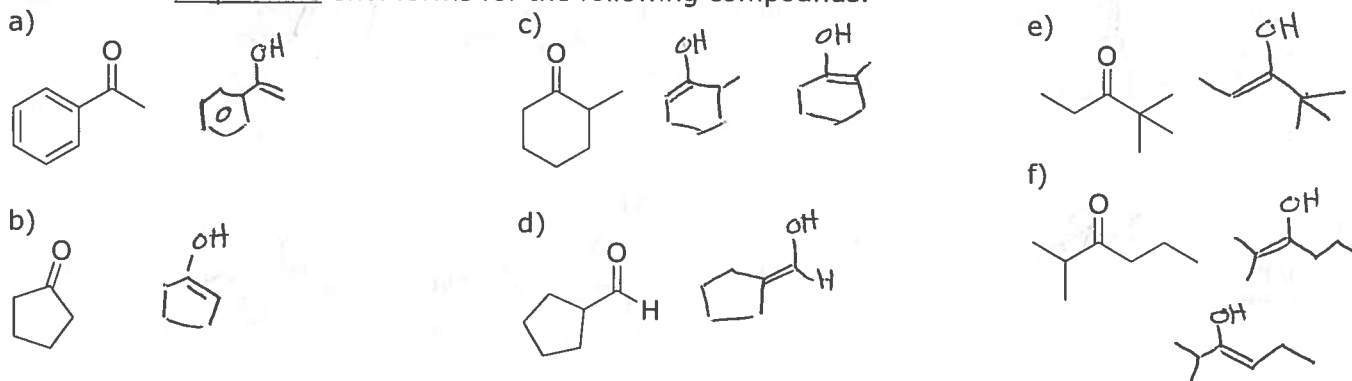


PRACTICE PROBLEMS - UNIT 20

20A. Draw the enol or enolate form of aldehydes and ketones.

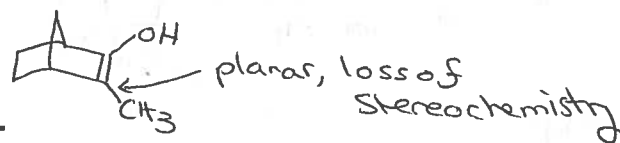
20A.1 Draw all possible enol forms for the following compounds.



20A.2 Briefly explain why the following isomerization occurs in the presence of an acid or base catalyst.



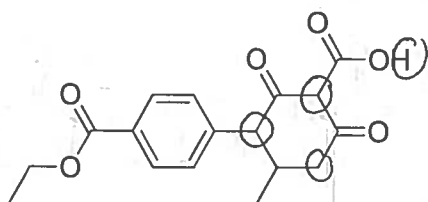
once in the enol form, the molecule can equilibrate to the more stable isomer



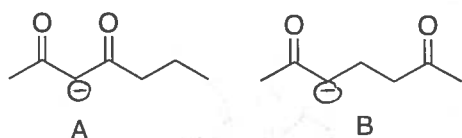
20B. Predict acid-base properties of carbonyl compounds.

20B.1 Which of the following will form enolates?

1. Indicate all acidic protons ($pK_a < 25$) on the molecule below.



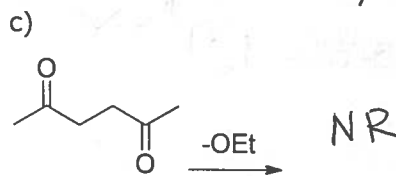
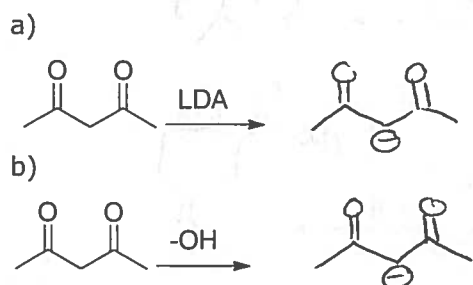
20B.2. Explain why compound A is more acidic than compound B.

