

Name: KEY

chm228test2sum2014

Problem

1. Draw the structure of the product of the following reaction.



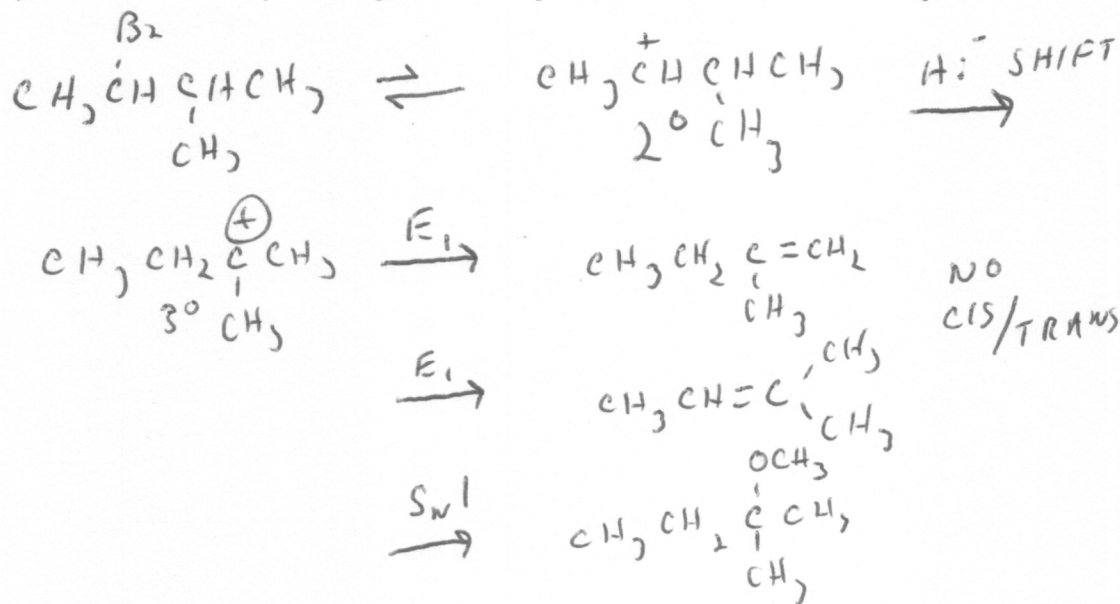
Multiple Choice

Identify the choice that best completes the statement or answers the question.

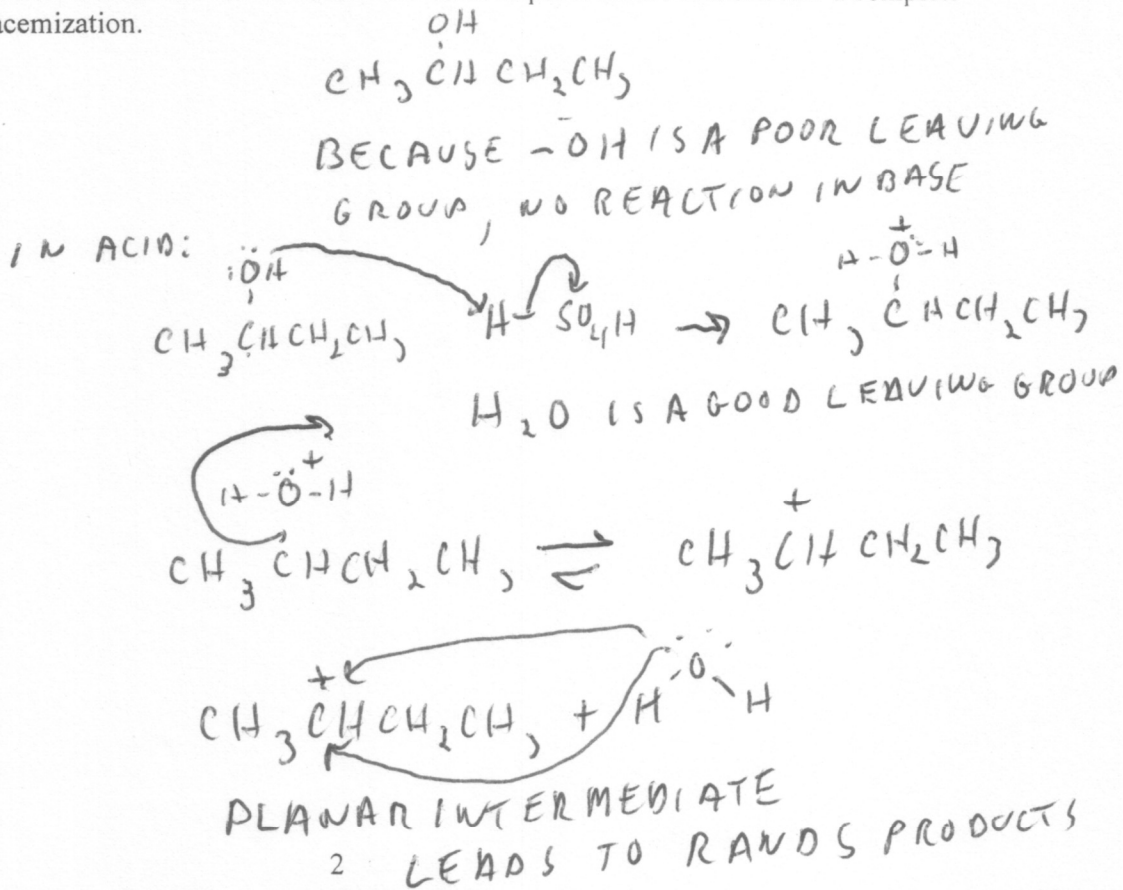
- E 2. Which conditions favor an efficient (fast, high yield)  $S_N2$  reaction between an appropriate alkyl halide and a nucleophile with a charge?
- high concentration of a strong nucleophile, polar protic solvent
  - high concentration of a weak nucleophile, nonpolar solvent
  - low concentration of a strong nucleophile, polar aprotic solvent
  - low concentration of a weak nucleophile, nonpolar solvent
  - high concentration of a strong nucleophile, polar aprotic solvent
- B 3. Which of the following statements about an  $S_N1$  reaction is true?
- the reaction occurs in one-step
  - there is no effect on reaction rate by nucleophile
  - primary alkyl halides react faster than secondary alkyl halides
  - the reaction proceeds with inversion of stereochemistry
  - the reaction is favored by aprotic solvents

