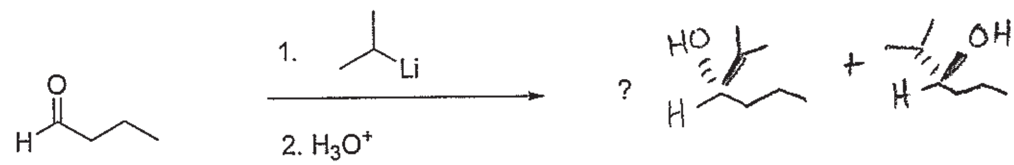
Key - Exam 3 - Summer 2011
CHEM 3331

4 pts

Select the single best answer to each multiple choice question (1-14). (~~8~~ pts each)

1. When the reaction shown here occurs, the product(s) will be:

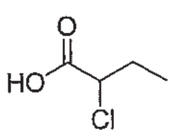
B



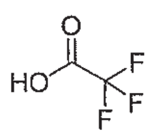
a. a single achiral molecule
b. a racemic mixture
c. an unequal mixture of enantiomers
d. an equal mixture of diastereomers
e. an unequal mixture of diastereomers

2. Which of the following is the **least** acidic species?

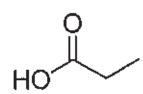
C



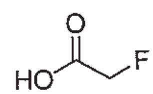
A



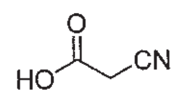
B



C



D

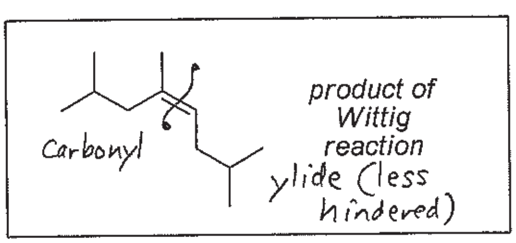


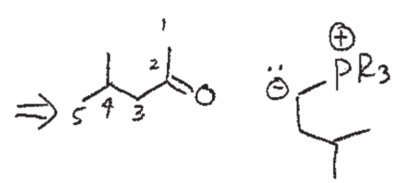
E

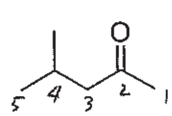
All others have EWG's that increase acidity

3. A Wittig reaction was performed and resulted in the product shown. What is the structure of the carbonyl compound that was used to synthesize the ~~ylide in~~ alkene this reaction? (The correct answer is the one that uses the most efficient possible synthetic route.)

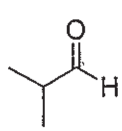
A



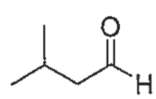




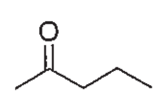
A



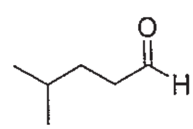
B



C



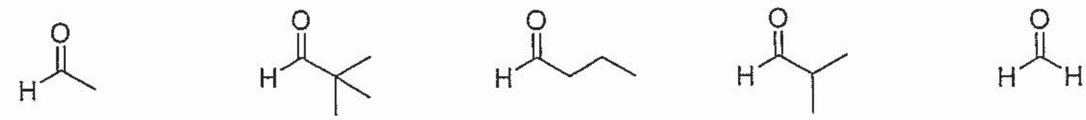
D



E

4. Which of the following aldehydes do you expect to have the *smallest* value of $K_{hydration}$?

B

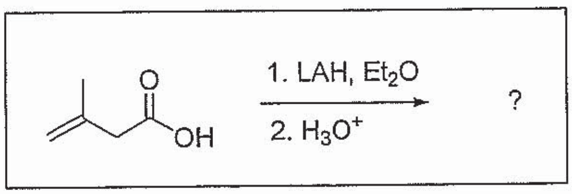


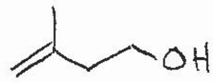
A B C D E

most sterically hindered → least amount of hydrate

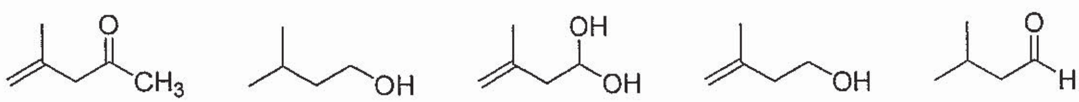
5. What is the major organic product of the following reaction?

