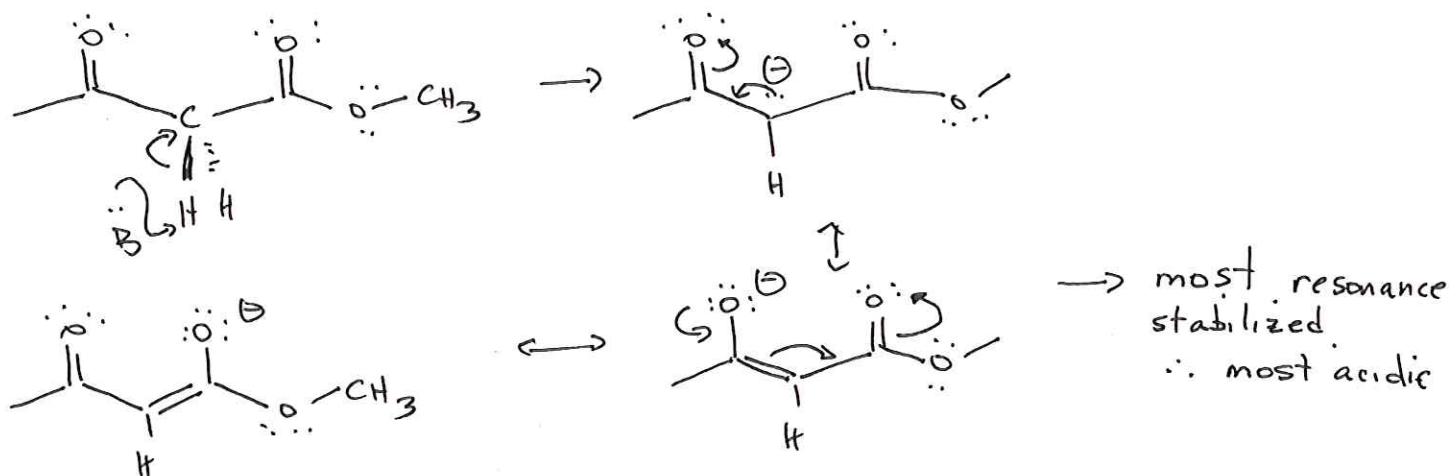
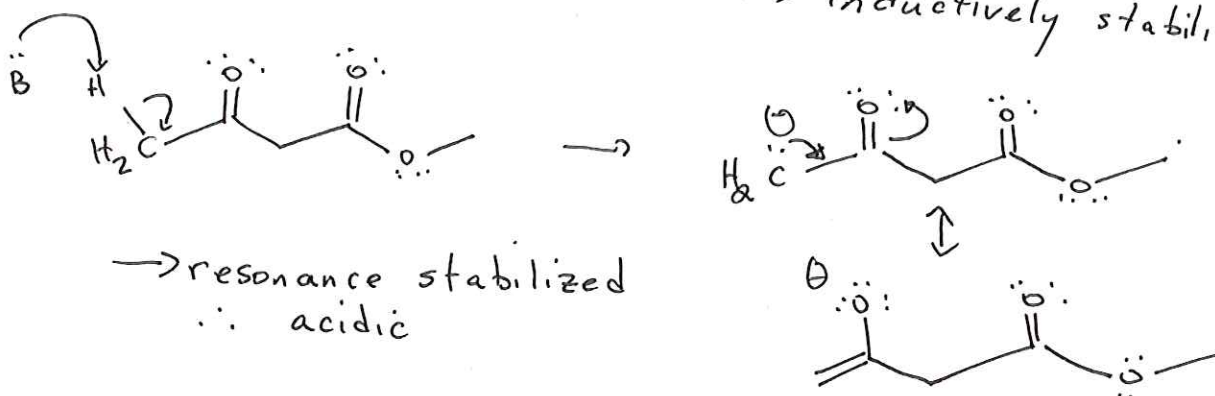
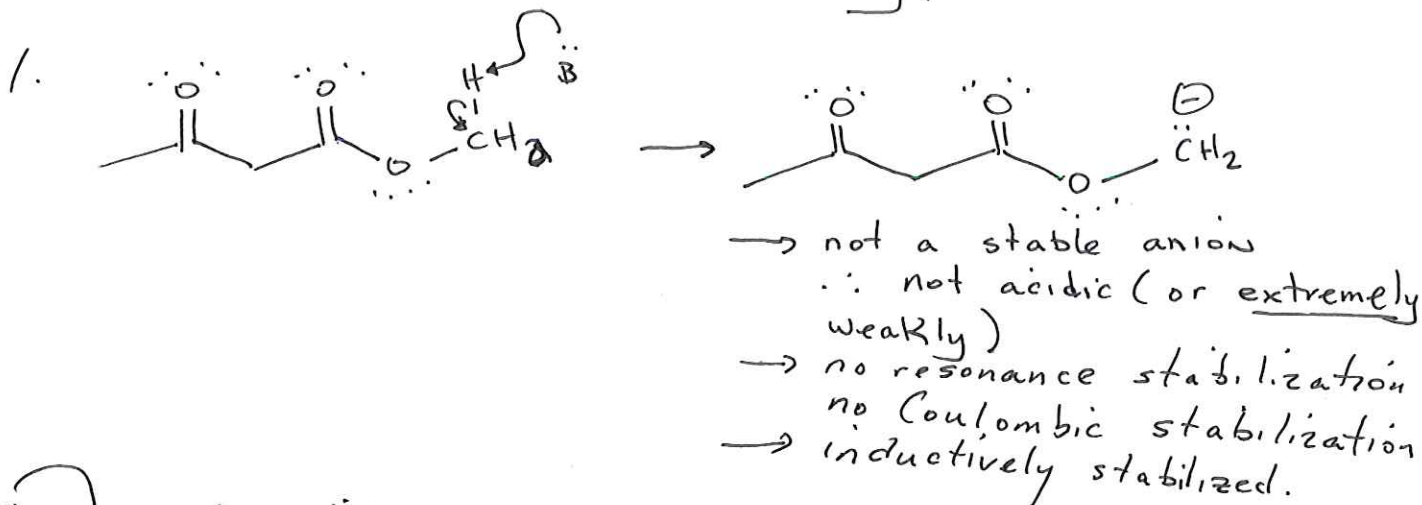
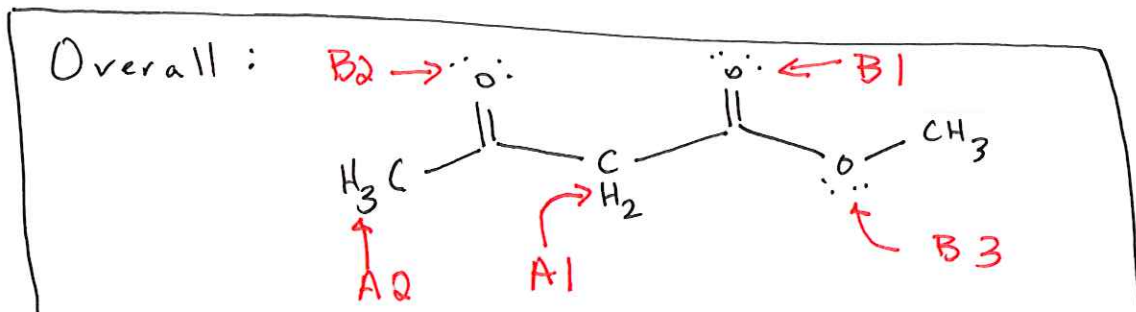
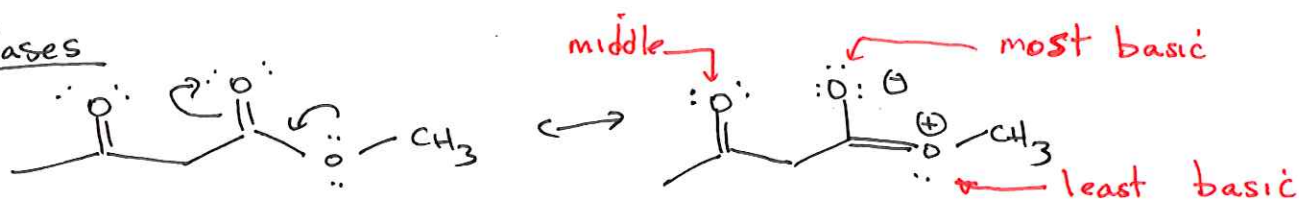


