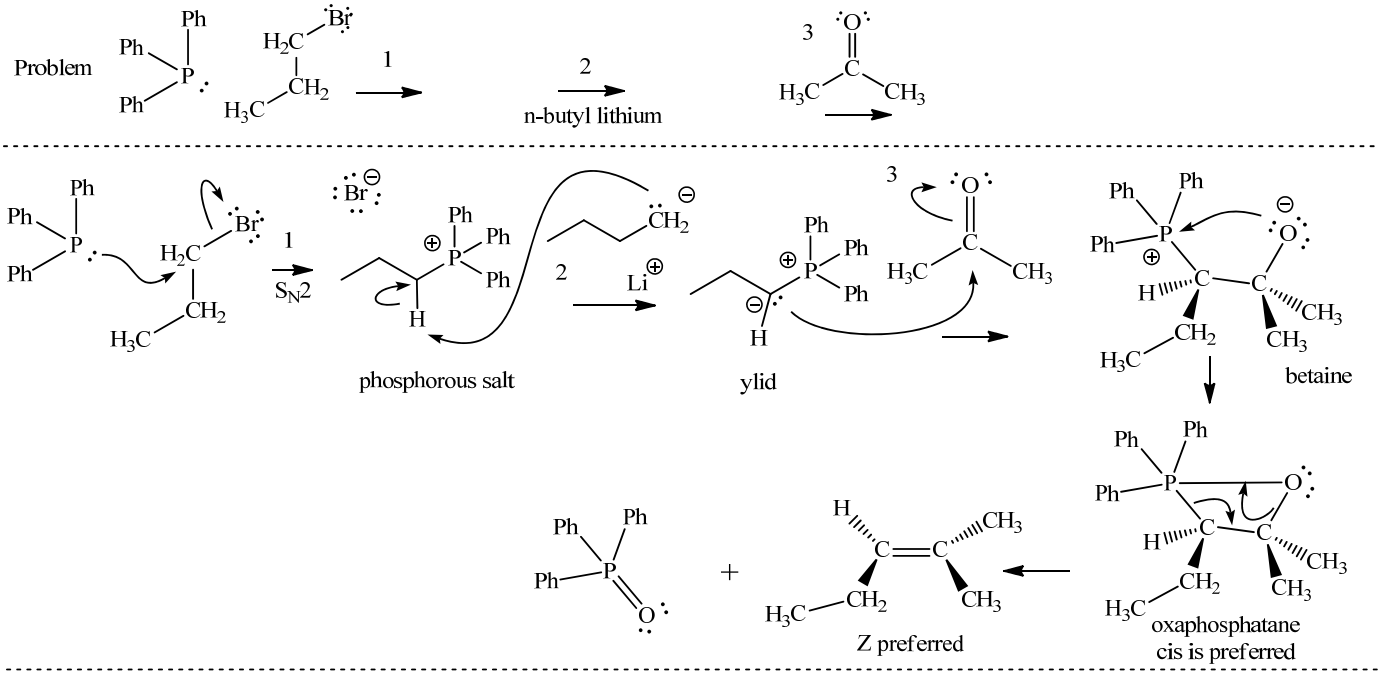




11. Sulfur ylid (make from a. diphenylsulfide + RBr (S_N2) b. sulfur salt + n-butyl lithium c. carbonyl compound)

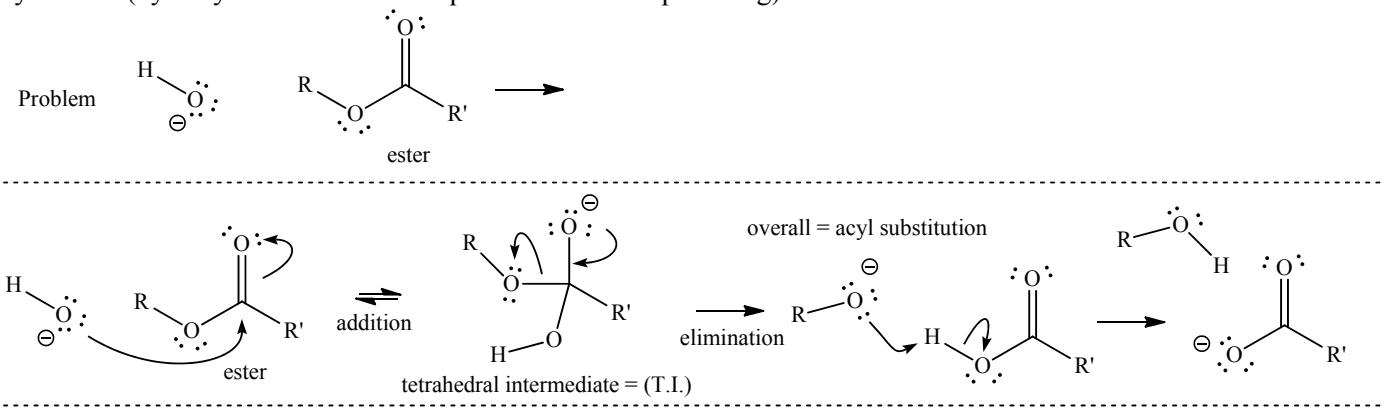


12. Phosphorous ylid (Wittig reaction = make from a. triphenylphosphine + RBr (S_N2) b. phosphorous salt + n-butyl lithium c. carbonyl compound)

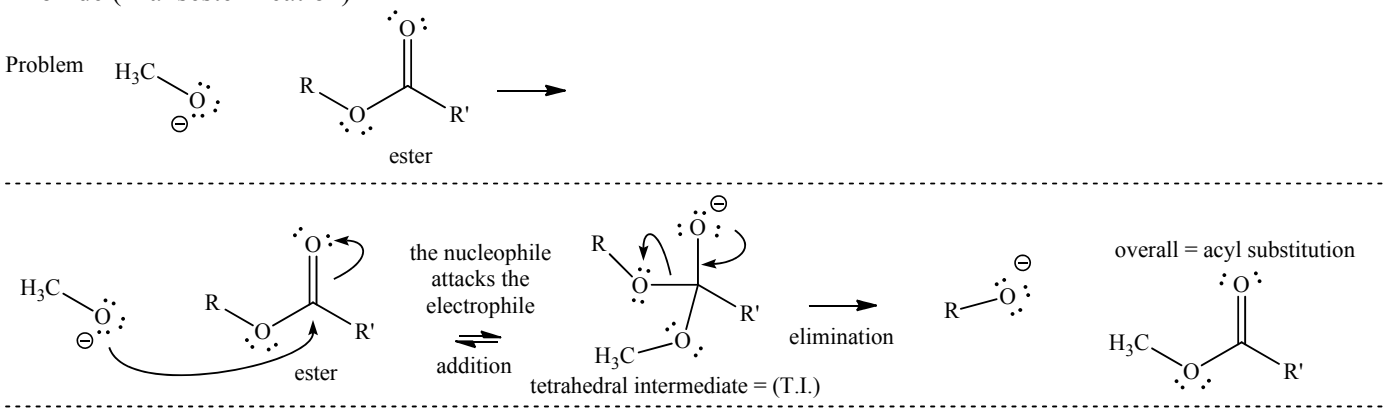


Esters (and carbonates)

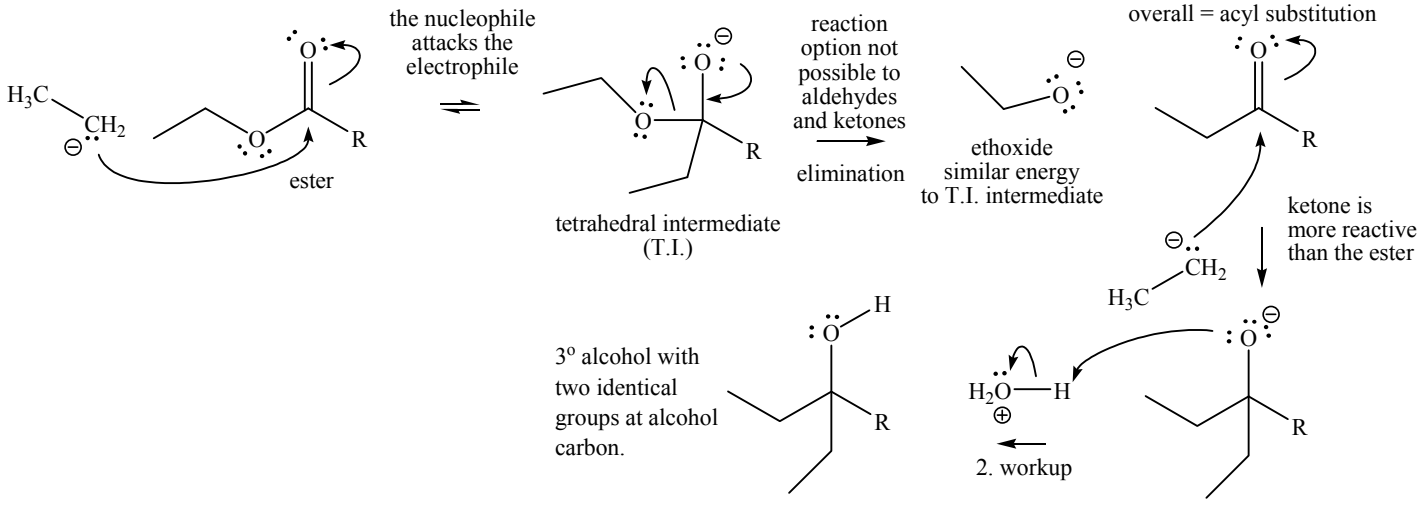
1. Hydroxide (hydrolysis is also called saponification = soap making)



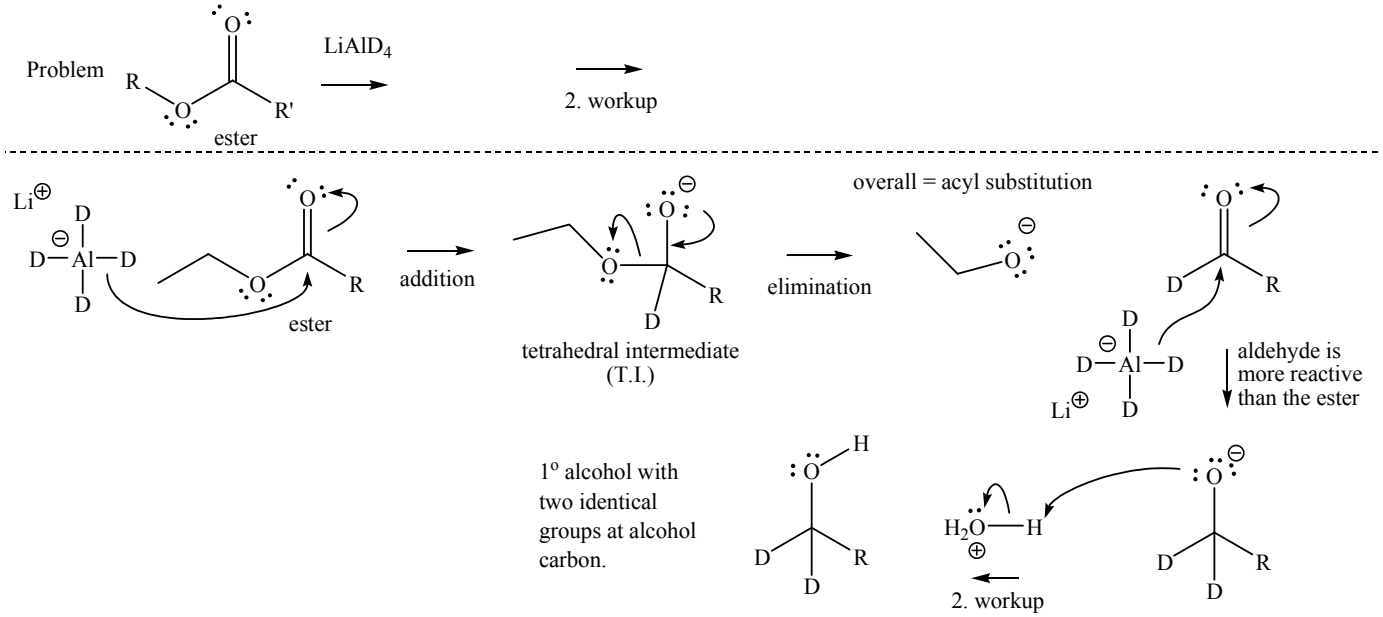
2. Alkoxide (Transesterification)



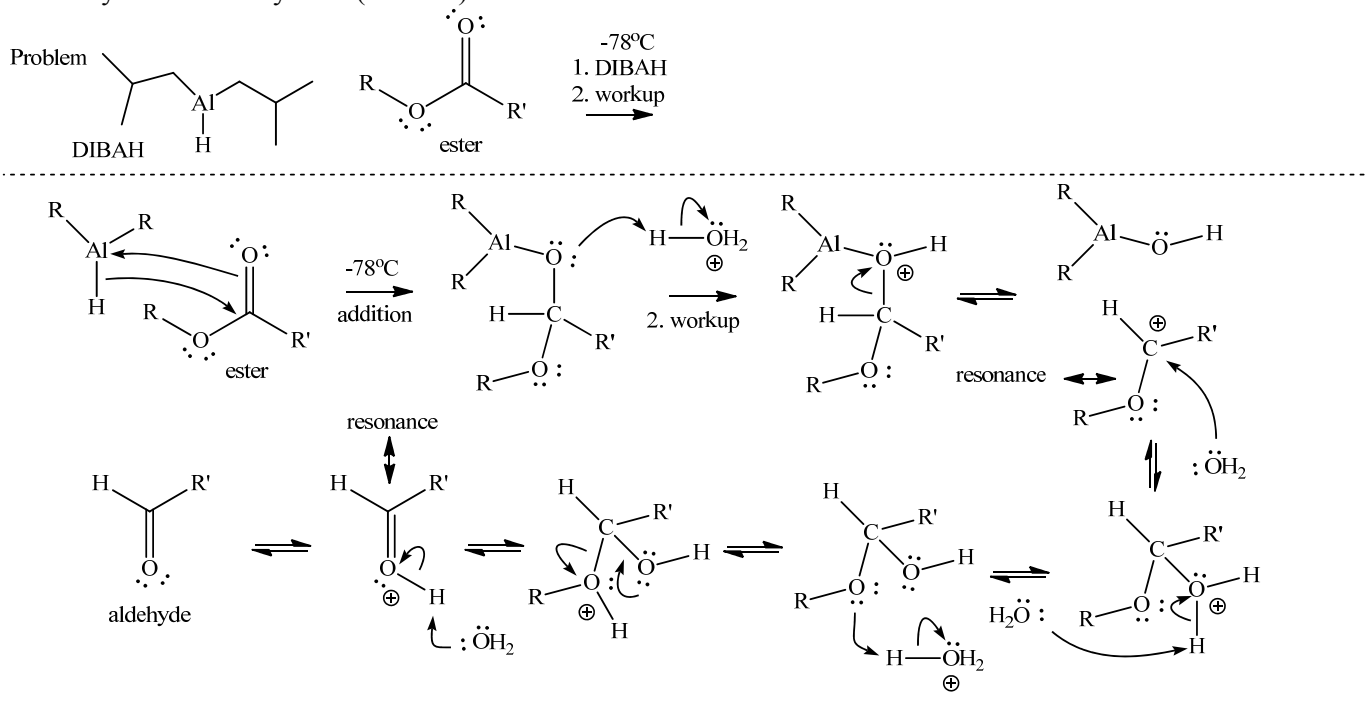
3. Organometallics (Li and Mg reagents)



4. Lithium aluminum hydride or sodium borohydride (or deuteride)



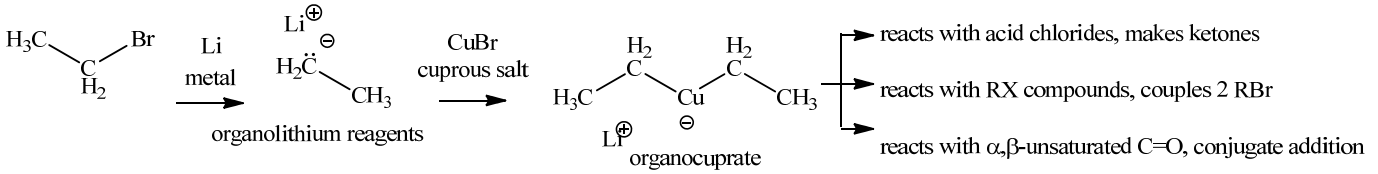
5. Diisobutylaluminium hydride (DIBAH)



