國　立　清　華　大　學　命　題　紙

99 學年度 生醫工程與環境科學系乙組(環境分子科學組) 碩士班入學考試

科目 有機化學及物理化學 科目代碼 2404 共 4 頁第 1 頁 *請在【答案卷卡】內作答

一、有機化學 (50%；務必作答於答案卷內)

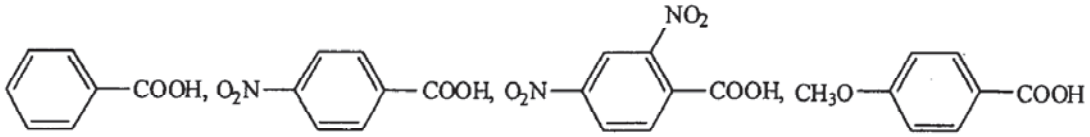
1. Rank each of the following groups of organic compounds in order of decreasing acidity. (5%)

(a) $CH_3CH_2CO_2H$, $CH_3\overset{\overset{O}{\|}}{C}CH_2OH$, $CH_3CH_2CH_2OH$

(b) $BrCH_2CO_2H$, $ClCH_2CO_2H$, FCH_2CO_2H

(c) $CH_3\overset{\overset{Cl}{|}}{C}HCH_2CO_2H$, $ClCH_2CH_2CH_2CO_2H$, $CH_3CH_2\overset{\overset{Cl}{|}}{C}HCO_2H$

(d) CF_3CO_2H, CBr_3CO_2H, $(CH_3)_3CCO_2H$

(e) 

2. For each of the following pairs of reactions indicate which one will be faster and explain briefly why you think so. (8%)

(a) 1. $CH_3CH_2CH_2Br + Na^+CN^- \xrightarrow[\text{dimethyl sulfoxide}]{} CH_3CH_2CH_2CN + Na^+Br^-$

2. $CH_3\underset{\underset{Br}{|}}{C}HCH_3 + Na^+CN^- \xrightarrow[\text{dimethyl sulfoxide}]{} CH_3\underset{\underset{CN}{|}}{C}HCH_3 + Na^+Br^-$

(b) 1. $CH_3CH_2CH_2Br + CH_3O^-Na^+ \xrightarrow[H_2O]{} CH_3CH_2CH_2OCH_3 + Na^+Br^-$

2. $CH_3CH_2CH_2Br + CH_3S^-Na^+ \xrightarrow[H_2O]{} CH_3CH_2CH_2SCH_3 + Na^+Br^-$

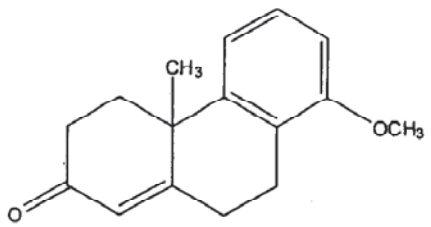
(c) 1. $H_3C\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br + H_2O \longrightarrow H_3C\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + HBr$

2. $CH_3CH_2CH_2CH_2Br + H_2O \longrightarrow CH_3CH_2CH_2CH_2OH + HBr$

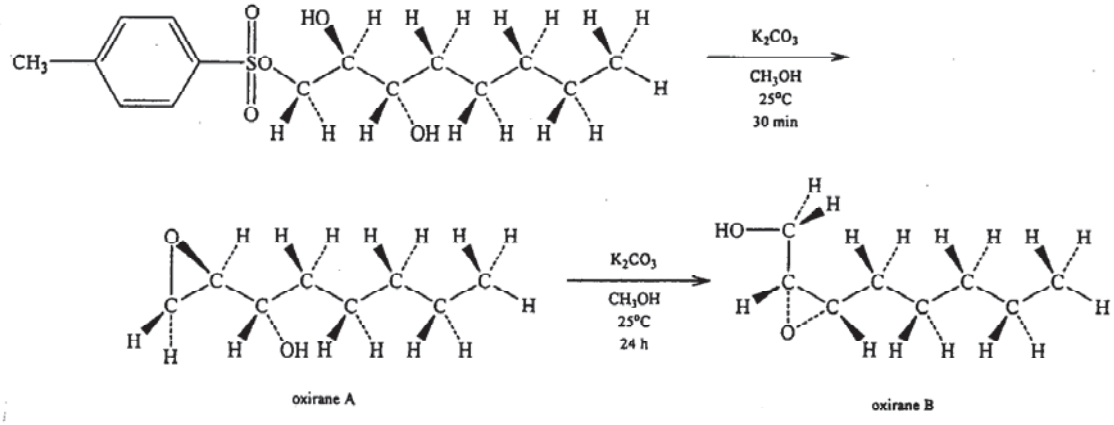
(d) 1. $CH_3CH_2CH{=}CH_2 + HCl \longrightarrow CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3$

