

# 國立臺灣師範大學 100 學年度碩士班招生考試試題

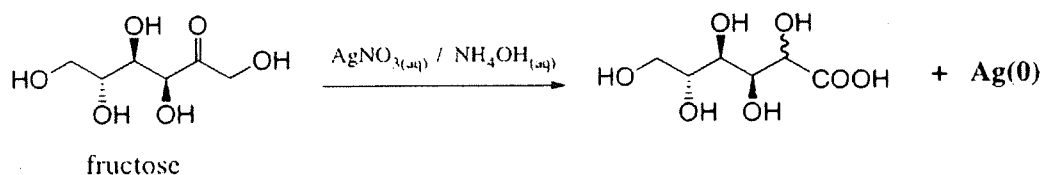
科目：有機化學

適用系所：化學系

注意：1. 本試題共 10 頁，請依序在答案卷上作答，並標明題號，不必抄題。2. 答案必須寫在指定作答區內，否則不予計分。

**答題注意事項：**作答時需按題號順序依次作答，每大題內的小題亦需按小題號順序作答，否則皆不予計分。

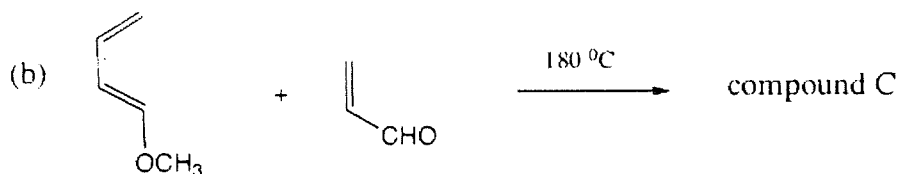
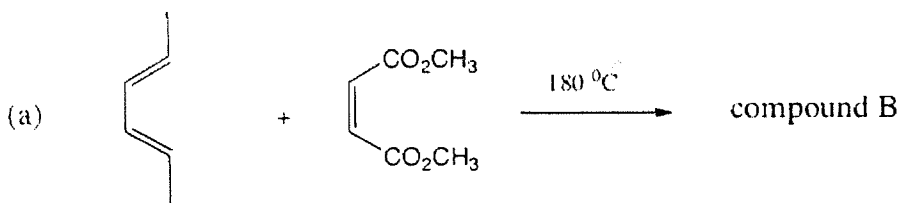
1. Although fructose has a ketone functional group, it converts to acid upon treating with Tollen's reagents ( $\text{AgNO}_3(\text{aq})$ , and  $\text{NH}_4\text{OH}(\text{aq})$ ) and a silver mirror is found. Draw a reasonable reaction mechanism for the transformation. (6 points)



2. When cyclohexanol is treated with dimethylsulfoxide (DMSO), oxalyl chloride and triethylamine at  $-60^\circ\text{C}$  in dichloromethane for 2 h, a major compound (A) is formed. The IR spectrum of A shows a significant absorption at  $1750\text{ cm}^{-1}$ , and  $^{13}\text{C}$  NMR shows a peak at 220 ppm. Based on the above information, answer the following questions.

- (a) Draw the structure for compound A. (2 points)  
 (b) Propose a reaction mechanism for the above transformation. (6 points)

3. Diels-Alder reaction is considered a very efficient way to synthesize 6-membered ring skeletons with high regio- and stereoselectivities. Draw the products for the following two reactions. Show the right stereochemistry for both two products (Compound B and C, 6 points each).

