CH 254, Spring 2008 **Name** KEY

Exam #3, 18 April 2008 **(PRINT CLEARLY PLEASE!)**

Question #	Points Possible	Points Received
1	20	
2	15	
3	7	
4	8	
5	12	
6	18	
7	10	
8	5	
9	5	
Subtotal	100	
Extra Credit	7	
Total	107	

1. (20 points) Multiple Choice. For each question, circle ONE answer.

a. In acyl substitution reactions:

i. protonation of the carbonyl is followed immediately by loss of the leaving group

ii. loss of the leaving group is followed by rearrangement of the carbocation

(iii.) addition to the carbonyl by a nucleophile is followed by loss of the leaving group

iv. ester hydrolysis is followed by deprotonation

v. an S_N2 reaction occurs

b. Acetyl chloride undergoes nucleophilic substitution at a faster rate than methyl acetate because:

i. the ester is more sterically hindered than the acid chloride

ii. the acid chloride is more sterically hindered than the ester

iii. methoxide is a better leaving group than the chloride

iv. esters hydrolyze faster than acid chlorides

(v.) chloride is a better leaving group than methoxide

c. Which of the following is (are) formed in the reaction between ethyl butanoate and ethyl amine?

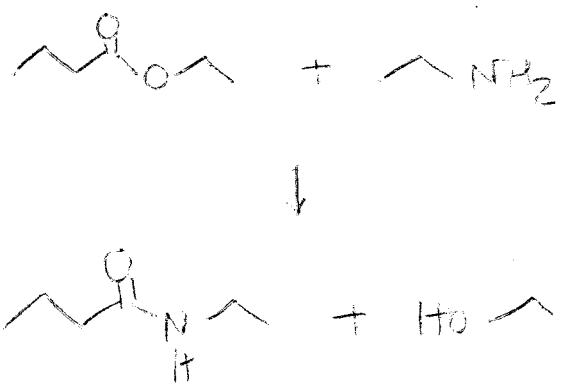
i. ethanol

ii. 1-butanol

iii. *N*-ethylbutanamide

(iv.) both i and iii

v. both ii and iii



d. Which of the following conditions will drive the equilibrium of the Fischer esterification towards ester formation?

i. addition of water

ii. removal of water as it is formed

iii. addition of an inorganic acid as a catalyst

iv. addition of alcohol

(v.) both ii and iv

e. Why do aldehydes undergo nucleophilic addition reactions while esters undergo nucleophilic acyl substitution reactions?

i. the carbonyl carbon of an ester is more electrophilic than that of an aldehyde

ii. aldehydes are more sterically hindered than esters

iii. once the nucleophile adds to an aldehyde, the tetrahedral intermediate is too sterically hindered to eliminate one of the attached groups

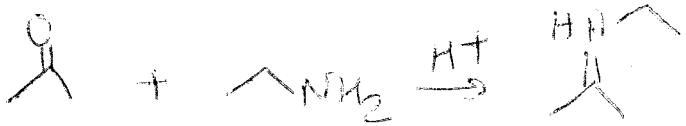
iv. the ester carbonyl carbon is sp^3 hybridized while the aldehyde carbonyl carbon is sp^2 hybridized

(v.) once the nucleophile adds to the aldehyde, neither H^- nor R^- can be eliminated since they are strongly basic

f. Which reagent would best serve as the basis for a simple chemical test to distinguish between acetaldehyde and acetone?

i. $I_2/NaOH$ ii. Br_2/CCl_4 iii. 2,4-DNP (iv.) $Ag(NH_3)_2^+$ v. $NaHCO_3/H_2O$

g. What class of organic compound is produced when a ketone reacts with a primary amine in the presence of an acid catalyst?



i. A cyanohydrin

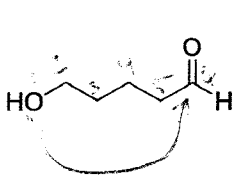
ii. A hydrazone

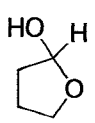
(iii.) An imine

iv. An enamine

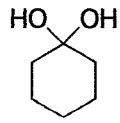
v. An oxime

h. The compound shown below can form a hemiacetal by reacting with itself in solution. What is the structure of the hemiacetal?