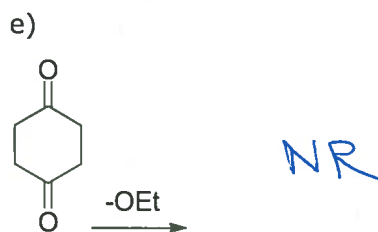
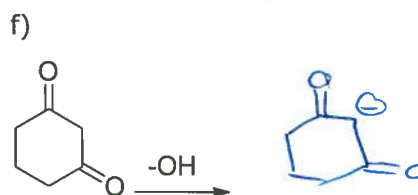
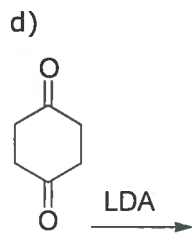


The conjugate base of A has 3 resonance forms, B only has 2. The extra stability of A's conjugate base makes it more acidic.

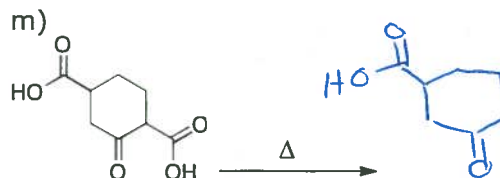
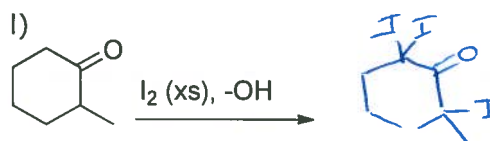
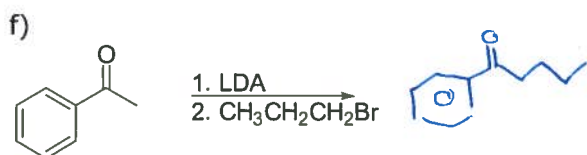
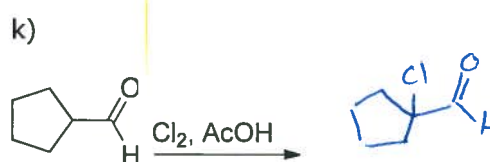
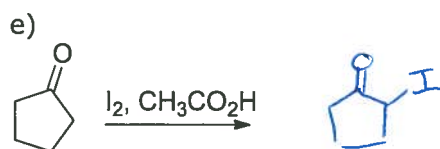
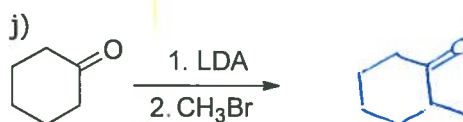
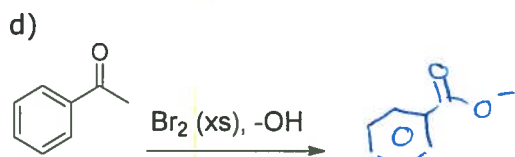
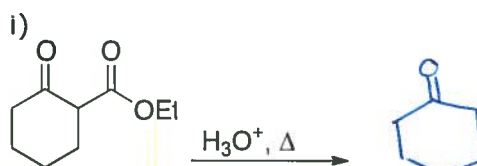
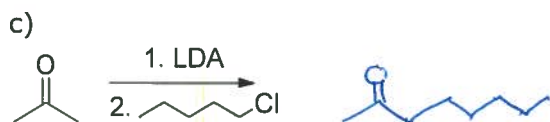
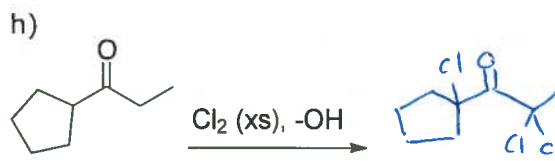
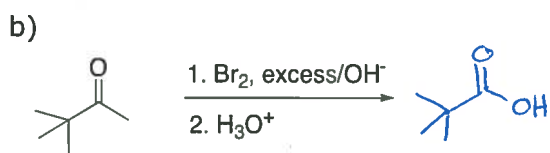
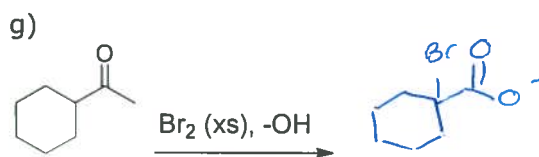
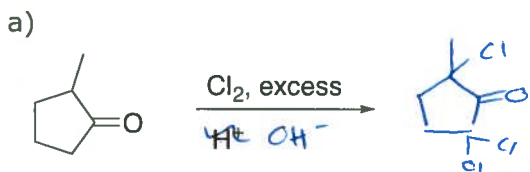
20B.3 What is the advantage of using LDA over $LiNH_2$ as a base? LDA is too large to be nucleophilic - it can only act as a base