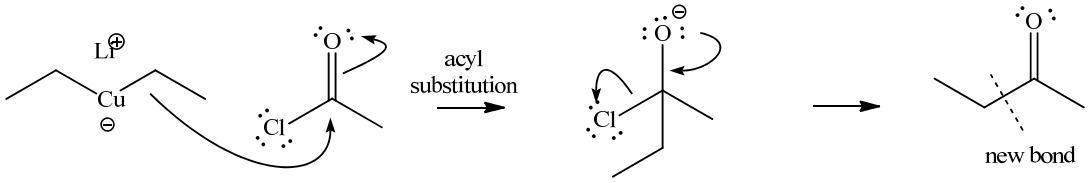
6. Amines

7. Lithium diisopropylamide (LDA), run at -78°C

8. Cuprate reactions – three variations for us that complement the lithium and magnesium organometallics

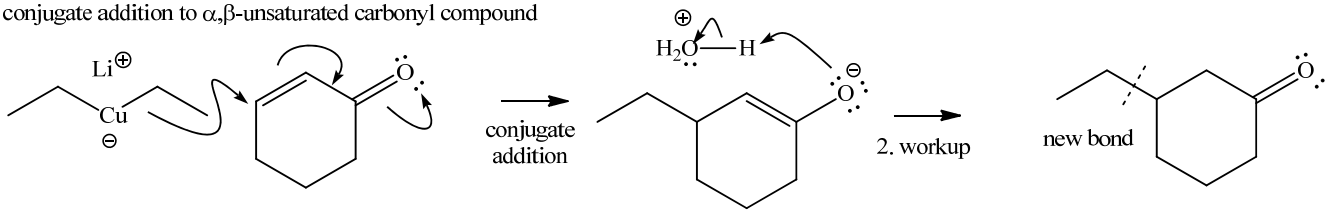


reacts with acid chlorides to make ketones



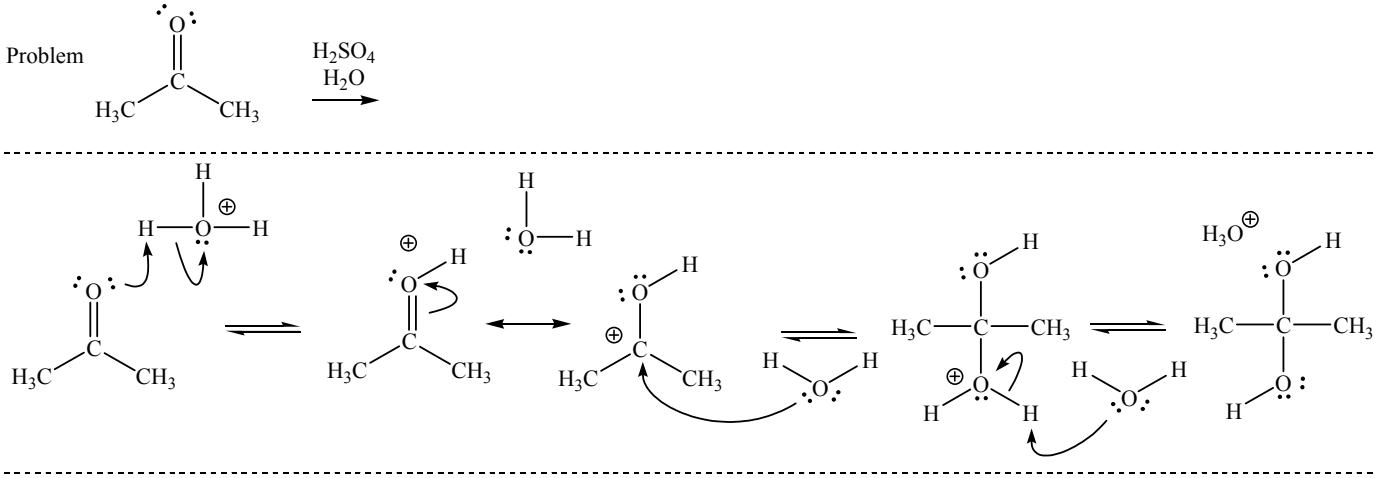
reacts with RX compounds

conjugate addition to α,β-unsaturated carbonyl compound

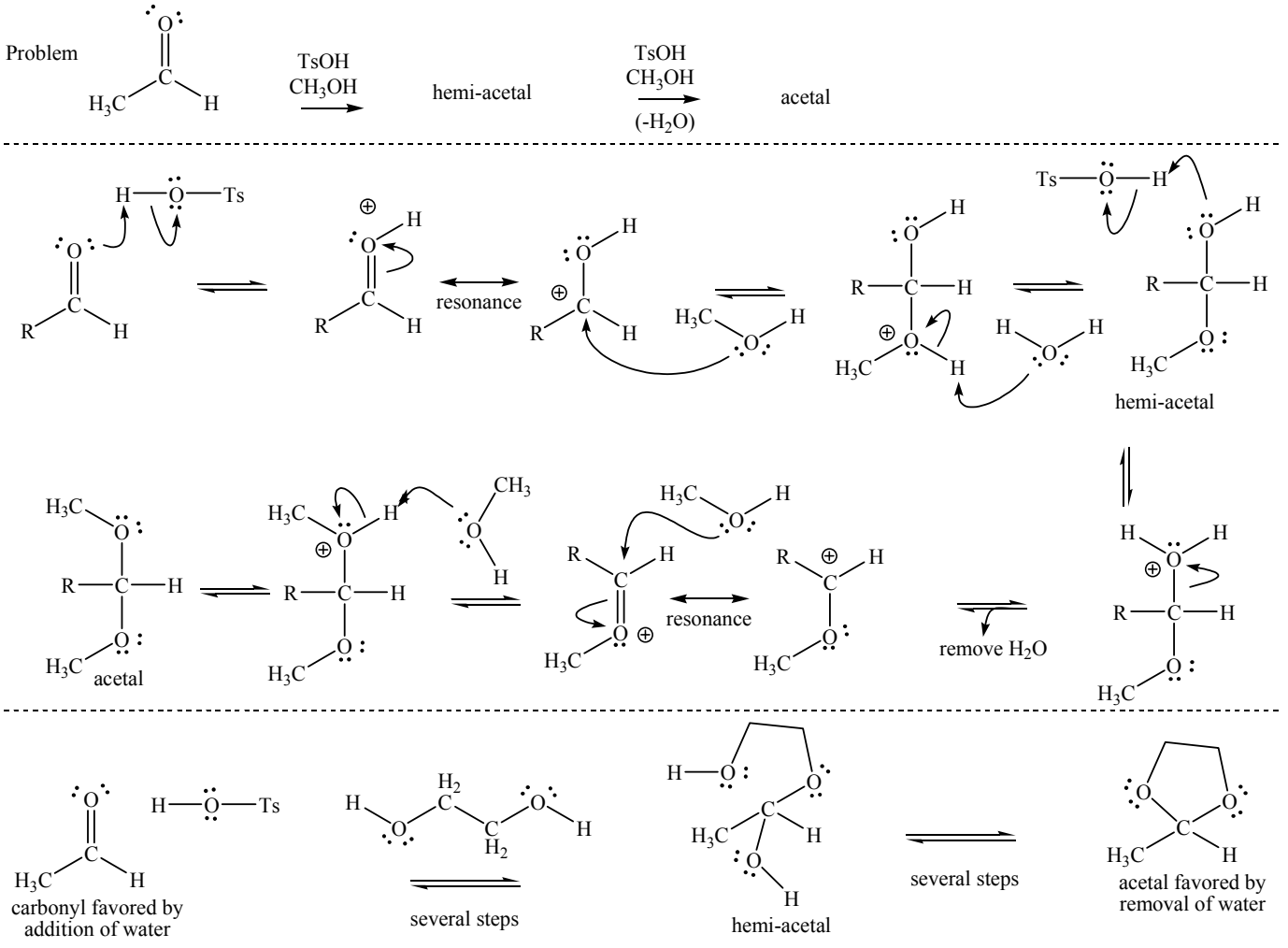


Carbonyls (aldehydes, ketones, esters, amides, nitriles) in Strong Acid/Electrophile mixtures

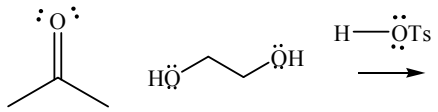
1. Aqueous acid makes carbonyl hydrates



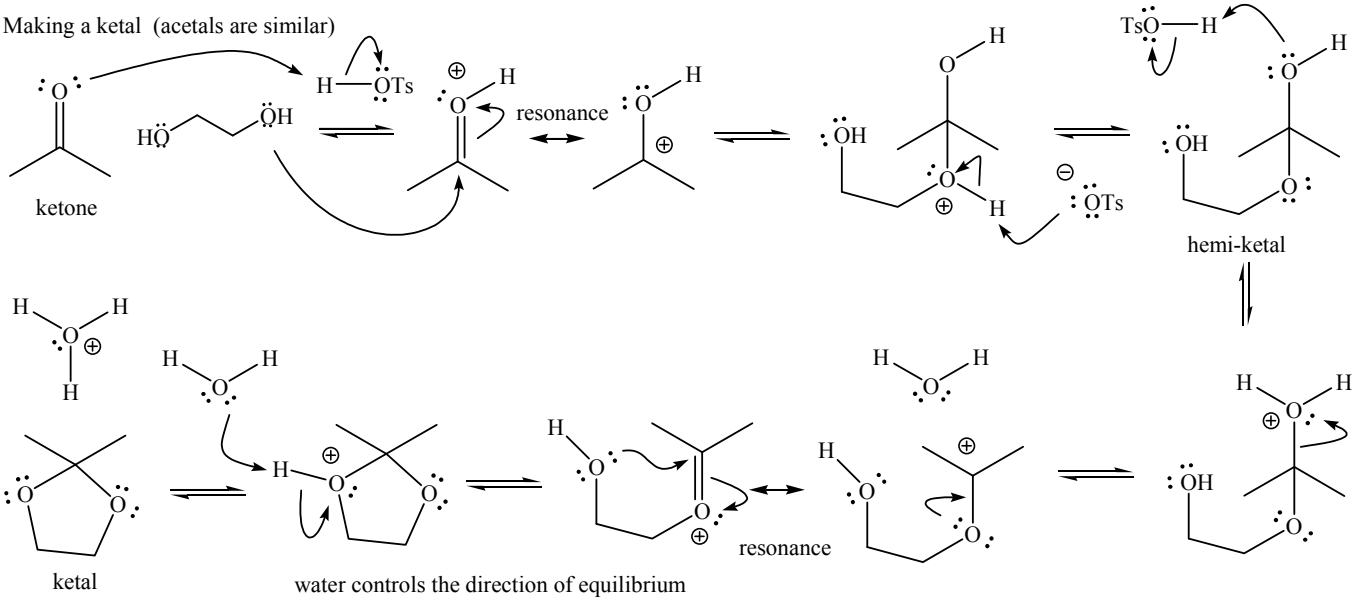
2. Carbonyl (aldehyde or ketone) + ROH + TsOH (-H_2O) makes hemi-acetals and acetals and hemi-ketals and ketals



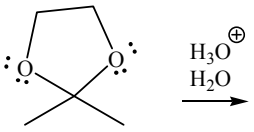
Problem



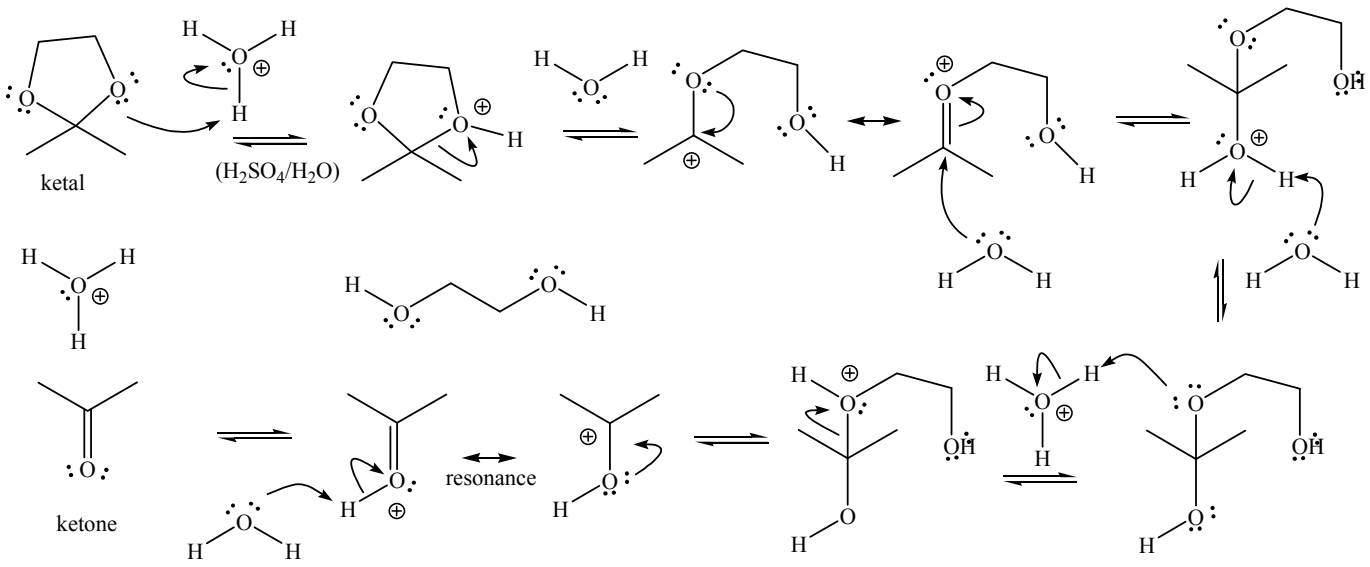
Making a ketal (acetals are similar)



Problem

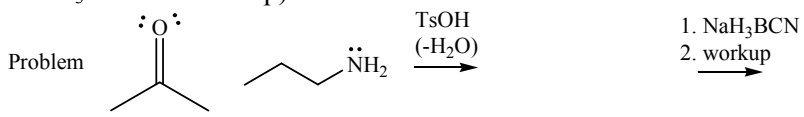


Hydrolysis of a ketal back to a ketone and ethylene glycol (acetals are similar and go back to aldehydes and ethylene glycol)

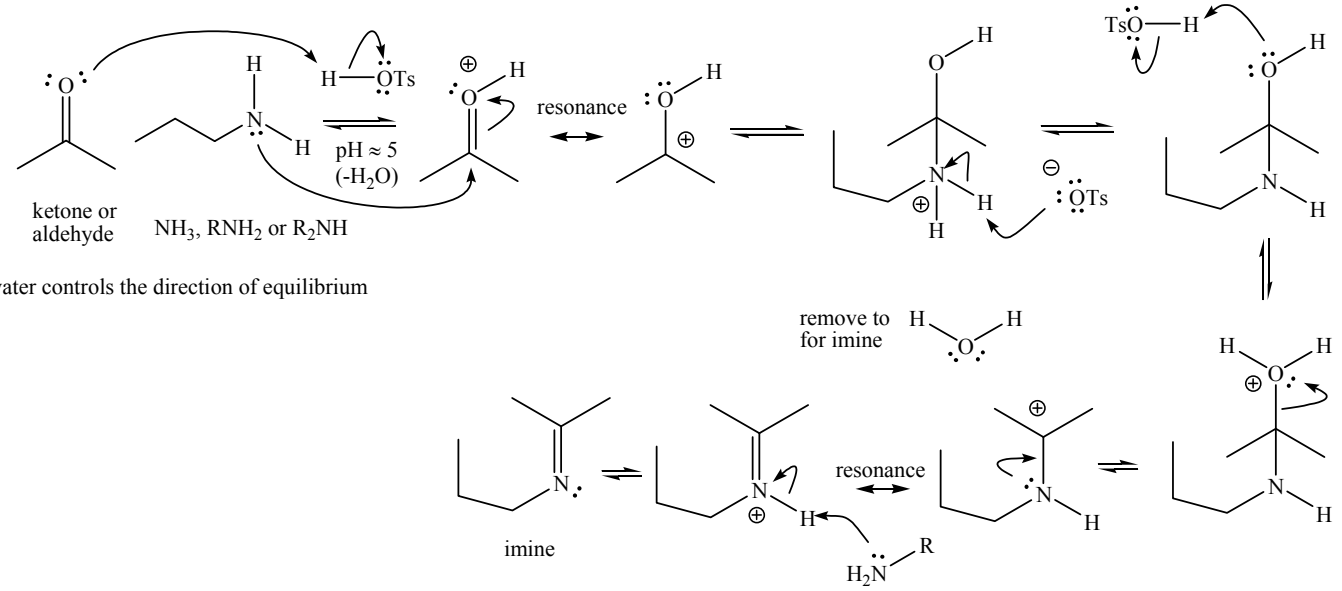


3. Carbonyl (aldehyde or ketone) + RNH_2 + TsOH ($-H_2O$) / pH = 5, makes imines that can be reduced

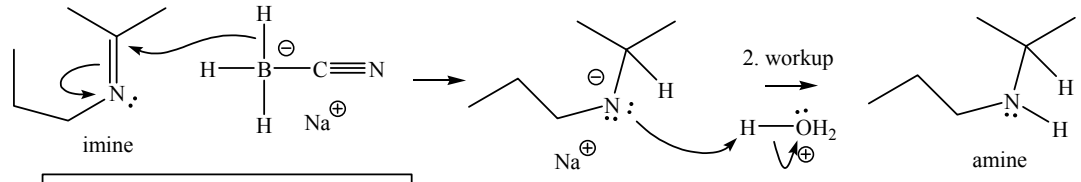
(a. NaH_3BCN b. workup) to amines.



Making an imine from a ketone or aldehyde and NH_3, RNH_2 or R_2NH. Then making the imine into a 1°, 2° or 3° amine using NaH_3BCN and workup.

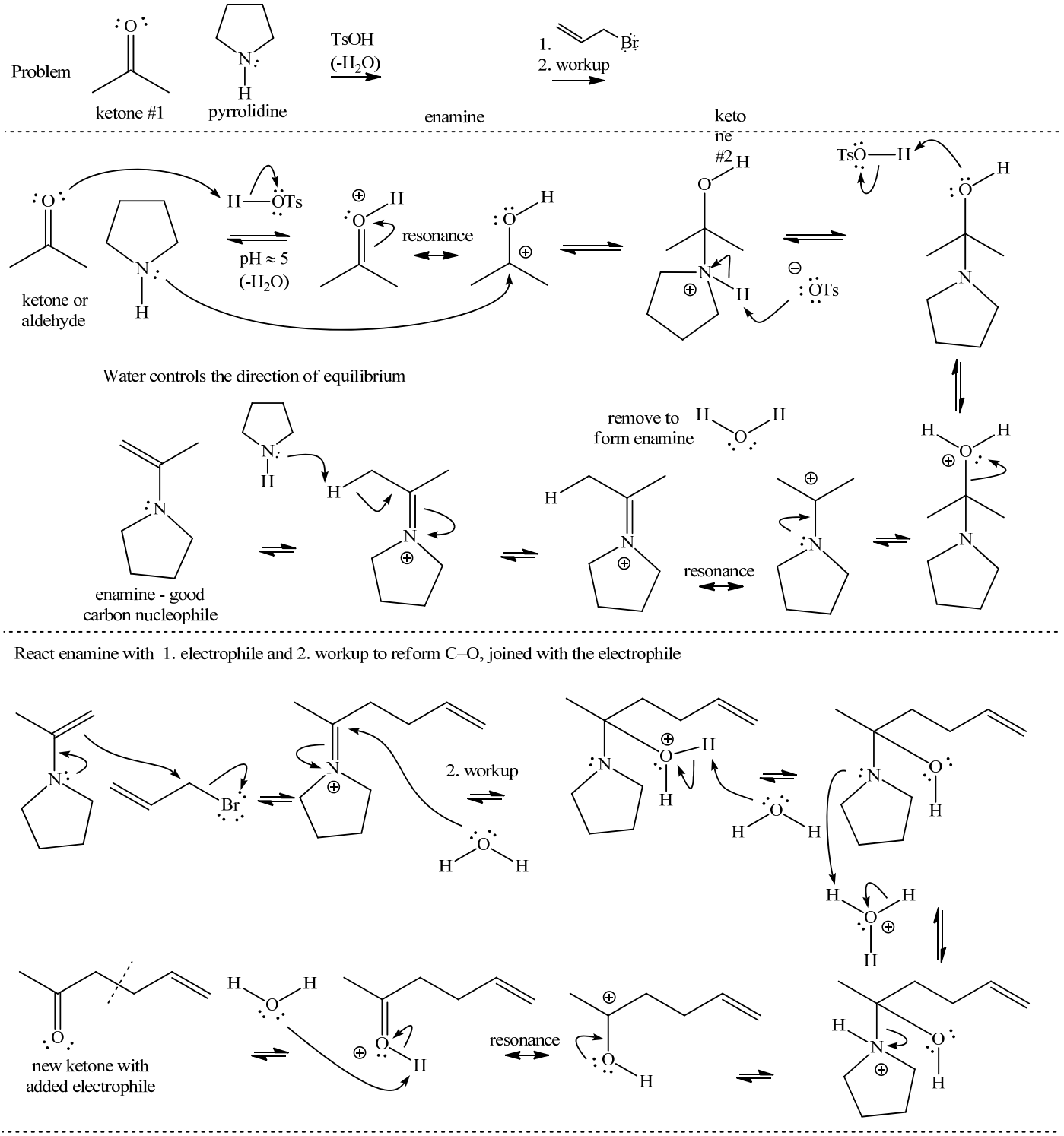


Reduce imine to amine with 1. sodium cyanoborohydride and 2. workup

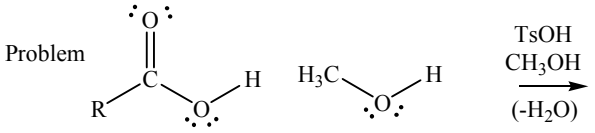


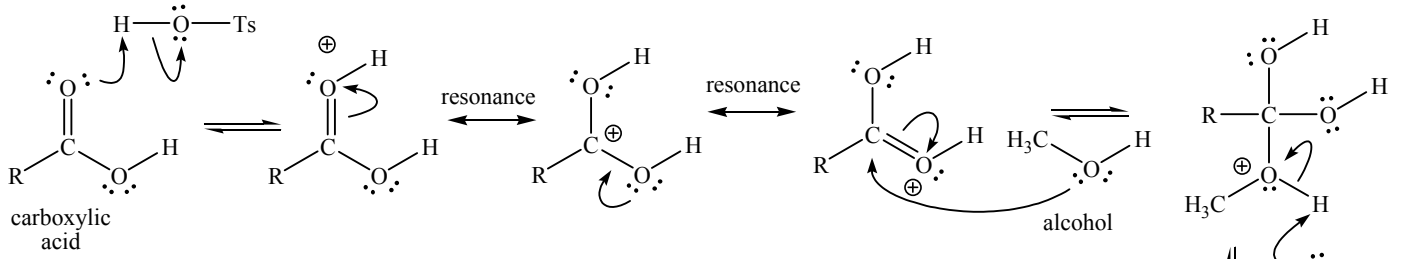
Transformations
C=O + NH_3 → primary amines
C=O + 1° amines → secondary amines
C=O + 2° amines → tertiary amines

4. Carbonyl (aldehyde or ketone) + R2NH + TsOH (-H_2O) / pH = 5, makes enamine that can be alkylated and hydrolyzed back to a ketone