D





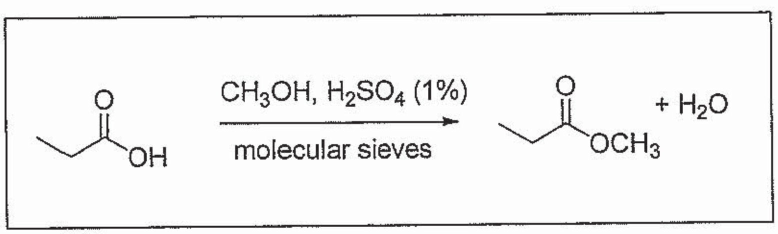
LAH reduces RCO_2H to 1° ROH and does not reduce alkenes



A B C D E

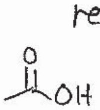
6. A carboxylic acid was esterified in the manner shown below (in the box). Which of the methods listed could also be used to synthesize this ester?

D



A	B	C	D	E
DCC CH_3OH	CH_2N_2	K_2CO_3 CH_3I	All of these methods would work	None of these methods would work

A ✓ Coupling reagent

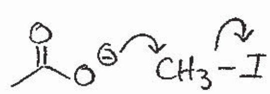


+ CH_3OH

→ 

B ✓ makes a methyl ester

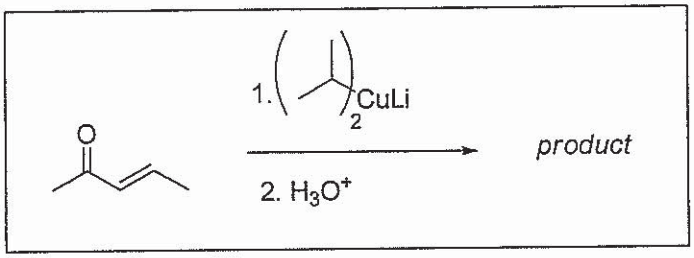
C ✓

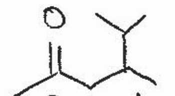


CH_3-I

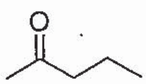
D

7. What is the product of the reaction conditions shown?

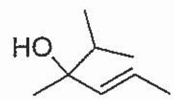




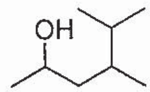
Cuprates give conjugate addition product



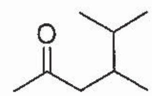
A



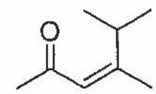
B



C



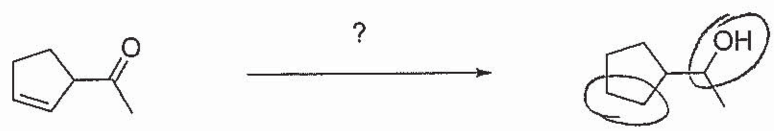
D



E

D

8. Which reagent would you use to accomplish this transformation?



Both alkene and carbonyl were reduced

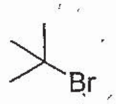
a. LAH
b. $NaBH_4$
c. NaH
d. Raney Ni/H_2
e. Either "a" or "b"

B

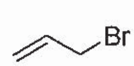
9. Which of the alkyl halides shown would be the least appropriate choice to use as a precursor to an ylide for a Wittig reaction?

CH_3Br

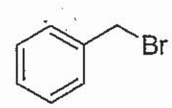
A



B



C



D

All of these can be made into ylides with no problem

E

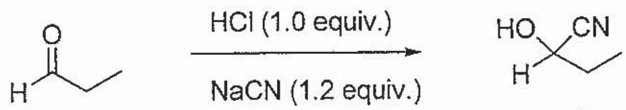
Too hindered – ylide is made through S_N2 reaction of R_3P: and R–X

10. Which of these statements is false?

C

T a. LAH is a stronger reducing agent than $NaBH_4$.
T b. The Al-H bond is longer than the B-H bond.
F ~~c.~~ Na coordinates (attaches) more tightly to O than Li. The opposite is true
T d. $NaBH_4$ can be used with protic solvents like water and alcohols.
T e. LAH can be used to reduce carboxylic acids.

11. Think about the mechanism of cyanohydrin formation that occurs under the following conditions:

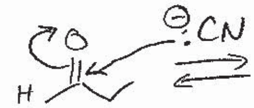


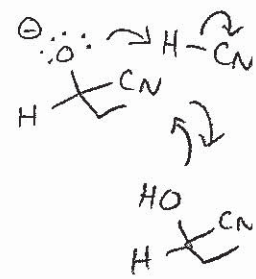
$$\underset{1.2}{NaCN} + \underset{1.0}{HCl} \longrightarrow \underset{1.0}{HCN} + \underset{1.0}{NaCl} + \underset{0.2}{NaCN}$$

Which of these statements is *true*?