2. $CH_3\overset{\overset{CH_3}{|}}{C}{=}CH_2 + HCl \longrightarrow CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}CH_3$

3. Propose synthesis of the following compound by using Michael addition followed by aldol condensation (i.e., Robinson annulation). (4%)



4. When the monotosylate of the 1,2,3-octanetriol shown below is treated with potassium carbonate in methanol for 30 minutes, oxirane A is formed. If, however, the reaction is allowed to continue for 24 hours, oxirane B is the product. (10%)



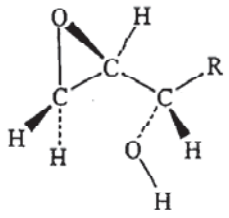
oxirane A oxirane B

(a) Identify any stereocenters in the monotosylate of the 1,2,3-octanetriol and assign configuration, *R* or *S*, to them.

(b) Draw a Newman projection of the tosylate in the conformation and looking down the bond between the *first* and *second* carbon atoms of the chain, as numbered in the naming of the compound. Is this the conformation in which the monotosylate reacts to give oxirane A? Why or why not?

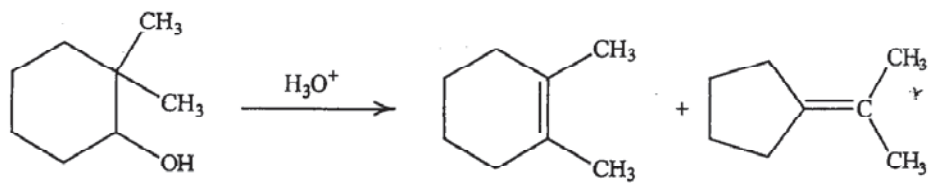
(c) What is the role of potassium carbonate? (Hint: the pK_a of HCO_3^- is 10.2, and the pK_a of CH_3CH_2OH is 17)

(d) How is oxirane B formed from oxirane A in the presence of base? Using the partial structure shown below and the curved-arrow representation for the movement of electrons, write a mechanism for the transformation of oxirane A to oxirane B.



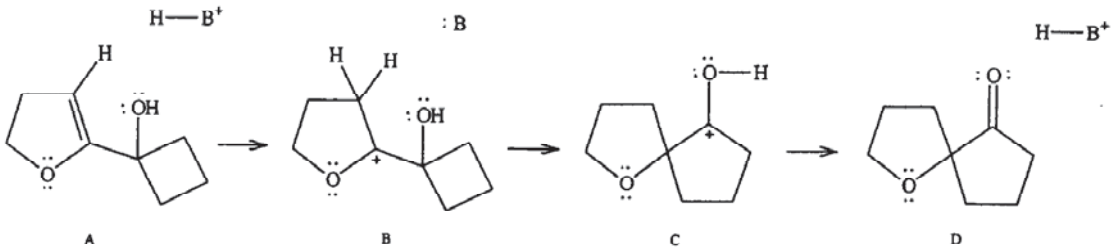
oxirane A

5. When 2,2-dimethylcyclohexanol is treated with acid, 1,2-dimethylcyclohexene and isopropylidenecyclopentane are the products obtained. Draw a detailed mechanism that explains this result. (4%)



2,2-dimethyl-cyclohexanol 1,2-dimethyl-cyclohexene isopropylidene-cyclopentane

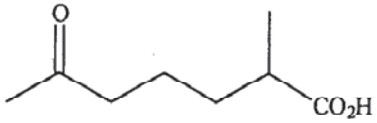
6. Research into the constituent of black tea that is responsible for its aroma involved the following set of reactions. (5%)



(a) Provide curved arrows that depict the mechanism of the transformations shown here.