Short Answer

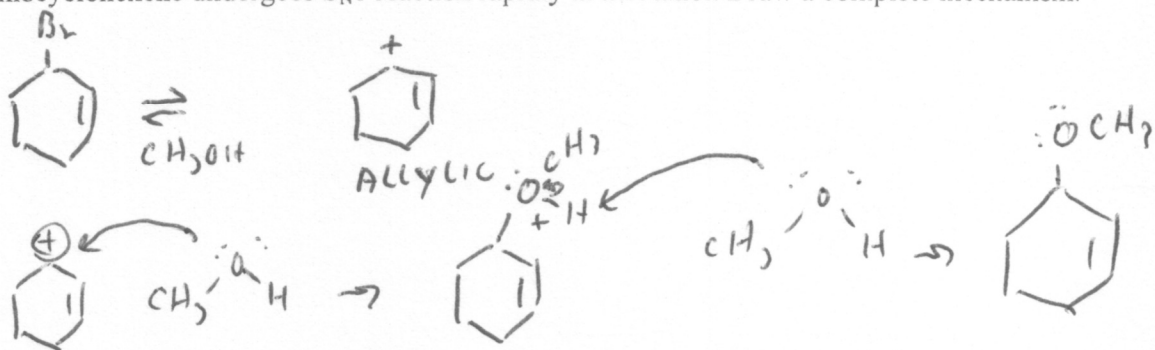
4. Solvolysis (in methanol) of 2-bromo-3-methylbutane gives several products. Draw structures of all products.



5. A pure enantiomer of 2-butanol retains its configuration indefinitely in contact with aqueous base, but is rapidly converted to a racemic mixture in dilute sulfuric acid. Explain these results. Draw a complete mechanism for the racemization.



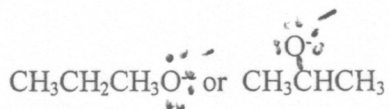
6. 3-bromocyclohexene undergoes  $S_N1$  reaction rapidly in methanol. Draw a complete mechanism.



7. Which is the strongest nucleophile? Choose one from each pair. Briefly explain your choice.

Iodide or chloride

→ POLARIZABLE



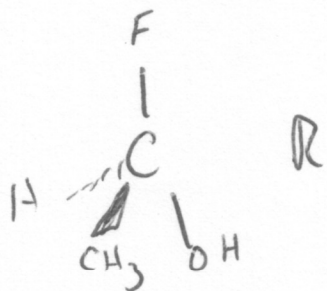
→ "SWIMMER" NO STERIC HINDRANCE

methanol or methoxide

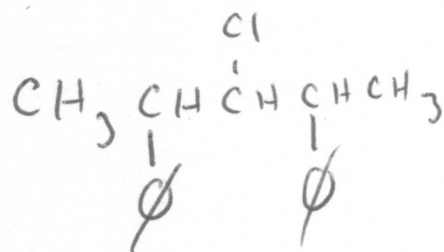
→ BASE FORM

8. Make a stereochemical drawing of the product.

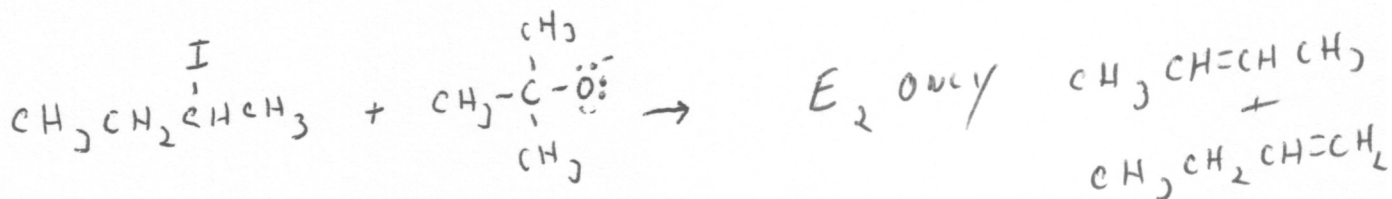
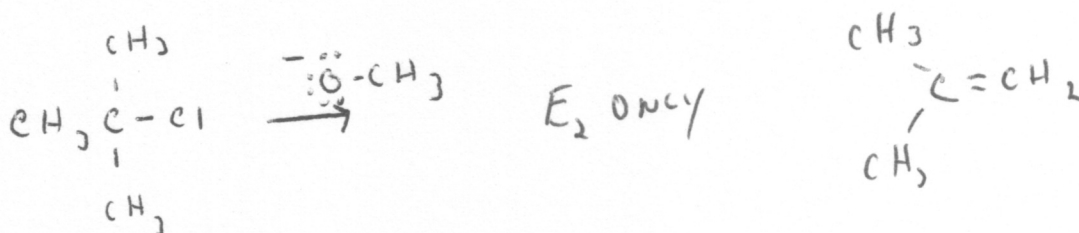
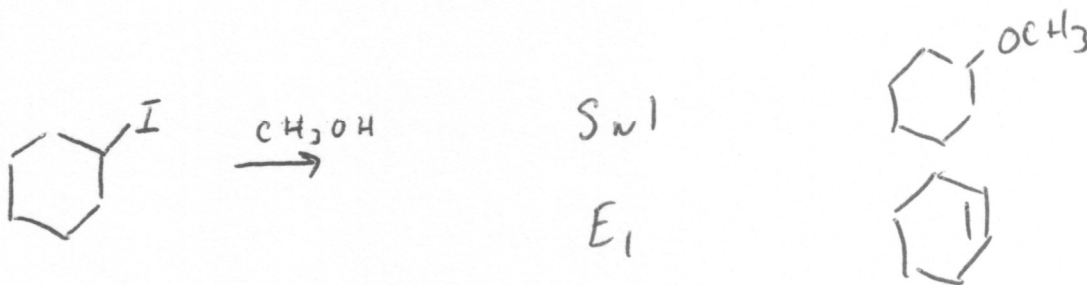
(S)-1-bromo-1-fluoroethane reacts with NaOH.



