

國立清華大學 102 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)

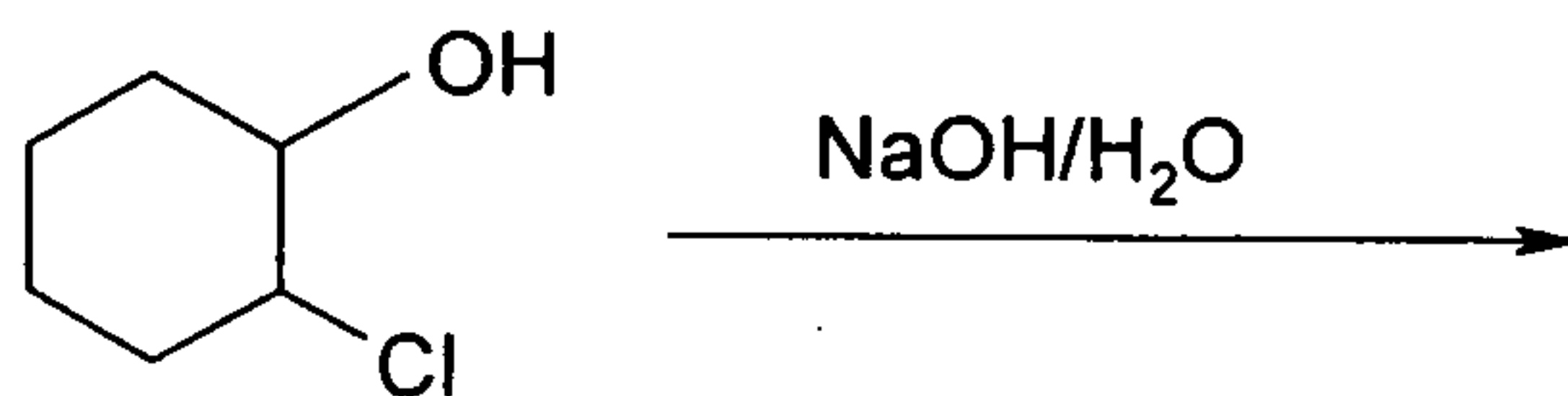
考試科目 (代碼)：有機化學及物理化學(2304)

共 5 頁，第 1 頁 *請在【答案卷、卡】作答

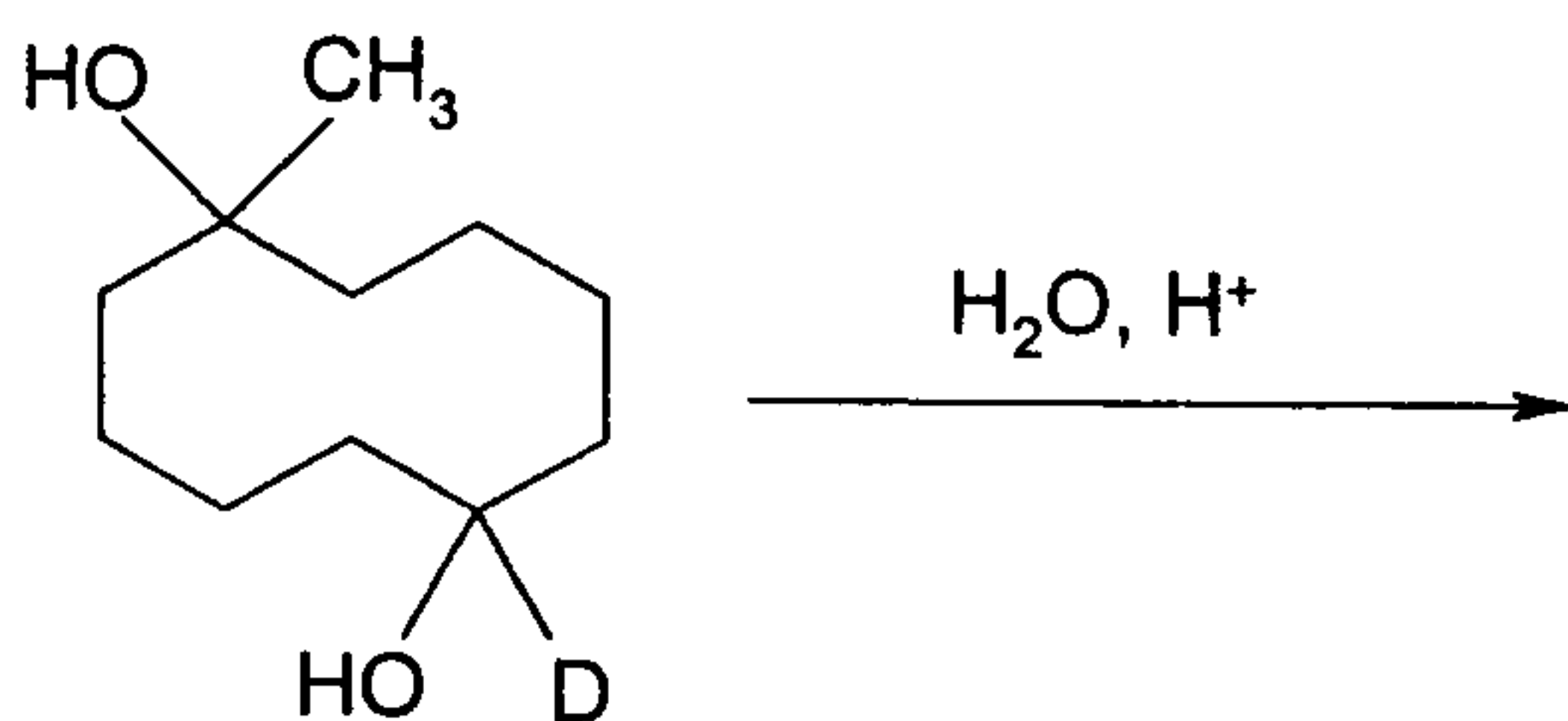
(一) 有機化學 (50%；務必作答於答案卷內)