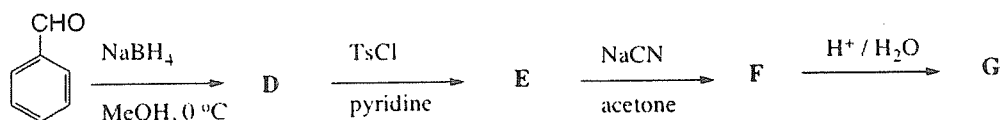


4. Draw the chemical structures for the following compounds. (2 points each).

(a) aniline (b) *p*-xylene (c) pyridine (d) ethylene oxide (e) formaldehyde

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5. Finish the following synthetic schemes. Write compounds D, E, F and G. (2 points each)



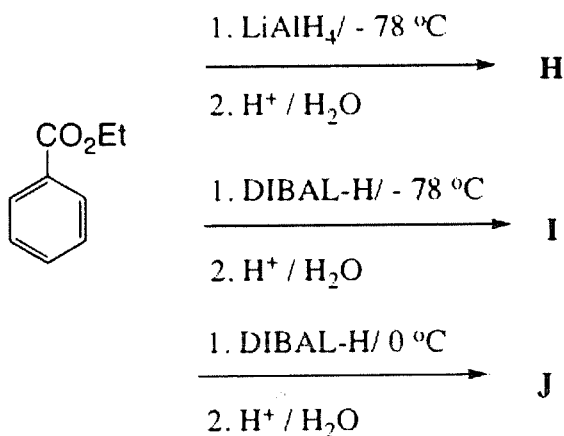
The spectroscopic data are for compound G:

IR : broad band at  $2900 - 3500\text{ cm}^{-1}$ , finger print peaks at  $1800$  to  $2000\text{ cm}^{-1}$ , broad intensive peak at  $1700\text{ cm}^{-1}$ .

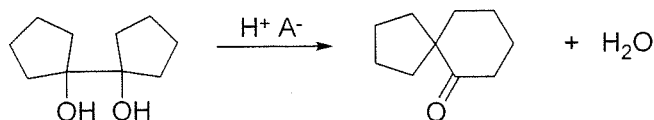
$^{13}\text{C}$  NMR : 1  $\text{sp}^2$  carbon at  $180\text{ ppm}$ ; 4  $\text{sp}^2$  carbons around  $120\text{ ppm}$ ; 1  $\text{sp}^3$  carbon at  $40\text{ ppm}$ .

$^1\text{H}$  NMR : only 5 peaks are detected.

6. Under different reaction conditions as shown below, ethyl benzoate can be reduced to various compounds. Draw the structures for compounds H, I, and J. (2 points each)

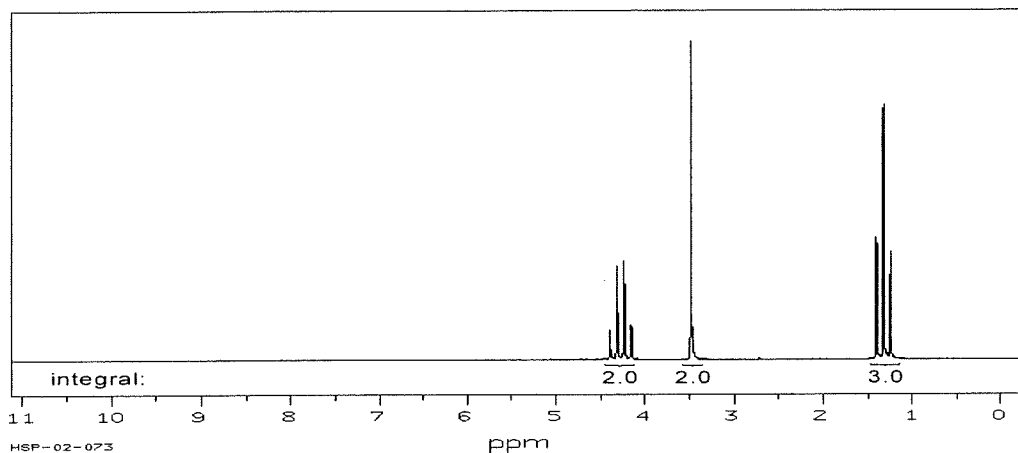


7. Write a detailed mechanism that explains the following transformation: (5 points)



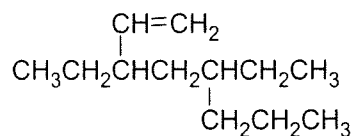
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8. The mass spectrum of the compound shows a molecular ion at  $m/z = 113$ , and the elementary analysis shows that this compound contains 4 different elements. The IR spectrum has characteristic absorptions at  $2270$  and  $1735\text{ cm}^{-1}$ , and the  $^{13}\text{C}$  NMR spectrum has five signals. The proton NMR spectrum is shown. Determine the structure of the compound. (5 points)