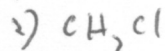
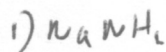
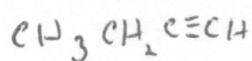
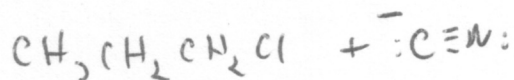
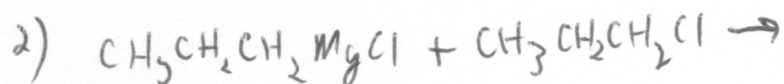
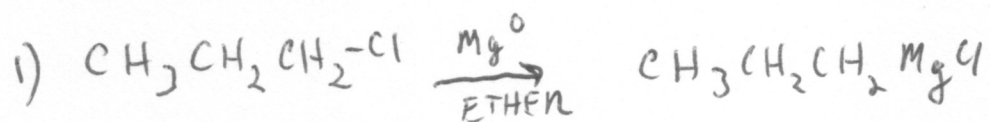
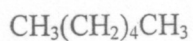
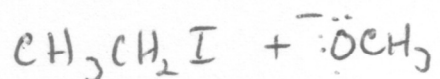
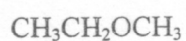
9. Draw the structure of an alkylhalide that will produce only 2,4-diphenylpent-2-ene in an E2 reaction.



10. Draw the structure of the product(s). Indicate the reaction mechanism name (e.g. S<sub>N</sub>2). If more than one mechanism or applies, so indicate.



11. Show how you might prepare the following compounds using a nucleophilic substitution at some step. You may use any reagent with 3 carbons or less.

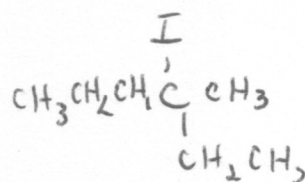


12. Why are the halide ions the only nucleophiles that work well in acidic conditions?

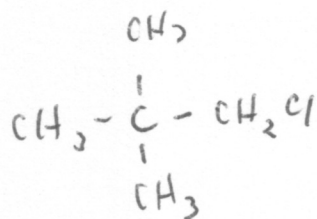
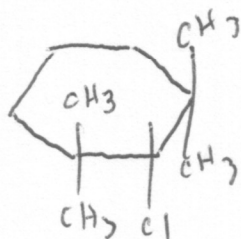
HALIDES ARE CONJUGATE BASES OF STRONG ACIDS  
THEY RETAIN NUCLEOPHILICITY IN ACID BECAUSE THEY ~~HAVE~~ DO NOT GET PROTONATED THE WAY BASIC NUCLEOPHILES DO

13. Propose structures that fit the following descriptions;

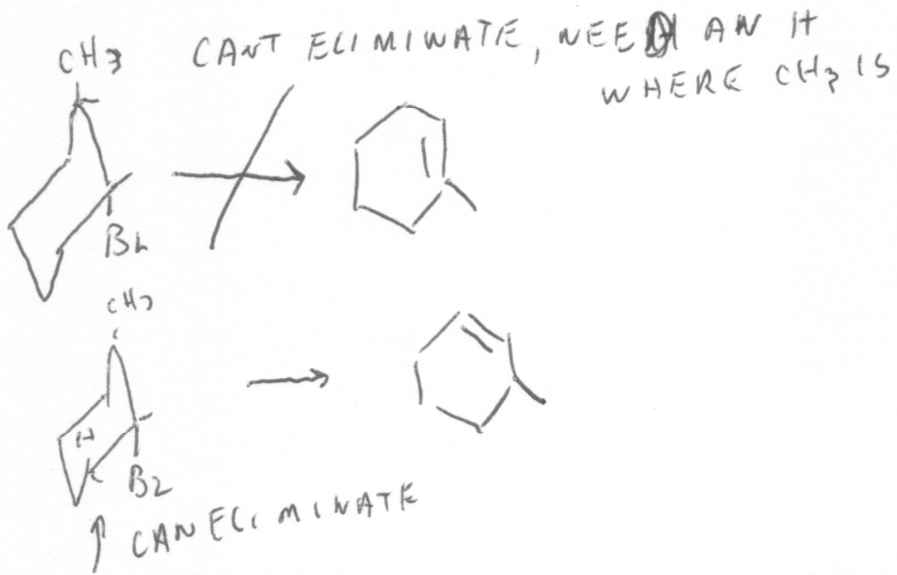
an alkyl halide that gives a mixture of three alkenes upon E2 reaction



an alkyl halide containing at least three carbons that cannot undergo elimination



14. trans-1-bromo-2-methylcyclohexane reacts with KOH via the E2 mechanism to form an alkene. Draw the structure of the product.



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Name: LEE

### CHM 228 Exam 3 Summer 2014

#### Problem

**Instructions:** Draw structures corresponding to each of the following names.

1. Draw:

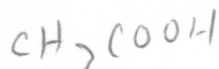
cyclohex-2-enone



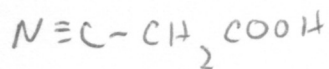
**Instructions:** Consider the data in the table below to answer the following question(s).

Acidities of Substituted Benzoic and Acetic Acids			
pK <sub>a</sub> at 25° C			
Y	Y-CH <sub>2</sub> COOH	Y-C <sub>6</sub> H <sub>4</sub> COOH	
		<i>meta</i>	<i>para</i>
H	4.75	4.19	4.19
CN	2.47	3.64	3.55
OCH <sub>3</sub>	3.57	4.09	4.46

2. Refer to instructions. Which of the acids in the table has the strongest conjugate base?

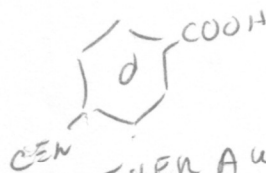


3. Refer to instructions. Explain (using structures) why cyanoacetic acid and methoxyacetic acid are more acidic than their correspondingly substituted benzoic acid counterparts.