(b) Cations B and C have special stability. What do they have in common? Draw a picture using either structure that illustrates the source of this stability.

7. Compound A, formula $C_8H_{14}O$, is converted by $CH_2=P(C_6H_5)_3$ into compound B, C_9H_{16}. Treatment of compound A with $LiAlH_4$ yields *two* isomeric products C and D, both $C_8H_{16}O$, in unequal yield. Heating either C or D with concentrated H_2SO_4 produces E, with the formula C_8H_{14}. Ozonolysis of E produces a keto aldehyde after $Zn-H^+$, H_2O treatment. Oxidation of this keto aldehyde with aqueous Cr(VI) produces

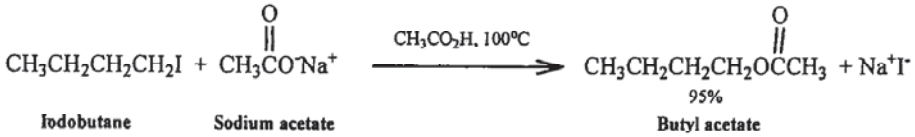


Identify compounds A through E. Pay particular attention to the stereochemistry of A. (8%)

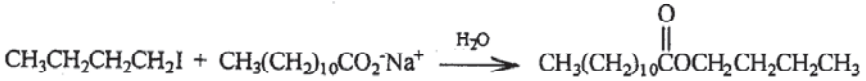
8. S_N2 reactions of simple carboxylate ions with haloalkanes in aqueous solution generally do not give good yields of esters. (6%)

(a) Explain why this is so.

(b) Reaction of 1-iodobutane with sodium acetate gives an excellent yield of ester if carried out in acetic acid (as shown here). Why is acetic acid a better solvent for this process than water?



(c) The reaction of 1-iodobutane with sodium dodecanoate proceeds surprisingly well in aqueous solution, much better than the reaction with sodium acetate (see the following equation). Explain this observation. (Hint: Sodium dodecanoate is a soap and forms micelles in water.)



二、物理化學 (50%；務必作答於答案卷內)

1. Define the "entropy" and show that entropy is a state function from the first law of thermodynamics, by considering (a) an ideal gas; (b) arbitrary substance. (10%)

2. When 1.0 mol glucose is oxidized to carbon dioxide and water at 25 °C, calorimetric measurements give $\Delta_r U° = -2808$ kJ/mol and $\Delta_r S° = +182.4$ J/molK at 25 °C. How much of this energy change can be extracted as (a) heat at constant pressure, (b) work? Compare (a) with (b) and explain your answer. (10%)

3. What is the degree of degeneracy of an energy level? For the particle in a cubic box with dimension l, what is the degree of degeneracy of the energy levels with the following values of $8ml^2E/h^2$? (a) 12; (b) 14 (10%)

4. Usually 10 minutes is required to hardboil an egg at 100 °C on the ground. On the top of a mountain 2500 m above sea level, it takes 12 hours to hardboil the egg. This dramatic change in rate with temperature is far beyond the chemist's rule of thumb. Assume that the temperature is constant at 300 K both on the ground and on the top of the mountain. Air is a single gas with molar mass 28 g/mol. The molar enthalpy change of vaporization of water is independent of temperature and equal to 40.7 kJ/mol.
   (a) What is the atmospheric pressure on the top of the mountain?
   (b) What is the boiling point of water on the top of the mountain?
   (c) Estimate the activation energy of the reaction.
   (d) Propose a reason why the dramatic change in rate with temperature occurs in hardboiling of eggs. (20%)