National Exams May 2017

BS-12, Organic Chemistry

3 hours duration

NOTES:

1. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper, a clear statement of any assumptions made.

2. This is a CLOSED BOOK EXAM.
   A Casio or Sharp approved calculator is permitted.

   One aid sheet written on both sides is permitted.

3. TEN (10) questions constitute a complete exam paper.
   The first 10 questions as they appear in the answer book will be marked.

4. Each question is of equal value.

Question 1:

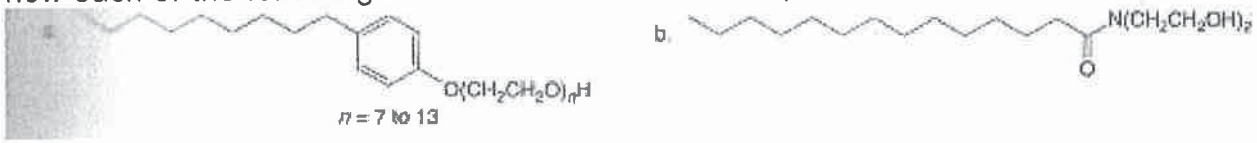
a) Dimethyl ether (CH_3OCH_3) and ethanol are isomers but CH_3OCH_3 has a pKa of 40 and CH_3CH_2OH has a pKa of 16. Explain why these pKa values are so different.

b) The indicated hydrogel in 1,4 pentadiene is more acidic than the indicated hydrogen in pentane. Explain.

1,4-pentadiene pentane

Question 2:

Unlike soap, which is ionic, some laundry detergents are neutral molecules. Explain how each of the following molecules behaves like soap and cleans away dirt.



Question 3:

Although penicillin G has two amide functional groups, one is much more reactive than the other. Which amide is more reactive and why?

penicillin G

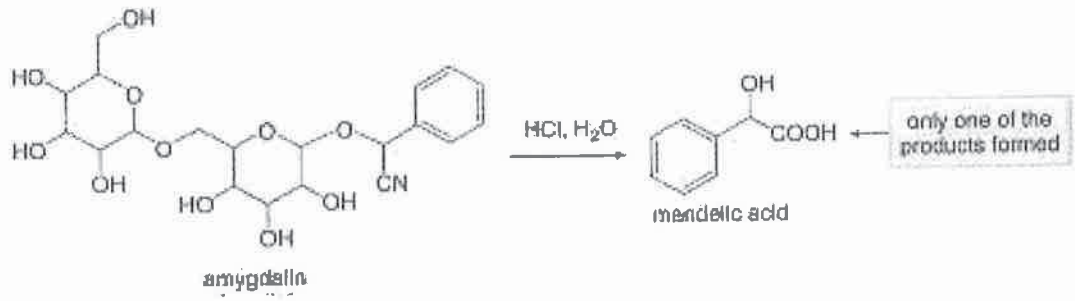
Question 4:

Amygdalin, a compound isolated from the pits of apricots, peaches and wild cherries, is commonly known as laetrile. Although it has no known therapeutic value, amygdalin has been used as an unsanctioned anticancer drug both within and outside of the United States. One hydrolysis product formed from amygdalin is mandelic acid, used in treating common skin problems caused by photoaging and acne.

a) How many stereogenic centres are present in amygdalin? What is the maximum number of stereoisomers possible?

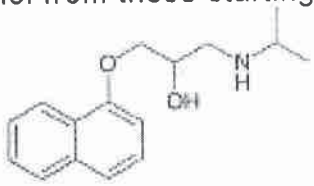
b) Draw both enantiomers of mandelic acid and label each stereogenic centre as R or S.

c) Pure (R)-mandelic acid has a specific rotation of -154. If a sample contains 60% of the R isomer and 40% of the enantiomer, what is [α] of this solution?