↑  
e<sup>-</sup> WITHDRAWN

IS 2 TO ACID (CLOSE)

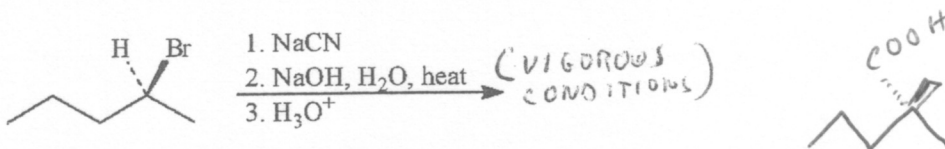


1

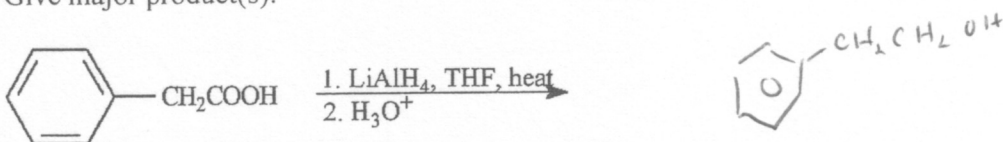
FARTHER AWAY, LESS  
INDUCTIVE EFFECT

**Instructions:** Give the major organic product(s) for each of the following reactions or sequences of reactions. Show all relevant stereochemistry.

4. Give major product(s):



5. Give major product(s):



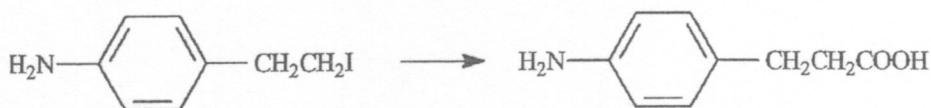
**Instructions:** Carboxylic acids are synthesized from alkyl halides via Grignard reagent carboxylation or nitrile hydrolysis. Choose the best method for affecting each of the following conversions. Explain each of your choices. If neither method is appropriate, explain.

6. Choose best method:



-C≡N WILL NOT WORK  
NO S<sub>N</sub>2 ON 3°  
USE GRIGNARD

7. Choose best method:



GRIGNARD WILL NOT WORK  
N-H IS TOO ACIDIC  
H  
USE -C≡N

### Multiple Choice

Identify the choice that best completes the statement or answers the question.

B 8. Which of the following is the correct order of *decreasing* acid strength (more acidic > less acidic)?

- a.  $\text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{F}_2\text{CHCOOH}$
- b.  $\text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{OH}$
- c.  $\text{CH}_3\text{CH}_2\text{OH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH}$
- d.  $\text{CH}_3\text{COOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{OH}$

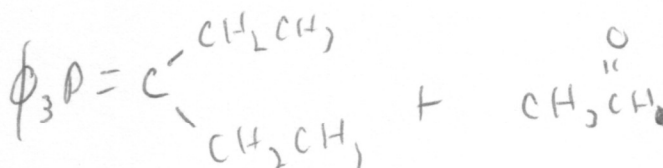
C 9. Which of the following has the highest boiling point?

- a. butanoic acid
- b. butan-2-ol
- c. hexanoic acid
- d. heptan-3-one

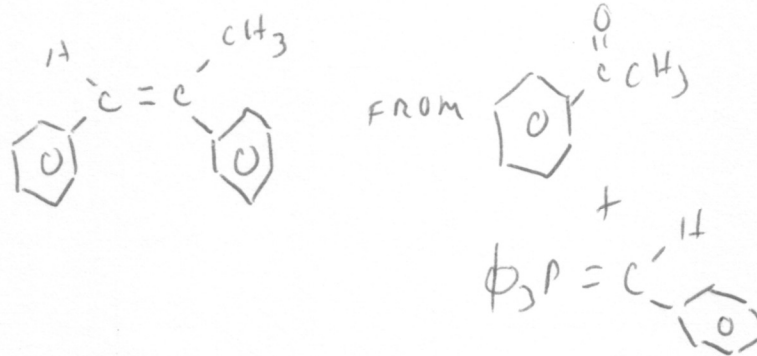
### Short Answer

10. Show how the Wittig synthesis could be used to make these alkenes. A list of reactants is all that is required.

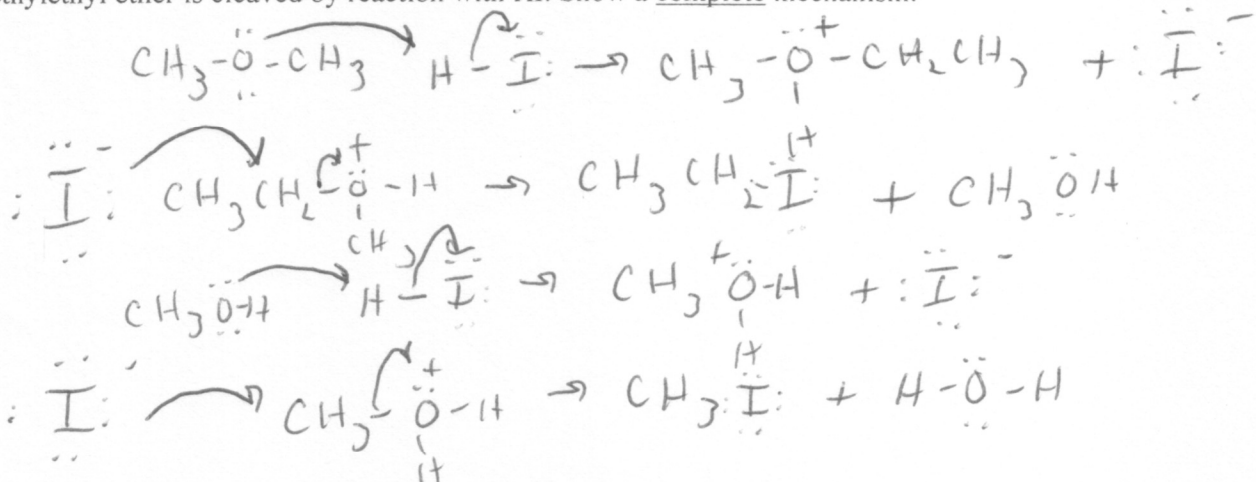
3-ethyl-2-pentene



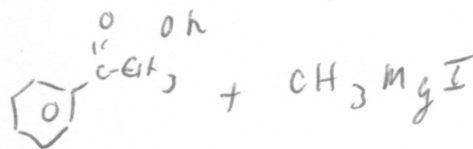
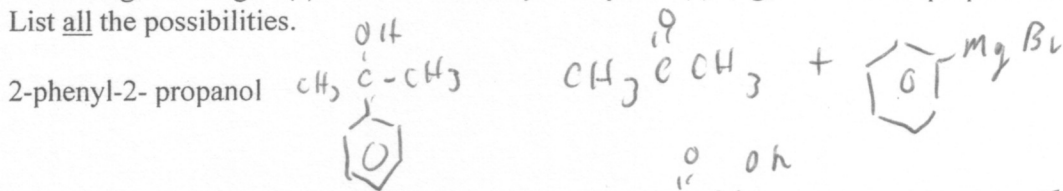
1,2-diphenyl-1-propene



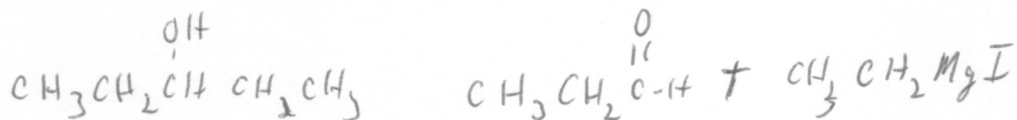
11. Methyl ethyl ether is cleaved by reaction with HI. Show a complete mechanism.