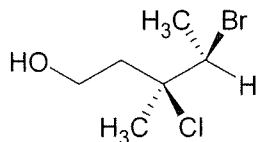
9. 選擇題 (每題 2 分):

(1). What is the IUPAC name of the following compound?



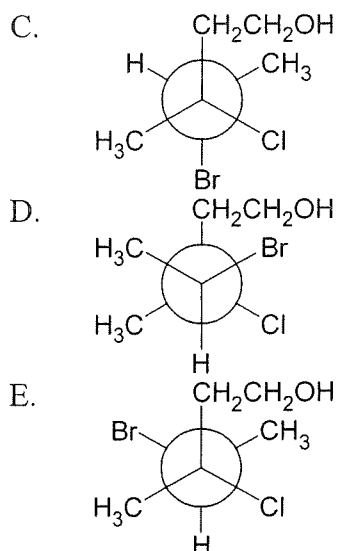
- A. 3-ethyl-propyl-1-heptene
- B. ethyl-3-vinyloctane
- C. 4,6-diethyl-1-octene
- D. 3,5-diethyl-1-octene
- E. 4,6-diethyl-7-octene

(2). What is the correct Newman projection for the following molecule?

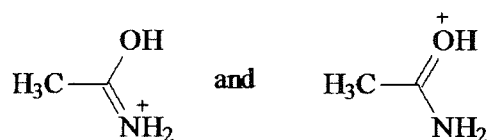


- A.
- B.

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(3). What is the relationship between the following two structures?



- A. resonance forms
- B. stereoisomers
- C. constitutional isomers
- D. tautomers
- E. diastereomers

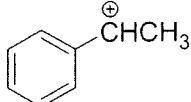
(4). Which of these compounds has the highest pKa?

- A. phenol
- B. 3-nitrophenol
- C. 4-nitrophenol
- D. benzoic acid
- E. *p*-toluenesulfonic acid

(5). Which of the following has the largest acid dissociation constant, Ka?

- A.  $\text{CH}_3\text{CH}_3$
- B.  $\text{H}_2\text{C}=\text{CH}_2$
- C.  $\text{HC}\equiv\text{CH}$
- D.  $\text{CH}_3\text{CH}_2\text{OH}$
- E.  $\text{CH}_3\text{COOH}$

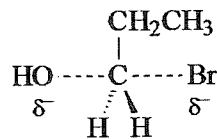
(6). Which of the following carbocations would most readily undergo a 1,2-hydride shift?

- A.  $(\text{CH}_3)_3\text{C}^+$
- B. 
- C.  $\text{CH}_3\text{CH}^+\text{C}(\text{CH}_3)_3$

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- D.  $\text{CH}_3\text{CH}^+\text{CH}(\text{CH}_3)_2$   
 E.  $(\text{CH}_3)_2\text{C}^+\text{CH}_2\text{CH}_3$

(7). The species shown below represents the transition state for the:

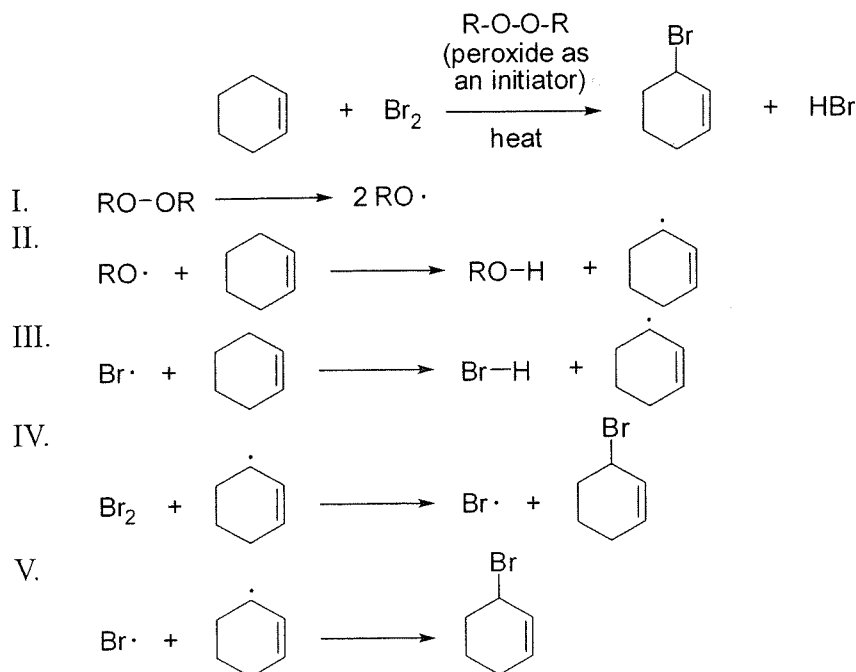


- A. reaction of 1-propanol with HBr  
 B. reaction of 1-bromopropane with NaOH  
 C. elimination of HBr from 1-bromopropane  
 D. addition of HBr to propene with peroxides  
 E. addition of  $\text{Br}_2$  to propene in  $\text{H}_2\text{O}$

(8). Which of the following compounds most readily undergoes a unimolecular elimination ( $\text{E1}$ ) reaction?

- A.  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$   
 B.  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{Br}$   
 C.  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$   
 D.  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{Br}$   
 E.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$

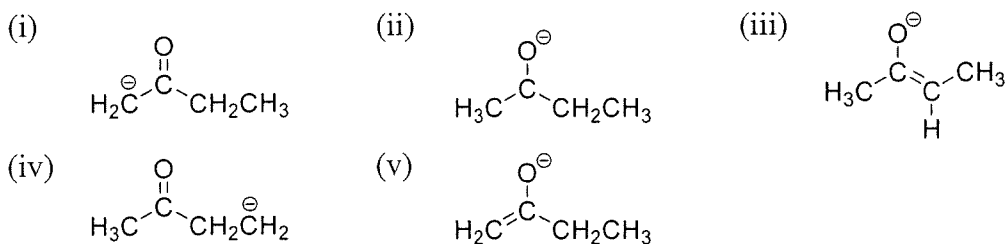
(9). Which of the following is(are) the propagation step(s) in the bromination of cyclohexene shown below:



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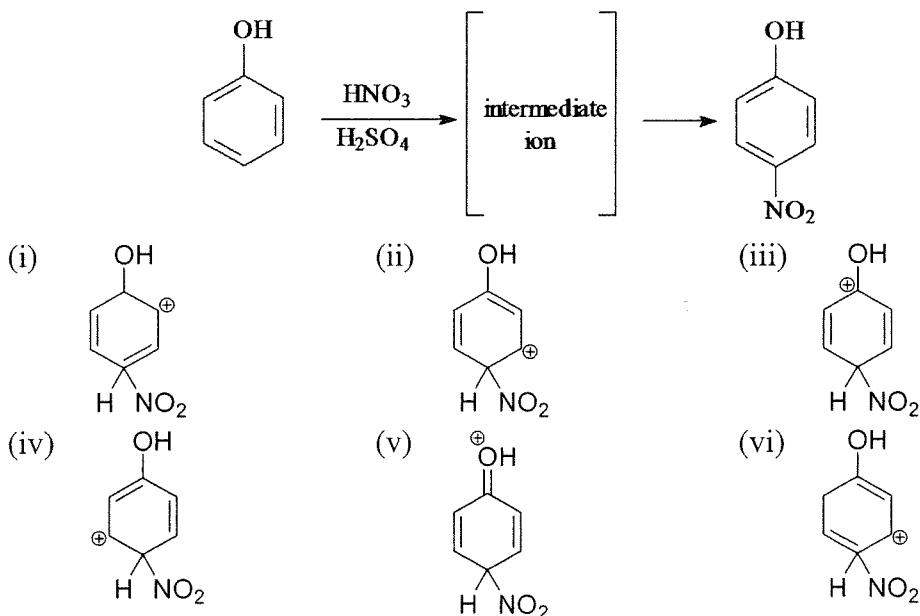
- A. I and II
- B. I only
- C. III, IV and V
- D. II and IV
- E. III and IV