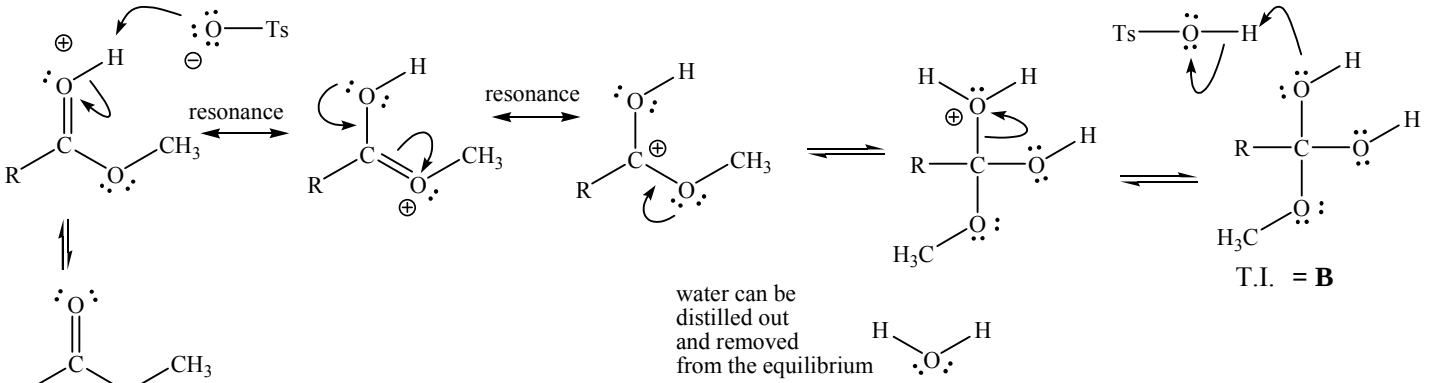


5. Fischer esterification ($RCO_2H + R'OH \rightarrow RCO_2R' + H_2O$ using TsOH as acid catalyst)





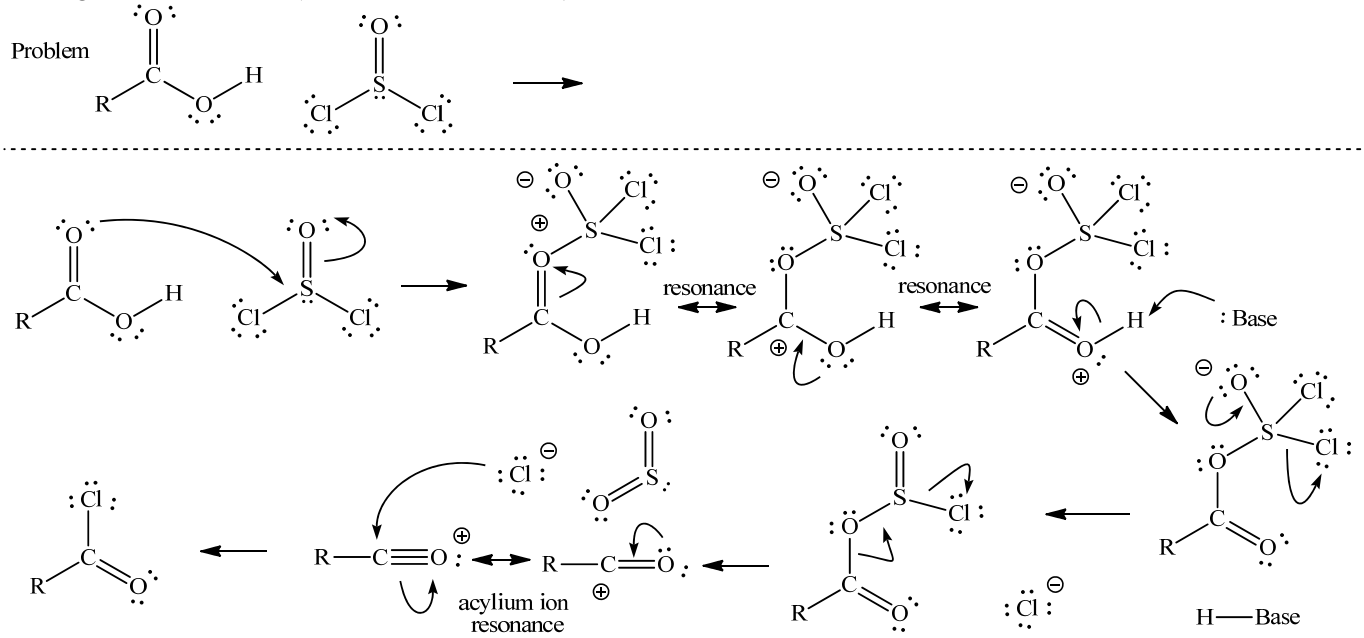
equilibrium is controlled by water, removing water shifts it to the right and adding water shifts it to the left



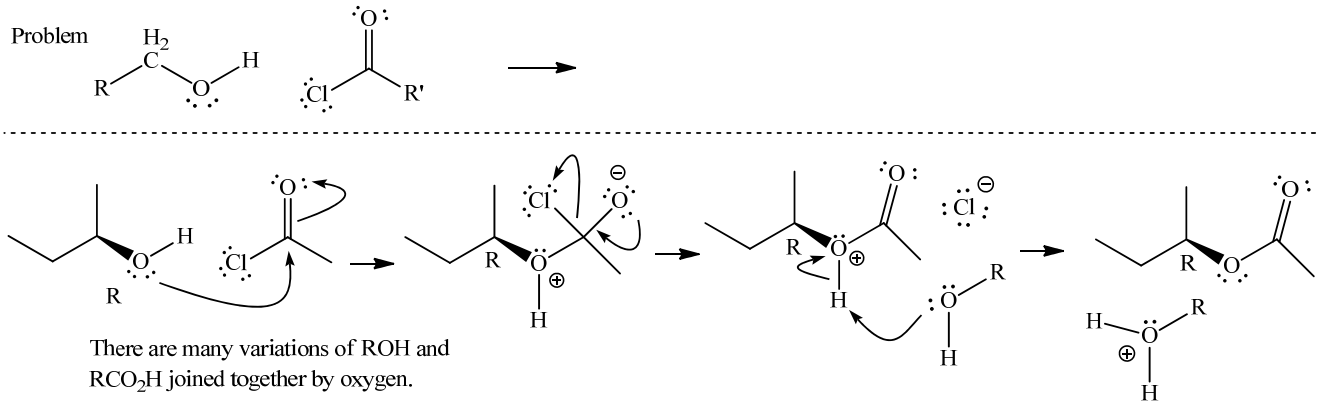
6.

Acid chlorides (and chloroformates, phosgene and equivalents, sulfur, nitrogen and phosphorous)

1. Making an acid chloride (from $RCO_2H + SOCl_2$)

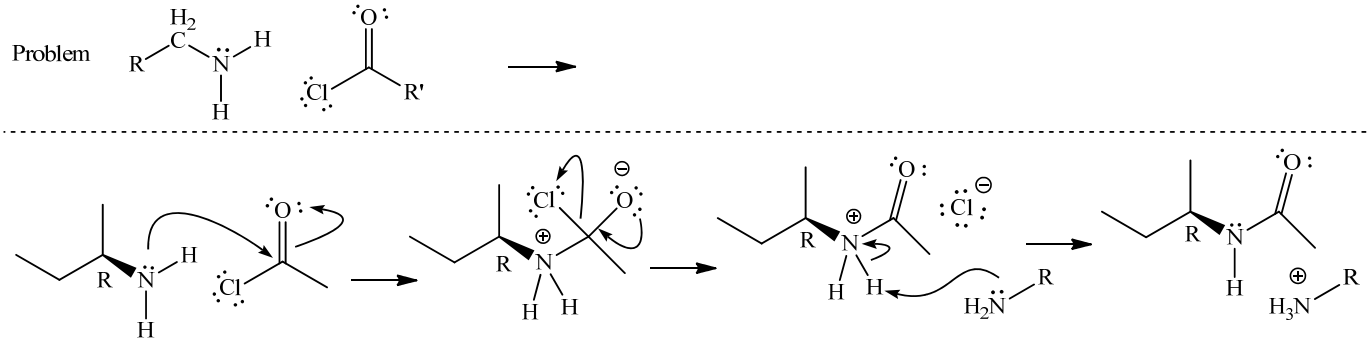


2. Alcohols make esters



There are many variations of ROH and RCO_2H joined together by oxygen.

3. Amines make amides



There are many variations of RNH_2 or R_2NH and RCO_2H joined together by nitrogen.

4. Organometallics (Li and Mg reagents) make tertiary alcohols
5. Lithium aluminum hydride or sodium borohydride make primary alcohols
6. Diisobutylaluminium hydride (DIBAH) makes ketones
7. Carboxylic acids make anhydrides
8. Water remakes the carboxylic acid (not desired)
9. Aromatics + AlCl3 makes aromatic ketones
10. Cuprates make ketones

Anhydrides (organic and mixed)

1. Hydroxide
2. Alkoxide
3. Organometallics (Li and Mg reagents)
4. Lithium aluminum hydride or sodium borohydride
5. Diisobutylaluminium hydride (DIBAH)
6. Amines
7. Lithium diisopropylamide (LDA)
8.

Acids

1. Hydroxide
2. Alkoxide
3. Organometallics (Li and Mg reagents)
4. Lithium aluminum hydride or sodium borohydride
5. Diisobutylaluminium hydride (DIBAH)
6. Amines
7. Lithium diisopropylamide (LDA)
8.

Amides (primary, secondary and tertiary)

1. Hydroxide
2. Alkoxide
3. Organometallics (Li and Mg reagents)
4. Lithium aluminum hydride or sodium borohydride
5. Diisobutylaluminium hydride (DIBAH)
6. Amines
7. Lithium diisopropylamide (LDA)
8.

Nitriles

1. Hydroxide
2. Alkoxide
3. Organometallics (Li and Mg reagents)
4. Lithium aluminum hydride or sodium borohydride
5. Diisobutylaluminium hydride (DIBAH)
6. Amines
7. Lithium diisopropylamide (LDA)
8.

Carbonyl Groups in Strong Protic or Lewis Acid Conditions

7. Aldehydes
8. Ketones (and carbon dioxide)
9. Esters (and carbonates)
10. Acid chlorides (and chloroformates, phosgene and equivalents, sulfur, nitrogen and phosphorous)
11. Anhydrides (organic and mixed)
12. Acids

13. Amides (primary, secondary and tertiary)

14. Nitriles

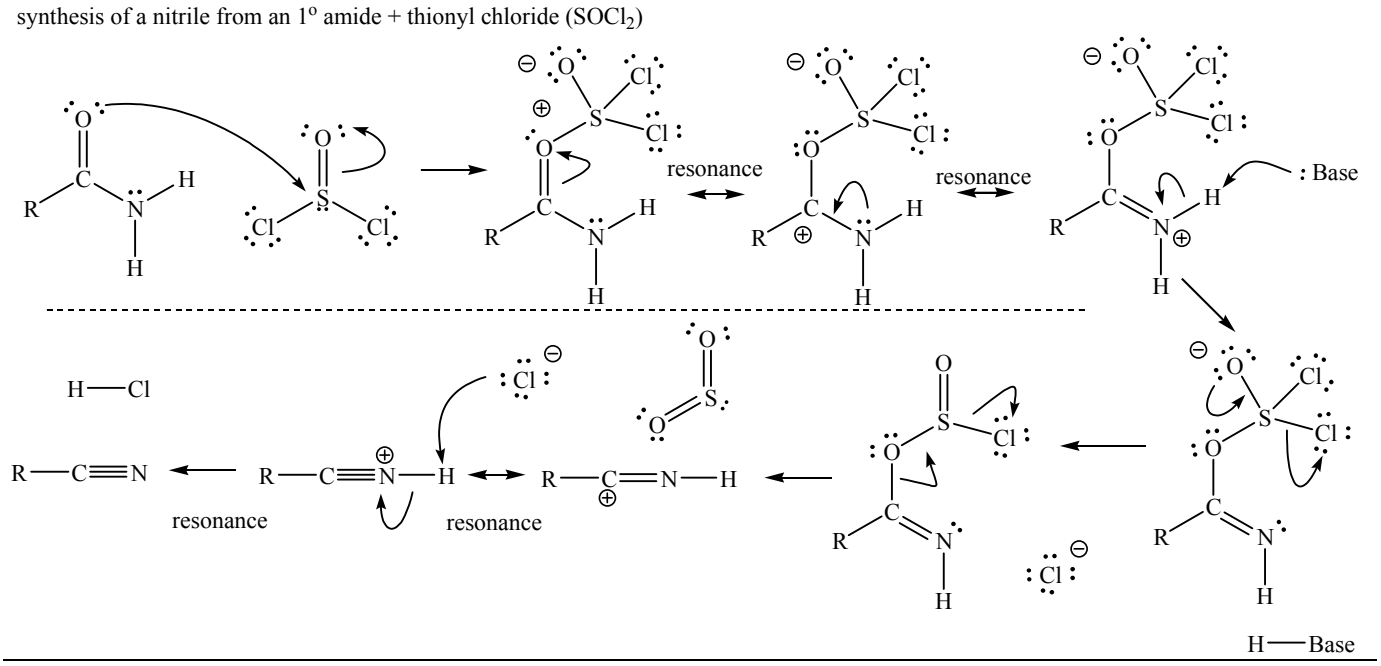
15.

Miscellaneous (Various name reactions)

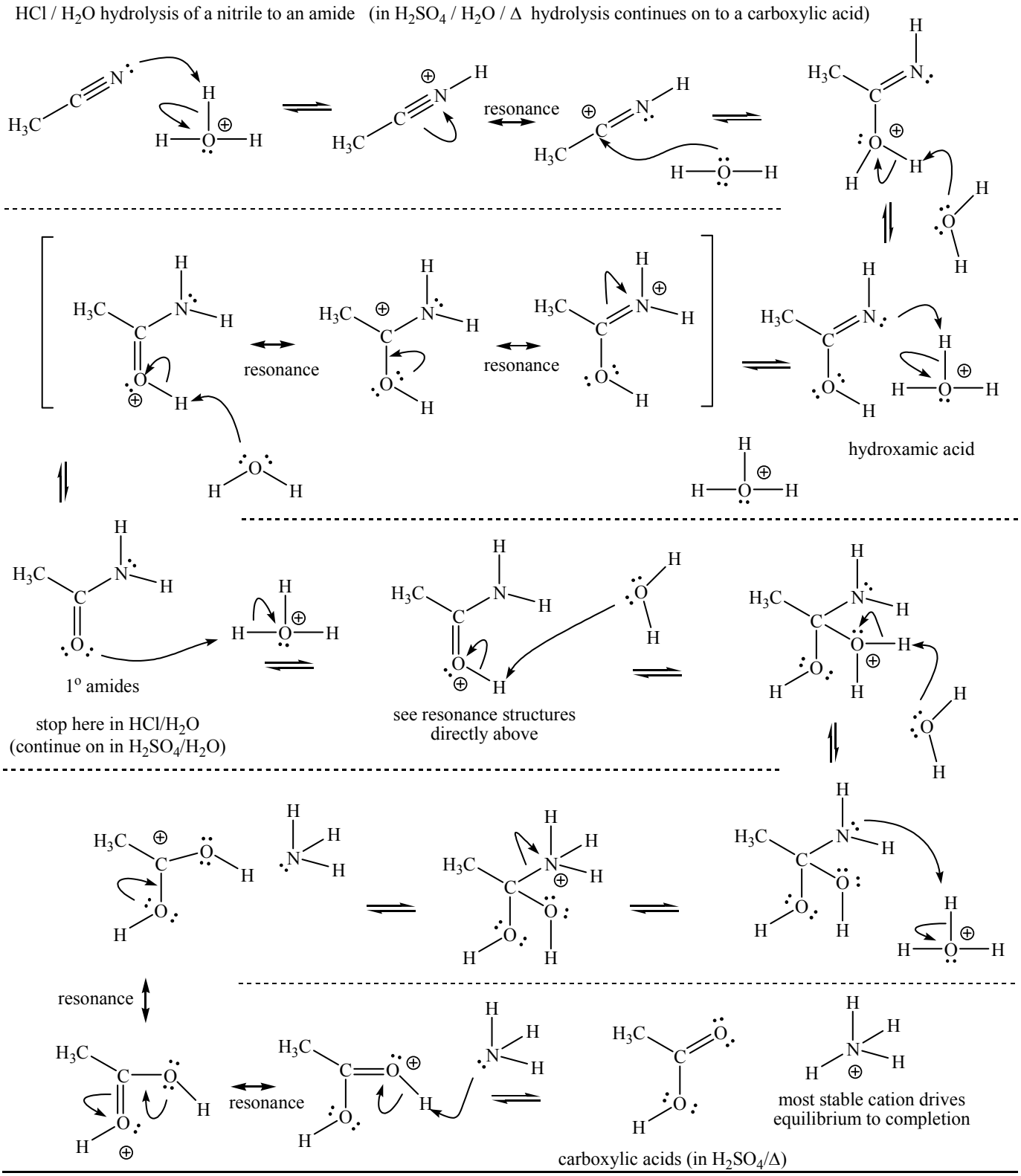
1. Baeyer Villigar reaction

2. Iodoform reaction

3. Nitrile synthesis from primary amide and $SOCl_2$



4. Hydrolysis of nitriles (moderate acid makes 1° amide, strong acid/heat makes carboxylic acids)



5. Ritter reaction

6.

7.

8.

9.

10.

11.

12.

13.

14.

15.

16.

17.

18.

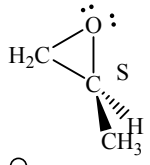
19.