12. What Grignard reagent(s) and what carbonyl compound(s) might be used to prepare the following alcohols? List all the possibilities.



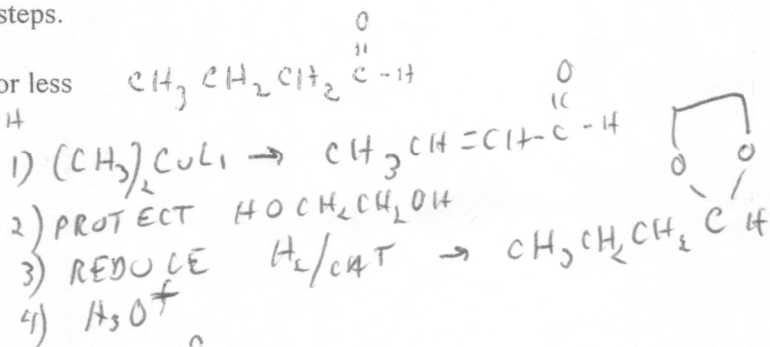
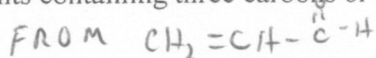
3-pentanol



13. A multistep synthesis is required. Show the steps.

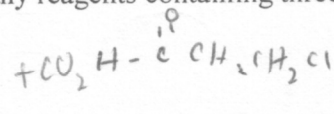
from any reagents containing three carbons or less

1,4 ADDITION

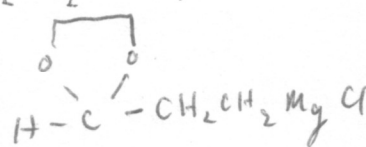


from any reagents containing three carbons or less

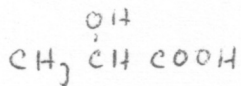
PROTECTED  
GRIGNARD



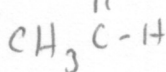
- 1) PROTECT  $\text{HOCH}_2\text{CH}_2\text{OH}$
- 2) GRIGNARD  $\text{Mg}^0/\text{ETHER} \rightarrow$
- 3)  $\text{CO}_2$
- 4)  $\text{H}_3\text{O}^+$



from acetaldehyde



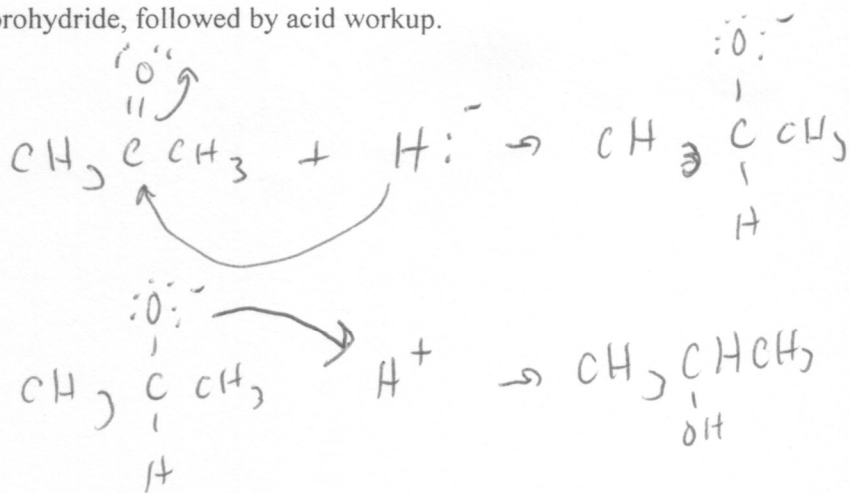
NITRILE  
+  
HYDROLYSIS



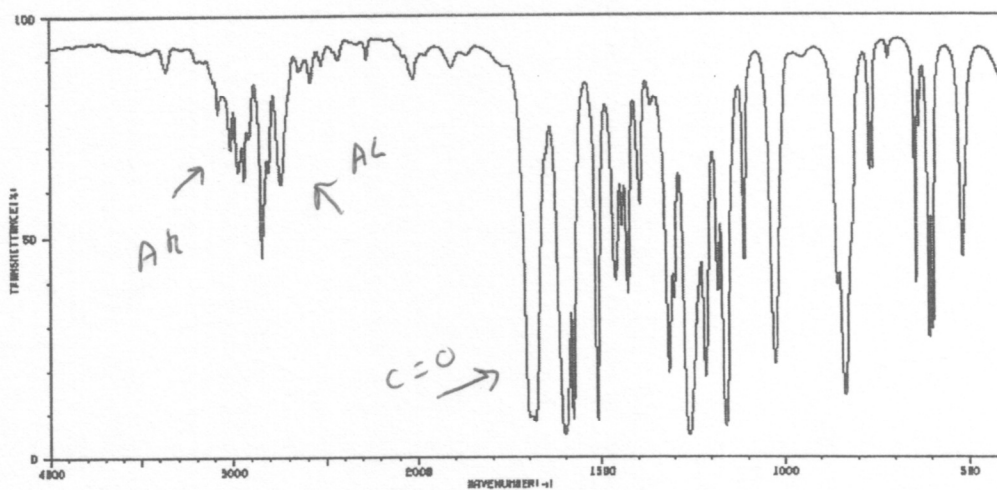
- 1)  $\text{C}\equiv\text{N} \rightarrow \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}\equiv\text{N}$
- 2)  $\text{H}^+$  WORKUP  $\rightarrow$
- 3)  $\text{H}_3\text{O}^+$  VIGOROUS HYDROLYSIS

14. Show a complete mechanism.

acetone reacts with sodium borohydride, followed by acid workup.