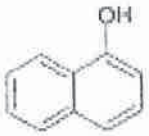


amygdalin mandelic acid

Question 5:
Propranolol, an antihypertensive agent is used in the treatment of high blood pressure, can be prepared from 1-naphthol, epichlorohydrin and isopropylamine using two successive nucleophilic substitution reactions. Devise a stepwise synthesis of propranolol from these starting materials.



propranolol

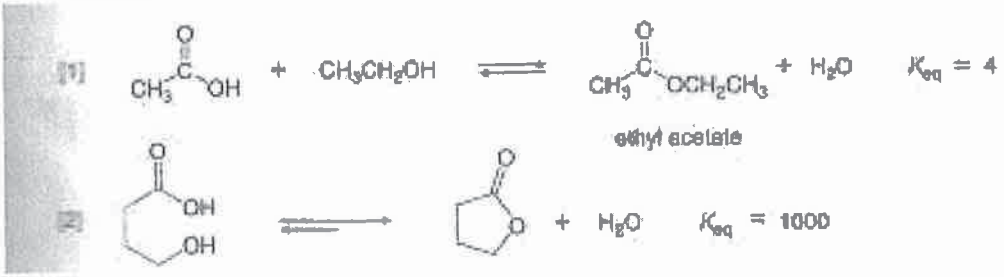


1-naphthol

epichlorohydrin

$(CH_3)_2CHNH_2$
isopropylamine

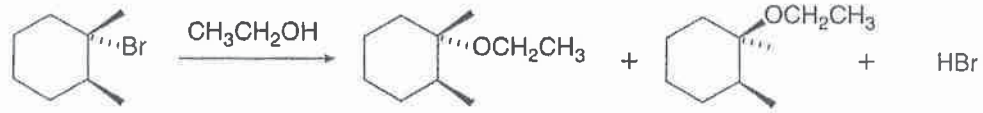
Question 6:
Esterification is the reaction of a carboxylic acid (RCOOH) and an alcohol (R'OH) to form as ester (RCOOR') with the loss of water. Equation 1) is an example of an intermolecular esterification reaction. Equation 2) is an example of an intramolecular esterification reaction; that is, the carboxylic acid and alcohol are contained in the same starting material forming a cyclic ester as product. The equilibrium constants for both reactions are given. Explain why K_{eq} is different for these two apparently similar reactions.



6.50

Question 7:

a) Draw a stepwise, detailed mechanism for each reaction, using curved arrows to show the movement of electrons.

a. 

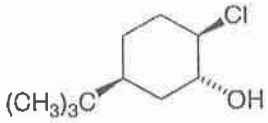
b. $CH_3CH_2CH_2CH_2NH_2 + CH_3I \xrightarrow{K_2CO_3} CH_3CH_2CH_2CH_2\overset{+}{N}(CH_3)_3 + I^-$

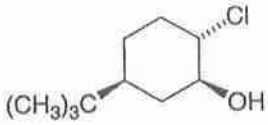
(excess)

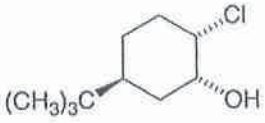
b) Although there are nine stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane, one stereoisomer reacts 7000 times more slowly than any of the others in an E2 elimination. Draw the structure of this isomer and explain why this is so.

Question 8:

Shown below are three isomers of halohydrins. One reacts rapidly to form an epoxide, one is intermediate in reactivity and one does not react at all. Identify which halohydrin corresponds to each kind of reactivity and explain why.

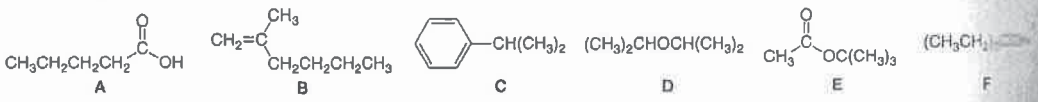
a. 

b. 

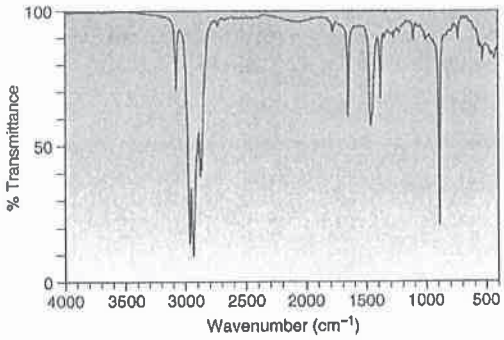
c. 

