國立清華大學 103 學年度碩士班考試入學試題

系所班組別：生醫工程與環境科學系乙組 (環境分子科學組)

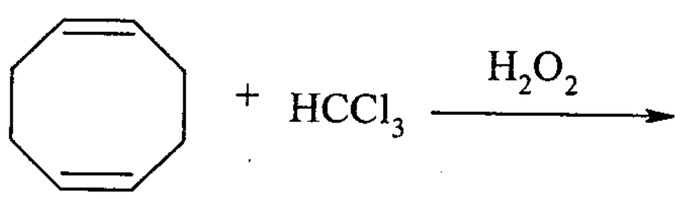
考試科目（代碼）：有機化學及物理化學(2404)

 *請在【答案卷、卡】作答

(一) 有機化學 (50%；務必作答於答案卷內)

[A] Please provide the structure of the major product(s) for each of the following reactions. Include stereochemistry where appropriate (18%, 3% of each).

(1)



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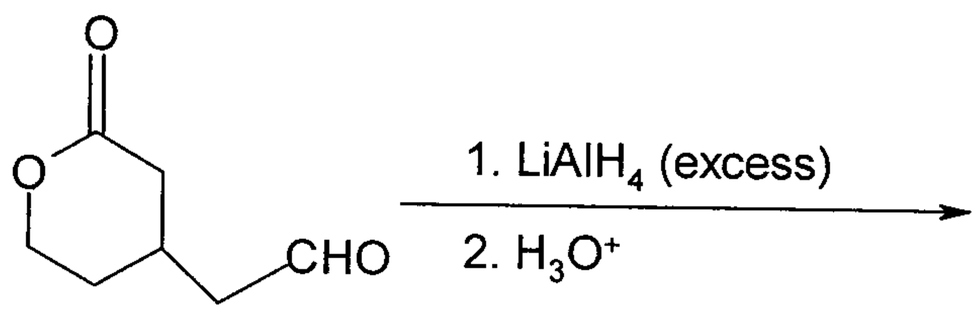

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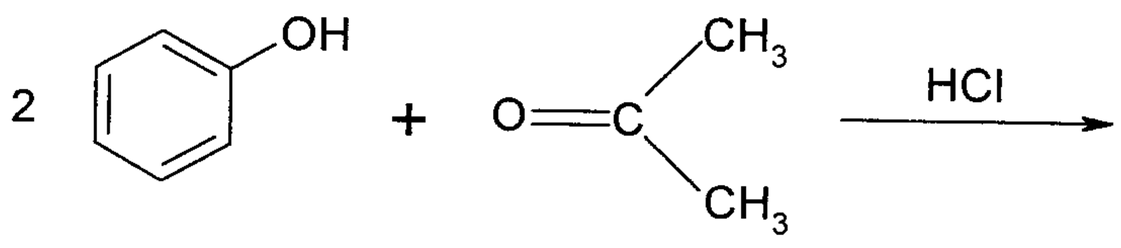

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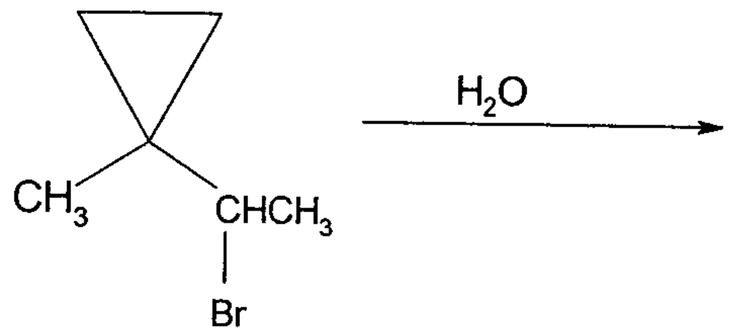

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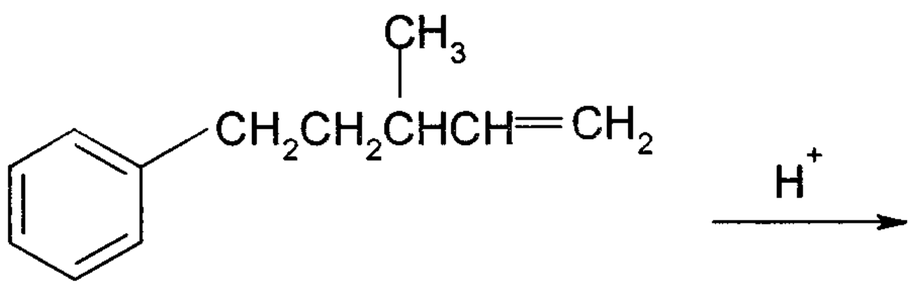