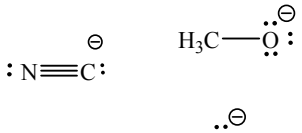
Cuprates

DIBAH

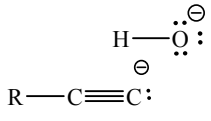
Nitriles

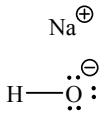
Thionyl chloride



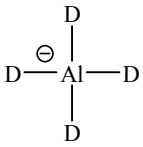


methyl RBr	= only S_N2
primary RBr	= S_N2 > E2
secondary RBr	= E2 > S_N2
tertiary RBr	= only E2



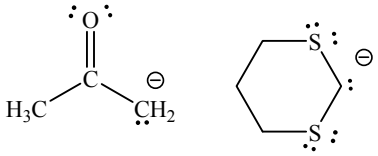


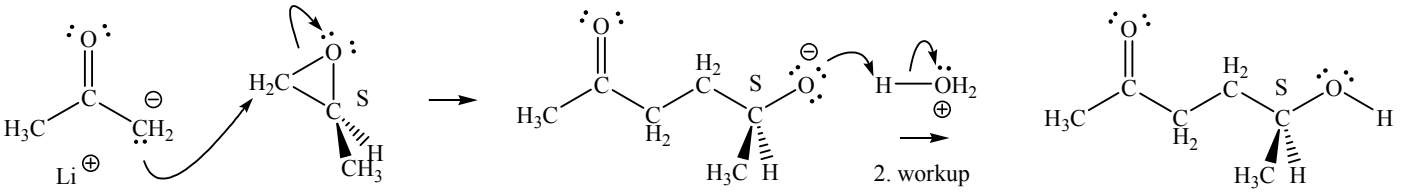
methyl RBr	= only S_N2
primary RBr	= mainly S_N2
secondary RBr	= mainly S_N2
tertiary RBr	= only E2

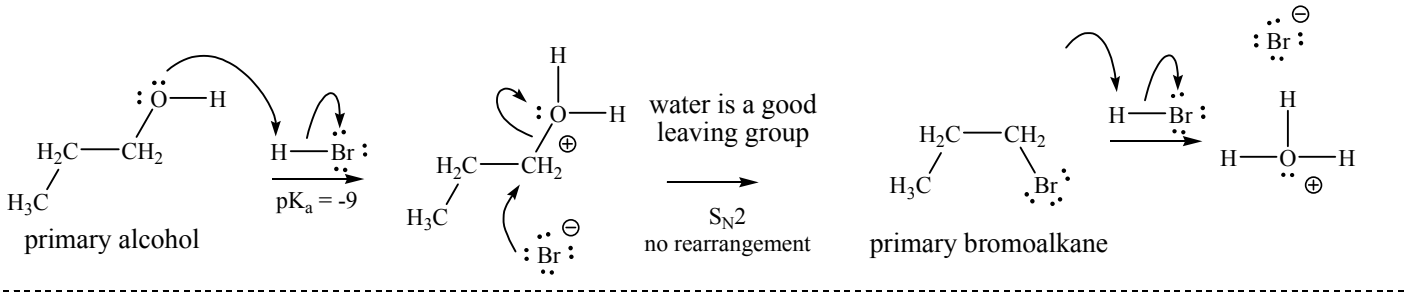


methyl RBr	= only S_N2
primary RBr	= S_N2 > E2
secondary RBr	= S_N2 > E2
tertiary RBr	= only E2

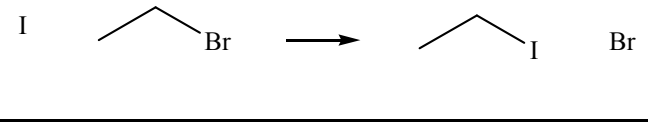
methyl RBr	= only S_N2
primary RBr	= S_N2 > E2
secondary RBr	= S_N2 > E2
tertiary RBr	= only E2



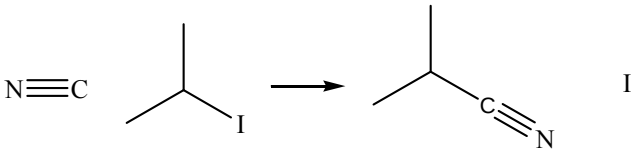




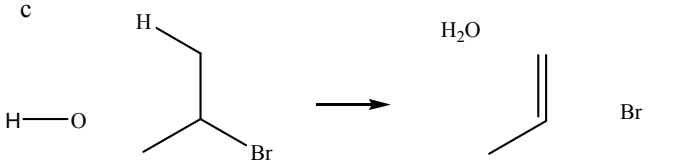
a


I
Br
I
Br

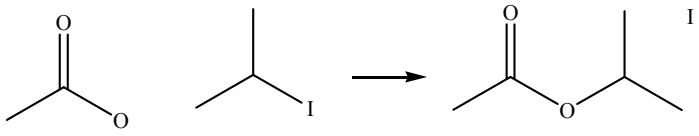
b


N≡C
I
C
N
I

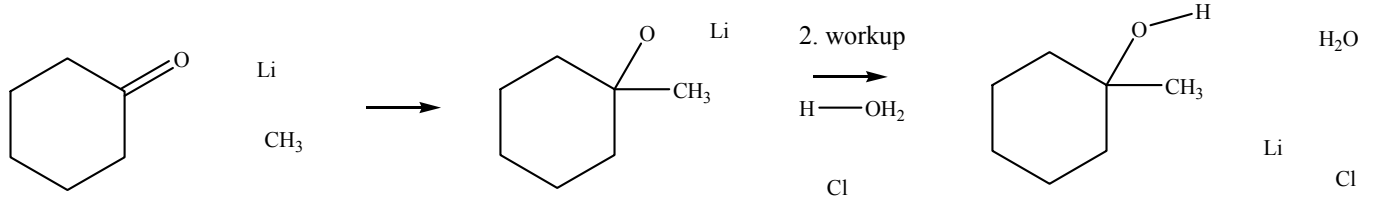
c


H
H—O
Br
H2O
Br

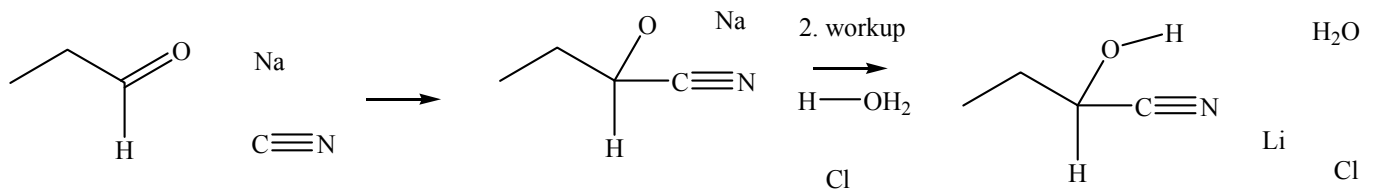
d


O
O
I
O
O
I

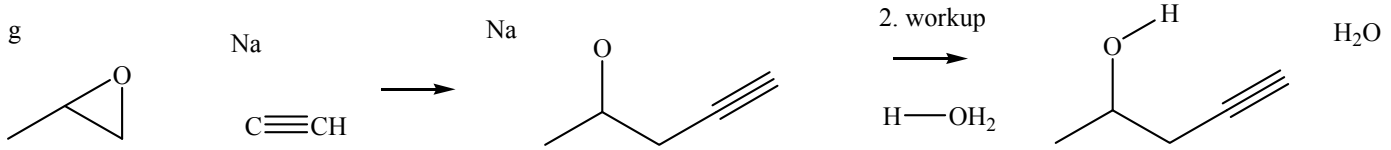
e


O
Li
CH3
O
Li
CH3
2. workup
H—OH2
Cl
O
H
CH3
H2O
Li
Cl

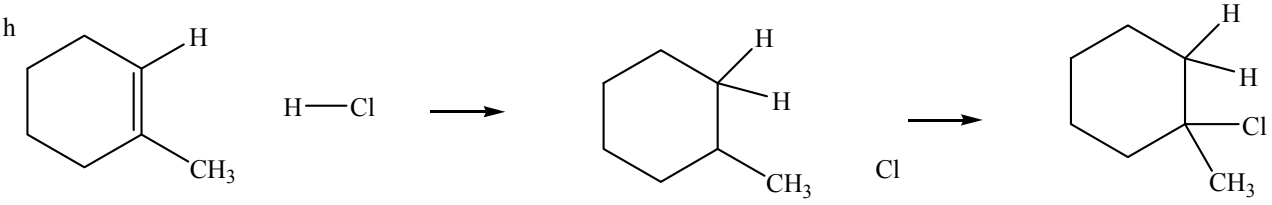
f


O
H
Na
C≡N
O
Na
C≡N
H
2. workup
H—OH2
Cl
O
H
C≡N
H
H2O
Li
Cl

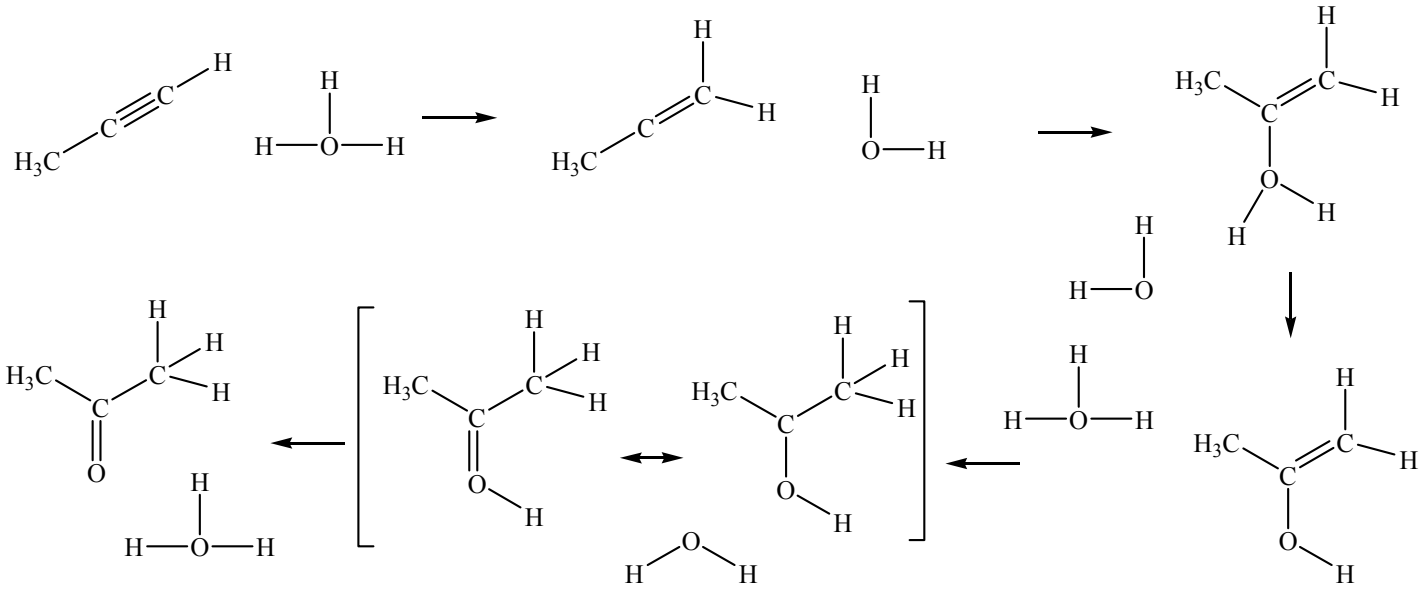
g


O
Na
C≡CH
Na
O
2. workup
H—OH2
O
H
H2O

h


H
CH3
H—Cl
H
H
CH3
Cl
H
H
Cl
CH3

i There isn't any lone pair, so you have to use the pi electrons as the nucleophile.



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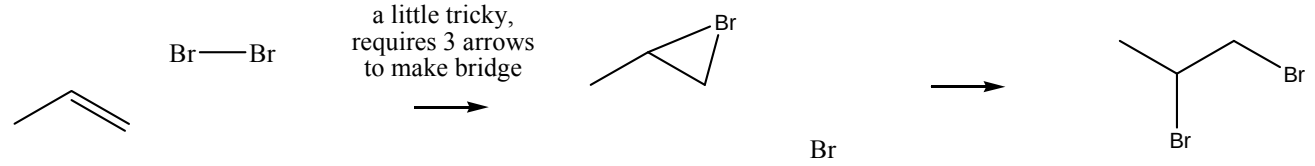
j



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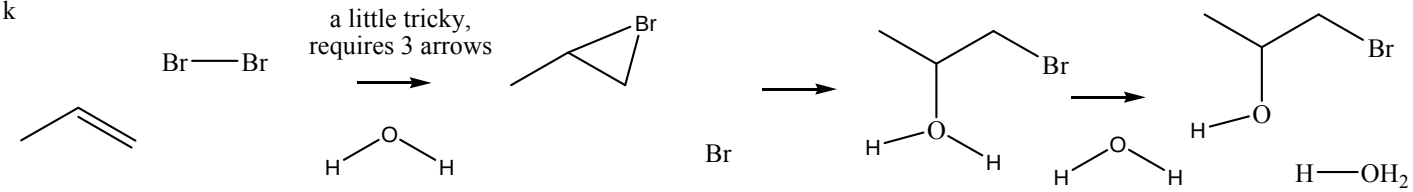
k



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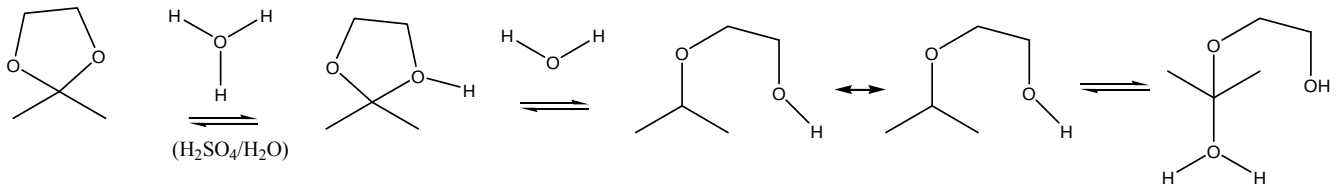
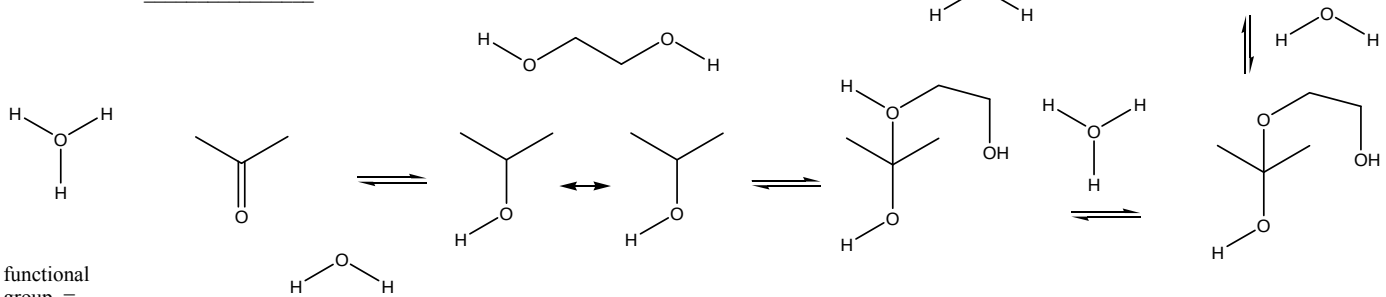
l Hydrolysis of a ketal back to a ketone and ethylene glycol (acetals are similar and go back to aldehydes and ethylene glycol)



common name = _____



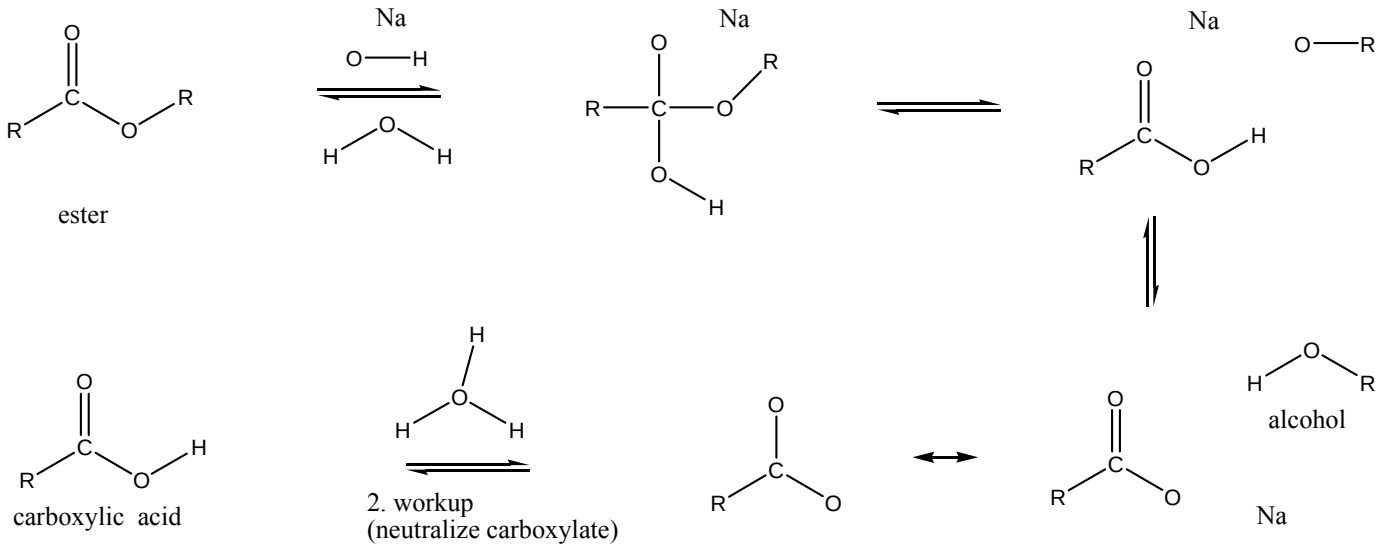
functional group = _____

Remove H_2O shifts equilibrium to the _____

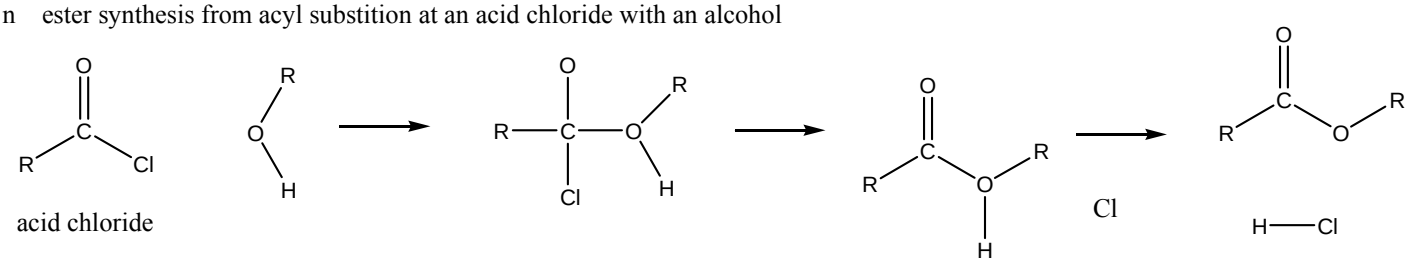
Adding H_2O shifts equilibrium to the _____

---

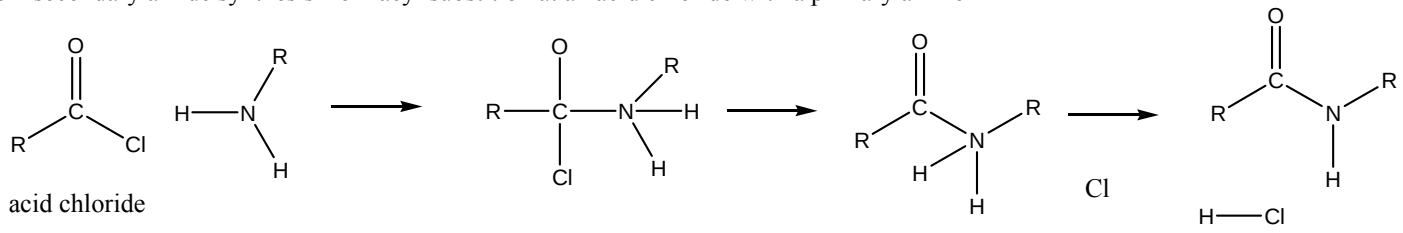
m ester base hydrolysis = saponification



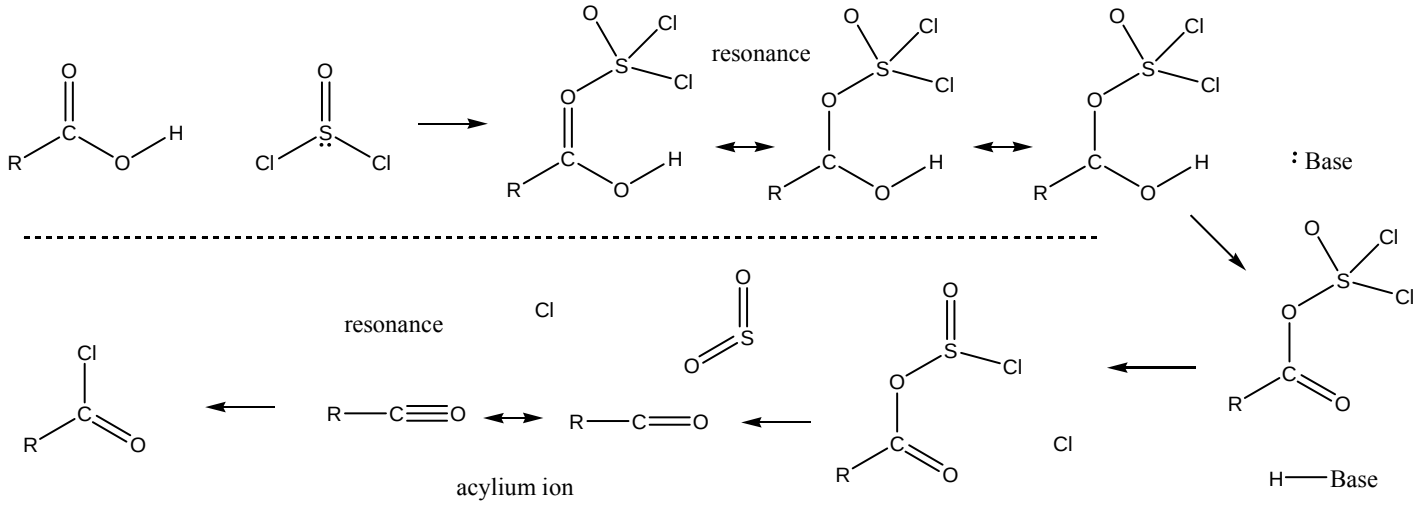
n ester synthesis from acyl substition at an acid chloride with an alcohol