Question 9:

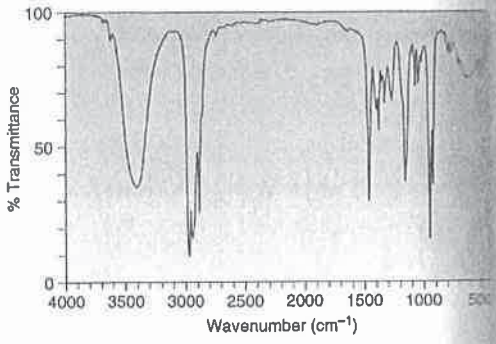
Match each compound to its IR-spectrum. Compound F is $(CH_3CH_2)_3COH$



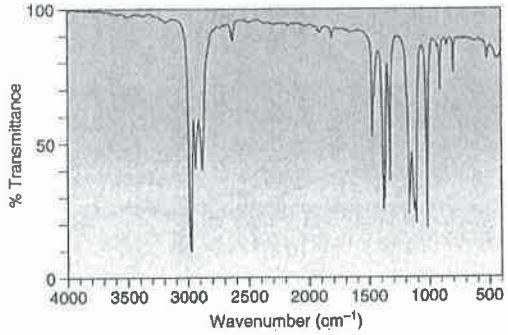
Spectrum [1]



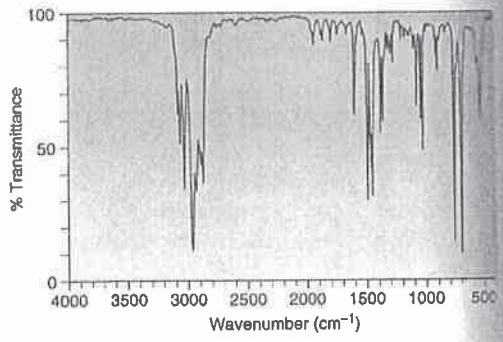
Spectrum [2]



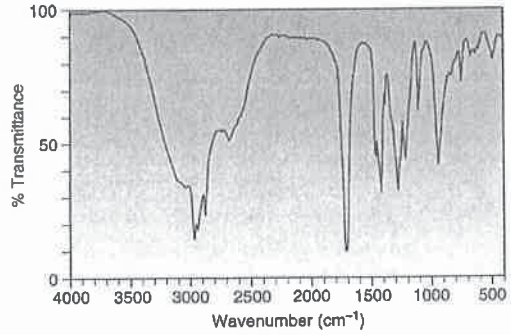
Spectrum [3]



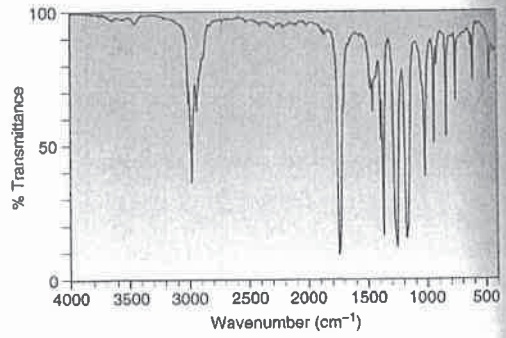
Spectrum [4]



Spectrum [5]



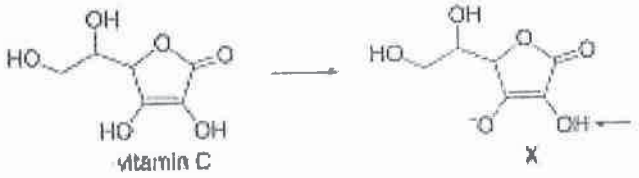
Spectrum [6]



Question 10:
Low molecular weight esters (RCO_2R) often have characteristic odors. Using its molecular formula and the 1H NMR spectral data, identify each ester.