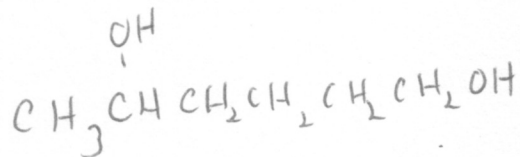
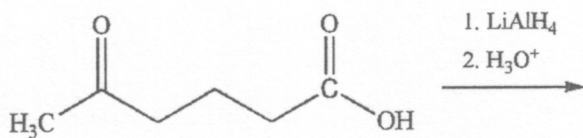
15. Based on the following IR spectrum, name the functional group(s)



Spectrum obtained from: SDBSWeb : <http://riodb01.ibase.aist.go.jp/sdbs/> (National Institute of Advanced Industrial Science and Technology, 11-06-08)

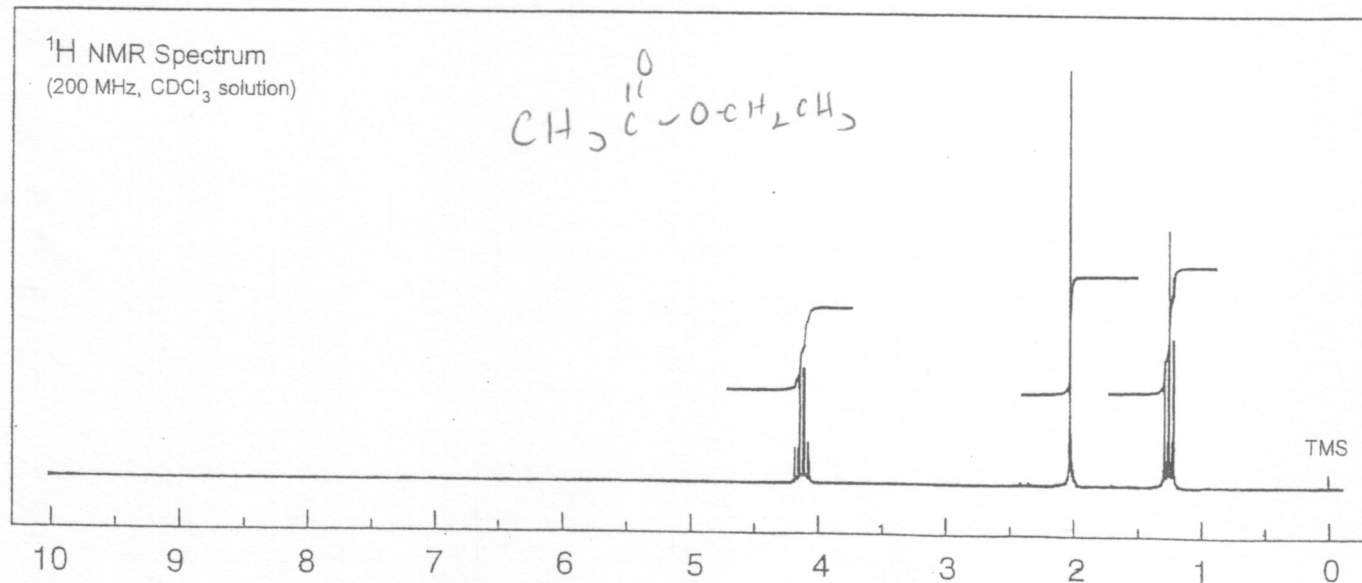
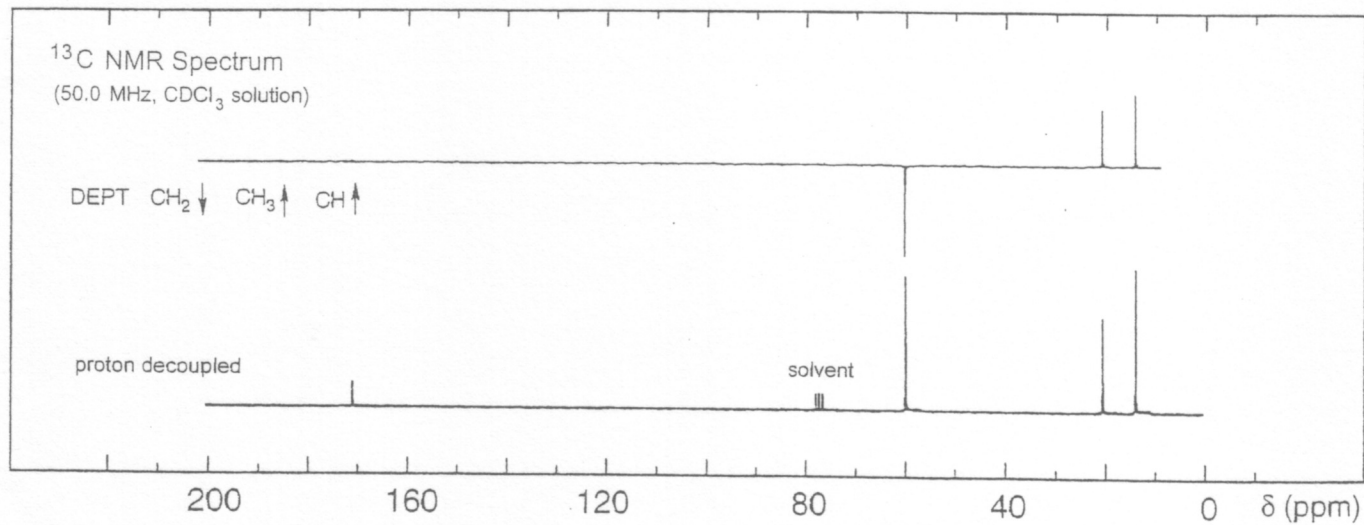
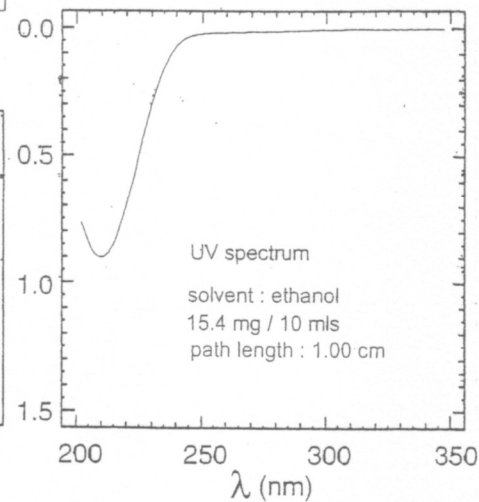
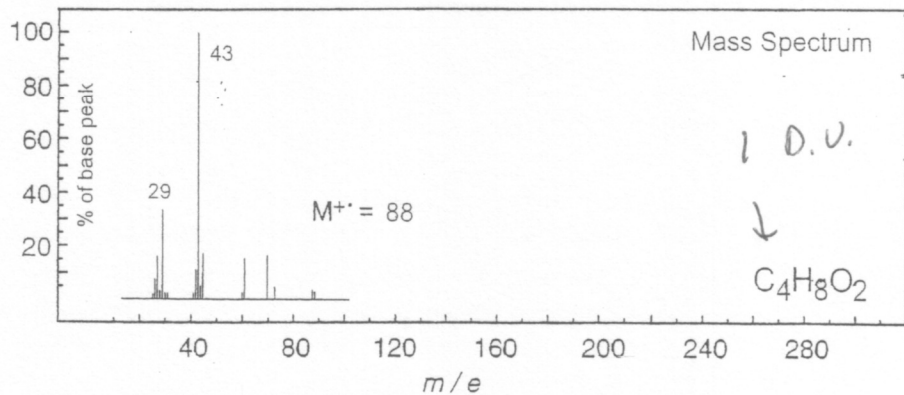
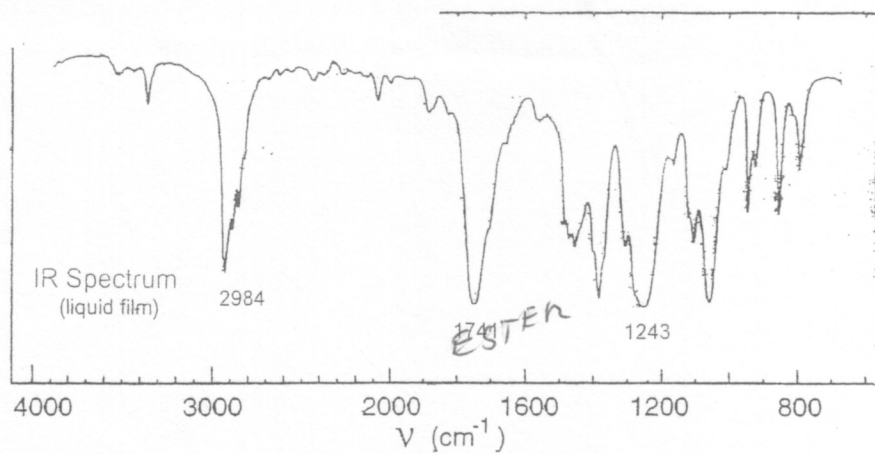
CONJUGATED AROMATIC ALDEHYDE

