

Student Name (first, last):

EXAM SOLUTION KEY

Student Number:

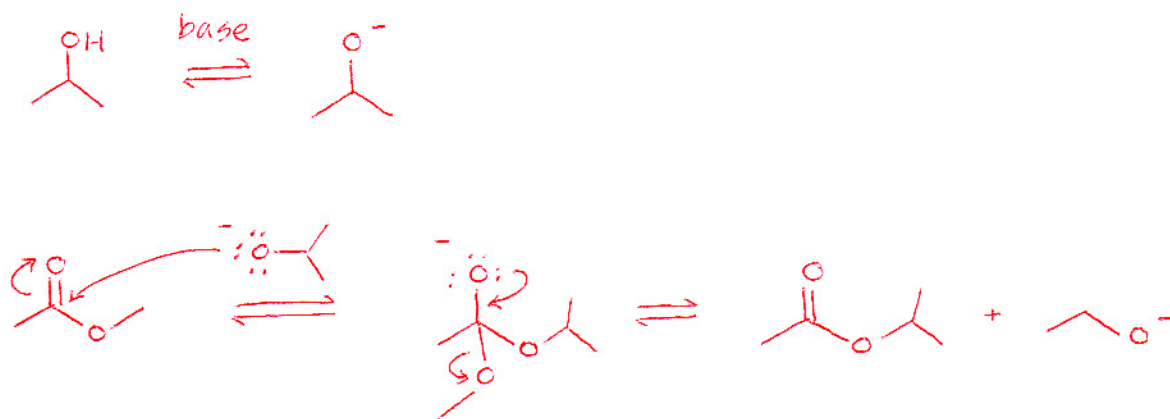
CHEMISTRY 3371  
FIRST MIDTERM EXAMINATION

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February 14, 2008

1. (20 points) Check the correct statements only:

- Alkyl esters of carboxylic acids  $\text{RCOOR}'$  react with lithium aluminum hydride (LAH) to yield primary alcohols  $\text{RCH}_2\text{OH}$  after workup.
- Allylmagnesium bromide reacts with alkyl halide  $\text{RX}$  to yield the hydrocarbon  $\text{CH}_2=\text{CHCH}_2\text{-R}$ .
- Basic hydrolysis of nitriles yields salts of carboxylic acids.
- The allene,  $\text{C}_2\text{H}_5\text{C}=\text{C}=\text{CHCH}_3$ , is not chiral.
- In solution, carboxylic acids do not form dimers by hydrogen bonding.
- A concentrated solution of soap in water is colloidal and contains micelles.
- Enolates of carboxylic esters can be produced by their reaction with lithium diisopropylamide.
- Heating of ammonium salts of carboxylic acids produces carboxamides.
- Trichloroacetic acid has a higher  $\text{pK}_a$  than acetic acid.
- Lithium diethylcuprate reacts with propanoyl chloride to yield diethyl ketone.
- Lithium diethylcuprate reacts with methyl vinyl ketone to yield ethyl vinyl ketone.
- Methyl acetate reacts with ammonia to yield acetamide in good yield.
- Chloroacetic acid reacts with thionyl chloride to yield chloroacetyl chloride.
- Hunsdieker reaction converts a silver salt of a carboxylic acid  $\text{RCOOAg}$  into a bromide  $\text{RBr}$ .
- Rosenmund reduction converts an acyl chloride  $\text{RCOCl}$  into a nitrile  $\text{RCN}$ .
- Butanoic acid reacts with diazomethane to produce methyl butanoate.
- Acetamide reacts with methanol to yield methyl acetate in good yield.
- A typical wavenumber at which the stretching vibration of a carbonyl group appears in the IR spectrum is  $17\,000\text{ cm}^{-1}$ .
- $\text{CO}_2$  reacts with vinylmagnesium bromide to yield acrylic acid after workup,  $\text{CH}_2=\text{CHCOOH}$ .
- Monobromination of carboxylic acids in position  $\alpha$  is best done by reaction with bromine and red phosphorus.