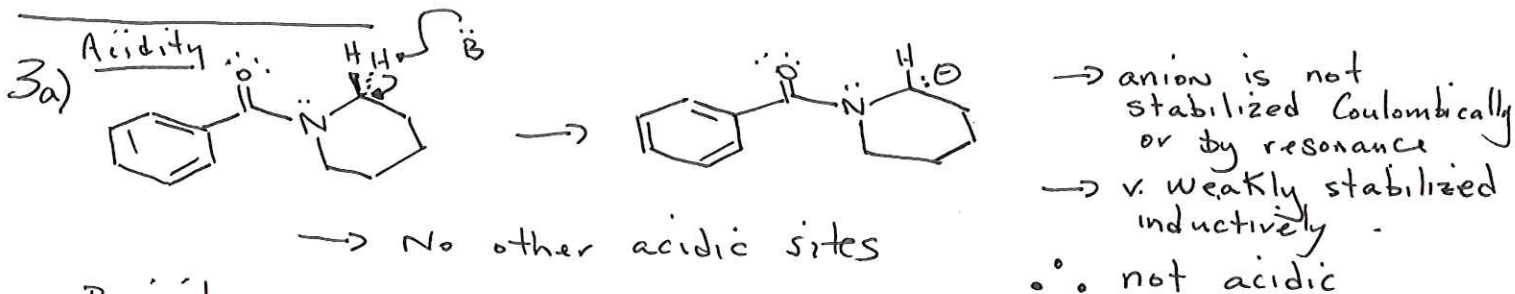
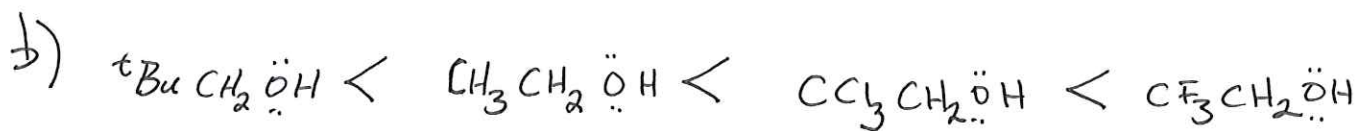
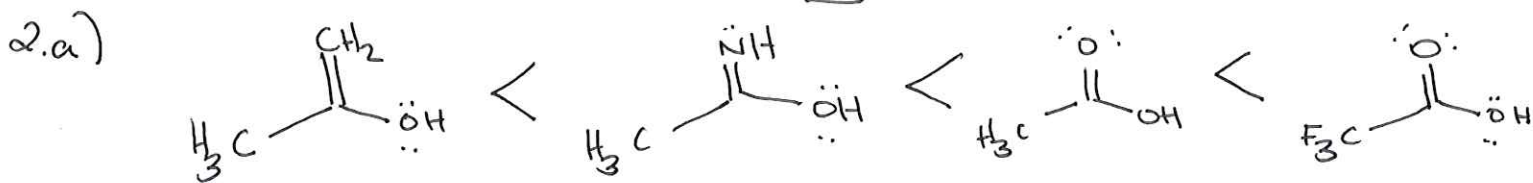
Assignment # 13 - Operational Species Answer Key.



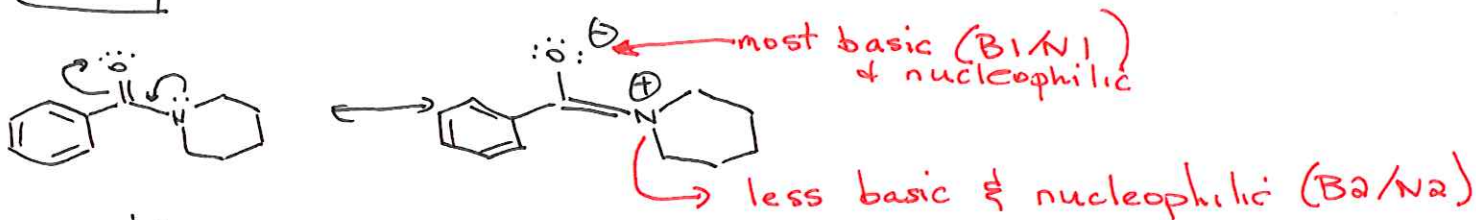
Bases



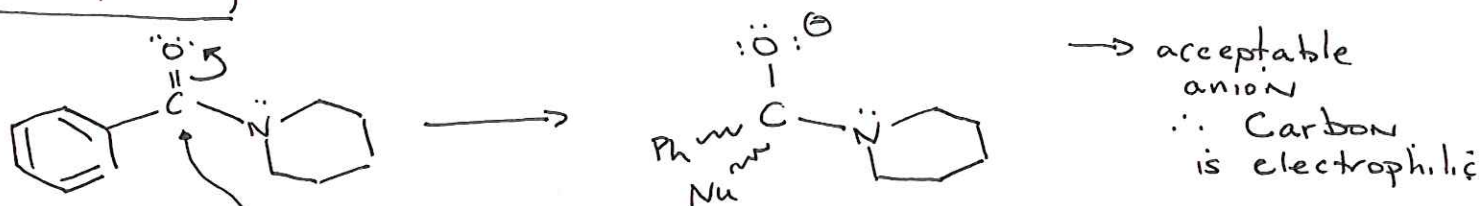
Chem 2500
Assignment #13 - Operational Species
Answer Key.



Basicity

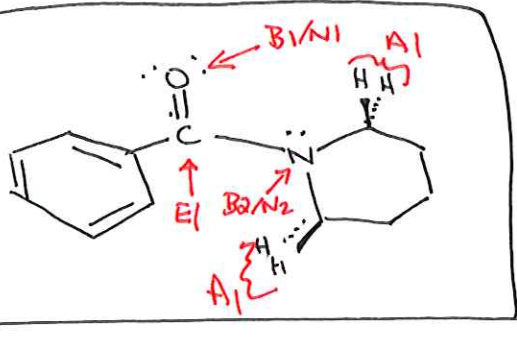


Electrophilicity



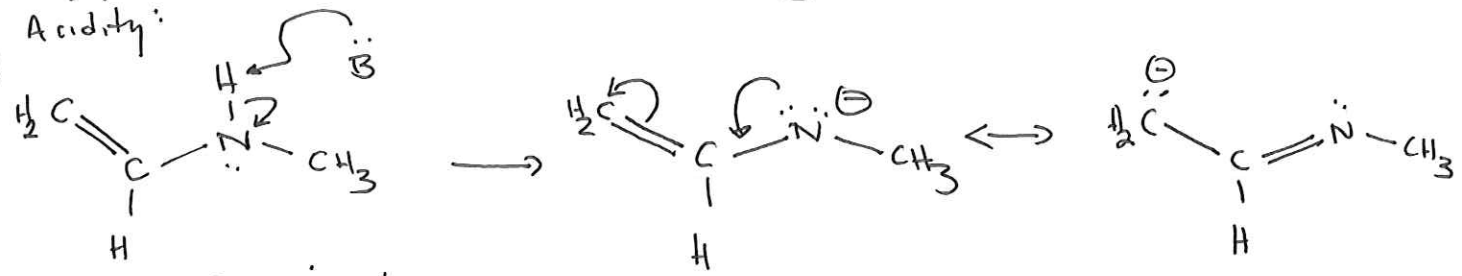
→ No other electrophilic sites.

