Exam #2

Chemistry 334

Principles of Organic Chemistry I

Thursday April 21, 2005

Name:_____.

The exam is worth a total of 100 points; there are six questions. Please show all work to receive full credit for an answer.

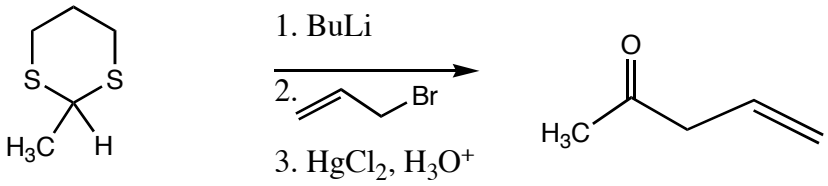
By putting your name on this exam, you agree to abide by California State University, Northridge policies of academic honesty and integrity

Molecular models are allowed for this exam. Calculators are not needed.

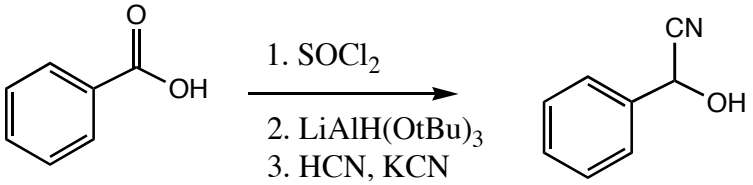
Good Luck!

1. Predict the product(s) of the following reactions, noting stereochemistry where appropriate and indicating when a racemic mixture of enantiomers is formed: (5 pts. each)

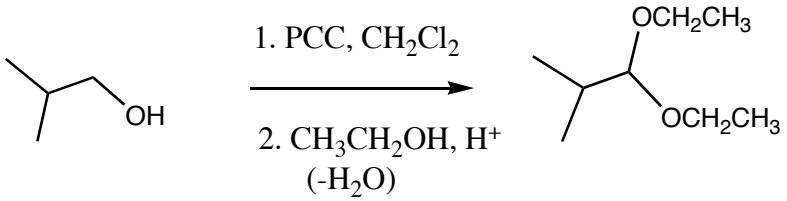
a.



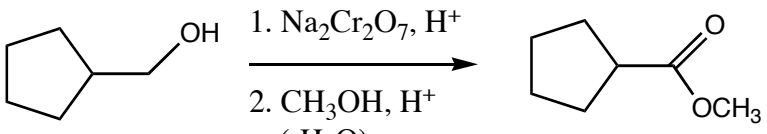
b.



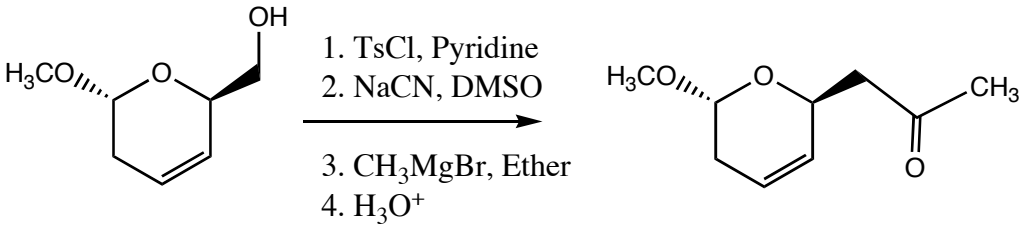
c.



d.



e.