(10). Which of the following are contributing resonance structures of the enolate formed by the treatment of 2-butanone with a base?



- A. (ii), (iv), (v)
- B. (i), (iii), (v)
- C. (ii), (iv), (v)
- D. (i), (iii), (iv), (v)
- E. (iii), (v)

(11). Which of the following are valid resonance structures for the intermediate species in the reaction shown below?



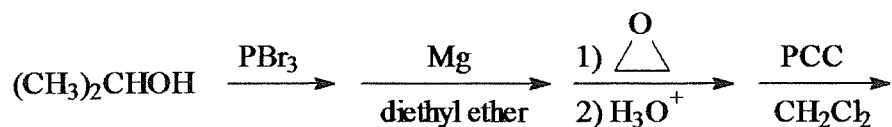
- A. (i), (ii), (iii), (iv), (v), (vi)
- B. (ii), (iii), (iv)
- C. (ii), (iii), (v)
- D. (ii), (iii), (iv), (v)
- E. (i), (ii), (iii)

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(12). Which of the following syntheses gives 3-methyl-1-hexanol?

- A. 
$$\text{3-methylhex-1-ene} \xrightarrow{\text{OsO}_4} \xrightarrow[\text{H}_2\text{O}]{\text{Na}_2\text{SO}_3}$$
- B. 
$$\text{2-bromopentane} \xrightarrow[\text{diethyl ether}]{\text{Mg}} \xrightarrow[2) \text{H}^+]{1) \text{epoxide}}$$
- C. 
$$\text{3-bromopentane} \xrightarrow[\text{diethyl ether}]{\text{Mg}} \xrightarrow[2) \text{H}^+]{1) \text{H}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{H}}$$
- D. 
$$\text{1-bromobutane} \xrightarrow[\text{diethyl ether}]{\text{Mg}} \xrightarrow[2) \text{H}^+]{1) \text{H}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3}$$
- E. 
$$\text{2-bromohexane} \xrightarrow[\text{diethyl ether}]{\text{Mg}} \xrightarrow[2) \text{H}^+]{1) \text{H}_2\text{C}=\text{O}}$$

(13). What is the final product of the following sequence of reactions?



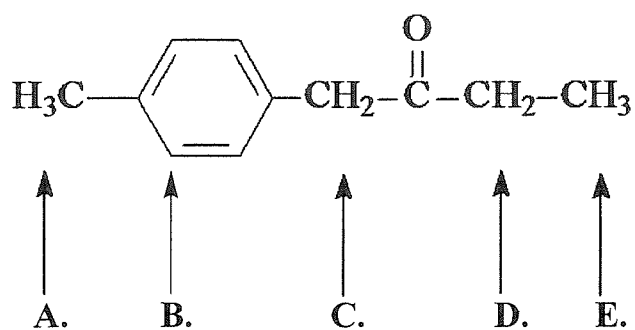
- A.  $(\text{CH}_3)_2\text{CHOCH}_2\text{CH}_2\text{OH}$
- B.  $(\text{CH}_3)_2\text{CH}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3$
- C.  $(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$
- D.  $(\text{CH}_3)_2\text{CHCH}_2\text{CO}_2\text{H}$
- E.  $\text{CH}_3-\overset{\text{Br}}{\underset{|}{\text{CH}}}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$

(14). A mixture of 1-hexanol and hexanoic acid in diethyl ether is shaken with an aqueous sodium bicarbonate solution. Which line below correctly describes the major organic species in the two resulting immiscible solutions?