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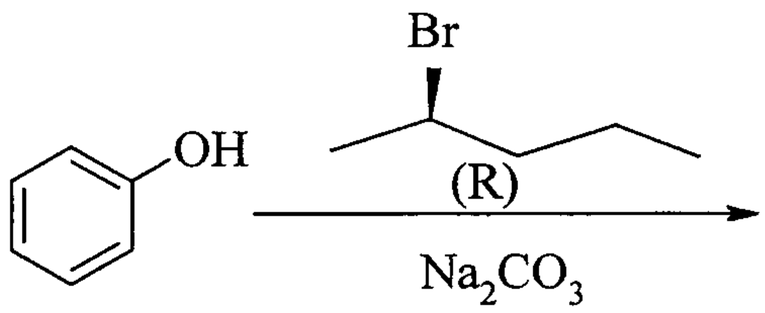
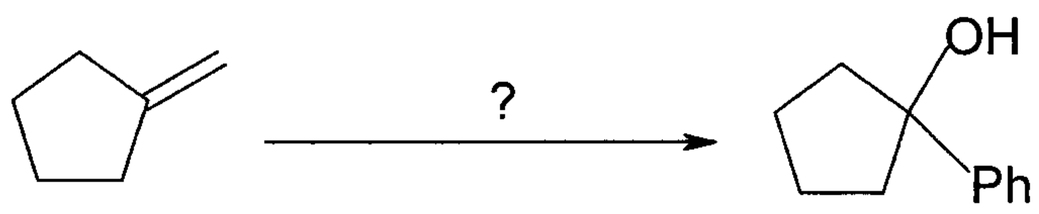


[B] Please provide the reagents necessary to accomplish to following transformation (9%, 3% of each)

(1)



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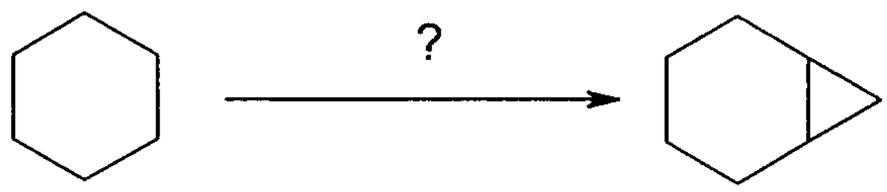

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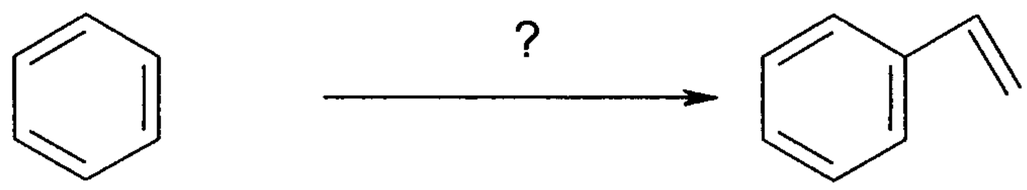
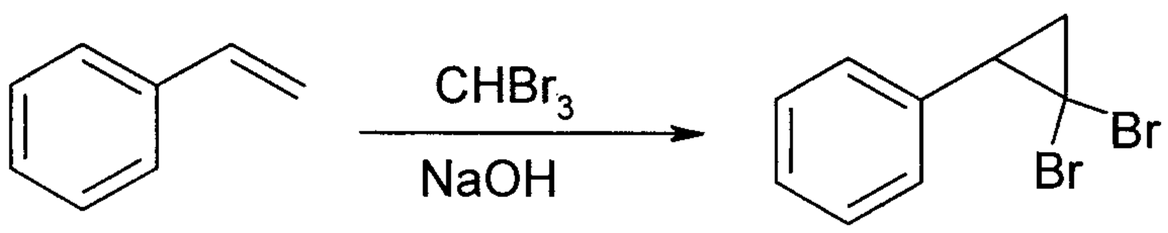


[C] Please provide a detailed, step-by-step mechanism for the following reactions. (12 %, 6% of each)

(1)



(2) The acid-catalyzed hydrolysis of 3-methylpentanamide to form 3-methylpentanoic acid in the presence of heat and sulfuric acid.

[D] Multiply Choice (11%)

(1) Which of the following are a pair of constitutional isomers?

(a) neohexane and 2,2-dimethylbutane

(b) neopentane and neohexane

(c) neopentane and 2,2-dimethylpropane

(d) isohexane and 2-methylpentane

(e) neopentane and isopentane

(2) Which of the following best explains why S_N1 reactions involving a neutral reactant are faster in polar solvent?

(a) The substrate is more soluble in polar solvents.

(b) The substrate is less soluble in polar solvents.