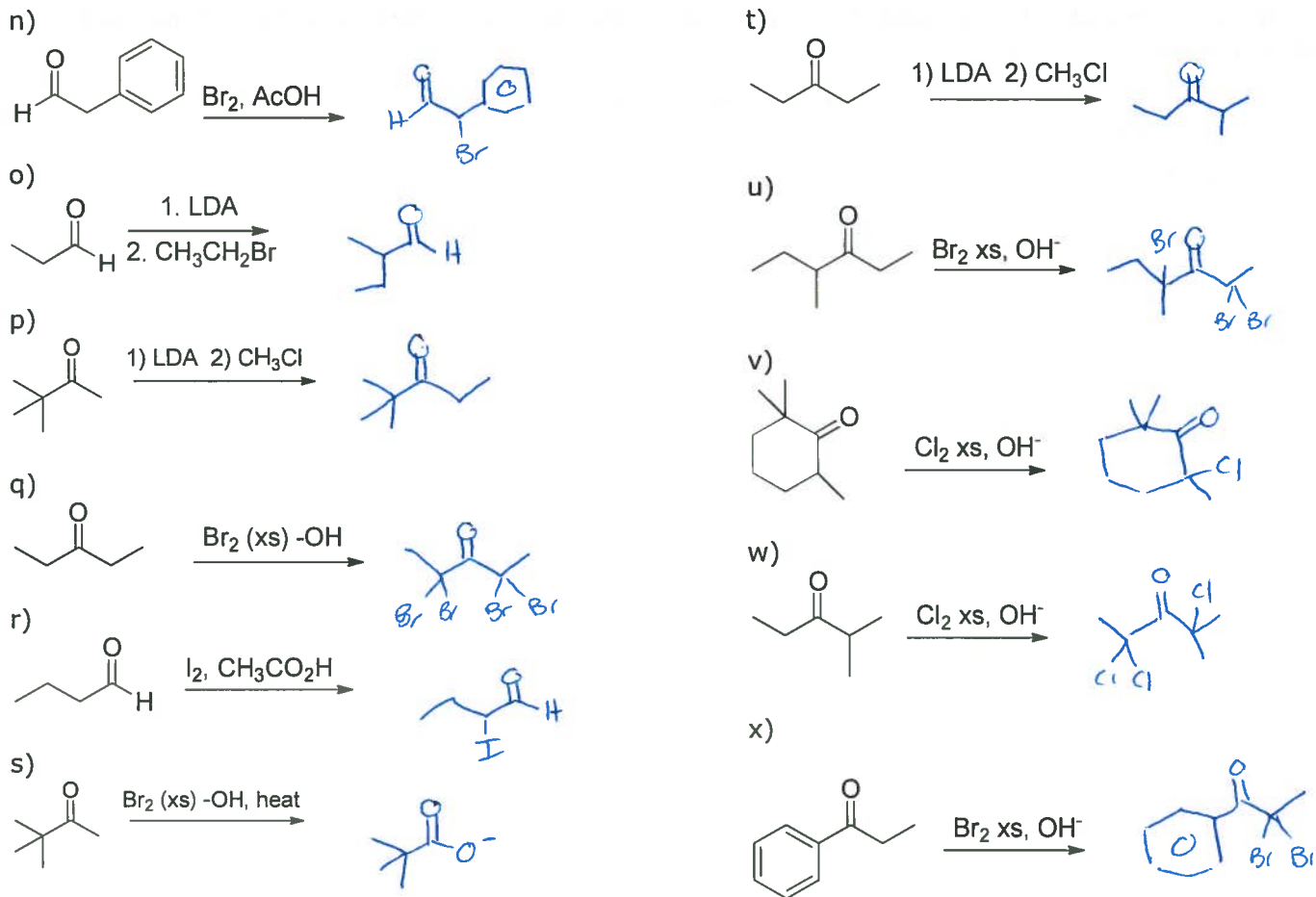
20B.4 Predict the product. If no reaction write NR.