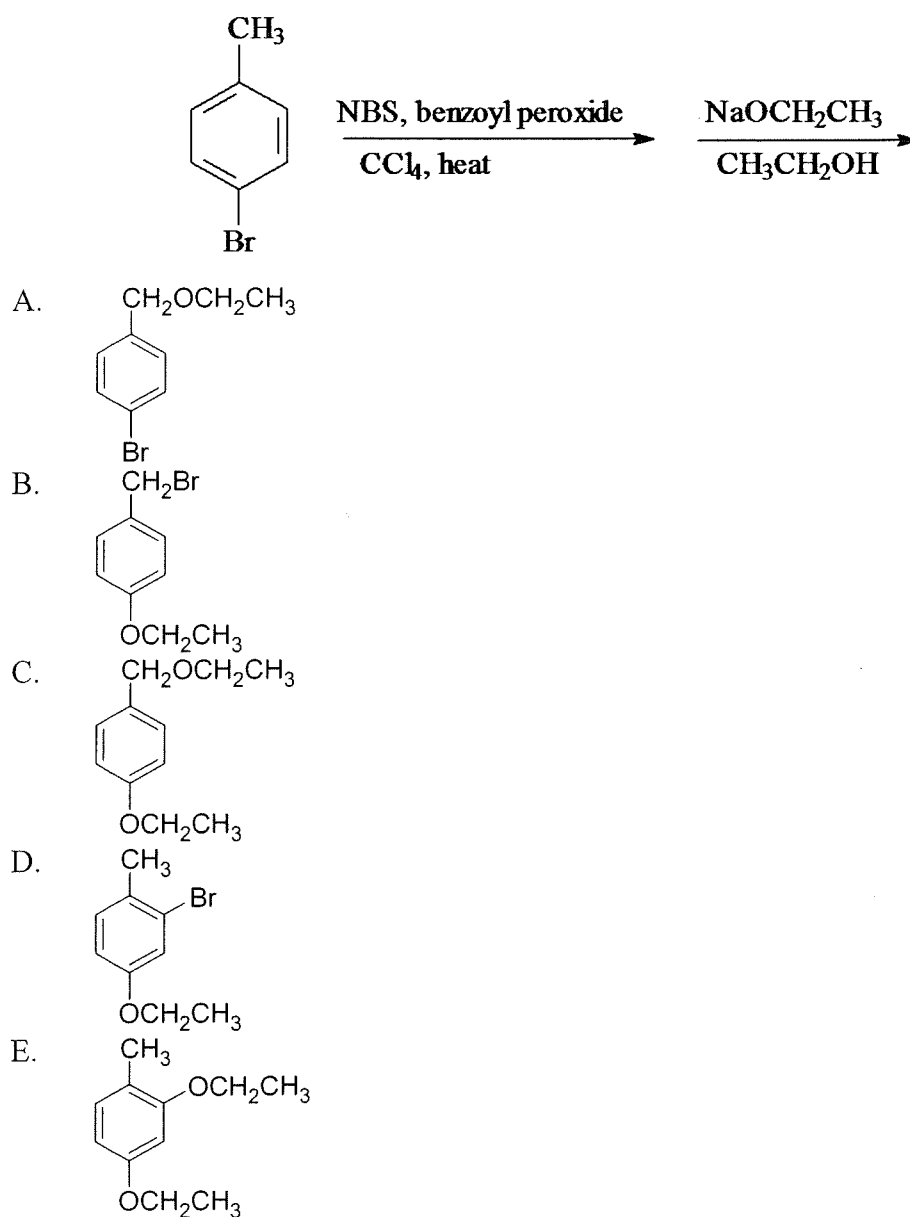
- | <u>ether solution</u>          | <u>sodium bicarbonate solution</u> |
|--------------------------------|------------------------------------|
| A. hexanoic acid               | 1-hexanol                          |
| B. 1-hexanol                   | hexanoic acid                      |
| C. sodium hexanoate            | 1-hexanol                          |
| D. 1-hexanol                   | sodium hexanoate                   |
| E. 1-hexanol and hexanoic acid | none                               |