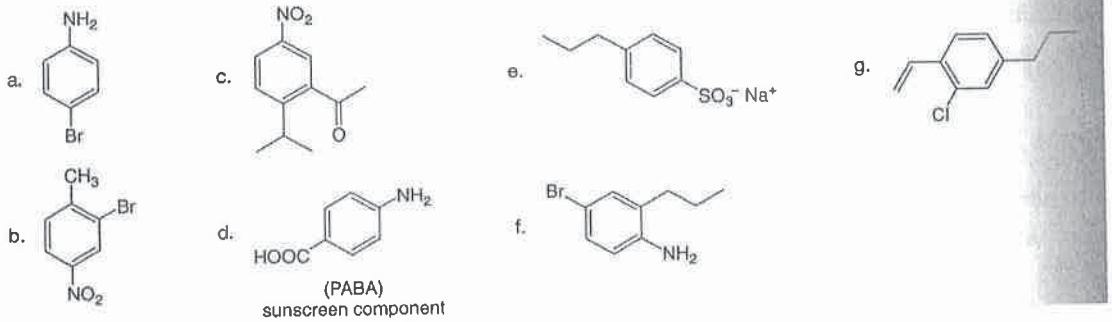
a) Compound A, the odor of banana: $C_7H_{14}O_2$; 1H NMR: 0.93 (doublet, 6 H), 1.52 (multiplet, 2 H), 1.69 (multiplet, 1 H), 2.04 (singlet, 3 H), and 4.10 (triplet, 2 H) ppm.
b) Compound B, the odor of rum: $C_7H_{14}O_2$; 1H NMR: 0.94 (doublet, 6 H), 1.15 (triplet, 3 H), 1.91 (multiplet, 1 H), 2.33 (quartet, 2 H) and 3.86 (doublet, 2 H) ppm.

Question 11:
In cells, Vitamin C exists largely as its conjugate base, X. X is an antioxidant because radicals formed in oxidation processes abstract the indicated H atom, forming a new radical that halts oxidation. Draw the structure of the radical formed by H abstraction and explain why this H atom is the most easily removed.

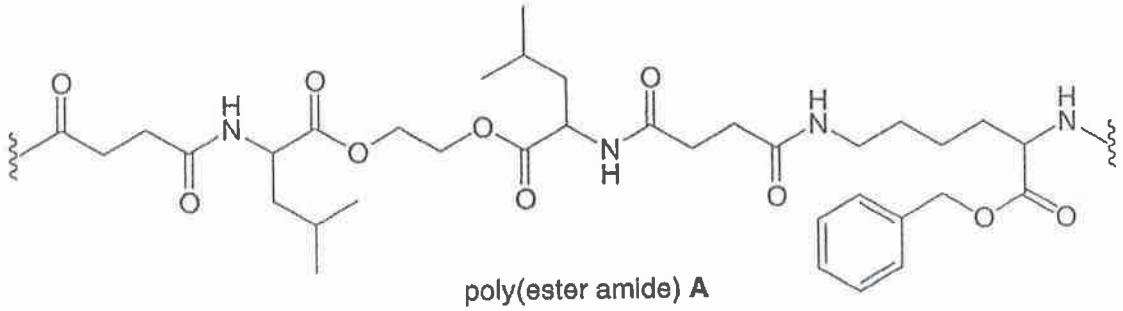


Vitamin C X

Question 12:
Synthesize each compound from benzene and any other organic or inorganic reagents.



Question 13:
Compound A is a novel poly(ester amide) copolymer that can be used as a bioabsorable coating for the controlled release of drugs. A is a copolymer of four monomers, two of which are amino acids or amino acid derivatives. The body's enzymes recognize the naturally occurring amino acids in the polymer backbone, allowing for controlled enzymatic breakdown of the polymer and the steady release of an encapsulated drug. Identify the four monomers used to synthesize A and name the two amino acids.



poly(ester amide) **A**