(c) The nucleophile is solvated by polar solvents.

(d) Solvation by polar solvents stabilizes the carbocation.

(e) Solvation by polar solvents stabilizes the transition state.

(3) The bond dissociation energies for the F-F bond, for the double bond of ethene, and for C-F bonds are 38, 61 and 108 kcal mol^{-1}. Which statement correctly describes the addition of F_2 to ethene?

(a) Exothermic by 117 kcal mol^{-1}

(b) Exothermic by 315 kcal mol^{-1}

(c) Endothermic by 117 kcal mol^{-1}

(d) Endothermic by 9 kcal mol^{-1}

(e) Exothermic by 9 kcal mol^{-1}

(4) When 1,3-cyclopentadiene reacts with the cis-isomer of NCCH=CHCN, the major product is

(a) optically active.

(b) a meso compound.

(c) a racemic mixture.

(d) a spirocyclic compound.

(e) a fused bicyclic compound.

(5) Which of the following statements best explains the information we can obtain from mass spectrometry?

(a) It allows us to determine the number of protons in a compound.

(b) It allows us to determine the kinds of functional groups in a compound.

(c) It allows us to determine the molecular weight and the mass of some fragments of a compound.

(d) It allows us to determine the presence and nature of a carbocation in the compound.

(e) It allow us to determine the presence and nature of a free radical in the compound.

(6) Referring to the priority rules for *E/Z* nomenclature, which of the following statement is not correct?

(a) CCl_3 priority > CF_3 priority

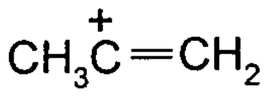
(b) CD_3 priority > CH_3 priority

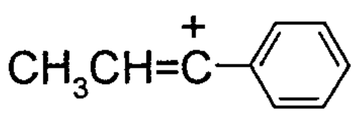
(c) $(CH_3)_3C$ priority > CH_3 priority

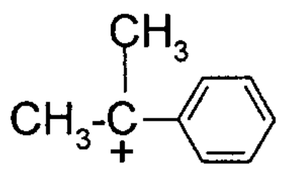
(d) $CH_2{=}CH$ > CH_3CH_2

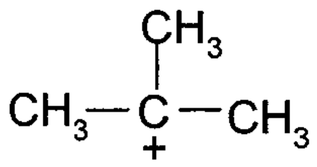
(e) $CH_3CH_2CH(CH_3)CH_2$ > $CH_3CH_2CH(CH_3)$

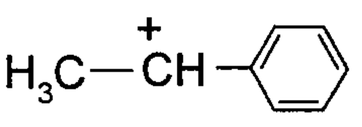
(7) Which of the following is the most stable cation?

(a) 

(b) 

(c) 

(d) 

(e) 

(8) The Walden Inversion (inversion of configuration) is associated with which of the following?

(a) E1 reaction

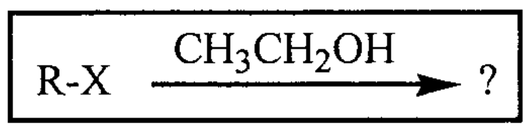
(b) free radical halogenation

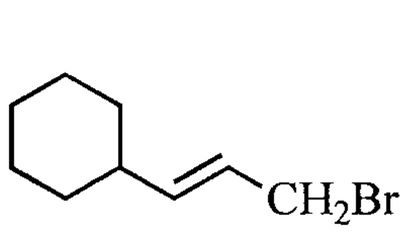
(c) S_N1 reaction

(d) S_N2 reaction

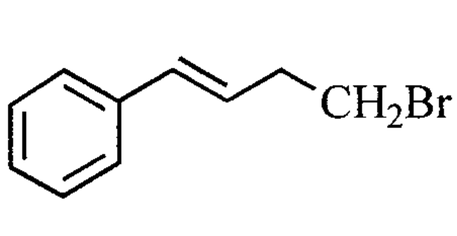
(e) E2 reaction.

(9) In order of decreasing reactivity, how would the bromides below rank in the following reaction?