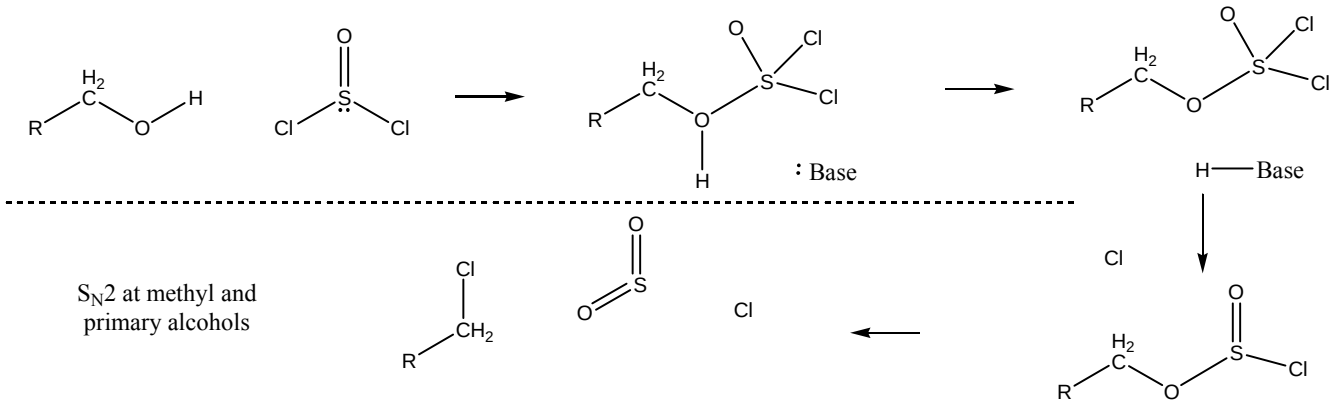
o secondary amide synthesis from acyl substition at an acid chloride with a primary amine



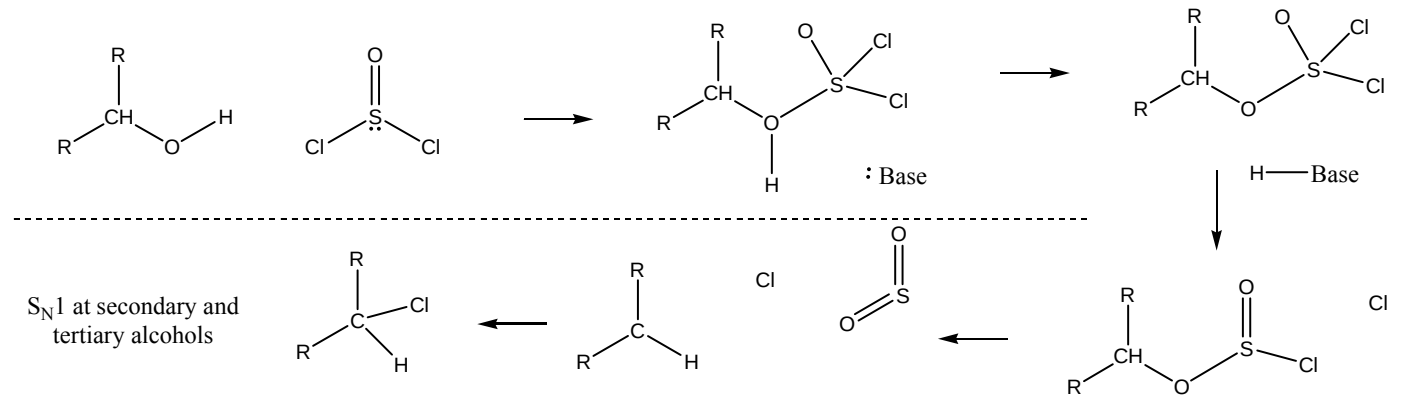
p synthesis of an acid chloride from an acid + thionyl chloride ($SOCl_2$)



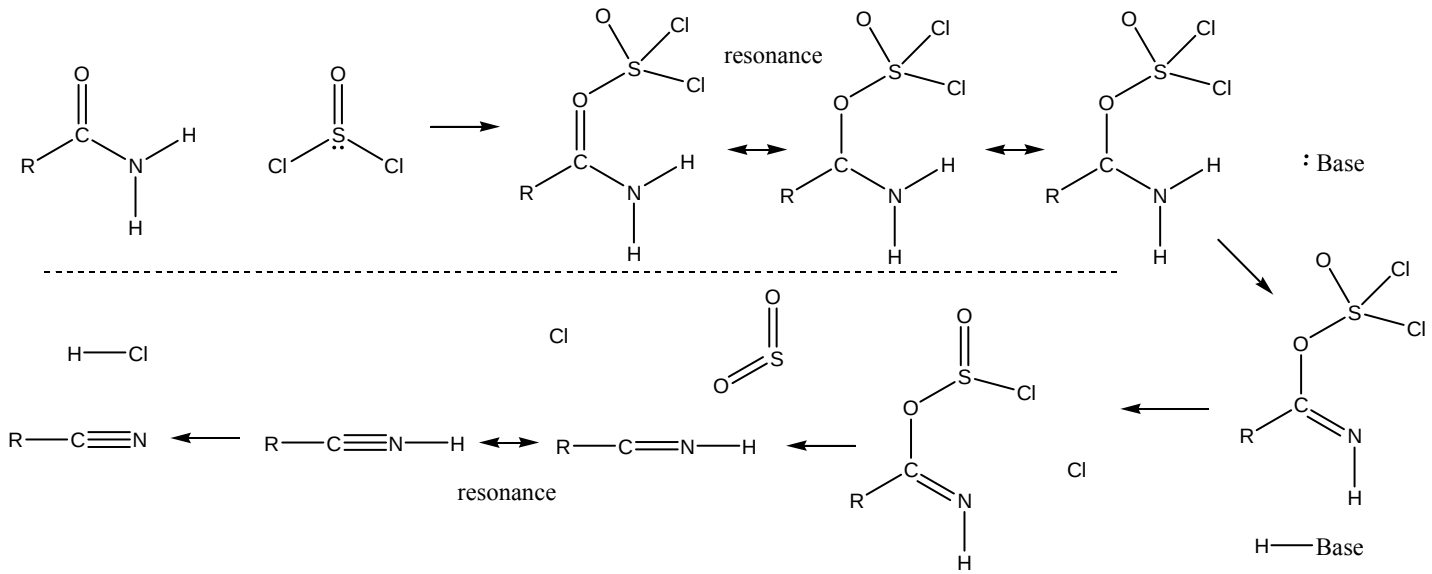
q synthesis of an alkyl chloride from an alcohol + thionyl chloride ($SOCl_2$) [can also make RBr from $SOBr_2$]



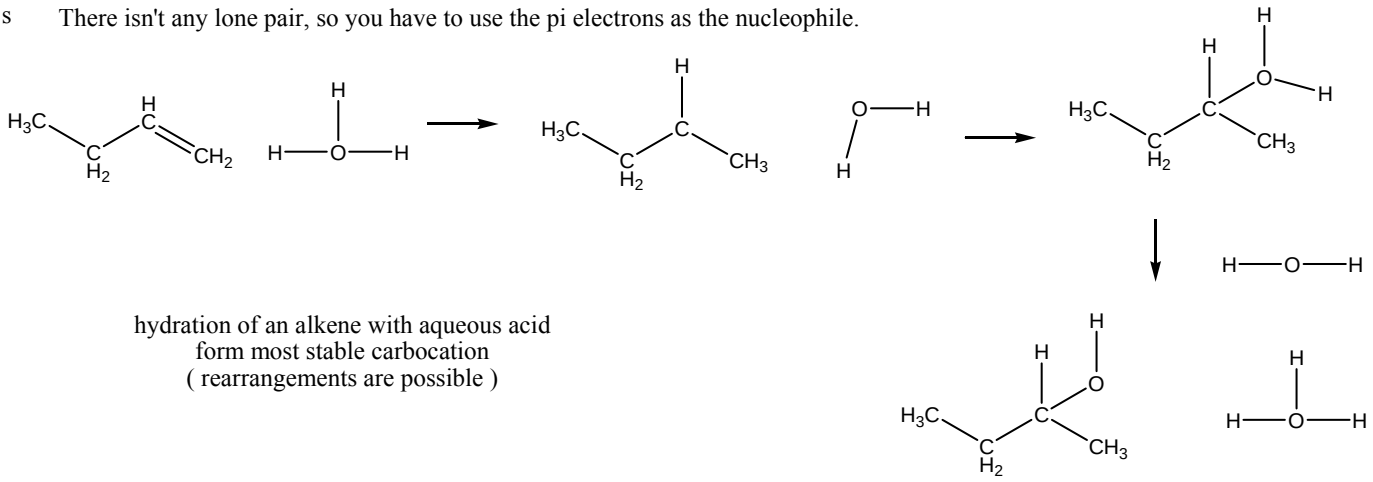
r synthesis of an alkyl chloride from an alcohol + thionyl chloride ($SOCl_2$) [can also make RBr from $SOBr_2$]



r synthesis of a nitrile from an 1° amide + thionyl chloride ($SOCl_2$)



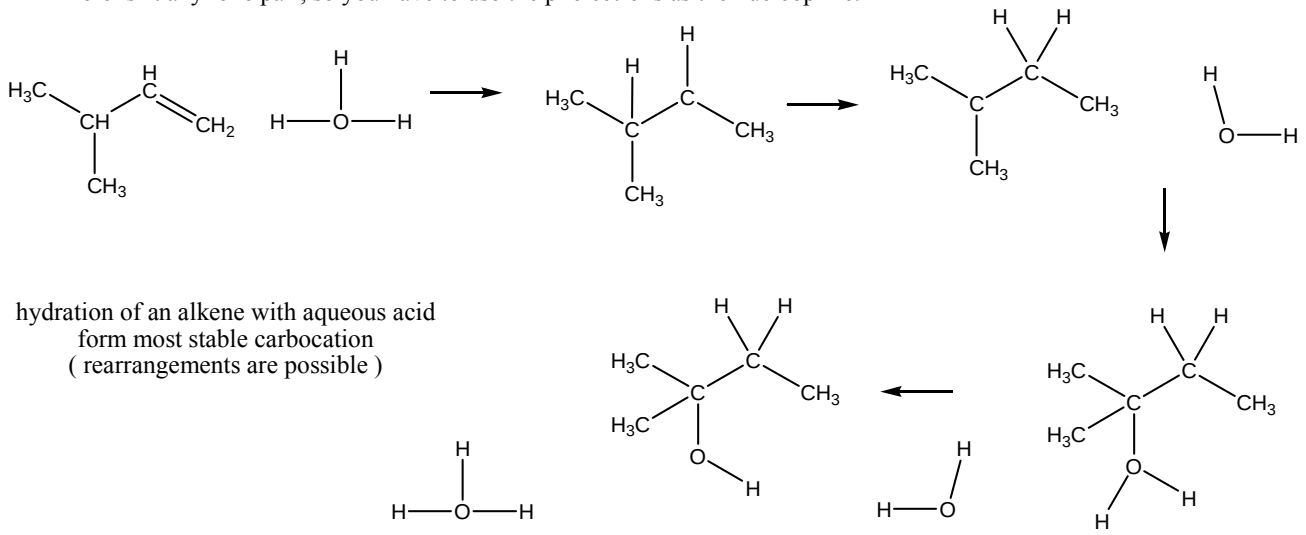
s There isn't any lone pair, so you have to use the pi electrons as the nucleophile.



hydration of an alkene with aqueous acid
form most stable carbocation
(rearrangements are possible)

---

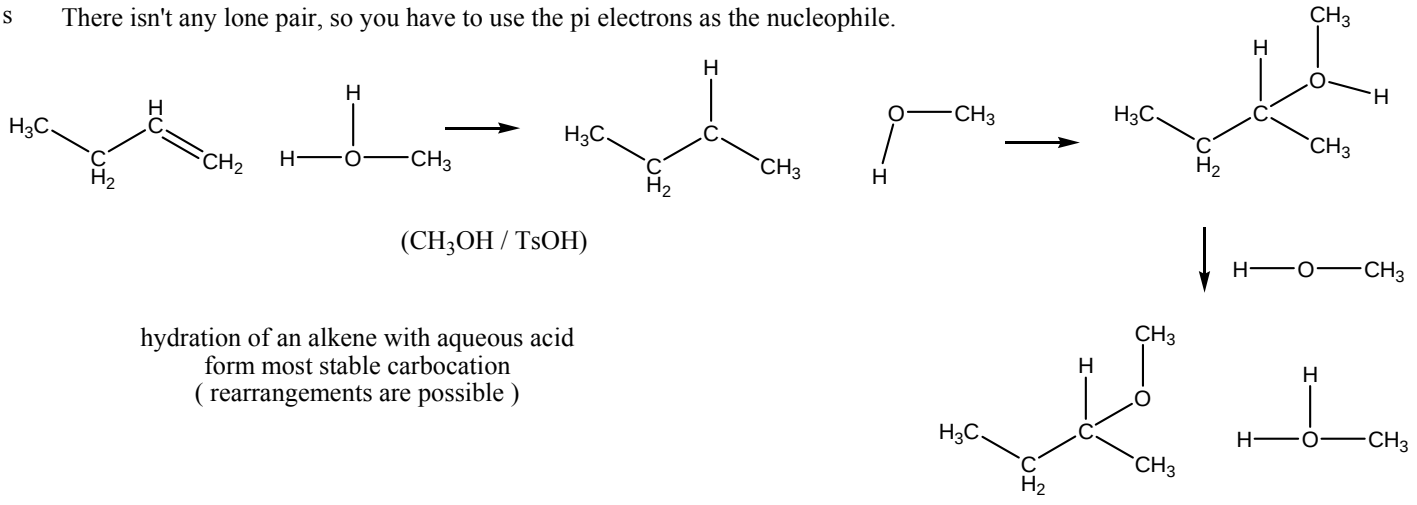
t There isn't any lone pair, so you have to use the pi electrons as the nucleophile.



hydration of an alkene with aqueous acid
form most stable carbocation
(rearrangements are possible)

---

s There isn't any lone pair, so you have to use the pi electrons as the nucleophile.

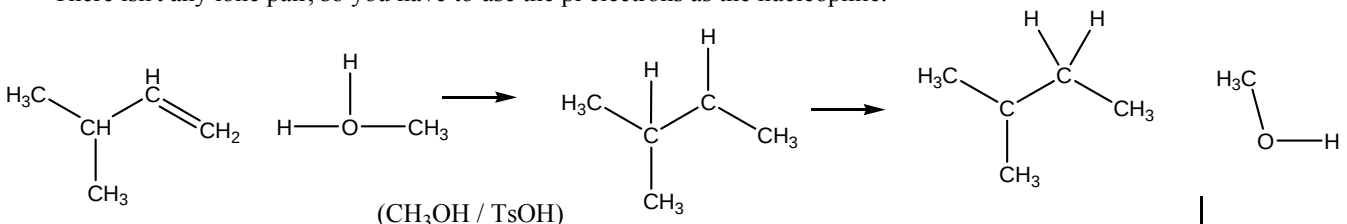


(CH_3OH / TsOH)

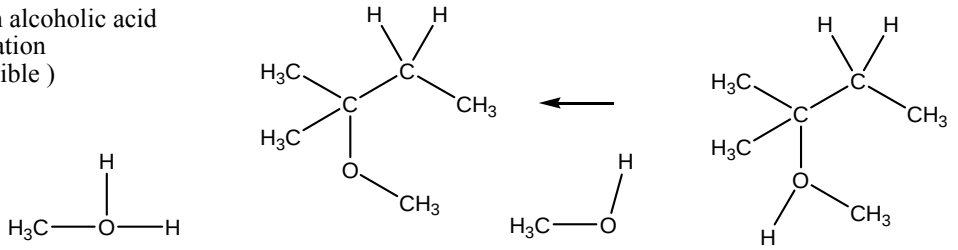
hydration of an alkene with aqueous acid
form most stable carbocation
(rearrangements are possible)

---

t There isn't any lone pair, so you have to use the pi electrons as the nucleophile.



ether synthesis from an alkene with alcoholic acid
form most stable carbocation
(rearrangements are possible)



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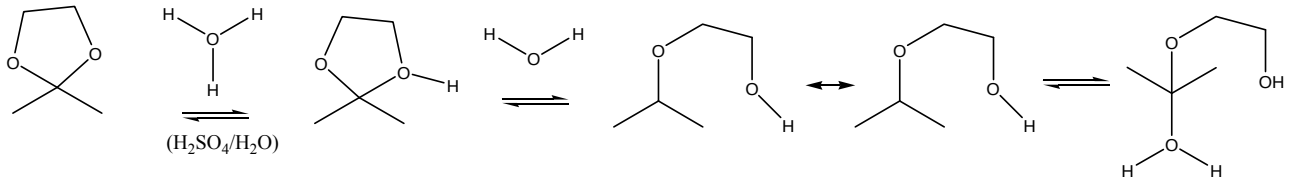
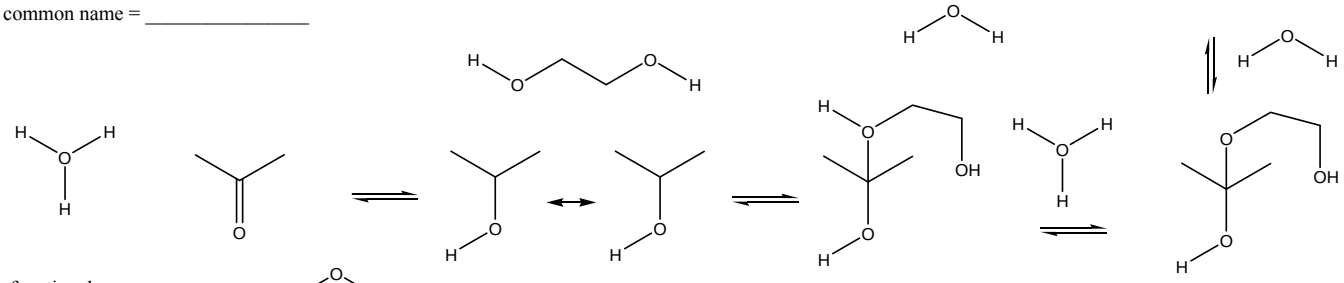
l Hydrolysis of a ketal back to a ketone and ethylene glycol (acetals are similar and go back to aldehydes and ethylene glycol)