C

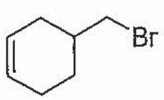
~~a.~~ The carbonyl oxygen is protonated by HCN.
~~b.~~ The carbonyl oxygen is protonated by HCl.
✓ c. The alkoxide intermediate is protonated by HCN.
~~d.~~ The alkoxide intermediate is protonated by HCl.
~~e.~~ There is no proton transfer step in this mechanism.





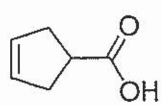
12. Compound **X** can be used to form an ylide. It can also be reacted with a carboxylate ion to produce an ester. When treated with ozone, it gives no reaction, but when treated with bromine and $FeBr_3$ a reaction occurs. Which of these structures is compound **X** ?

D

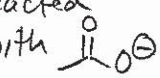


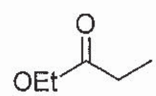
~~A~~

Gives rxn with O_3

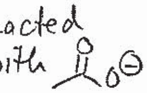


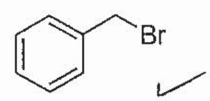
B

- Can't be reacted with  to form ester

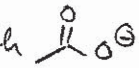


C

- Can't be reacted with  to form ester

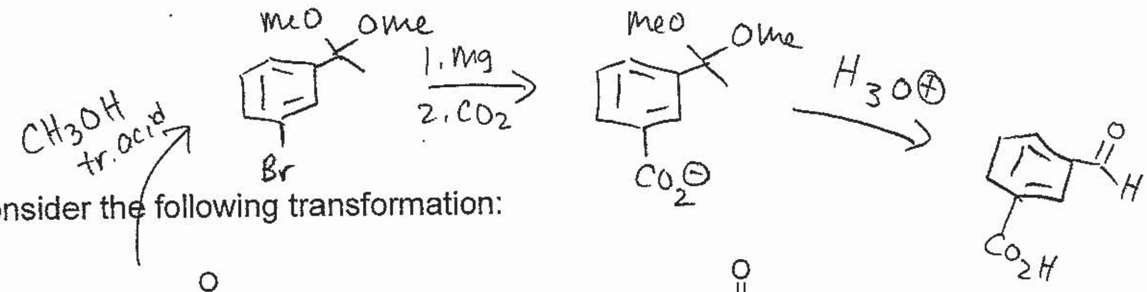


D ✓

- Reacts with Br_2 and $FeBr_3$
- Can be used to make an ylide
- Doesn't react with O_3
- Can react with  to form an ester

None of these is Compound X

E



13. Consider the following transformation:

C

Which of the following multi-step synthetic pathways would successfully accomplish this transformation? (Assume appropriate solvents and aqueous workups where not explicitly written.)

X a.
1. $KMnO_4$
2. Mg
3. CO_2, then H_3O^+
4. 0.5 equiv LAH, then H_3O^+

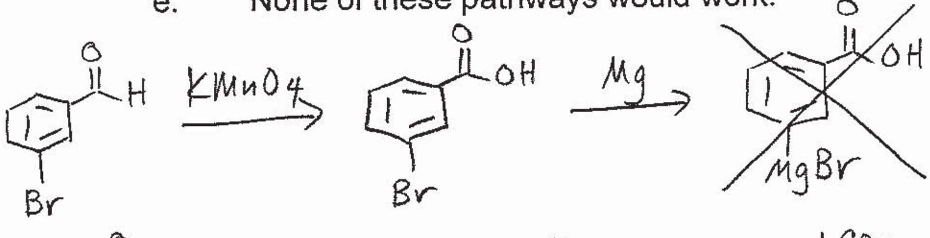
X b.
1. Clemmensen or Wolff-Kishner reduction
2. Mg
3. CO_2, then H_3O^+
4. MnO_2

✓ c.
1. CH_3OH, trace H_2SO_4, molecular sieves
2. Mg
3. CO_2, then H_3O^+ See above
4. H_3O^+

X d.
1. LAH, then H_3O^+
2. Mg
3. CO_2, then H_3O^+
4. MnO_2

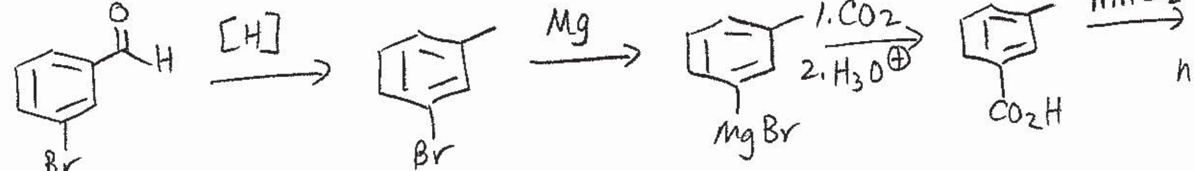
e. None of these pathways would work.