16. What is the major organic product obtained from the following reaction?



Identify the compound.

# Problem 3



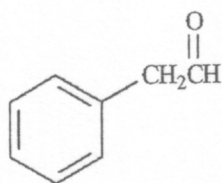
Name: KEY

### CHM 228 Exam 4 Summer 2014

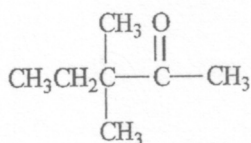
#### Multiple Choice

Identify the choice that best completes the statement or answers the question.

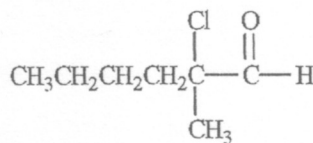
- C 1. Which of the following best describes the key mechanistic steps in the reaction of an acid chloride and an alcohol to form an ester?
- elimination followed by addition
  - addition followed by decarboxylation
  - addition followed by elimination
  - substitution followed by addition
- D 2. Which of the following is the correct order of decreasing reactivity in hydrolysis reactions (more reactive > less reactive)?
- anhydrides > amides > acid chlorides
  - amides > acid chlorides > anhydrides
  - anhydrides > acid chlorides > amides
  - acid chlorides > anhydrides > amides
- E 3. Which of the following would form an enolate ion on treatment with a base?