common name = _____



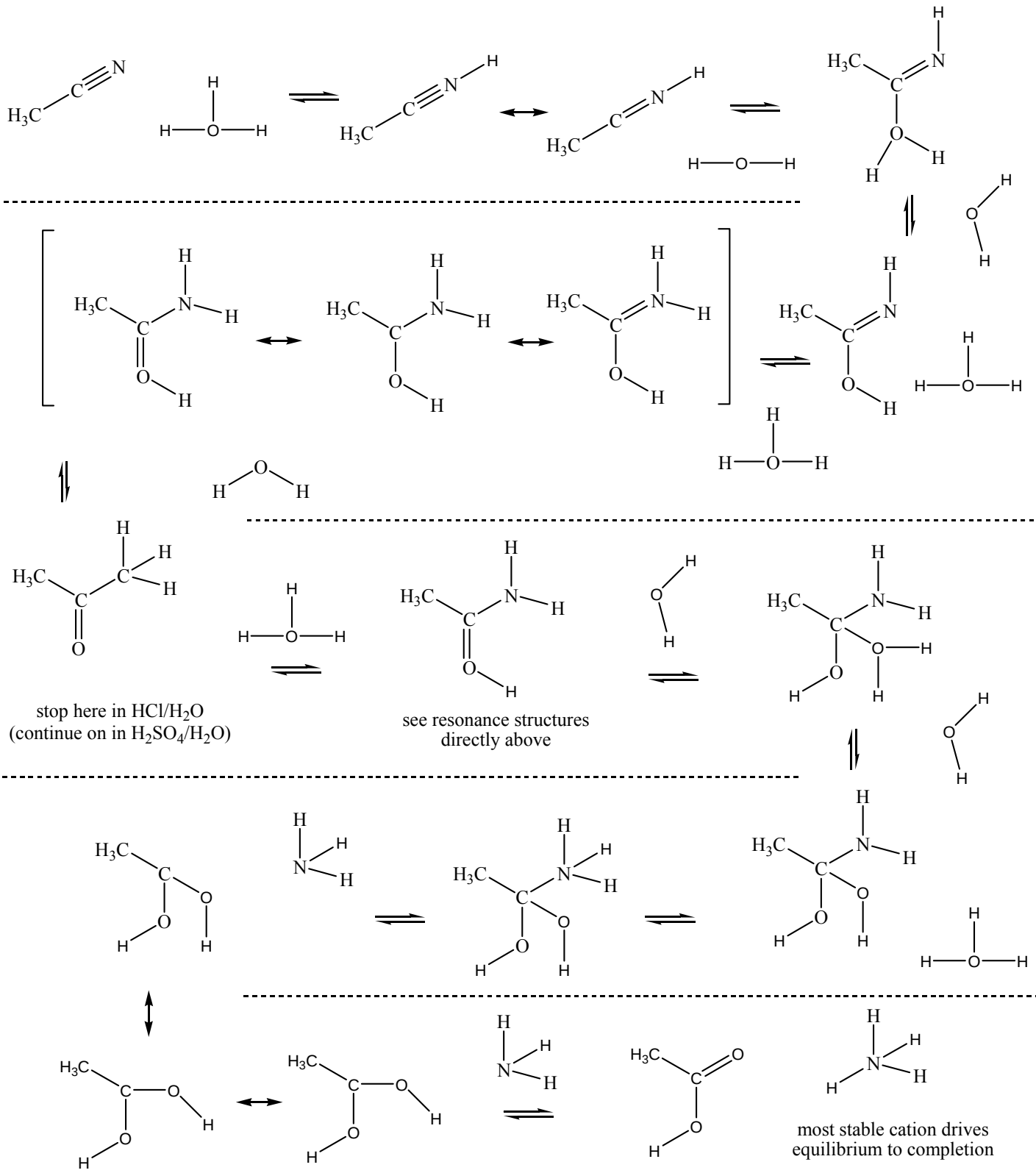
functional
group = _____

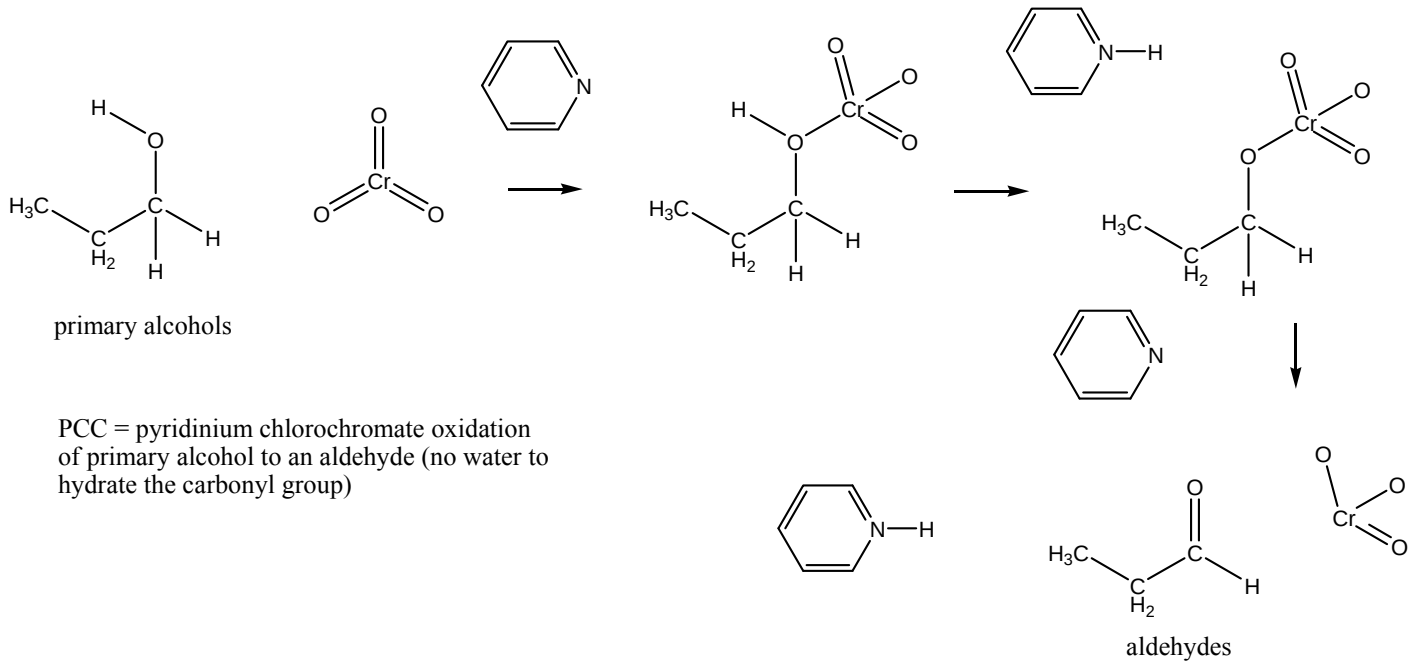
Remove H_2O shifts equilibrium to the _____

Adding H_2O shifts equilibrium to the _____

---

i HCl / H_2O hydrolysis of a nitrile to an amide (in H_2SO_4 / H_2O hydrolysis continues on to a carboxylic acid)

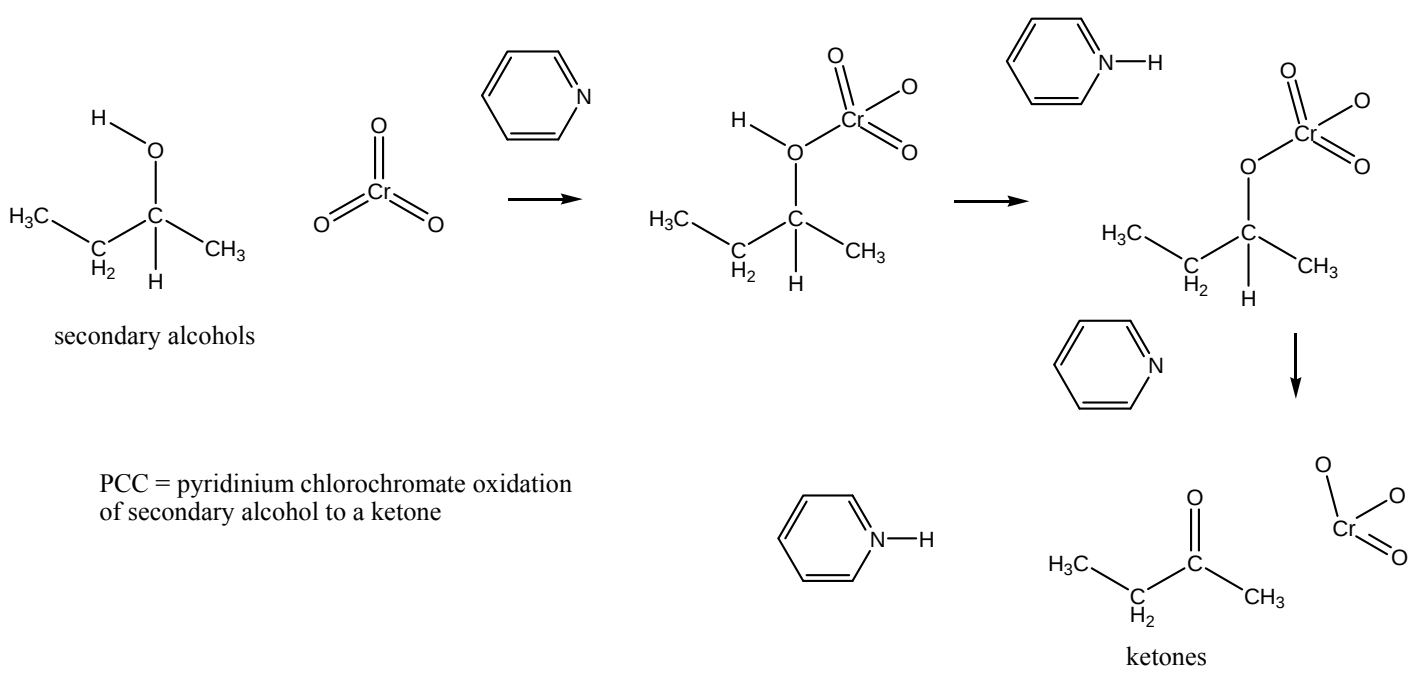




primary alcohols

PCC = pyridinium chlorochromate oxidation of primary alcohol to an aldehyde (no water to hydrate the carbonyl group)

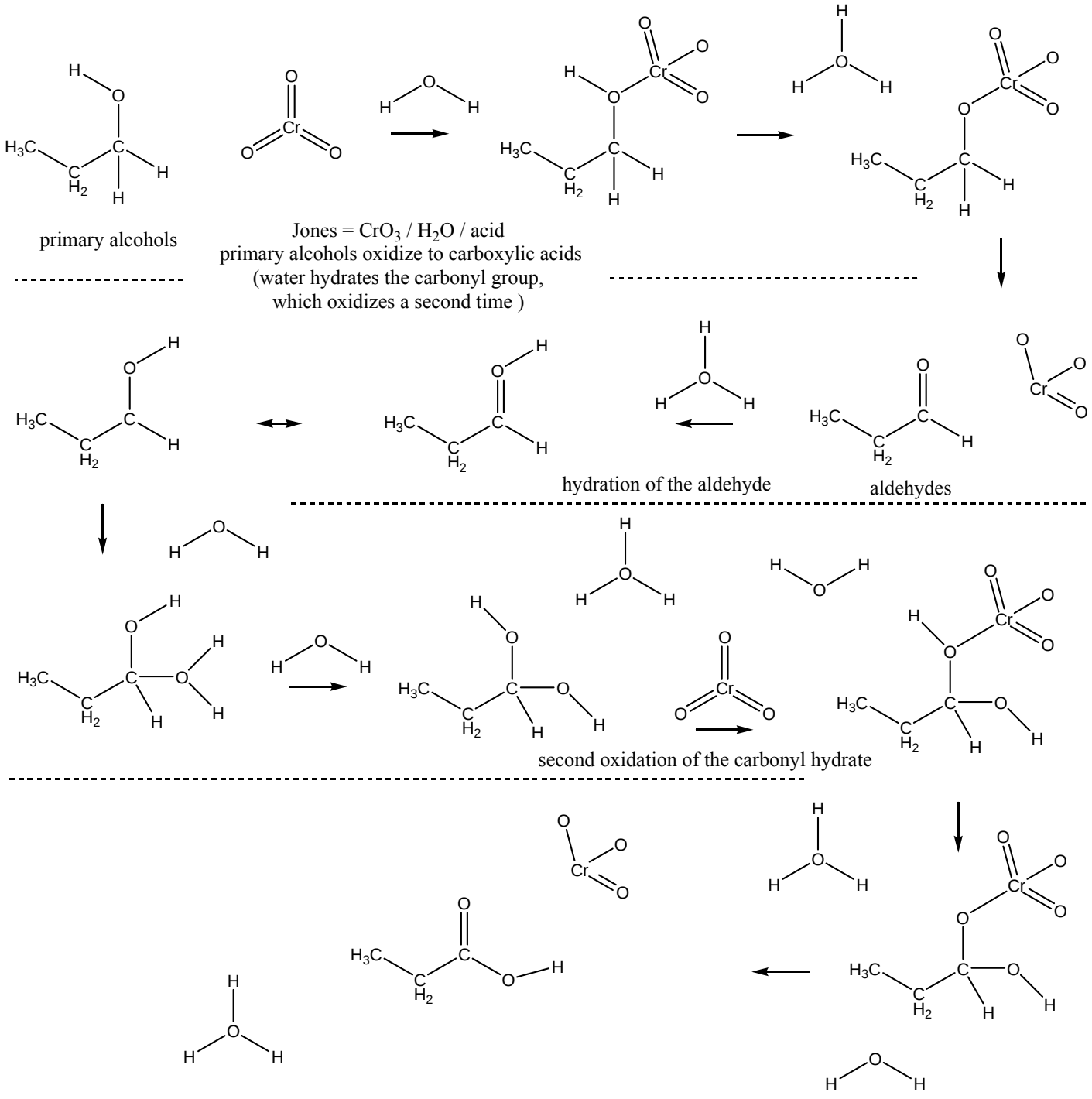
aldehydes

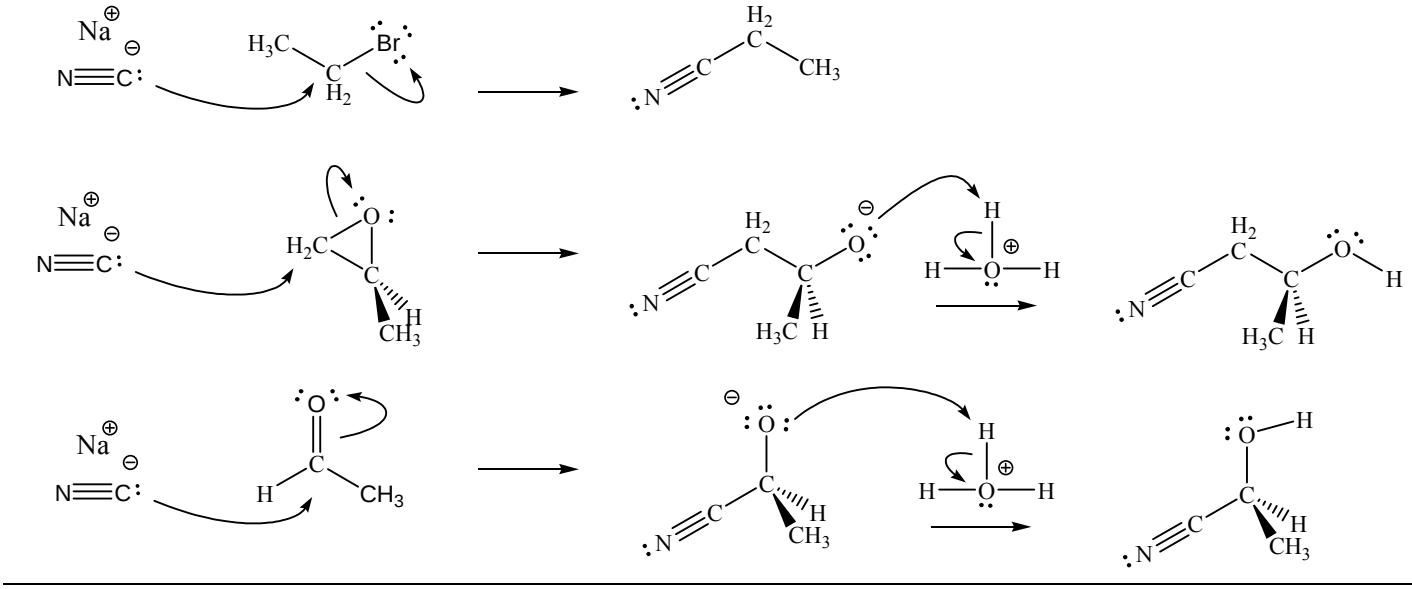


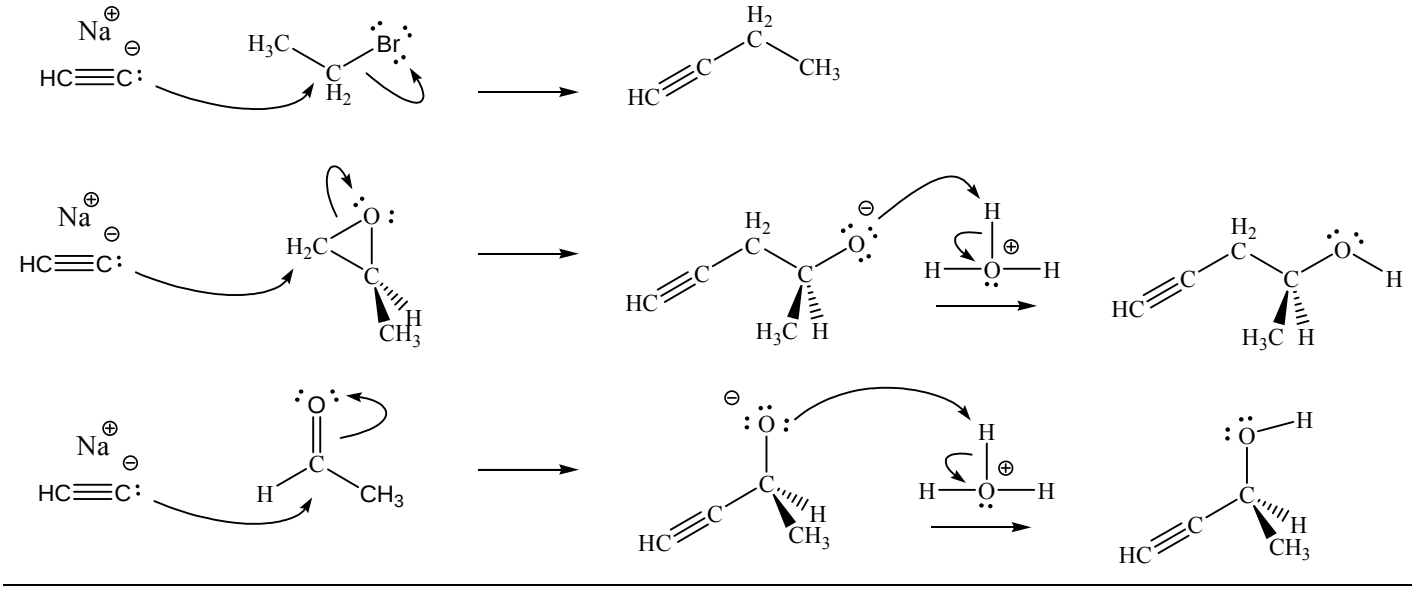
secondary alcohols

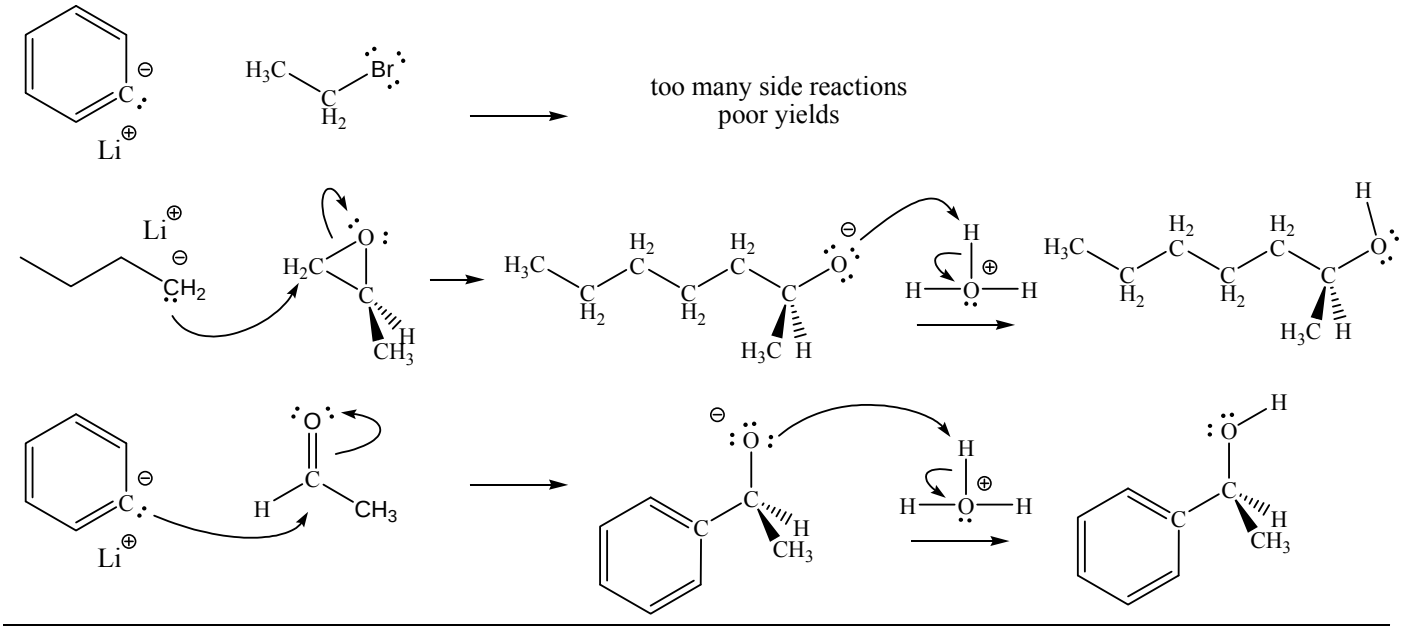
PCC = pyridinium chlorochromate oxidation of secondary alcohol to a ketone