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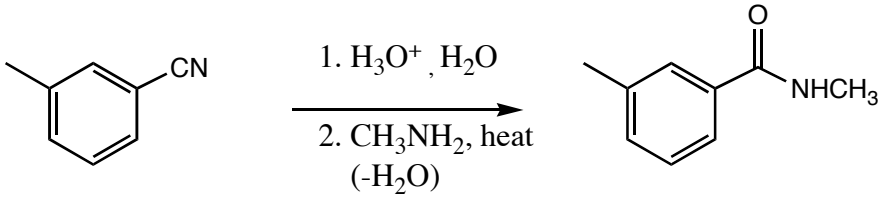
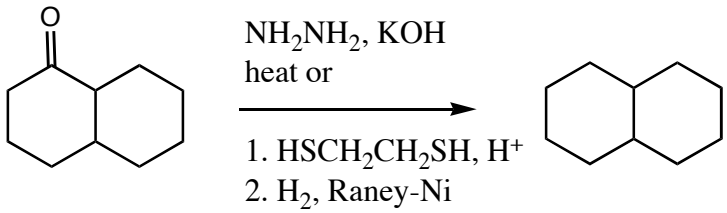
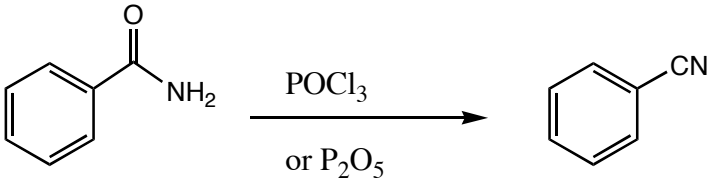


2. Indicate reagents to accomplish the following transformations.(20 pts)

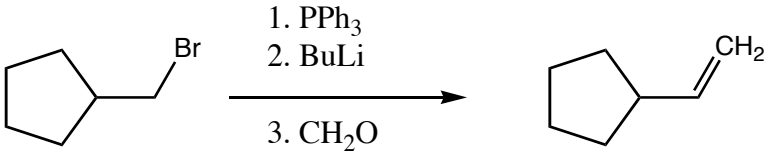
a.



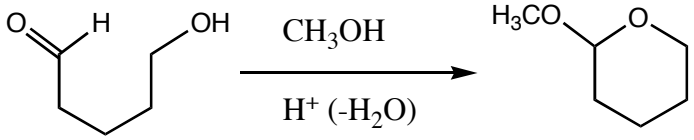
b.



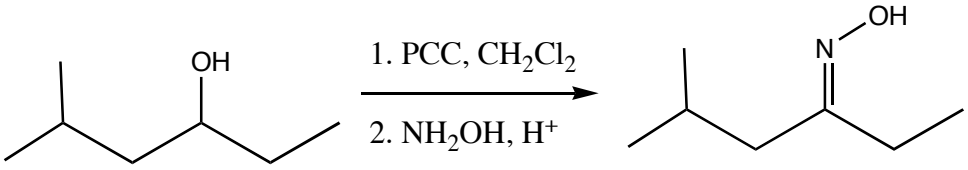
c.