(A)



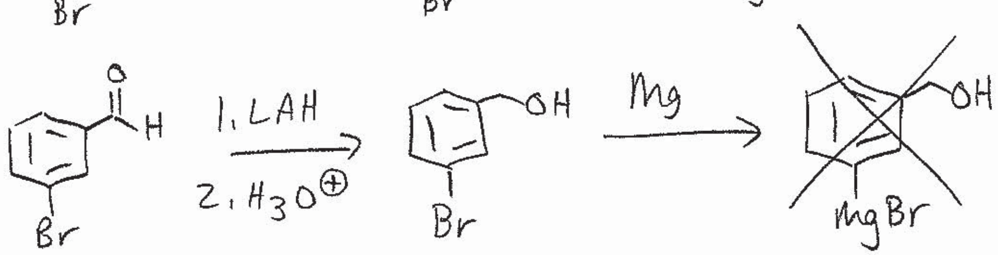
Can't have RMgX and RCO_2H in same molecule

(B)



N.R.
no alcohol to oxidize

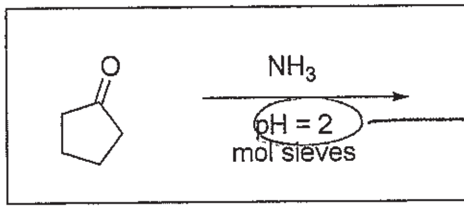
(D)



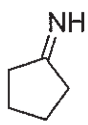
Can't have RMgX and ROH in same molecule

14. What is the most likely result of the reaction conditions shown?

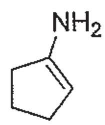
E



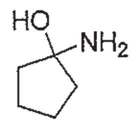
Too acidic! NH_3 will be protonated and can't act as a nucleophile.
pH must be ≈ 5