2. (20 pts) Write a plausible mechanism for the base-catalyzed transesterification of ethyl acetate with isopropyl alcohol (include all steps and intermediates and use curved arrows to indicate electron movement in each step).

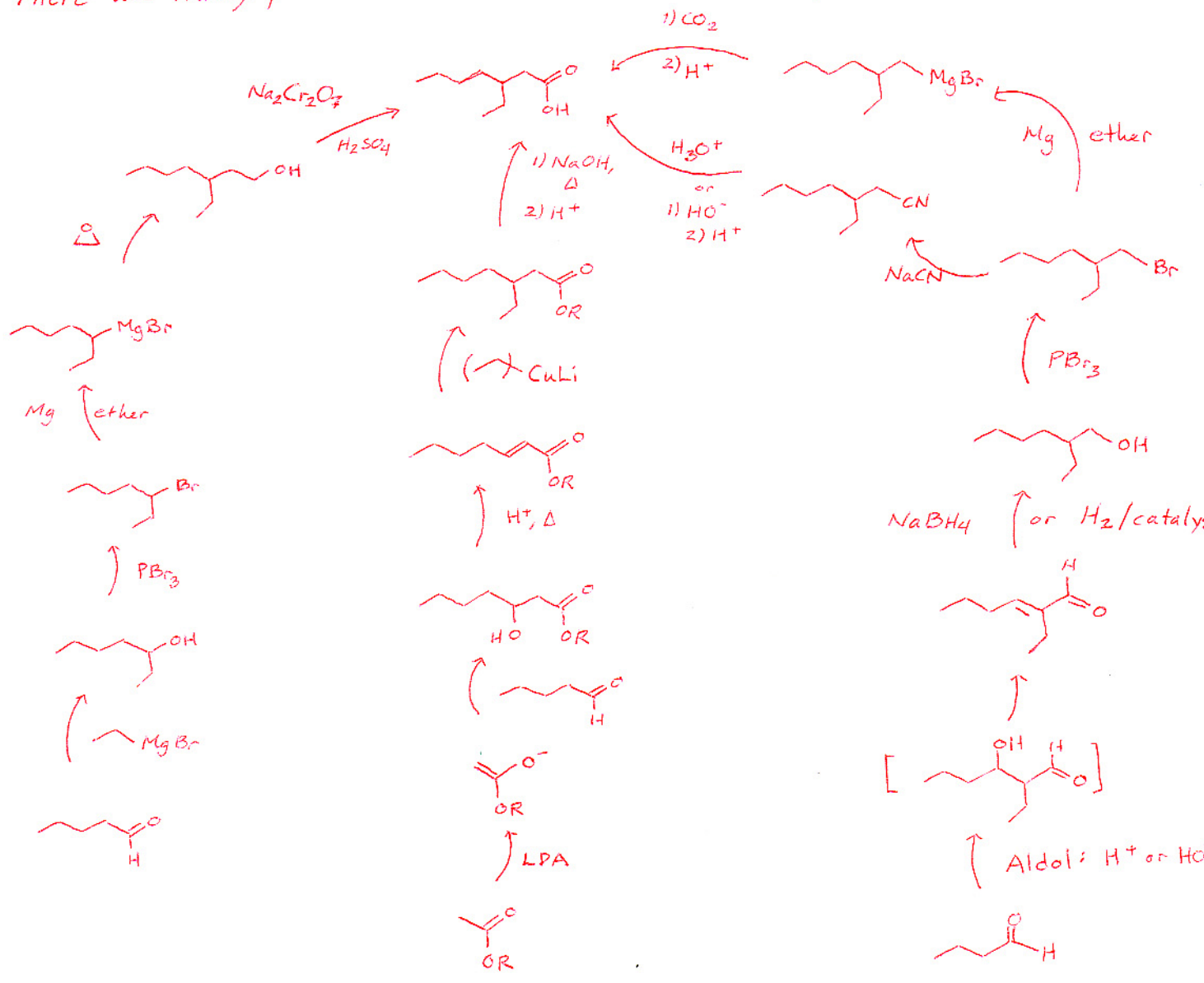


In basic solution, isopropoxide will be a better nucleophile than isopropanol.