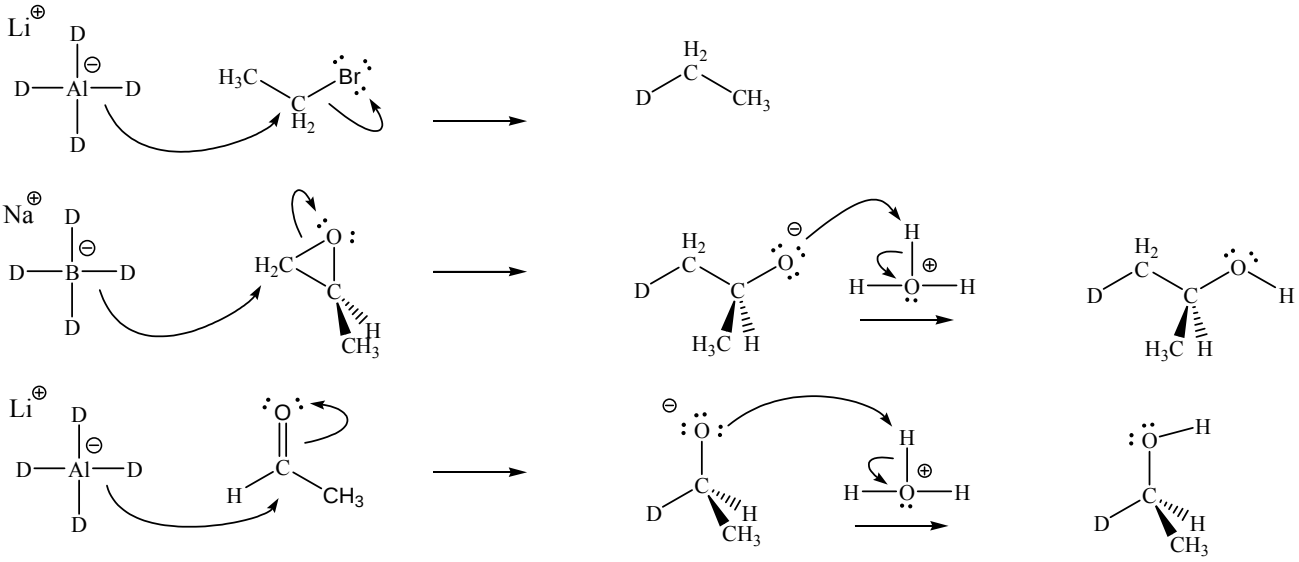
ketones

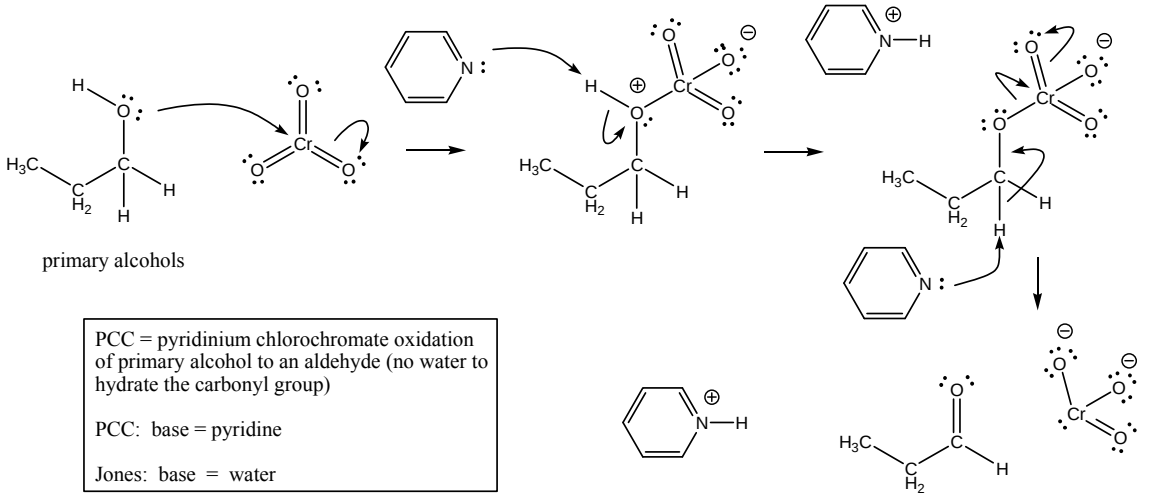

primary alcohols
Jones = CrO_3 / H_2O / acid
primary alcohols oxidize to carboxylic acids
(water hydrates the carbonyl group,
which oxidizes a second time)
hydration of the aldehyde
aldehydes
second oxidation of the carbonyl hydrate

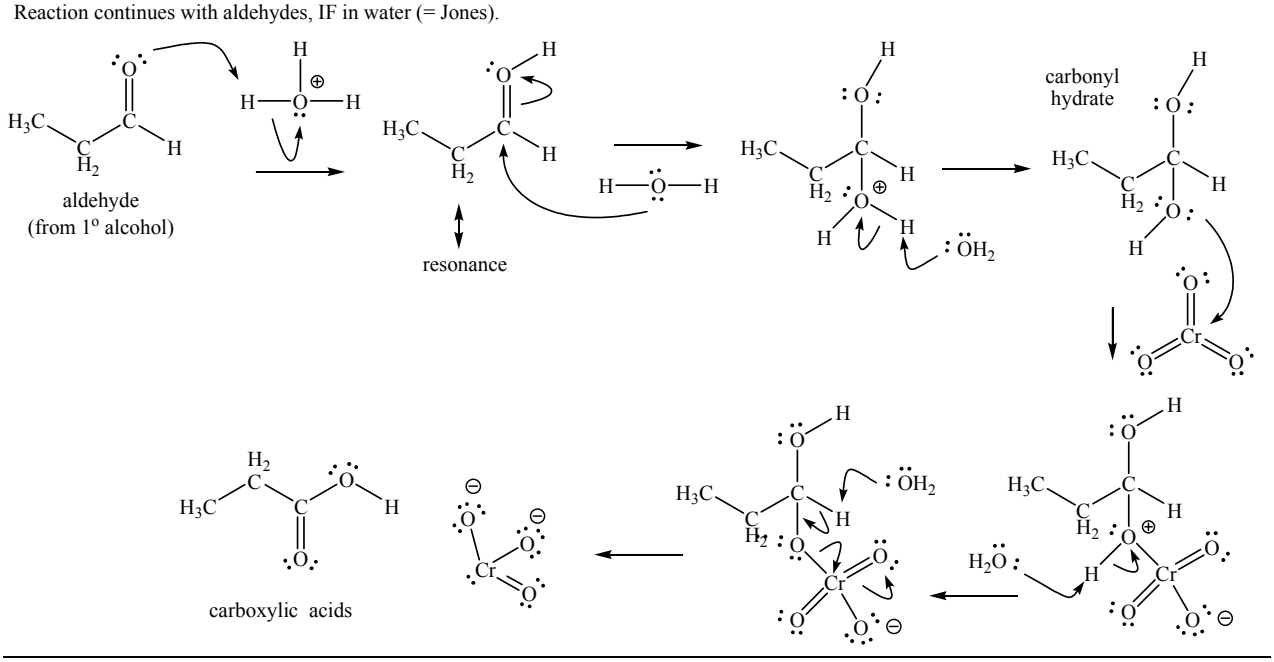





too many side reactions
poor yields

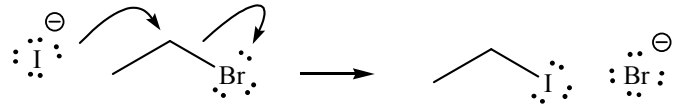



primary alcohols
PCC = pyridinium chlorochromate oxidation of primary alcohol to an aldehyde (no water to hydrate the carbonyl group)
PCC: base = pyridine
Jones: base = water
aldehydes


Reaction continues with aldehydes, IF in water (= Jones).
aldehyde
(from 1° alcohol)
resonance
carbonyl
hydrate
carboxylic acids

Possible Keys –Check for mistakes. I often make a few with all of the necessary computer clicks.

a



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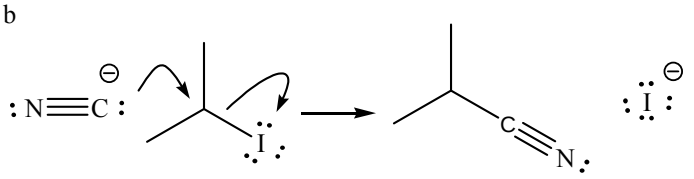

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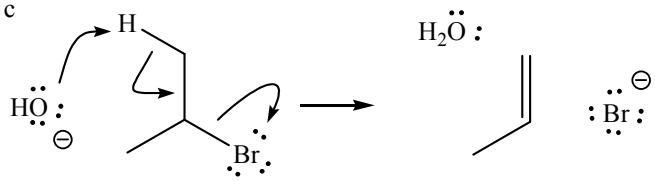
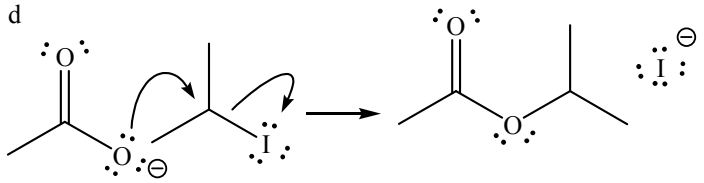
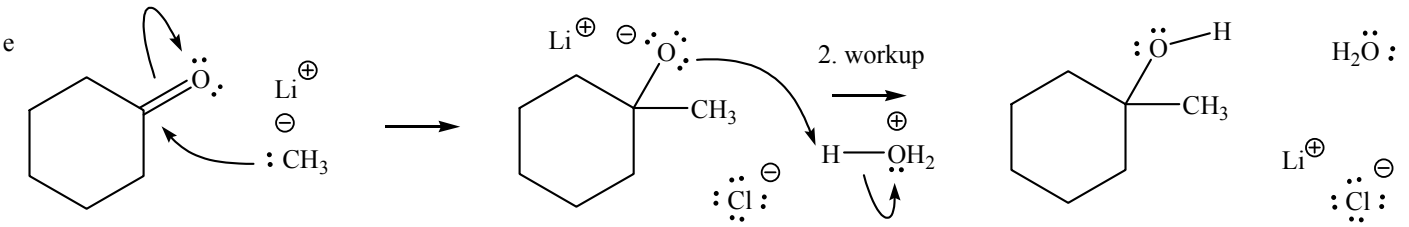


d



e



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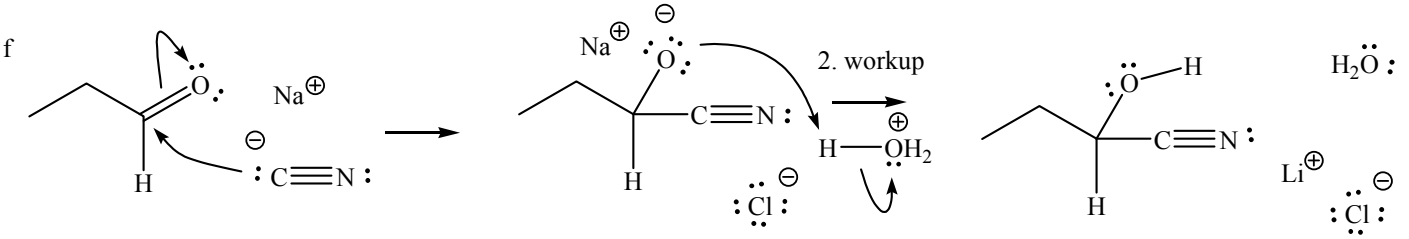

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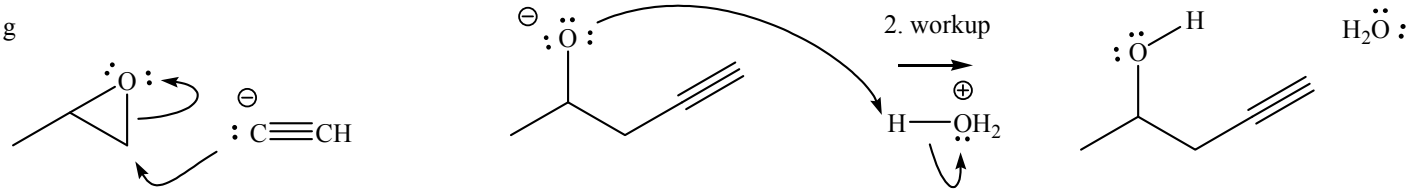

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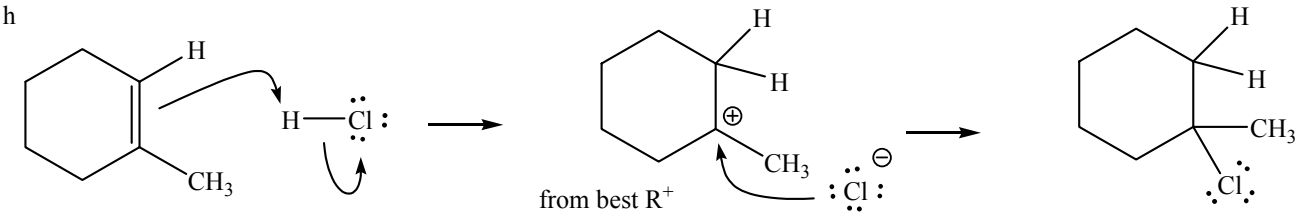
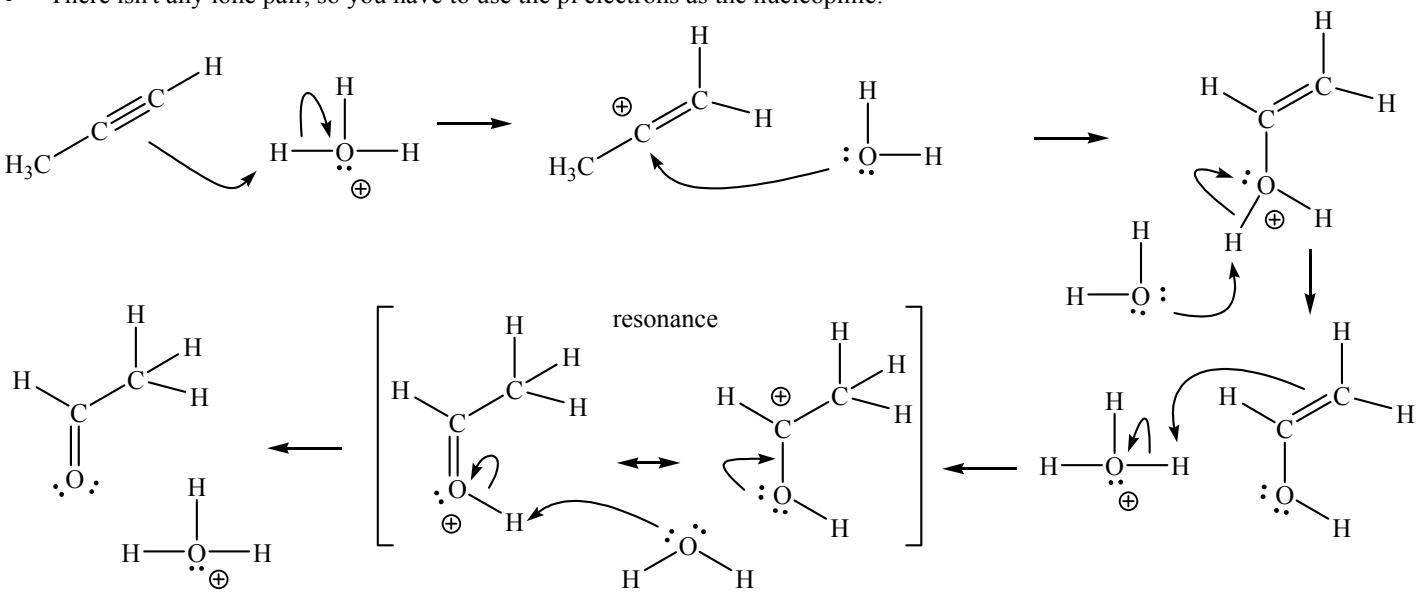


i There isn't any lone pair, so you have to use the pi electrons as the nucleophile.



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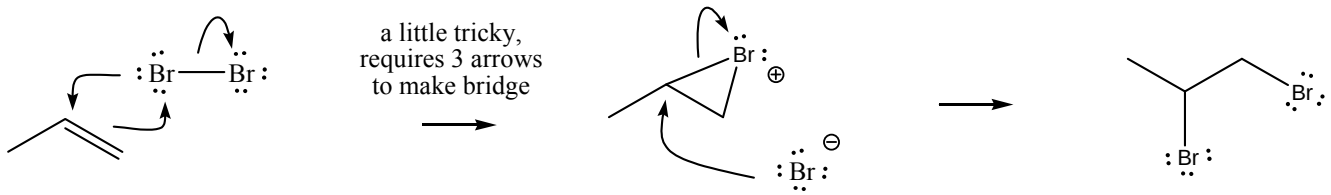