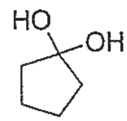
A



B



C

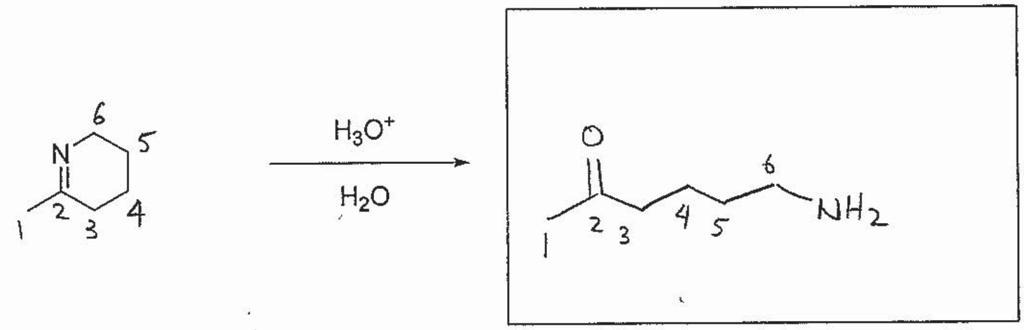


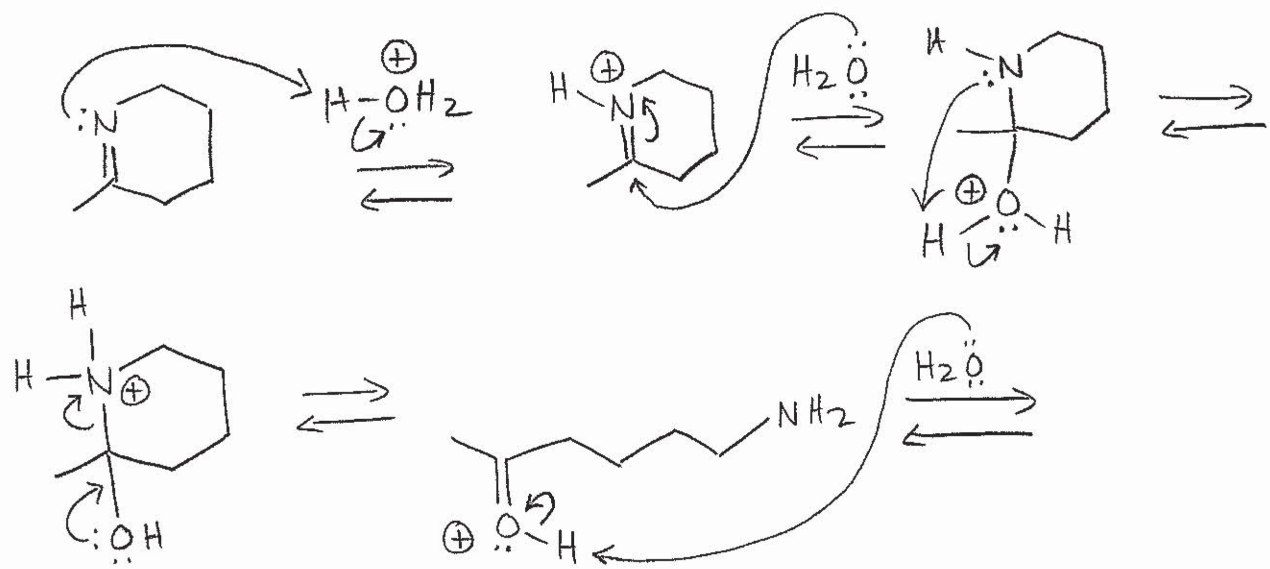
D

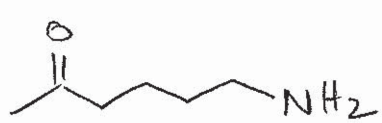
No reaction

E

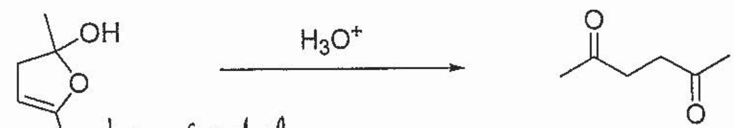
15. Predict the major organic product of the conditions shown and draw a mechanism to rationalize its formation. Include all curved arrows, intermediates, necessary electrons, and nonzero formal charges for full credit. (15 pts)



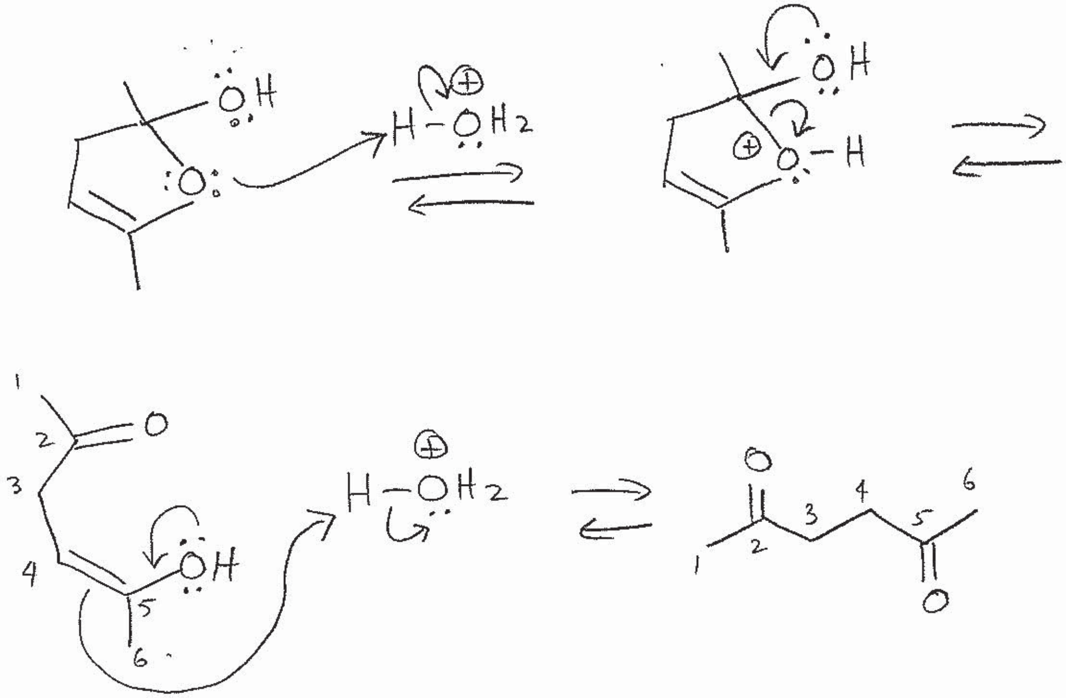




16. Draw a mechanism to illustrate the transformation shown. Include all curved arrows, intermediates, necessary electrons and nonzero formal charges for full credit. (15 pts)



hemiacetal



17. Design a multi-step synthesis for each of the following transformations. Show the reagents needed for each step and the product of each step. Do not draw any mechanisms. Do not provide a list of reagents without showing the product of each step. (18 pts)