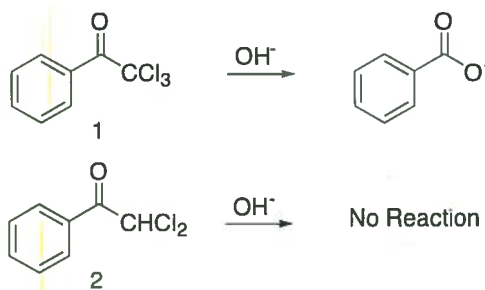


20C. Predict products of α -halogenation, α -alkylation and the haloform reaction.





20C.2 Explain why compound 1 is reactive to base but compound 2 is not.

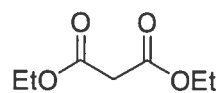


$\ominus\text{CCl}_3$ is an ok leaving group

$\ominus\text{CHCl}_2$ is not as good \rightarrow the negative is not as stabilized

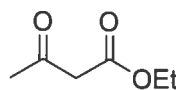
20D.1

a)



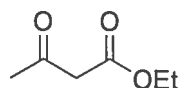
1. -OEt.
2. CH₃Br
3. H₃O⁺ / Δ

i)



1. -OEt.
2. Br-CH₂-C₆H₅
3. H₃O⁺ / Δ

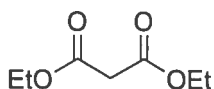
b)



1. -OEt.
2. Br-CH₂-CH₂-CH₃
3. -OEt
4. Br-CH₂-CH₂-CH₂-CH₃
5. H₃O⁺ / Δ

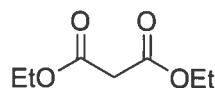
j) Bromobenzene is sp² hybridized and cannot undergo an S_N2 reaction.

c)



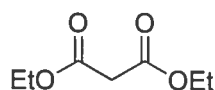
1. -OEt.
2. CH₃Br
3. -OEt
4. Br-CH₂-CH₂-CH₂-CH₂-CH₃
5. H₃O⁺ / Δ

k)



1. 2. -OEt.
2. Br-CH₂-CH₂-CH₂-CH₂-Br
3. H₃O⁺ / Δ

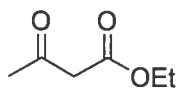
l)



1. -OEt
2. Br-CH₂-CH₂-CH₂-CH₂-Cl
3. -OEt
4. PhCH₂Br
5. H₃O⁺, Δ

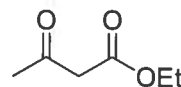
d) The product of malonic ester synthesis must have one alpha proton which comes from the decarboxylation step.

e)



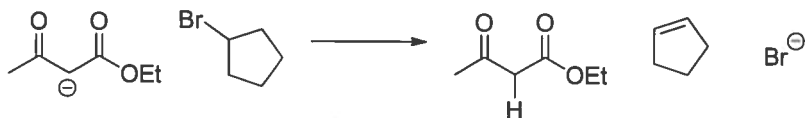
1. -OEt.
2. Br-CH₂-CH(CH₃)-CH₃
3. H₃O⁺ / Δ

f)

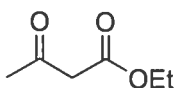


1. -OEt.
2. Br-CH₂-CH=CH-CH₂-CH₃
3. H₃O⁺ / Δ

g) This synthesis doesn't work because the 2° halide would undergo elimination rather than substitution.



h)



1. 2. -OEt.
2. Br-CH₂-CH₂-CH₂-CH₂-CH₂-Br
3. H₃O⁺ / Δ

m) Not possible – t-butyl groups cannot undergo an S_N2 reaction

20 E. 1