Overall:

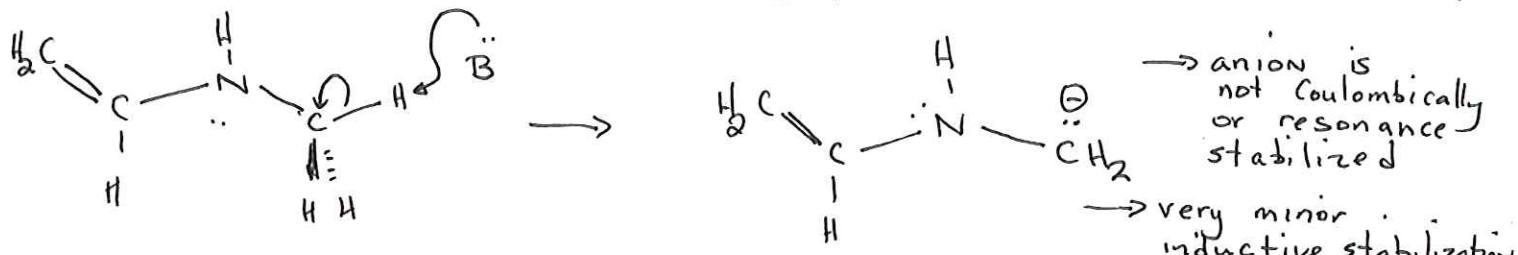


Assignment #13 - Operational Species
Answer Key.

3b) Acidity:

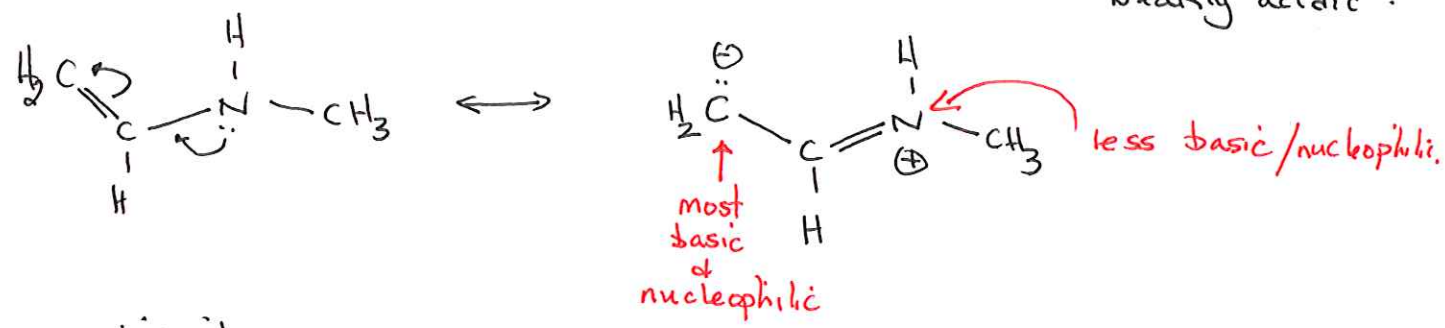


→ anion is acceptable because \ominus is on an electronegative atom and it is resonance stabilized.

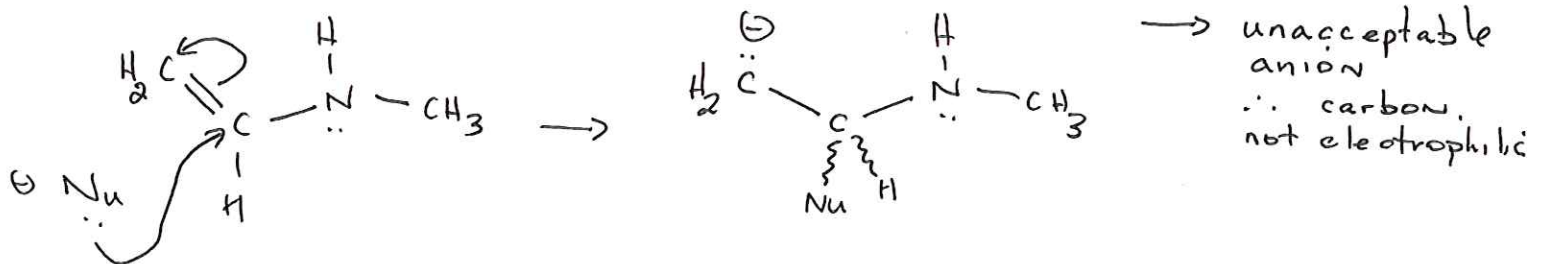


→ anion is not Coulombically or resonance stabilized
→ very minor inductive stabilization
∴ ~~not~~ not acidic or very, very weakly acidic.

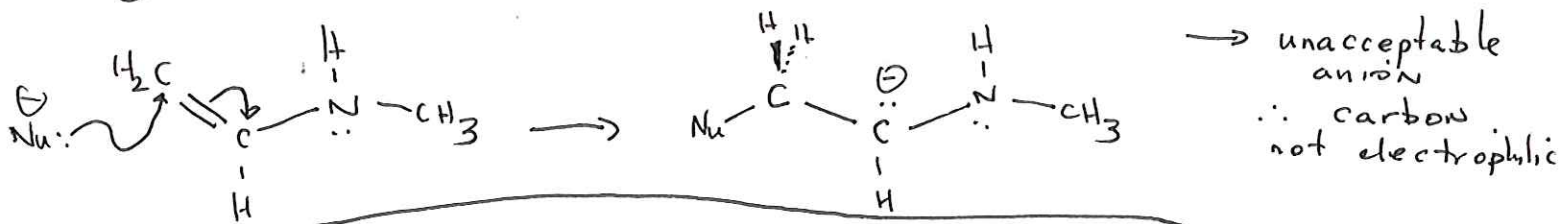
Basicity



Electrophilicity



→ unacceptable anion
∴ carbon, not electrophilic



→ unacceptable anion
∴ carbon, not electrophilic

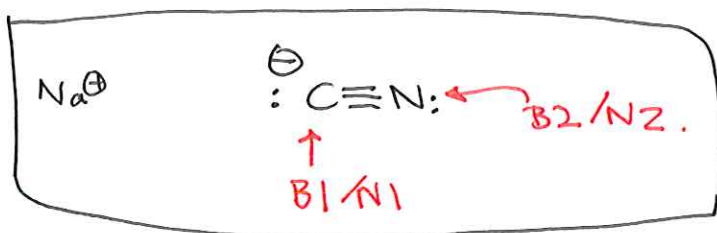
Overall:

A1 → H (alpha-carbon)
 B1/N1 → C (carbonyl carbon)
 B2/N2 → N (nitrogen)
 A2 → H (methyl group)

Assignment #13 - Operational Species

Answer Key.

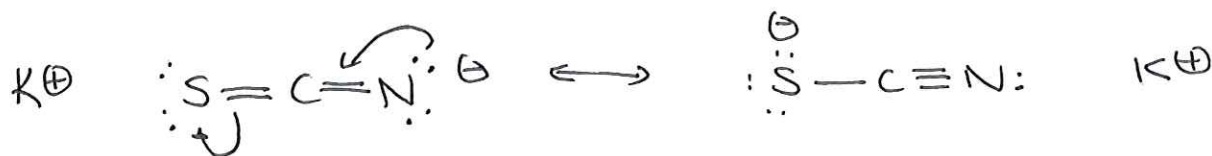
3c)



→ No H ∴ no acidic sites.