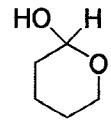




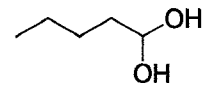
i



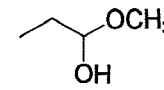
ii



iii

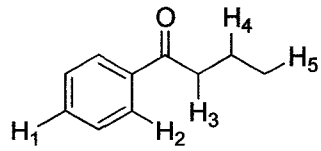


iv



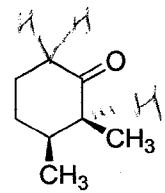
v

i. Which of the labeled hydrogens in the following structure is the most acidic?



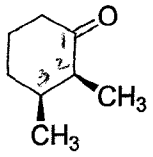
i. 1 ii. 2 iii. 3 iv. 4 v. 5

j. How many H's in the compound shown below are replaced by D's when the compound is shaken in D_2O containing trace amounts of NaOD?

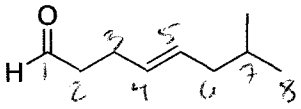


i. 1 ii. 2 iii. 3 iv. 6 v. 7

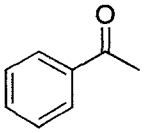
2. (15 points) Nomenclature. Name each of the following molecules using IUPAC approved methods. Don't forget to indicate stereochemistry where appropriate.



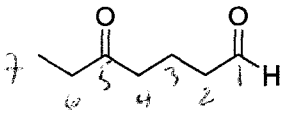
(2S, 3S)-2,3-dimethylcyclohexanone



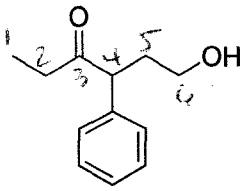
E-7-methyl-4-octenal



acetophenone

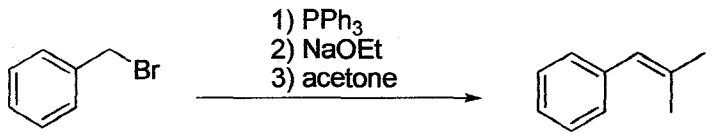


5-oxoheptanal

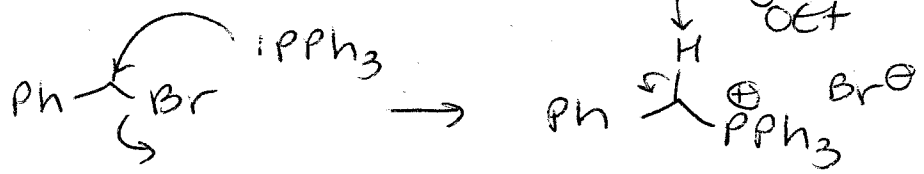


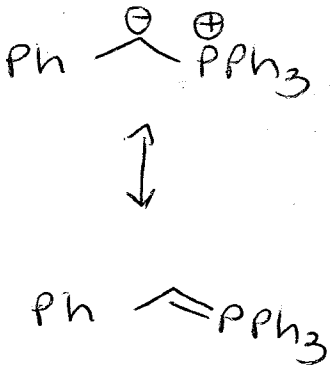
6-hydroxy-4-phenyl-3-hexanone

3. (7 points) Propose a mechanism for the following transformation, as shown in lecture, using proper electron-pushing formalisms and showing all important resonance structures.