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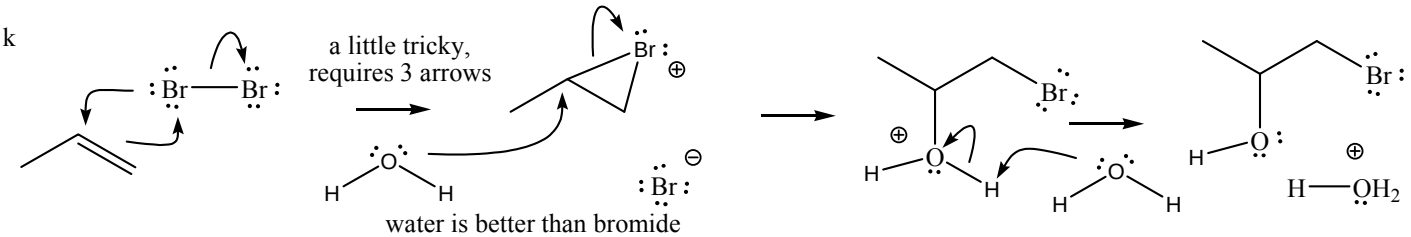
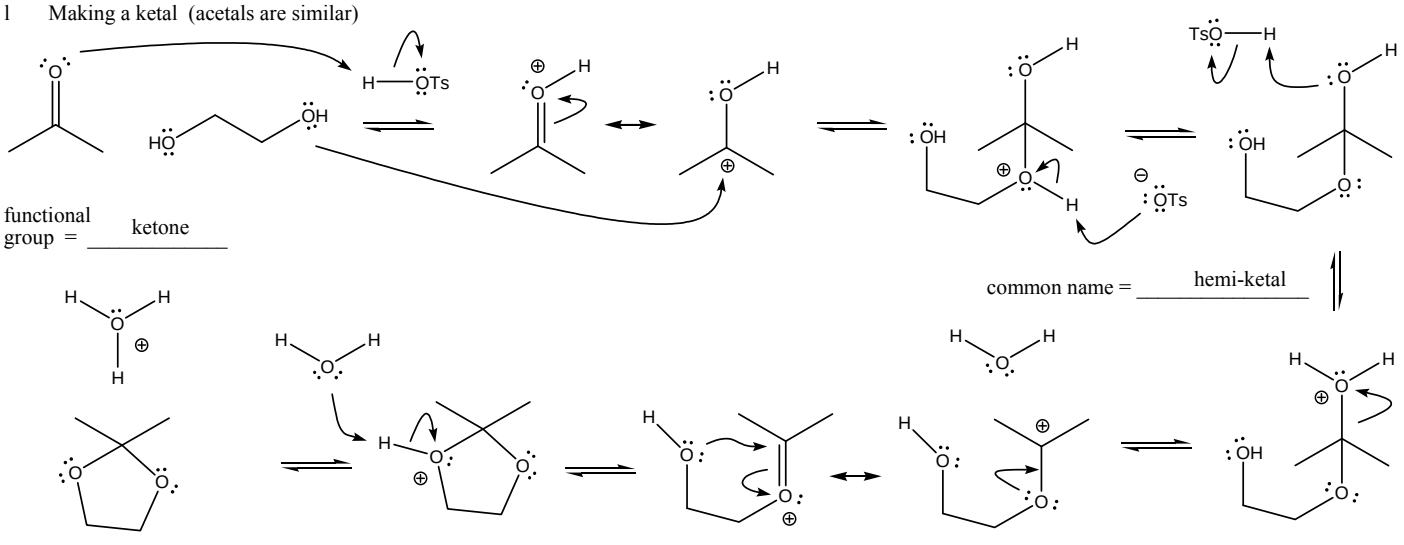


l Making a ketal (acetals are similar)



functional group = ketone

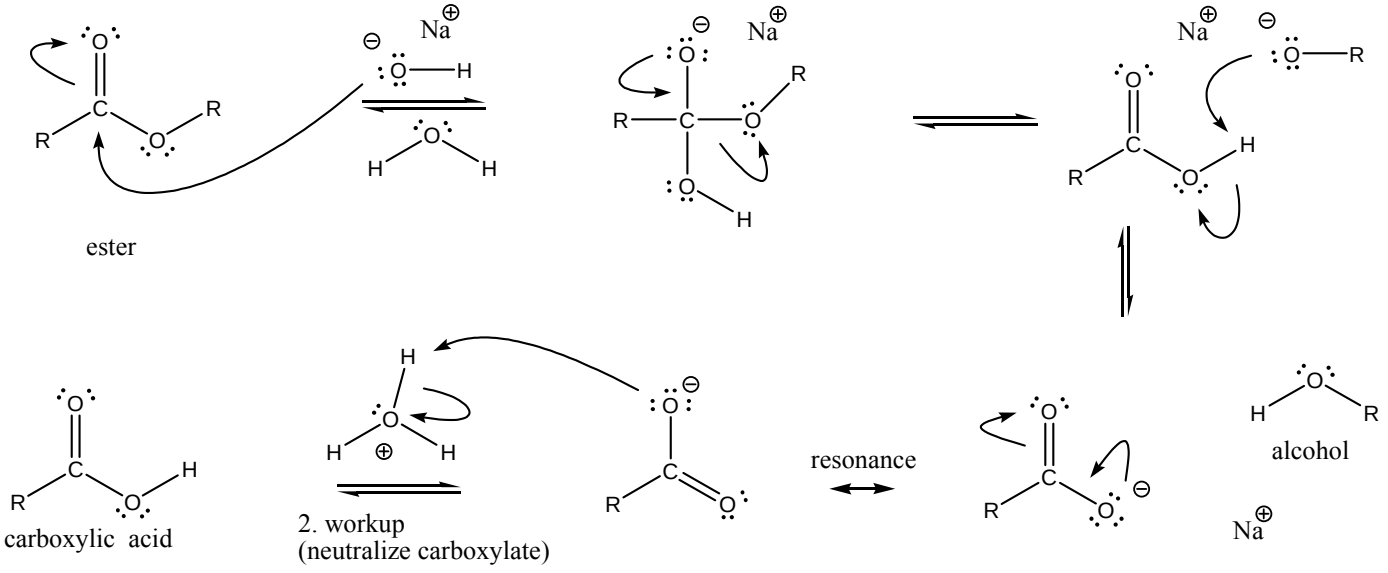
common name = hemi-ketal

common name = ketal

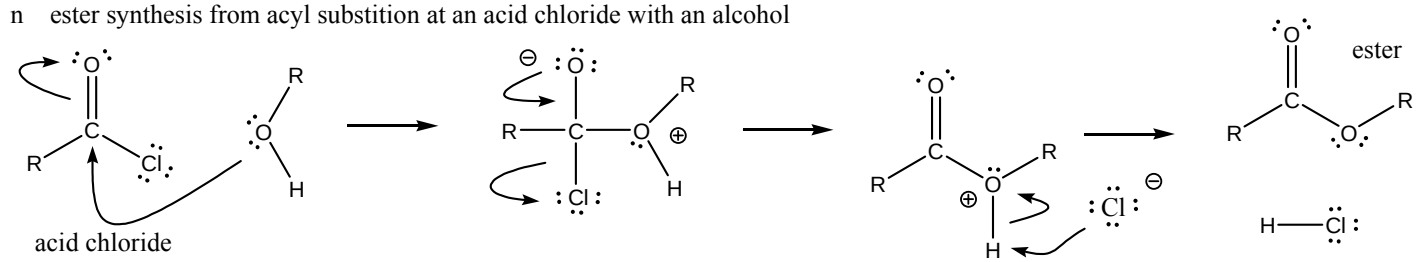
Remove H_2O shifts equilibrium to the right

Adding H_2O shifts equilibrium to the left

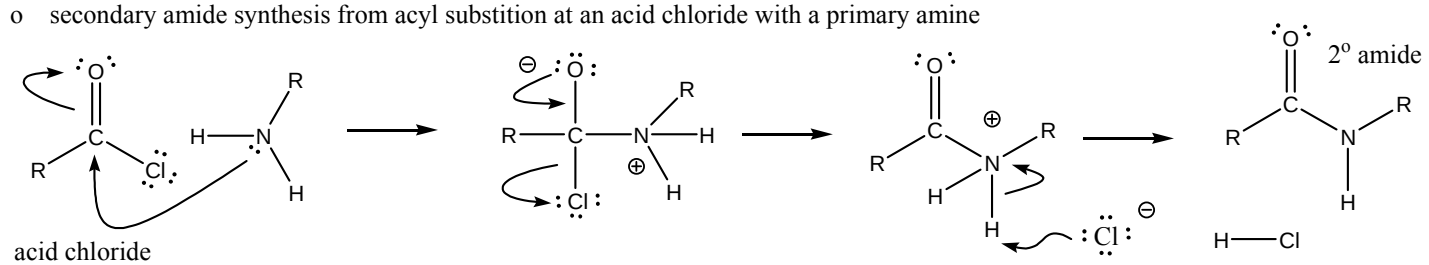
m ester base hydrolysis = saponification



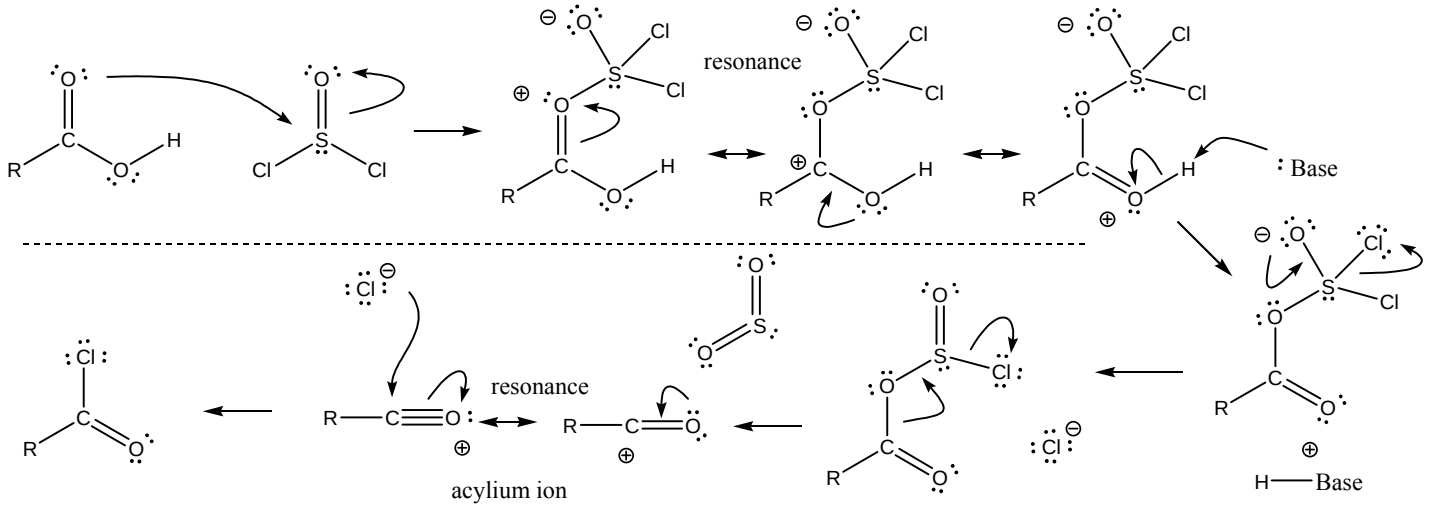
n ester synthesis from acyl substition at an acid chloride with an alcohol



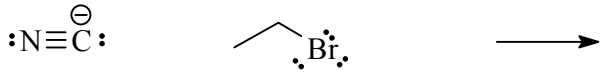
o secondary amide synthesis from acyl substition at an acid chloride with a primary amine



p synthesis of an acid chloride from an acid + thionyl chloride ($SOCl_2$)



Problem - Identify the nucleophile (Lewis base) and the electrophile (Lewis acid) in each equation and show the products of the following reactions. Add the curved arrows to show how each reaction proceeds.

a 

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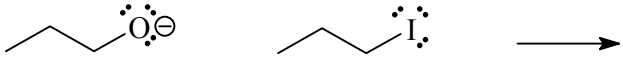
b 

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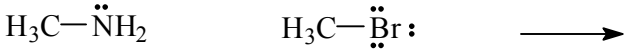
c 

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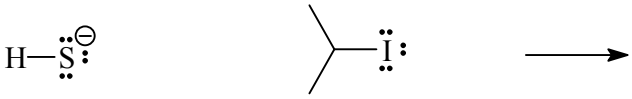
d 

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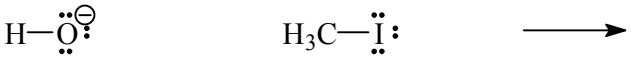
e 

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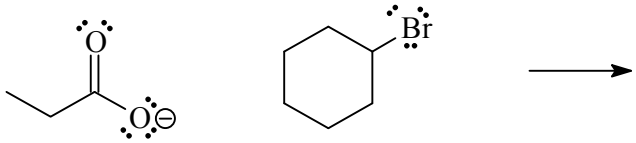
f 

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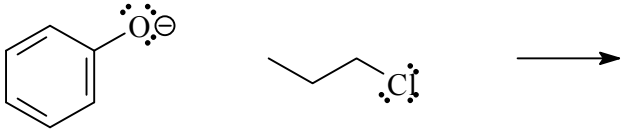
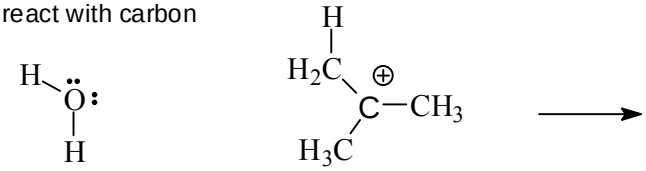
g 

h react with carbon



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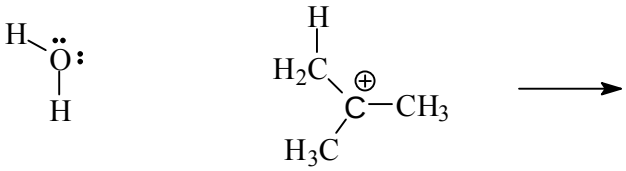
i react with proton



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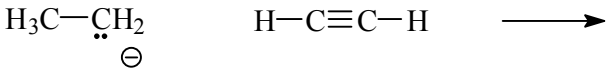
j



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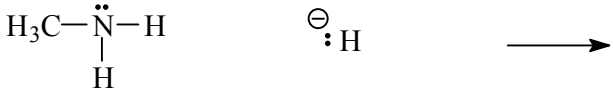

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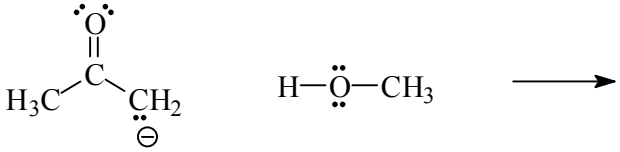

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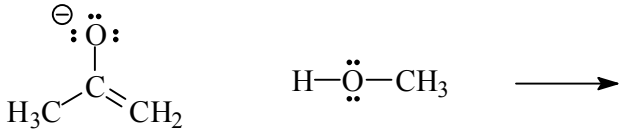

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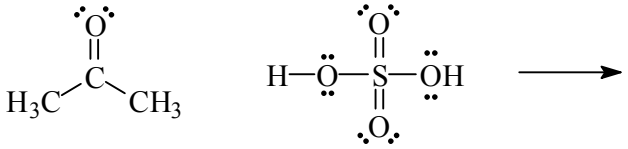
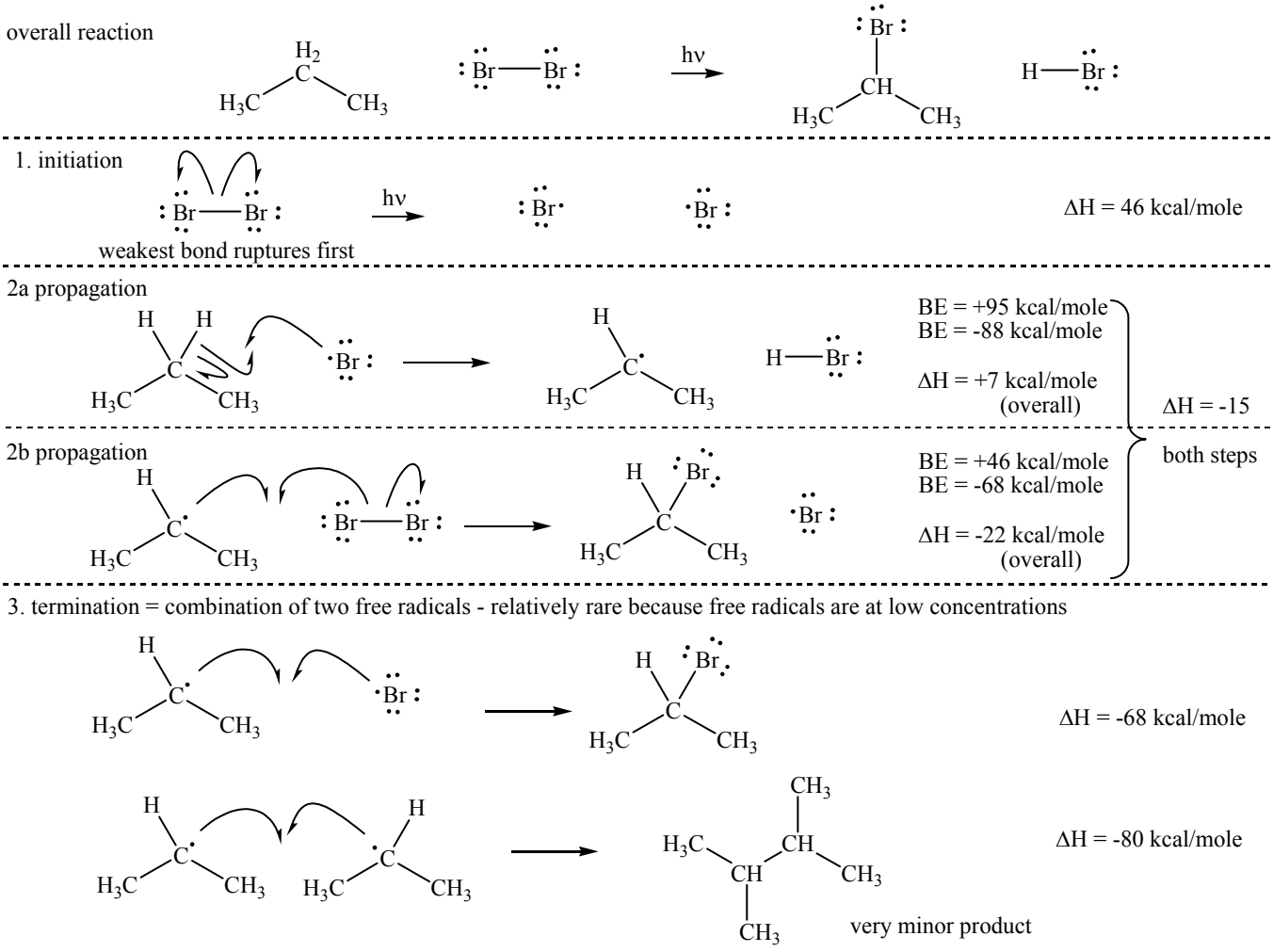
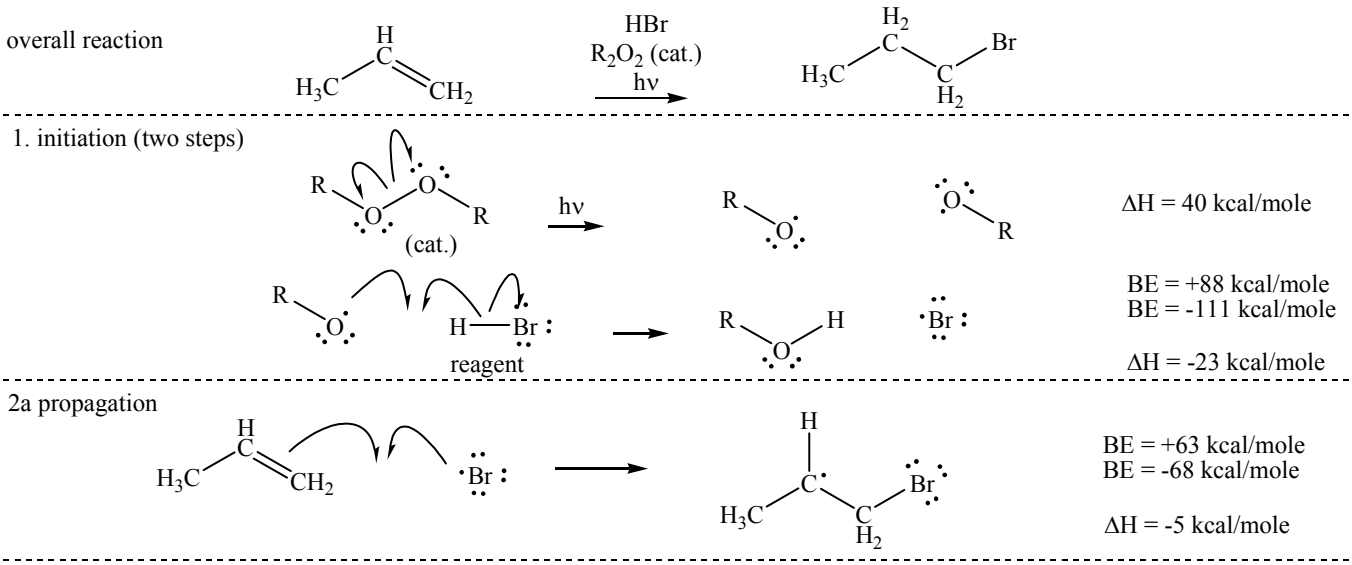


Problem - Which of the structures below can be a Lewis acid (show an arrow pushing reaction with base B:), a Lewis base (show a reaction with acid HA) or both an acid and a base (show both reactions)?

1. **Mechanism for free radical substitution of alkane sp^3 C-H bonds to form sp^3 C-Br bonds at weakest C-H position**



2. **Free radical addition mechanism of H-Br alkene pi bonds** (alkenes can be made from E2 or E1 reactions at this point in course) (anti-Markovnikov addition to alkenes)



2b propagation