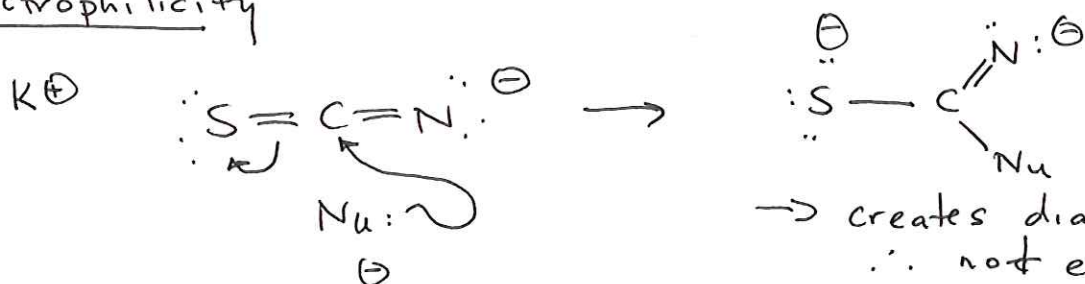
→ No electrophilic sites.

d)

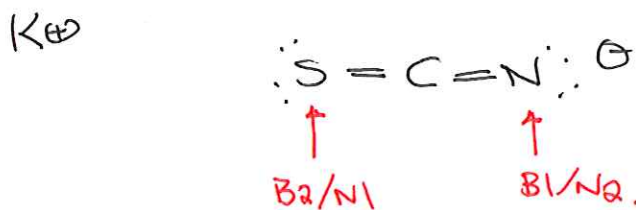


→ N is more basic, while S is more nucleophilic.

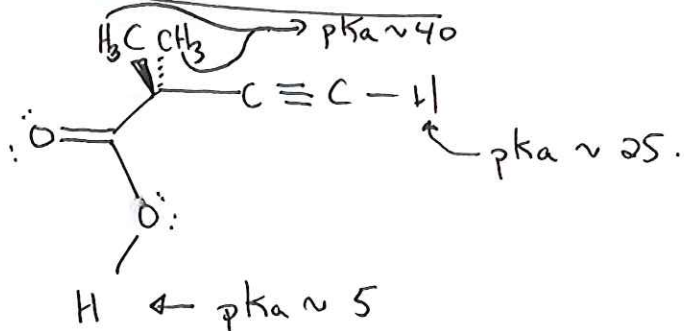
(basicity decreases while nucleophilicity increases down a group).

Electrophilicity

→ creates dianion ∴ not electrophilic

Overall

4.

→ use KOCH_3

Chem 2500
Assignment #13 - Operational Species
Answer Key.

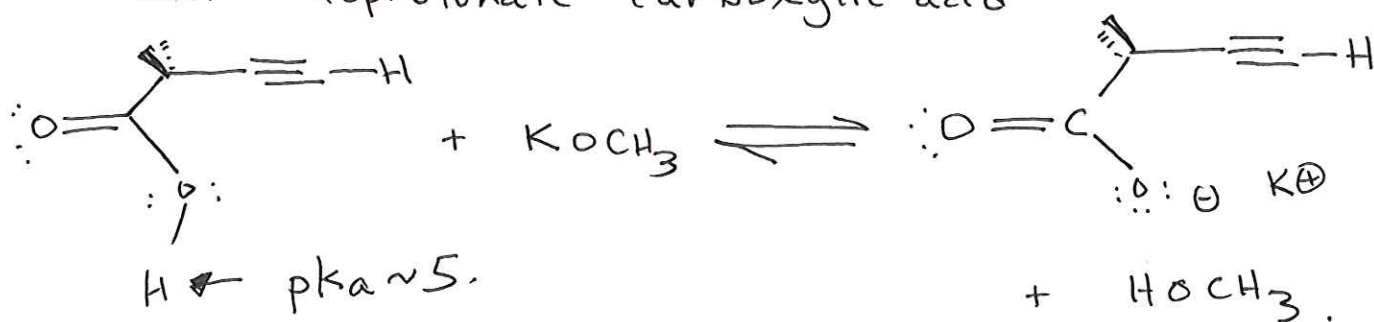
4. \rightarrow HBr is not ~~acid~~ basic. $pK_a \sim -7$.

\rightarrow both NaNH_2 & $t\text{BuLi}$ are sufficiently basic to deprotonate more than one site \therefore not selective

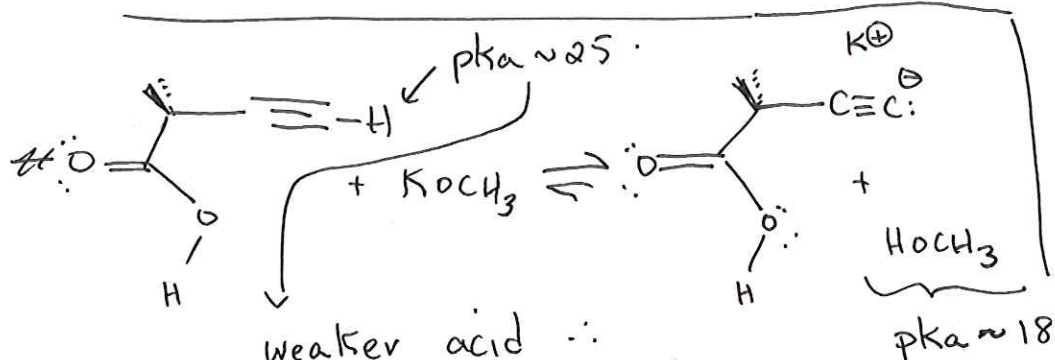
$pK_a \text{ NH}_3 \sim 36$
 $pK_a t\text{BuH} \sim 45$.

\rightarrow NaCl is not basic. $\rightarrow pK_a \text{ HCl} \sim -7$.

\rightarrow $\text{KOCH}_3 \rightarrow pK_a$ of $\text{HOCH}_3 \sim 18 \rightarrow$ not basic enough to deprotonate alkyne but will deprotonate carboxylic acid



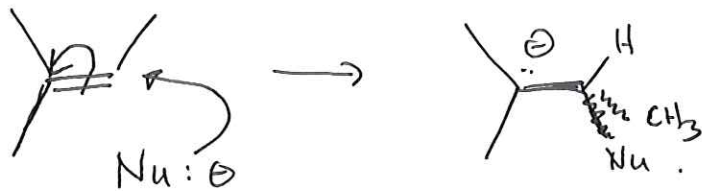
$+ \text{HOCH}_3$
 $pK_a \sim 18$
 \rightarrow weaker acid



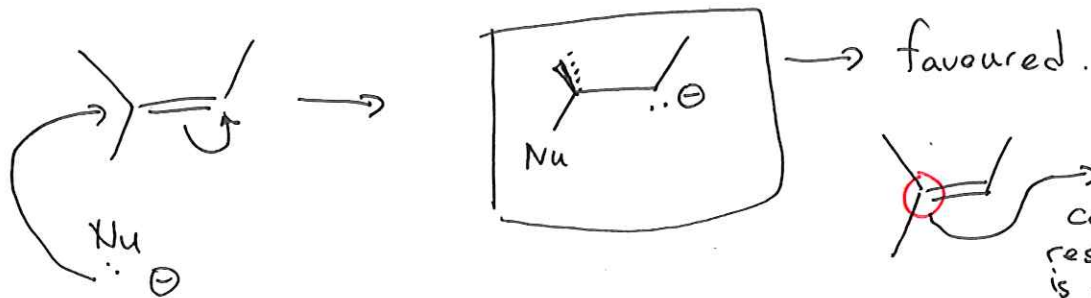
\therefore products
favoured &
deprotonation
occurs.