1. Please provide the structure of the major product(s) for each of the following reactions, and include stereochemistry where appropriate (18, 3% of each).

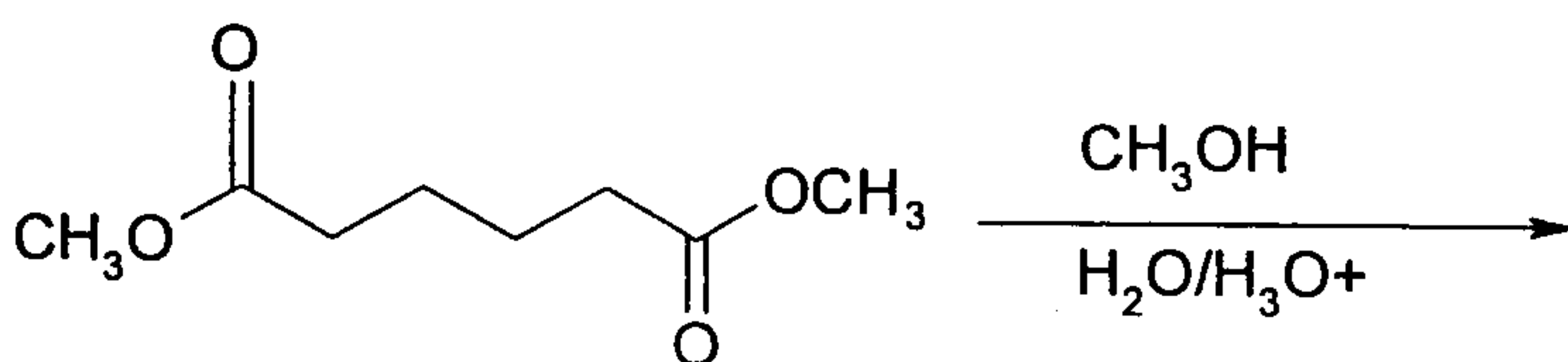
[A]