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(15). Identify the most acid hydrogen for the following compound:



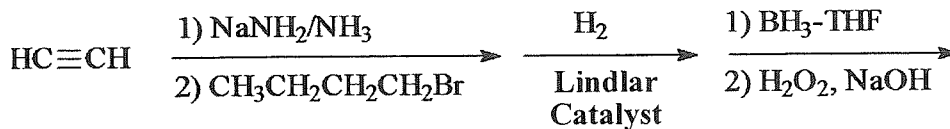
(16). What is the major product of the following reaction?





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(17). What is the product of the following reaction sequence?

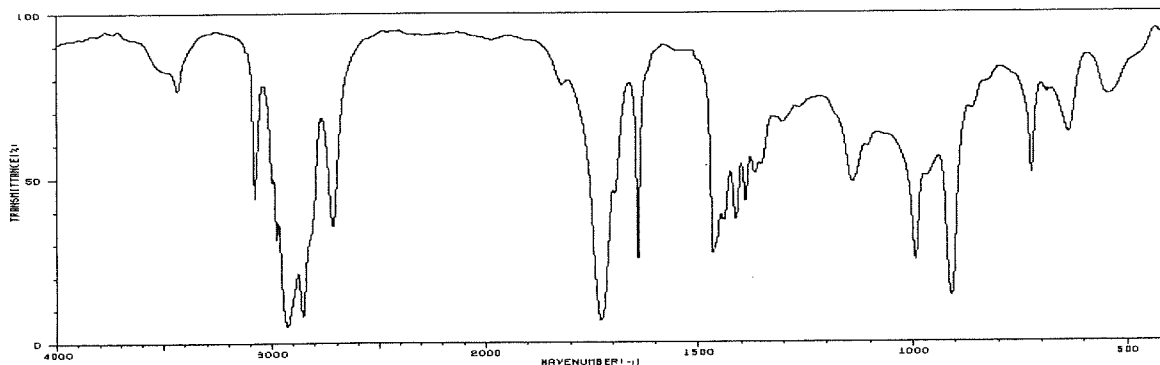


- A. 1-hexanol  
B. 2-hexanol  
C. 1,2-hexanediol  
D. 1-hexene  
E. *trans*-2-hexene

(18). Which of the following is the aldol condensation product of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ ?

- A.  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\text{CH}_3$
- B.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CH}$
- C.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\underset{\text{CHCH}_3}{\text{CH}}$
- D.  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}\underset{\text{CH}_2\text{CH}_3}{\text{CH}}\overset{\text{O}}{\parallel}\text{CH}$
- E.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\overset{\text{O}}{\parallel}\text{C}\underset{\text{CH}_2\text{CH}_3}{\text{CH}}$

(19). Identify which one of the following compounds has the infrared spectrum shown below:



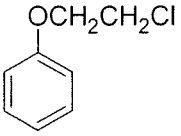
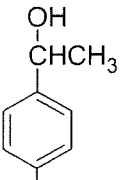
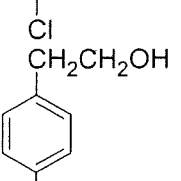
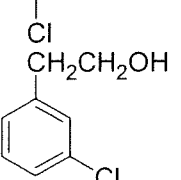
- A. 3-methylcyclohexanone  
B. 10-undecenal  
C. methyl pentanoate  
D. 3-butenic acid  
E. octanoic acid

(20). The proton NMR of a compound,  $C_8H_9ClO$ , has the following peaks. Which compound

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below best fits the data?

broad singlet	$\delta$ 2.41 (1H)
triplet	$\delta$ 2.75 (2H)
triplet	$\delta$ 3.69 (2H)
doublet	$\delta$ 7.02 (2H)
doublet	$\delta$ 7.50 (2H)

- A. 
- B. 
- C. 
- D. 
- E. 