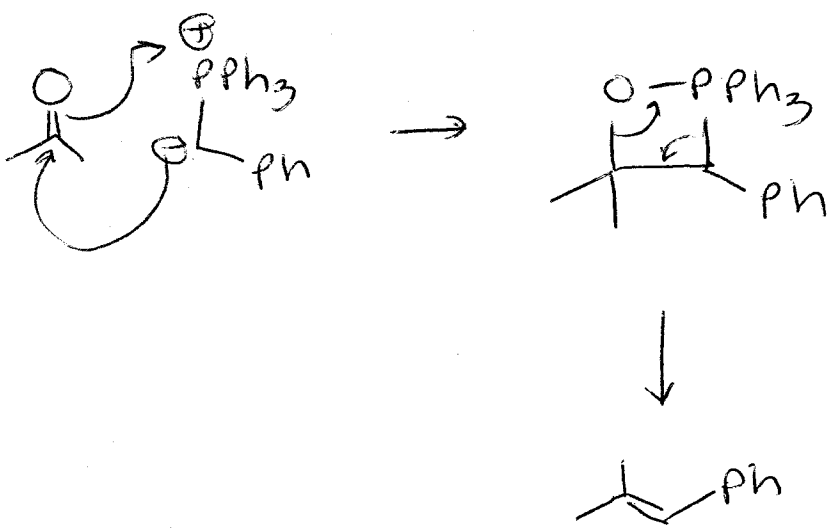


(1)

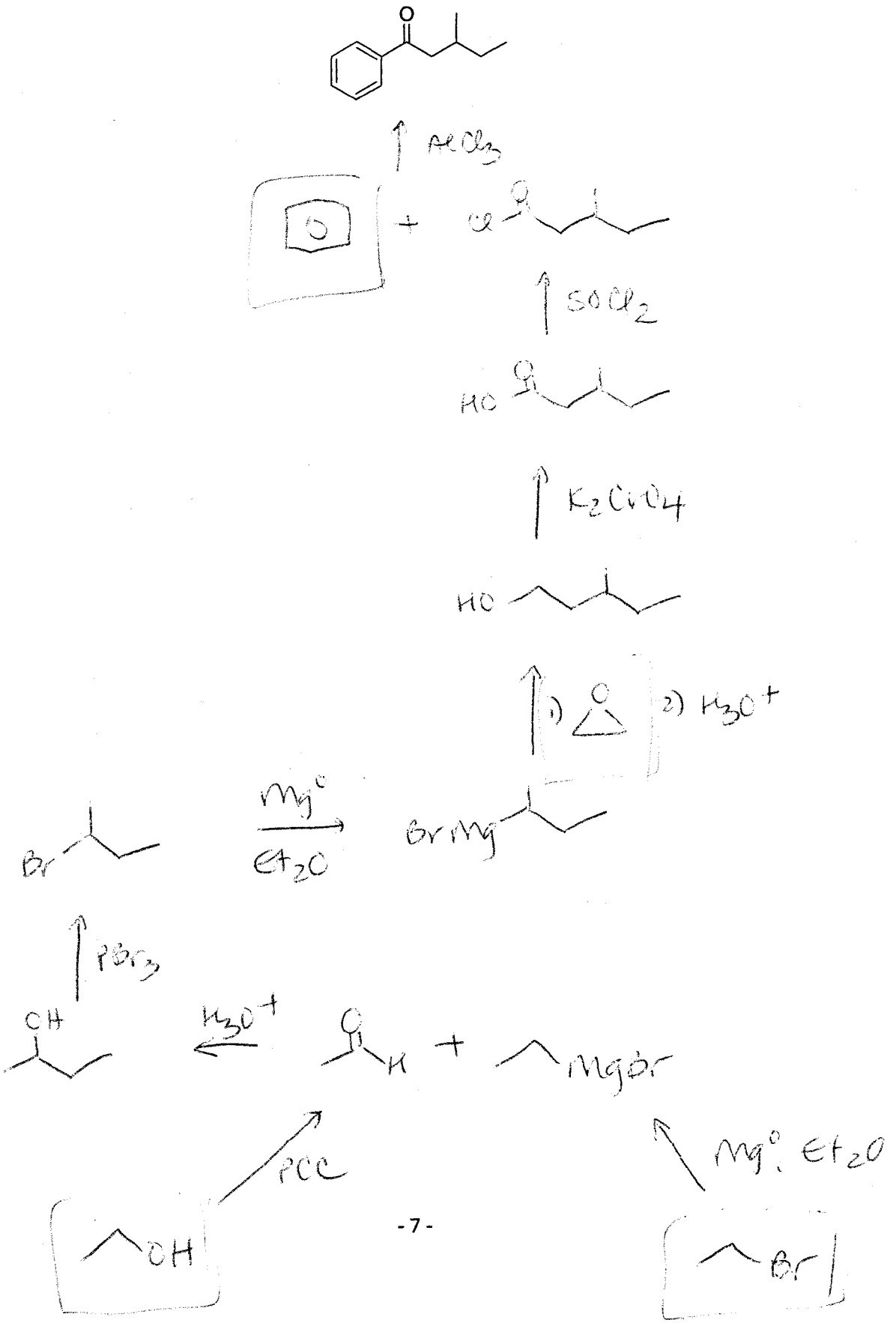




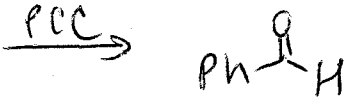
(2)