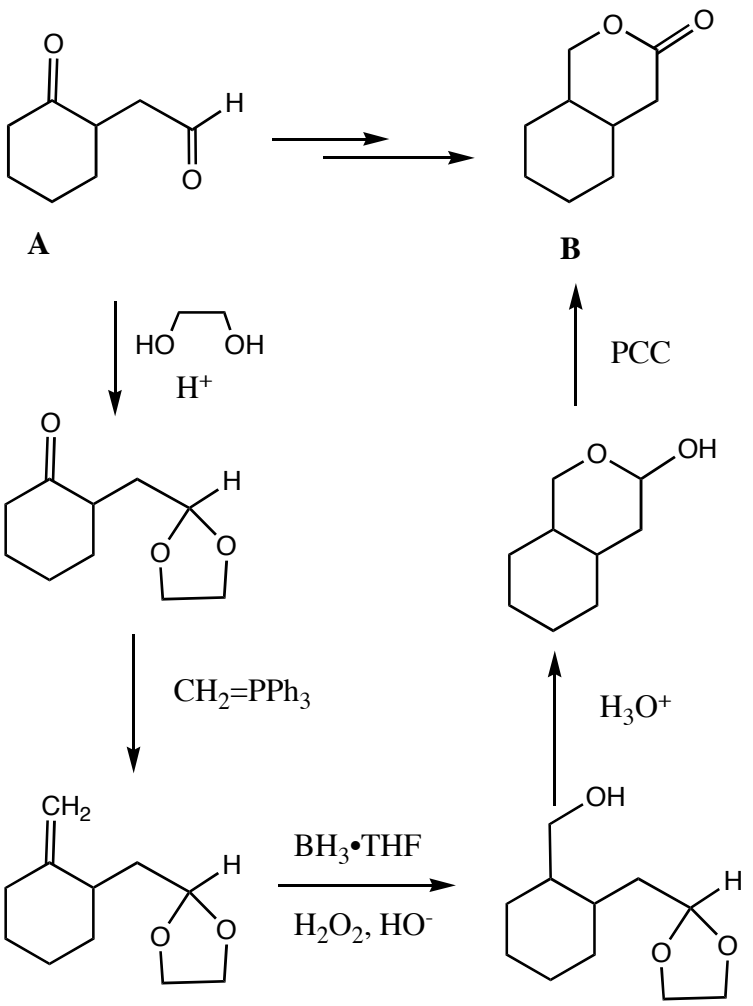
d



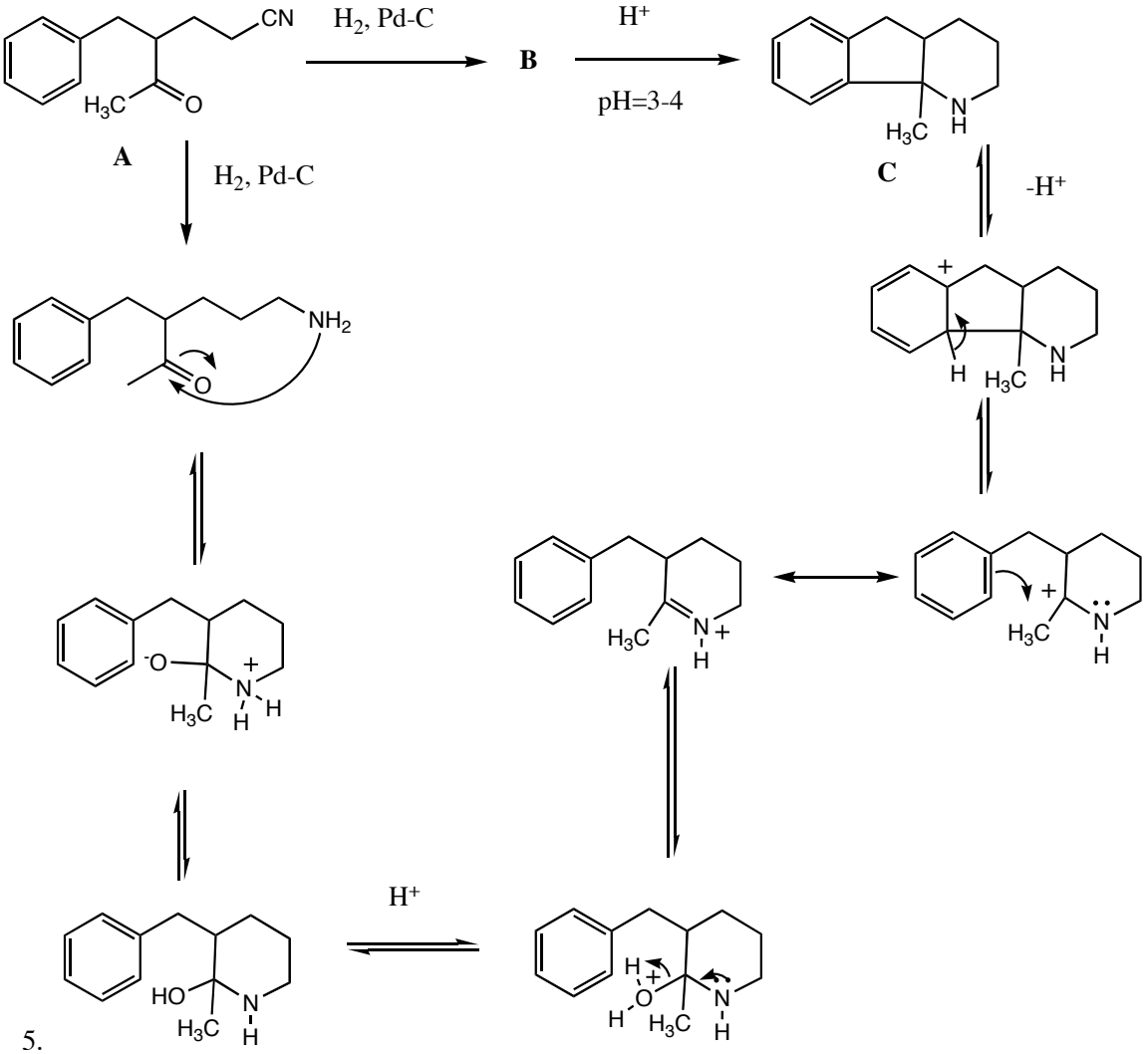
e.