Assignment # 13 - Operational Specifics
Answer Key.

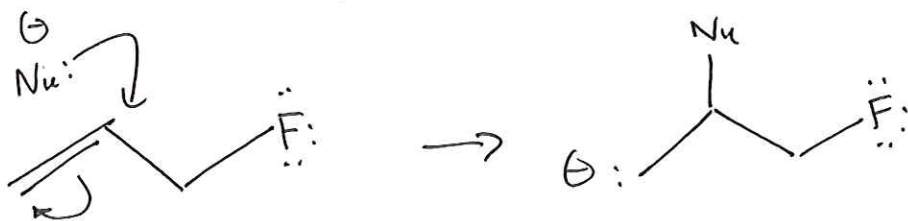
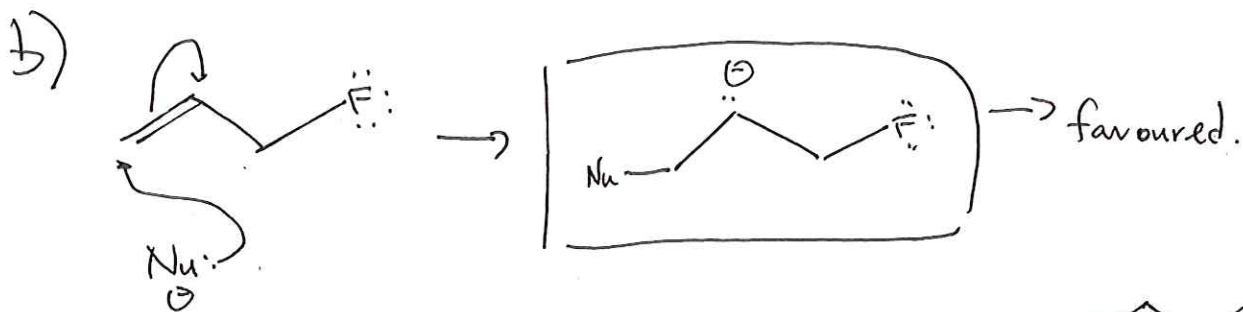
5a)