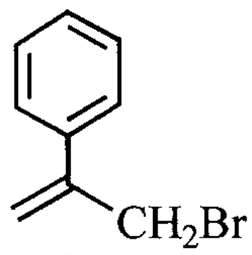




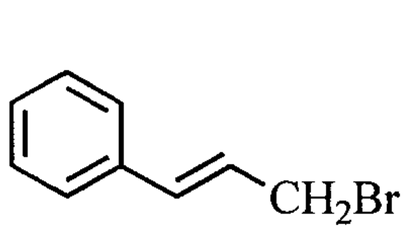
A



B



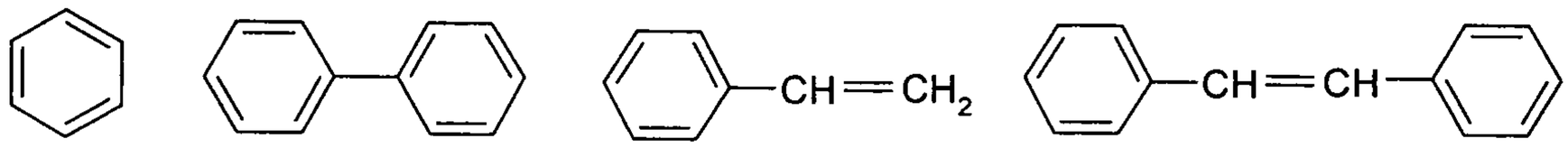
C



D

(a) B > A > D > C
(b) D > A > C > B
(c) A > C > D > B
(d) D > B > A > C
(e) C > D > B > A

(10) Which of the following is the correct order of decreasing λ_{max} in the following compounds of in order of decreasing



A　　B　　C　　D

(a) B > A > D > C
(b) A > D > C > B
(c) D > C > B > A
(d) D > B > A> C
(e) C > D > A > B

(11) Which of the following compounds exhibits the pattern of m/z values shown below?

m/z values　41, 43, 57, 87, 101, 106

(a) propylbromide
(b) isopropyl bromide
(c) sec-butyl isopropyl ether
(d) 2-hexanol
(e)2-butanone

(二) 物理化學（50%；務必作答於答案卷內）

Fundamental constants

$c = 3.0\times10^{8}$ m/s, $e = 1.6\times10^{-19}$ C, $N_A = 6.02\times10^{23}$ mol^{-1}, $R = 8.3145$ J/(K mol),

$k = 1.38\times10^{-23}$ J/K, $h = 6.626\times10^{-34}$ Js, $m_e = 9.11\times10^{-31}$ kg

1. A sample of 4.0 mol $CH_3OH_{(g)}$ is condensed isothermally and reversibly to liquid at 64°C. The standard enthalpy of vaporization of methanol at 64°C is 35.3 kJ/mol. Find q, w, ΔU, ΔS, and ΔG for this process. (10%)

2. The enthalpy of fusion of anthracene is 28.8 kJ/mol and its melting point is 490 K. Calculate its ideal solubility (g/kg) in benzene at 300K. (M.W. of anthracene = 178 g/mol) (10%)

3. Consider the equilibrium $N_2O_4(g) \leftrightarrows 2NO_2(g)$, which can be easily studied in the laboratory through a measurement of the vapor density of the equilibrium mixture. The degree of dissociation (α) of dinitrogen tetroxide is a function of the pressure (P).

(a) Show that if the mixture remains in equilibrium as the pressure is changed, the apparent compressibility $\kappa = (-1/V)(\partial V/\partial P)_T = (1/P)[1+\alpha_e(1-\alpha_e)/2]$ where α_e is the degree of dissociation of dinitrogen tetroxide in equilibrium.

(b) Calculate the equilibrium constant K_p at 298K and determine the pressure when the quantity of κP is at a maximum value. (10%)

Table 1. Thermodynamic data

Substance	ΔH_f° (kJ/mol)	S_m° (J/Kmol)	$C_{p,m}$ (J/Kmol)
$N_2O_4(g)$	9.179	305.376	77.28
$NO_2(g)$	33.095	240.034	37.20
$O_2(g)$	0	205.14	29.355
$N_2(g)$	0	191.609	29.125

*Standard molar enthalpies of formation, standard absolute entropies, and molar heat capacities are for 298 K.

4. An autocatalytic reaction is one in which a product acts as a catalyst. Assume that the reaction A → B has the rate law -d[A]/dt = k[A][B].

(a) Please derive the integrated rate law. (the assumption might be the initial concentrations of A and B are both nonzero)

(b) Find [A] at t = 10.0 min if $[A]_o$ = 0.50 mole/L, $[B]_o$ = 0.010 mole/L, and k = 0.1 L/(mol min). (10%)

5. The organic molecule benzene, C_6H_6, has a cyclic structure where the carbon atoms make a hexagon. The π electrons in the cyclic molecule can be approximated as having two-dimensional rotational motion. Calculate the diameter of this electron ring if it is assumed that a transition occurring at 260.0 nm corresponds to an electron going from m = 3 to m = 4. X-ray diffraction studies show that benzene is a completely flat and symmetrical molecule with all carbon-carbon and carbon-hydrogen bonds in benzene have lengths of 0.139 nm and 0.110 nm, respectively. Compare your result with the experimental data by X-ray and electron diffraction. (10%)