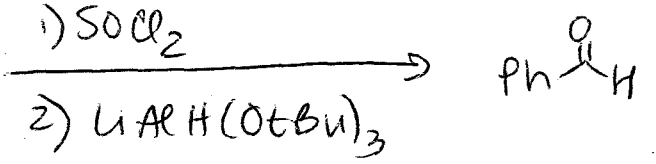


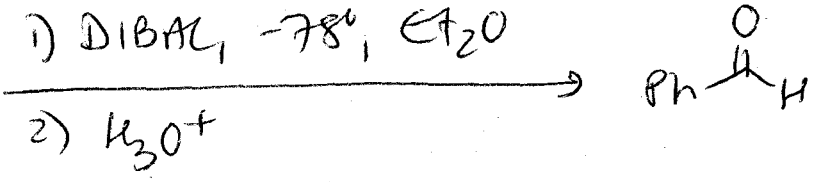
4. (8 points) Propose a synthesis of the following molecule. Allowable starting materials include any three-carbon (or less) alkyl halide, alcohol, or epoxide; or benzene. Any inorganic reagents are allowable. Please show all isolable intermediates; no mechanisms.

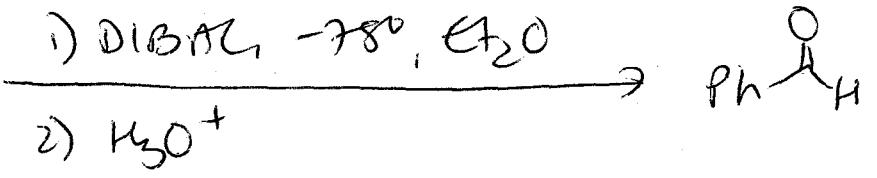


5. (12 points) Show how you would synthesize benzaldehyde *from* each of the following:

a) $PhCH_2OH$ 

b) $PhCO_2H$ 

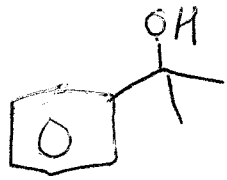
c) PhCN 

d) $PhCO_2CH_3$ 

(other ways also possible)

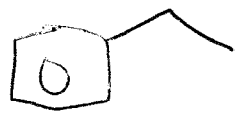
6. (18 points) Give the product of the reaction of acetophenone with each of the following:

a) CH_3MgBr; then H^+/H_2O

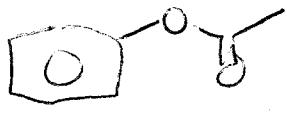


b) NH_2NH_2, NaOH, DMSO, Δ

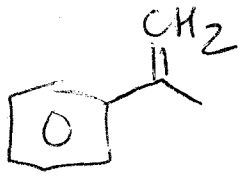
c) $HSCH_2CH_2SH$, H^+; then Raney Ni



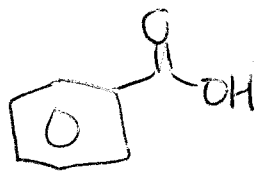
d) mCPBA



e) $CH_2=PPh_3$

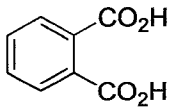


f) NaOH, xs I_2; then H^+/H_2O

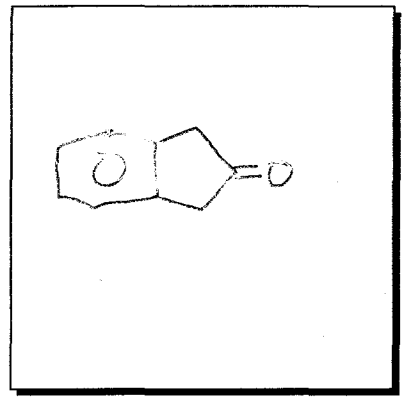


C=O SOAR=6

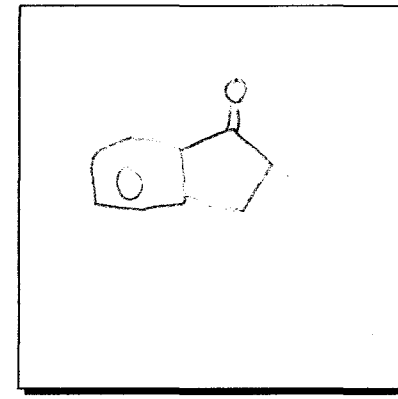
7. (10 points) Compounds **W** and **X** are isomers; they have the molecular formula C_9H_8O. The IR spectrum of each compound shows a strong absorption band near 1715 cm^{-1}. Oxidation of either compound with hot, basic potassium permanganate followed by acidification yields phthalic acid (see below). The ^1H NMR spectrum of **W** shows a multiplet at 7.3 ppm and a singlet at 3.4 ppm. The ^1H NMR spectrum of **X** shows a multiplet at 7.5 ppm, a triplet at 3.1 ppm, and a triplet at 2.5 ppm. Propose structures for **W** and **X**.



phthalic acid

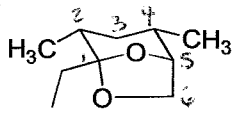


W



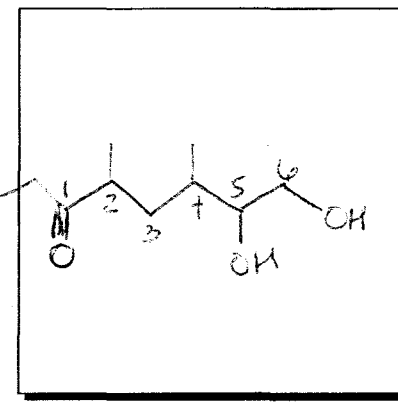
X

8. (5 points) Dutch elm disease is caused by a fungus transmitted to elm trees by the elm bark beetle. The female beetle, when she has located an attractive elm tree, releases several pheromones, including multistriatin (shown below). These pheromones attract male beetles, which bring with them the deadly fungus. Treating multistriatin with dilute aqueous acid at room temperature leads to the formation of a product, $C_{10}H_{20}O_3$, which shows a strong IR peak near 1715 cm^{-1}. Propose a structure for this product.

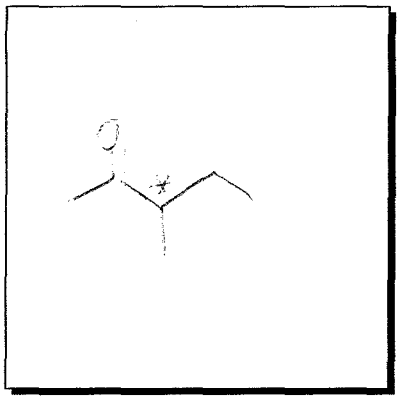


multistriatin

H_3O^+



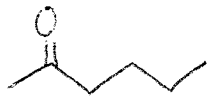
9. (5 points) An optically active compound, $C_6H_{12}O$, gives a positive test with 2,4-DNP but a negative test with Tollens' reagent. What is the structure of the compound?

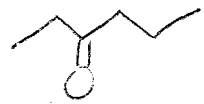


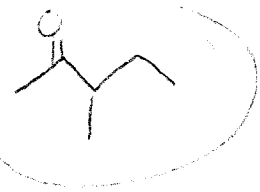
SODAR = 1

+ 2,4-DNP - aldehyde or ketone

- Tollens - ketone







optically active

Extra Credit:

1. Name reactions! Name each of the following.
   a. The reaction shown in #3. Wittig
   b. #6a Grignard
   c. #6b Wolff-Kishner
   d. #6d Baeyer-Villiger
   e. #6f haloform

2. What is "tinnitus"?

Ringing in the ears.