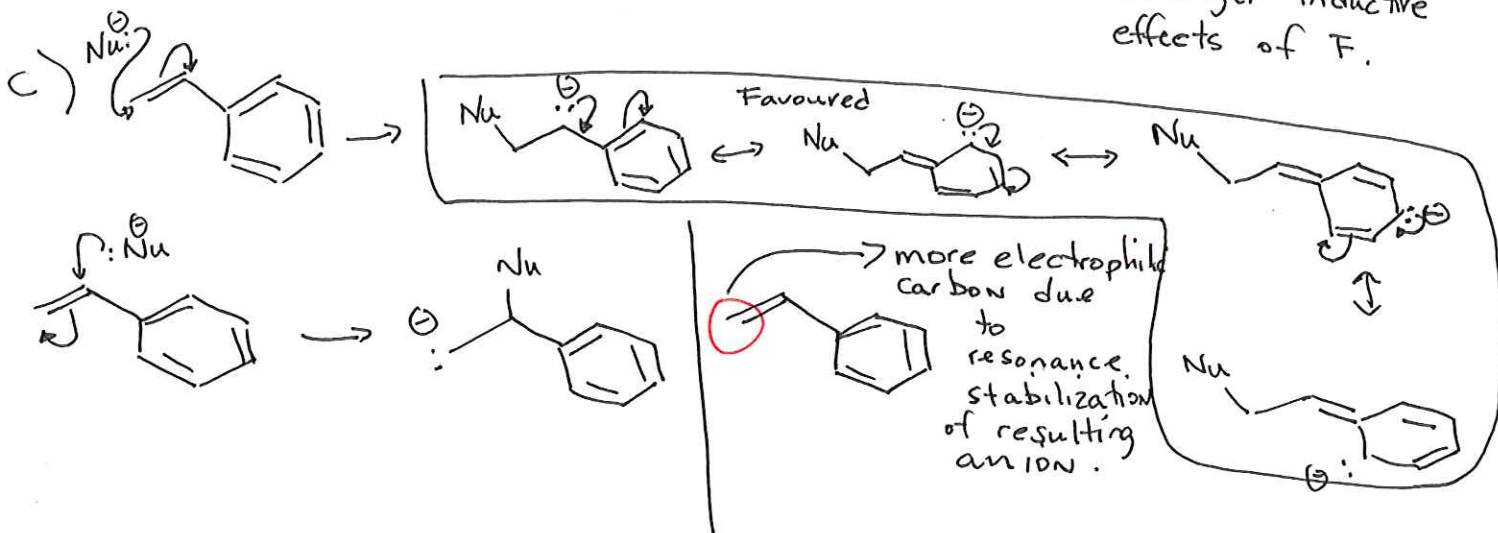
or



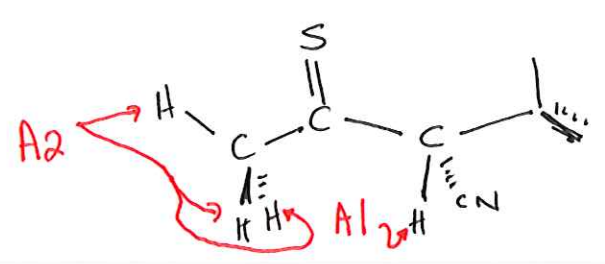
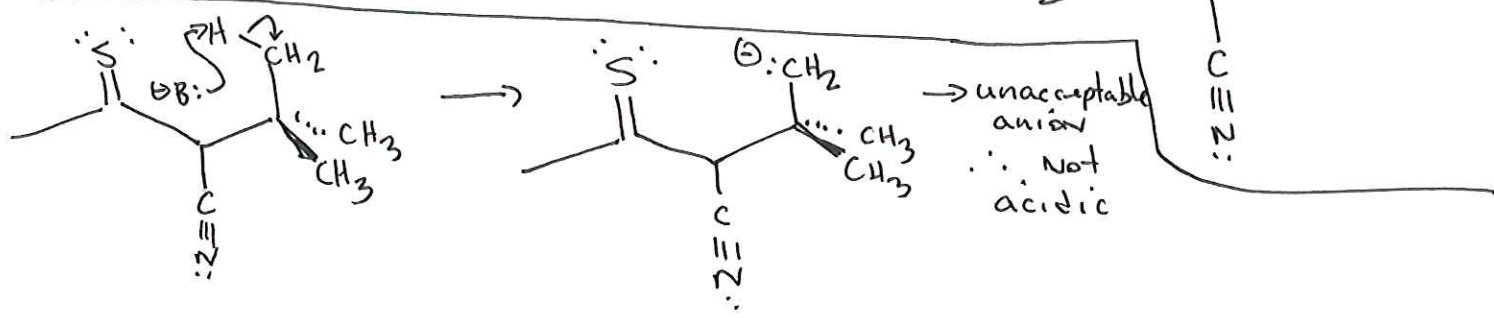
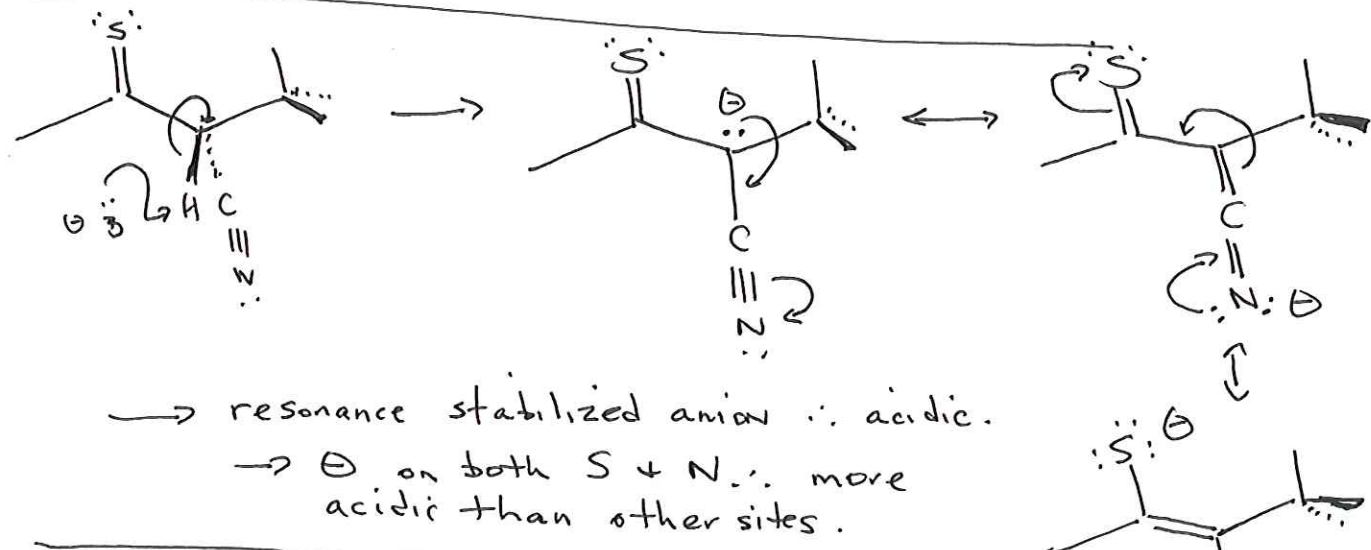
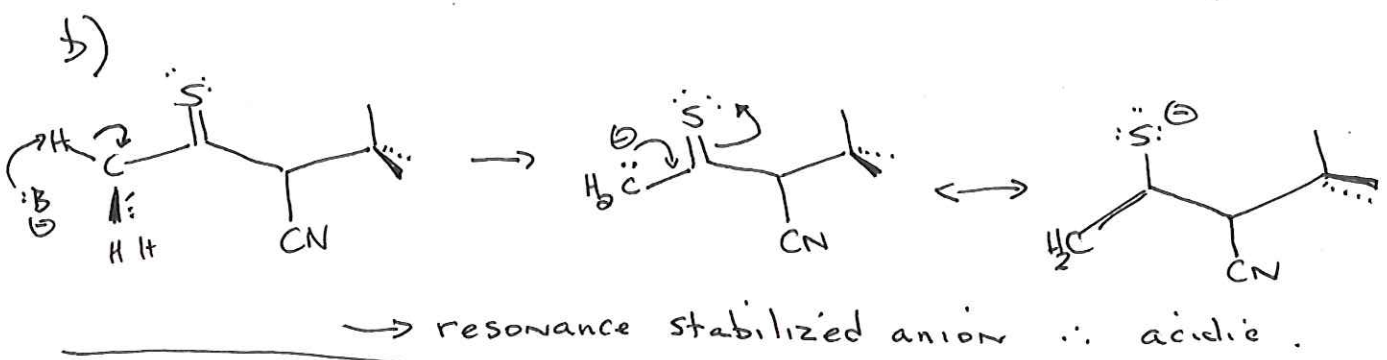
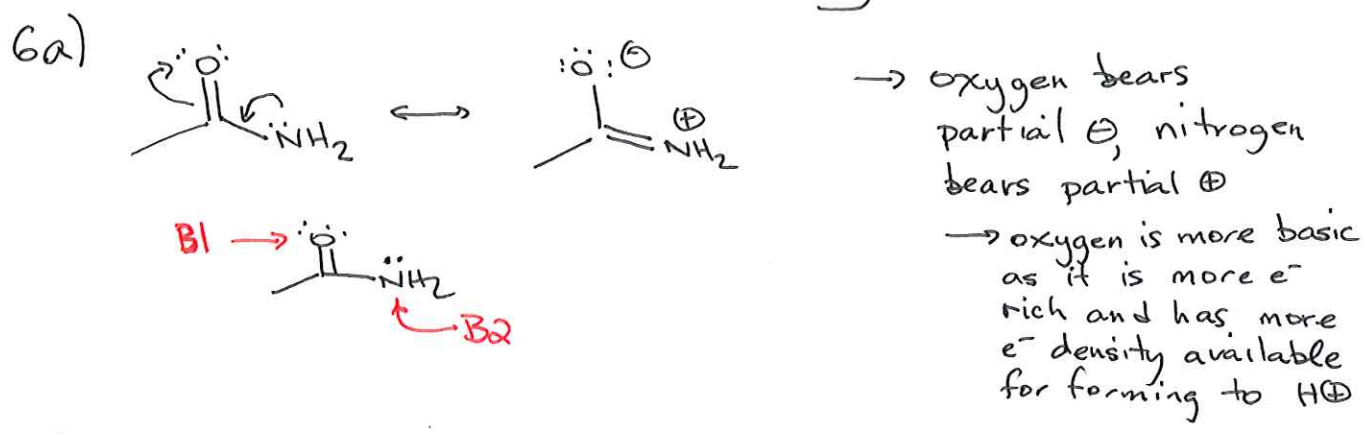
more electrophilic carbon because resulting anion is more stable 2° vs 3° .



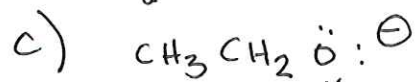
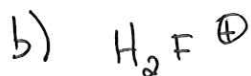
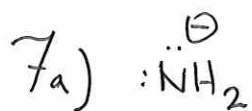
more electrophilic carbon because anion is more stable due to stronger inductive effects of F.



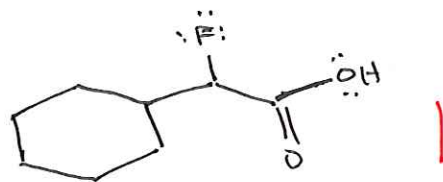
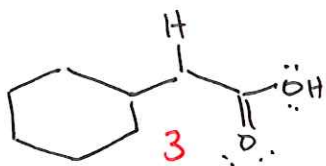
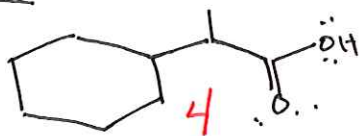
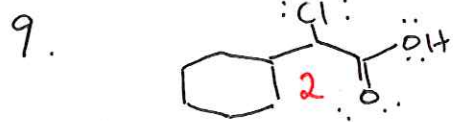
Chem 2500
 Assignment # 13 - Operational Species
 Answer Key.



Chem 2500
Assignment #13 Operational Species
Answer Key.



8. \rightarrow NaNH_2 is the correct reagent.
 \rightarrow pK_a of conjugate acid of $\text{:}\ddot{\text{N}}\text{H}_2^-$ (NH_3) is 36 which is greater than pK_a of $\text{Ph-C}\equiv\text{C-H}$ (~ 25). Hence, the equilibrium favours the side of NH_3 and deprotonation is expected.
- \rightarrow NaOH \rightarrow will not work because too weak of base
 \rightarrow pK_a of $\text{H}_2\text{O} = 15.7$.
- \rightarrow NaSH \rightarrow will not work because too weak of base
 \rightarrow pK_a of $\text{H}_2\text{S} \sim 11$.
- \rightarrow HCl \rightarrow will not work, as it is an acid, not a base.
- \rightarrow H_2O \rightarrow will not work because too weak of base
 \rightarrow pK_a of $\text{H}_3\text{O}^+ \sim 1.4$.