3. Indicate a sequence of synthetic steps to prepare lactone B from keto-aldehyde A. Useful reagents may include :($HOCH_2CH_2OH$, BH_3•THF, $CH_2=PPh_3$,PCC) (20 pts)

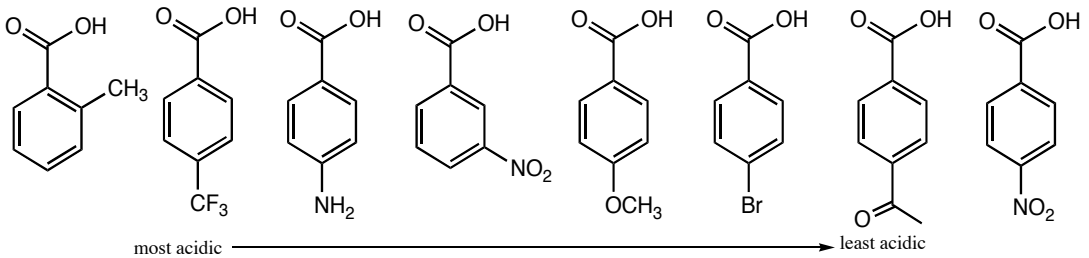


4. Hydrogenation of keto-nitrile A leads to a compound B. When the pH of a solution of compound B is lowered to between 3-4, compound C is rapidly produced. Draw the structure of compound B and show a mechanism for the conversion of B to C. (15 pts)

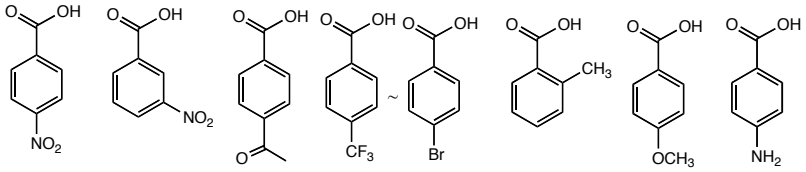


5.

5. Rank the following 8 substituted benzoic acids in order of their acidity, from most acidic to least acidic. Give a rationale for your ordering, including a discussion of resonance/inductive effects. (15 pts)

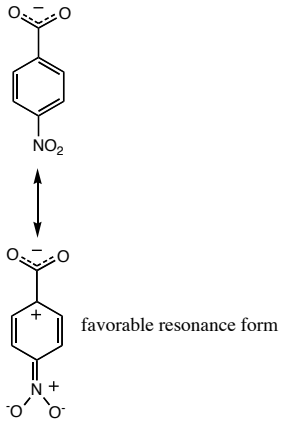


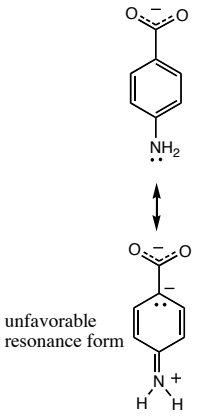
most acidic → least acidic



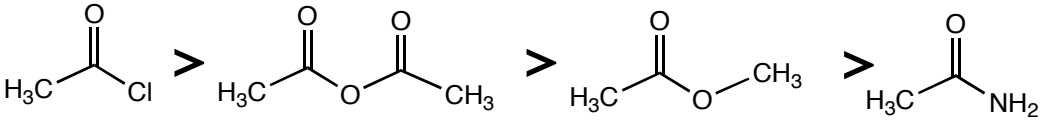
$$RCOOH + H_2O \underset{}{\overset{K_a}{\rightleftharpoons}} RCOO^- + H_3O^+$$