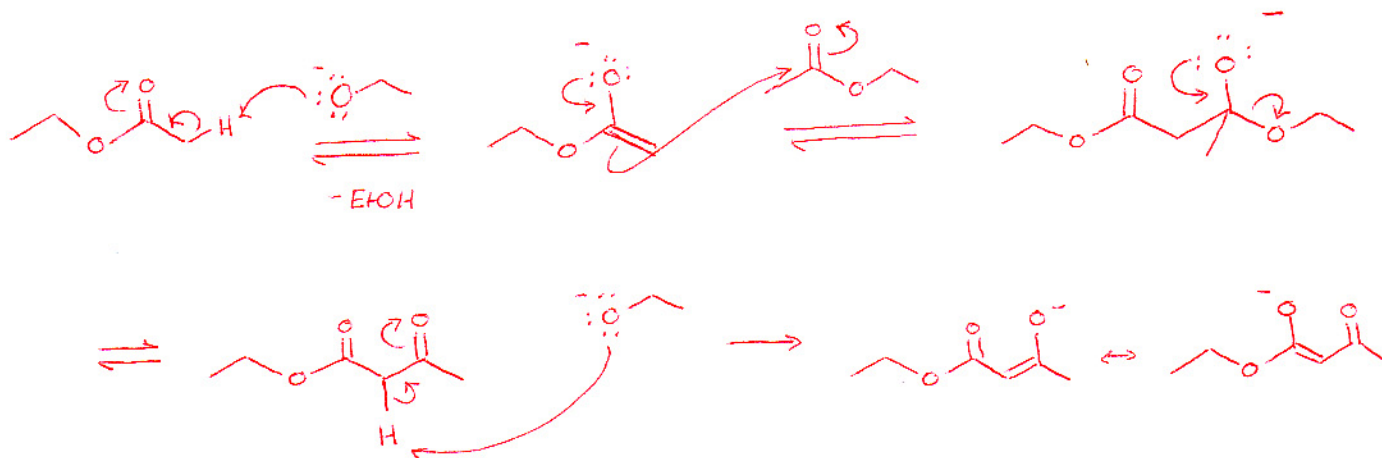
All steps are reversible: This reaction is under equilibrium control.

3. (20 pts) Propose a reaction sequence for the synthesis of 3-ethylheptanoic acid from compounds whose molecule contains no more than five carbons, and inorganic reagents. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents).

There are many possibilities. Consider the following:

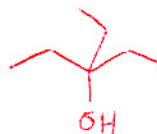


4. (20 pts) Write a plausible mechanism for the Claisen condensation of ethyl acetate in the presence of one full equivalent of sodium ethoxide in ethanol (include all steps and intermediates and use curved arrows to indicate electron movement in each step).

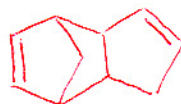


5. (20 pts) Write the structures of **all** principal organic products of the following reactions. You do not need to show solvents, mechanisms, or curved arrows.

(a)  $\text{C}_2\text{H}_5\text{-CO-OCH}_3 + 1. \text{C}_2\text{H}_5\text{MgI (excess)}, 2. \text{H}^+ \rightarrow$



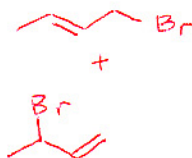
(b) cyclopentadiene, room temperature  $\rightarrow$



(c)  $\text{C}_3\text{H}_7\text{CONH}_2 + \text{SOCl}_2 \text{ (heat)} \rightarrow$



(d) *trans*- $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH} + \text{HBr} \rightarrow$



(e) 2-cyclohexenone + base, excess  $\text{D}_2\text{O}$ , long time  $\rightarrow$