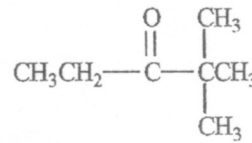
A



B



C



D

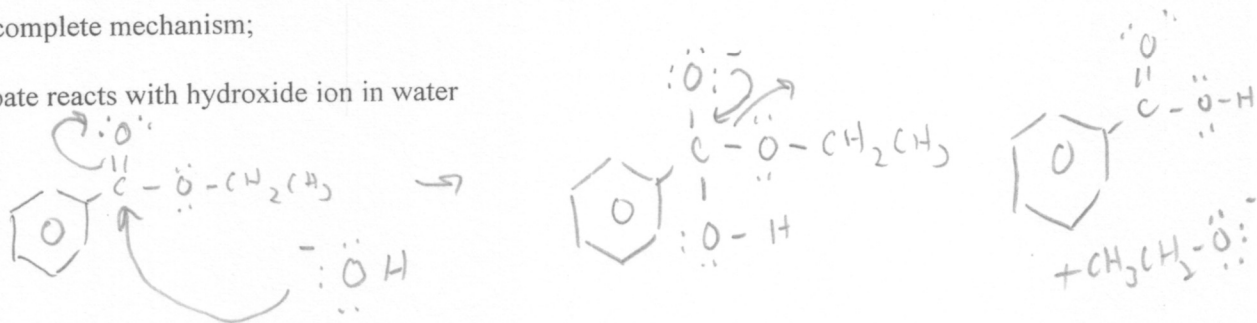
- A
- B
- C
- D
- All of these except C



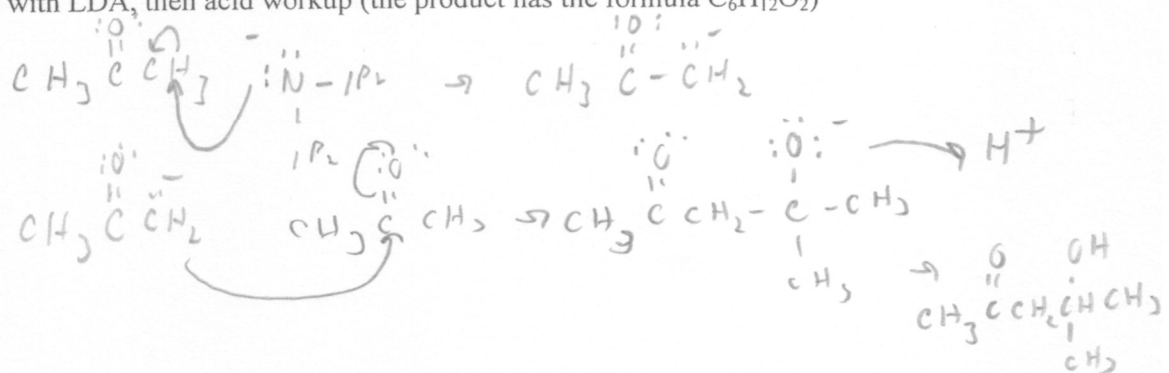
Short Answer

4. Show the complete mechanism;

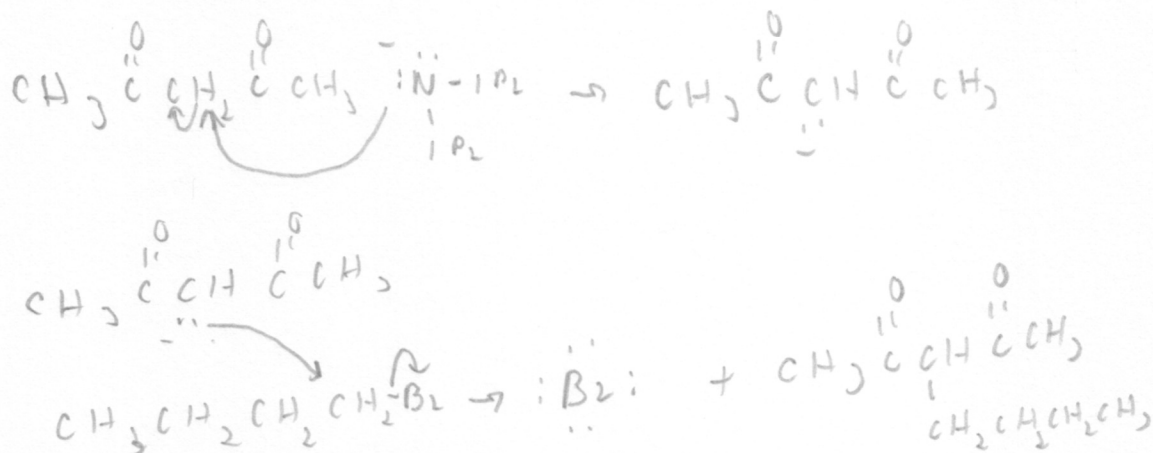
ethylbenzoate reacts with hydroxide ion in water



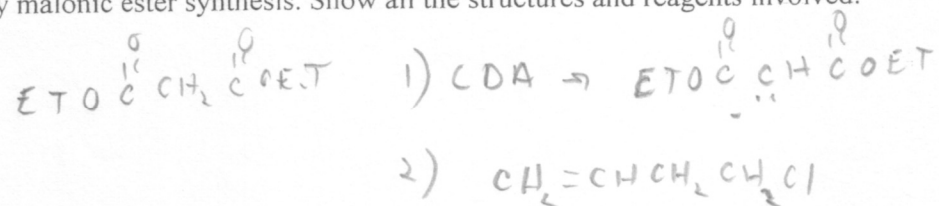
acetone is treated with LDA, then acid workup (the product has the formula  $\text{C}_6\text{H}_{12}\text{O}_2$ )



2,4-pentanedione is treated with LDA, then reacts with n-butyll bromide



5. Hex-5-enoic acid can be made by malonic ester synthesis. Show all the structures and reagents involved.

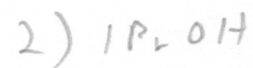
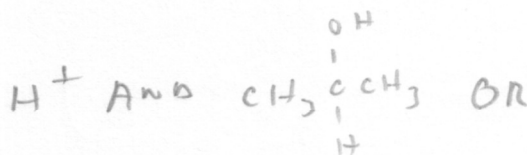


6. Show how you could prepare the following compounds from butanoic acid. Only a list of reagents is required.

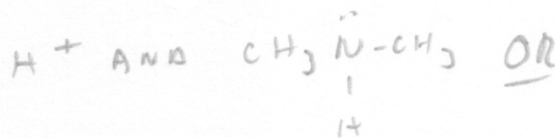
butan-1-ol



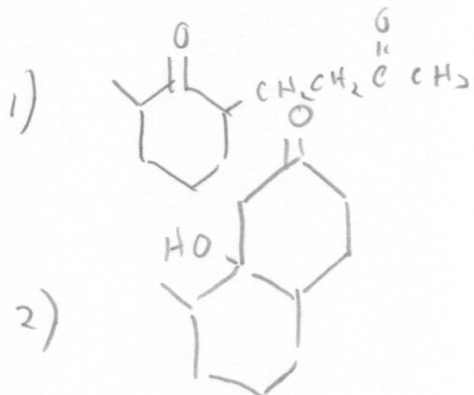
isopropylbutanoate



N,N-dimethyl butanamide

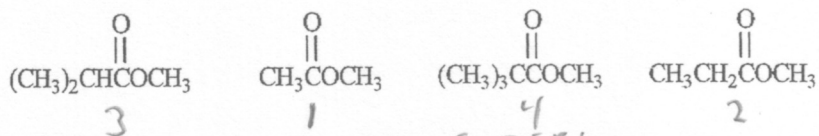


7. 2-methyl cyclohexanone is treated with LDA and then reacts with but-3-en-2-one. Draw the structure of the product. The product then reacts with LDA to form a new product. Draw its structure.



### Problem

8. Rank the following compounds in order of *increasing* reactivity with a nucleophile. (1 = most, 4 = least)



ALL ESTERS

ALL ALKYLs SO INDUCTIVE EFFECTS  
ARE VERY SIMILAR

SO, MUST BE STERIC