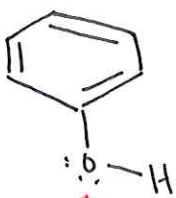


\rightarrow the most stable anion is generated for the most acidic compound.

$\text{F} > \text{Cl} > \text{H} > \text{CH}_3$
best inductive withdrawing capacity worst inductive withdrawing capacity.

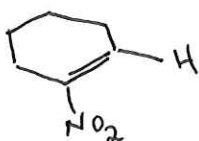
Chem 2500
 Assignment # 13 - Operational Species
 Answer Key

10a)



basic and nucleophilic.

b)



none of these

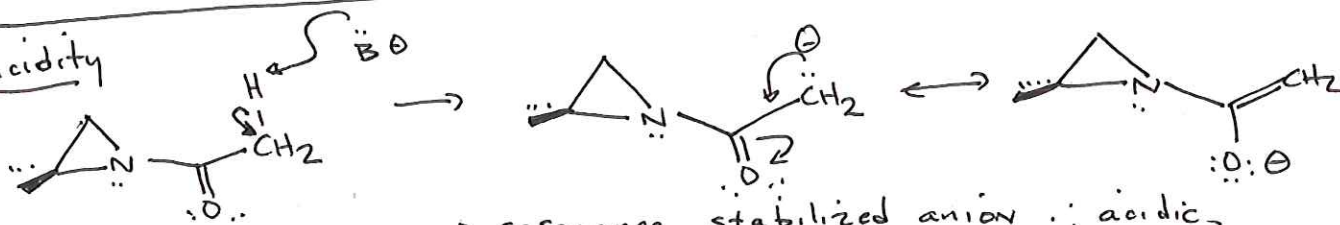
c)



electrophilic

11a)

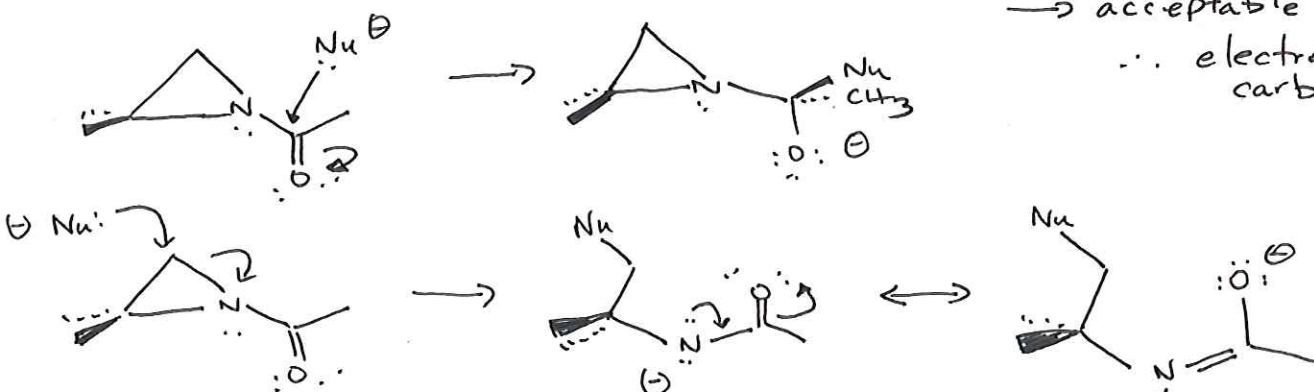
Acidity



→ resonance stabilized anion ∴ acidic

→ deprotonation at other sites does not produce stable anion.

Electrophilicity



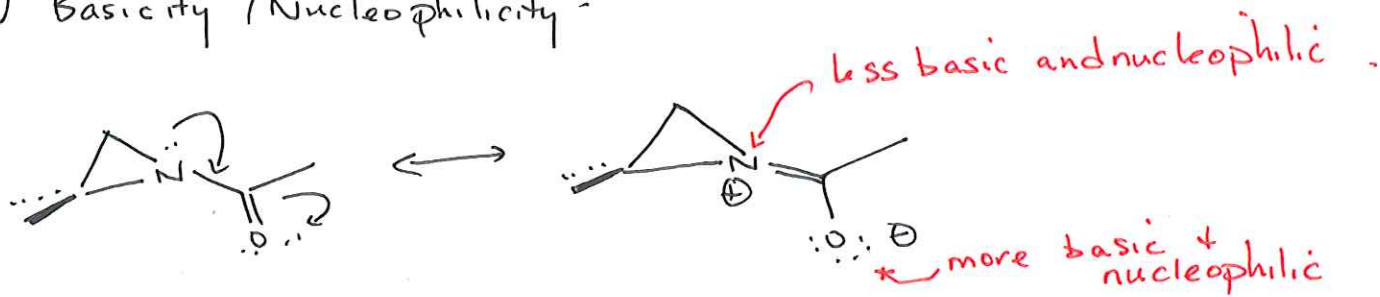
→ acceptable anion
 ∴ electrophilic carbon.

→ amides are very poor leaving groups, but more so than normal in this case because of ring strain.

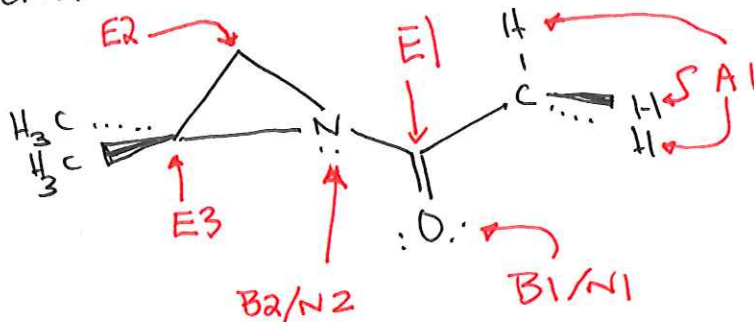
→ electrophilic for same reasons as last site but less so because of steric bulk @ carbon. Also, this carbon has less δ^+ due to inductive stabilization of Me groups.

Chem 2500
 Assignment #13 Operational Species
 Answer Key.

11a) Basicity / Nucleophilicity -

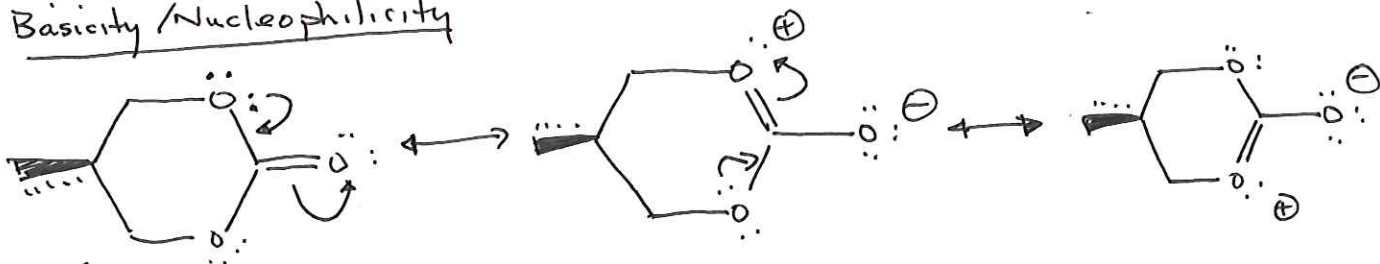


Overall :