acidity correlates with the stability of the cojugate base, $RCOO^-$, and thus groups on the aromatic ring which stabilize the negative charge of the carboxylate by inductive or resonance electron withdrawing groups will stabilize the conjugate base and thus increase the acidity of the parent acid. Groups which withdraw electron density by resonance (NO_2, $CH_3C{=}O$) will have a greater effect on carboxylate stability than groups which withdraw electron density inductively (Br, CF_3). Similarly, groups which donate electron density inductively (CH_3) will be more acidic than groups which donate electron density by resonance (OCH_3, NH_2). Finally, groups in the ortho and para position will have a greater affect on acidity than groups in the meta position, as we know from drawing resonance forms.



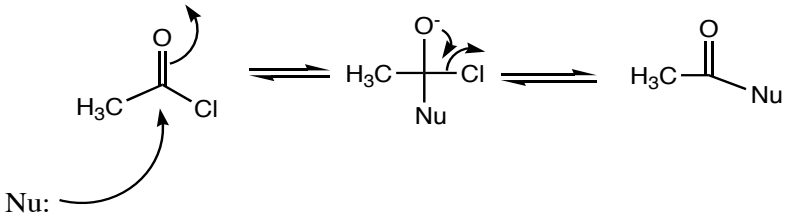


6. (Bonus) Explain the following substrate reactivity trend for nucleophilic acyl substitution:

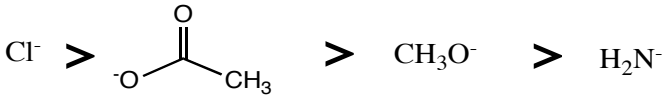


Be sure to include a discussion of the mechanism of nucleophilic acyl substitution, resonance stabilization of substrate, and leaving group ability. (10 points)

Nucleophilic acyl substitution:



Leaving group: best ability to stabilize negative charge:



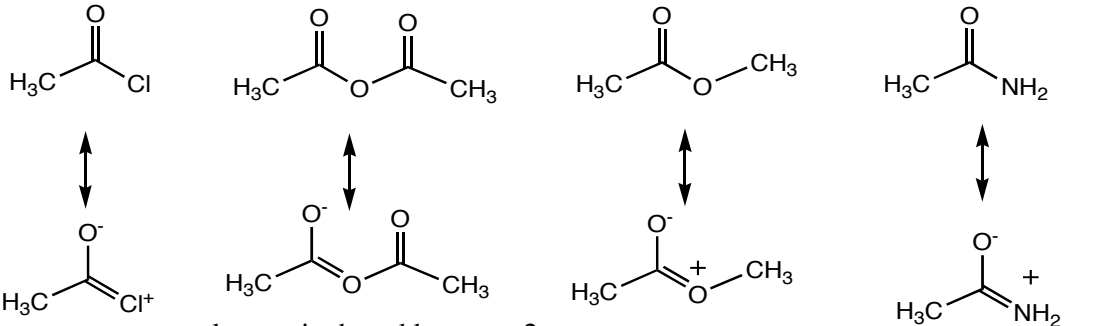
electronegative halogen

resonance

negative charge localized on O

negative charge localized on less electronegative N

Resonance: least resonance stabilization in acid chloride (poor overlap of Cl lone pairs with carbon p orbital); most resonance stabilization in amide



worst: + on Cl

lone pair shared between 2 carbonyls

+ on O

best: + on N, - on O

Congratulations!
Score:

1. _____/30
2. _____/20
3. _____/20
4. _____/15
5. _____/15
6. _____/10

Total: _____/100