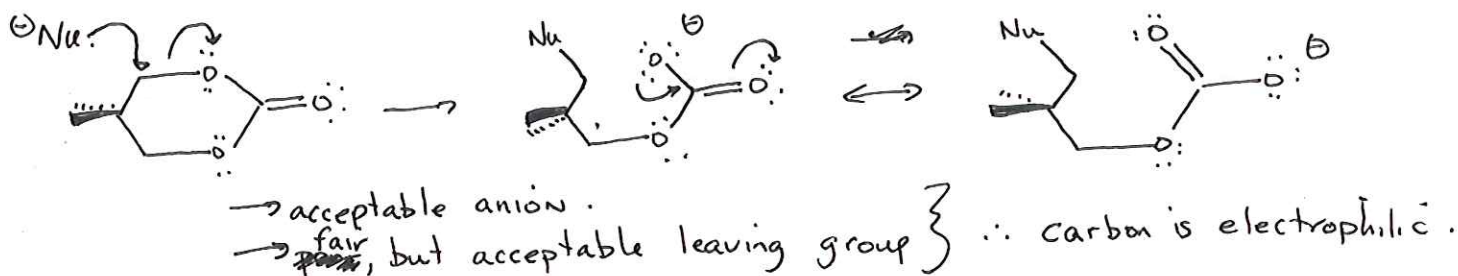
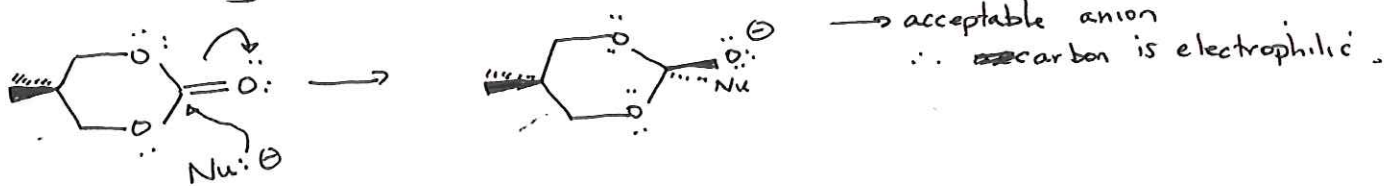


Basicity / Nucleophilicity

b)

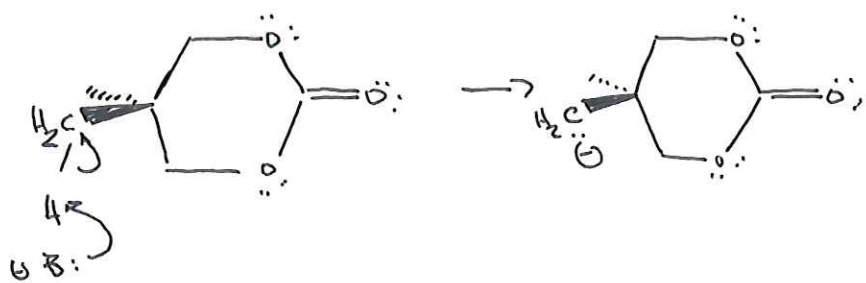


Electrophilicity

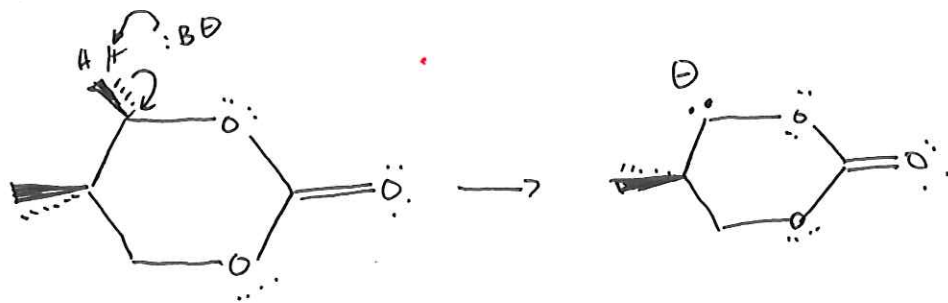


Assignment #13 - Operational Species
Answer Key.

11b) Acidity

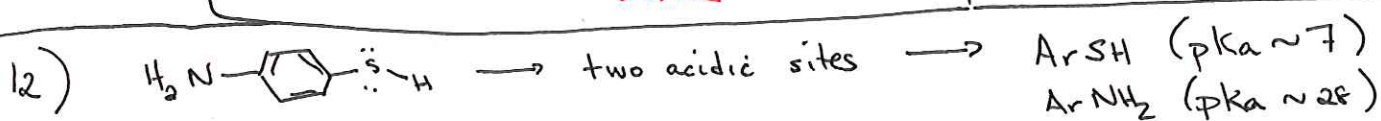
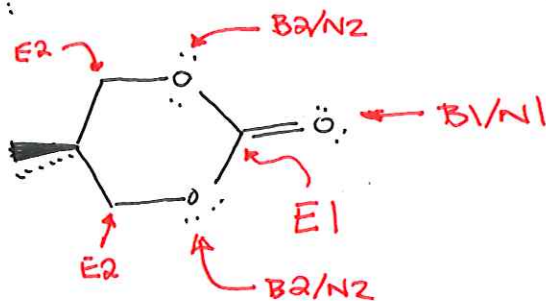


→ unacceptable
anion ∴ not acidic

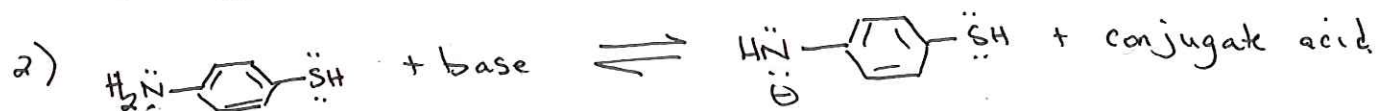
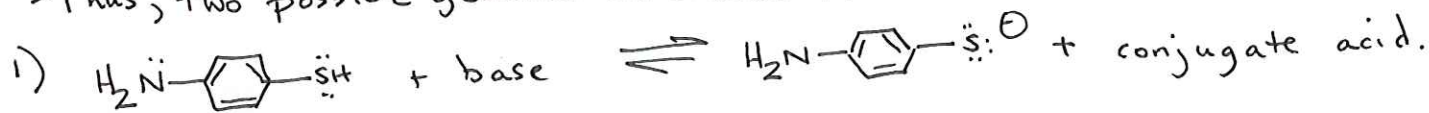


→ unacceptable
anion ∴ not acidic.

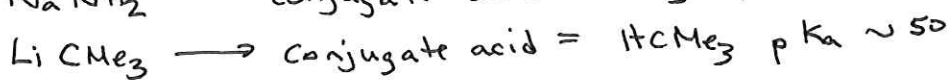
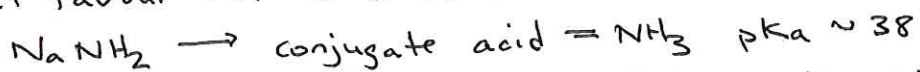
Overall:



Thus, two possible general acid/base reactions



→ Remember... acid/base reactions are equilibria
that favour the side with the weakest acid.



Assignment #13 — Operational Species.

Answer Key.

12)

→ If you substitute each reagent into the preceding general equations ~~shown~~, both NaNH_2 & Li^+Bu create very weak conjugate acids (weaker than either ArSH or NH_2Ar).

Thus, both of these reagents can deprotonate either functionality, and selectivity may not be achieved.

→ However, NaOH creates a conjugate acid w a $\text{pK}_a = 15.7$.

This is a weaker acid than ArSH , so NaOH can deprotonate this group. H_2O , though, is a stronger acid than ArNH_2 , thus the equilibrium would favour the starting material and no reaction will occur. In other words, NaOH is basic enough to deprotonate ArSH , but not basic enough to deprotonate ArNH_2 .

Thus, if you want to selectively deprotonate ArSH → use NaOH .