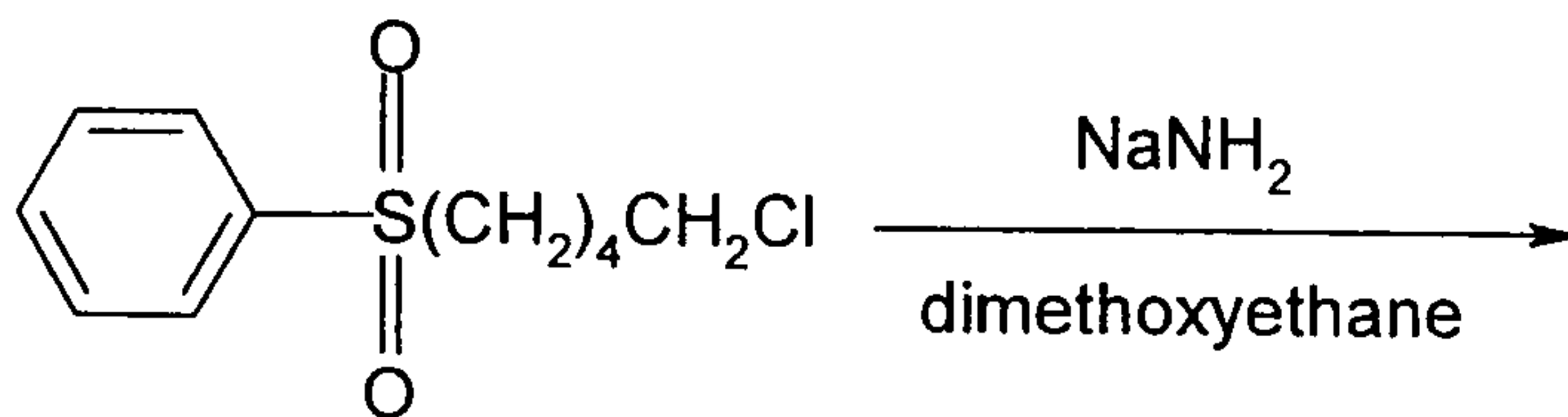
[B]



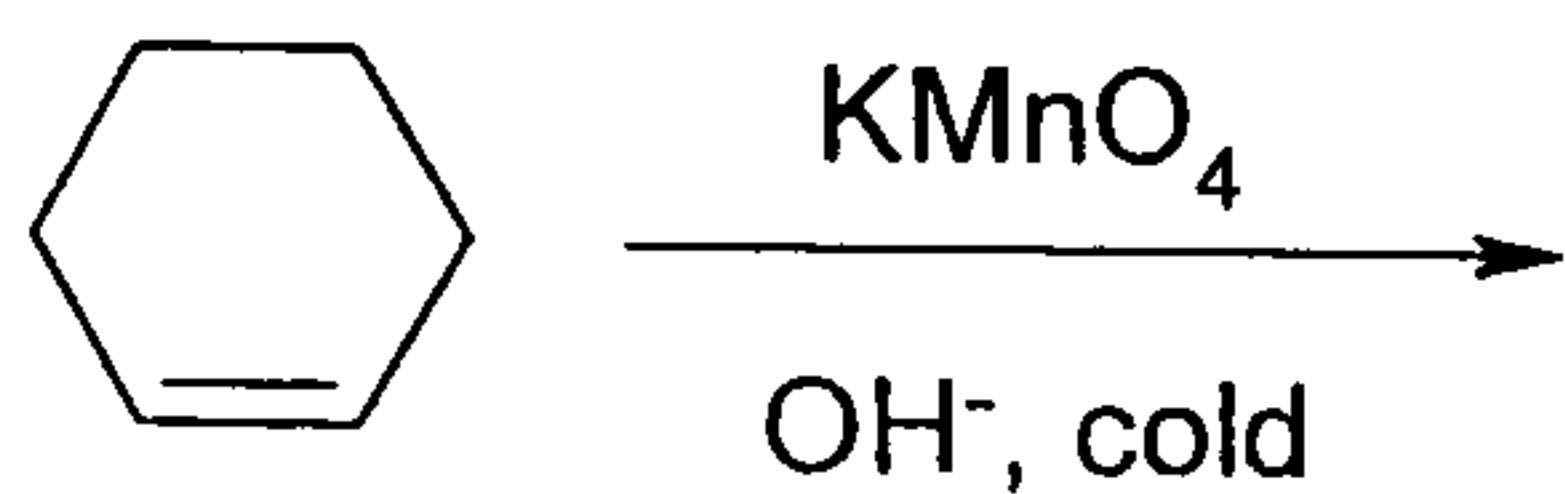
[C]



[D]



[E]



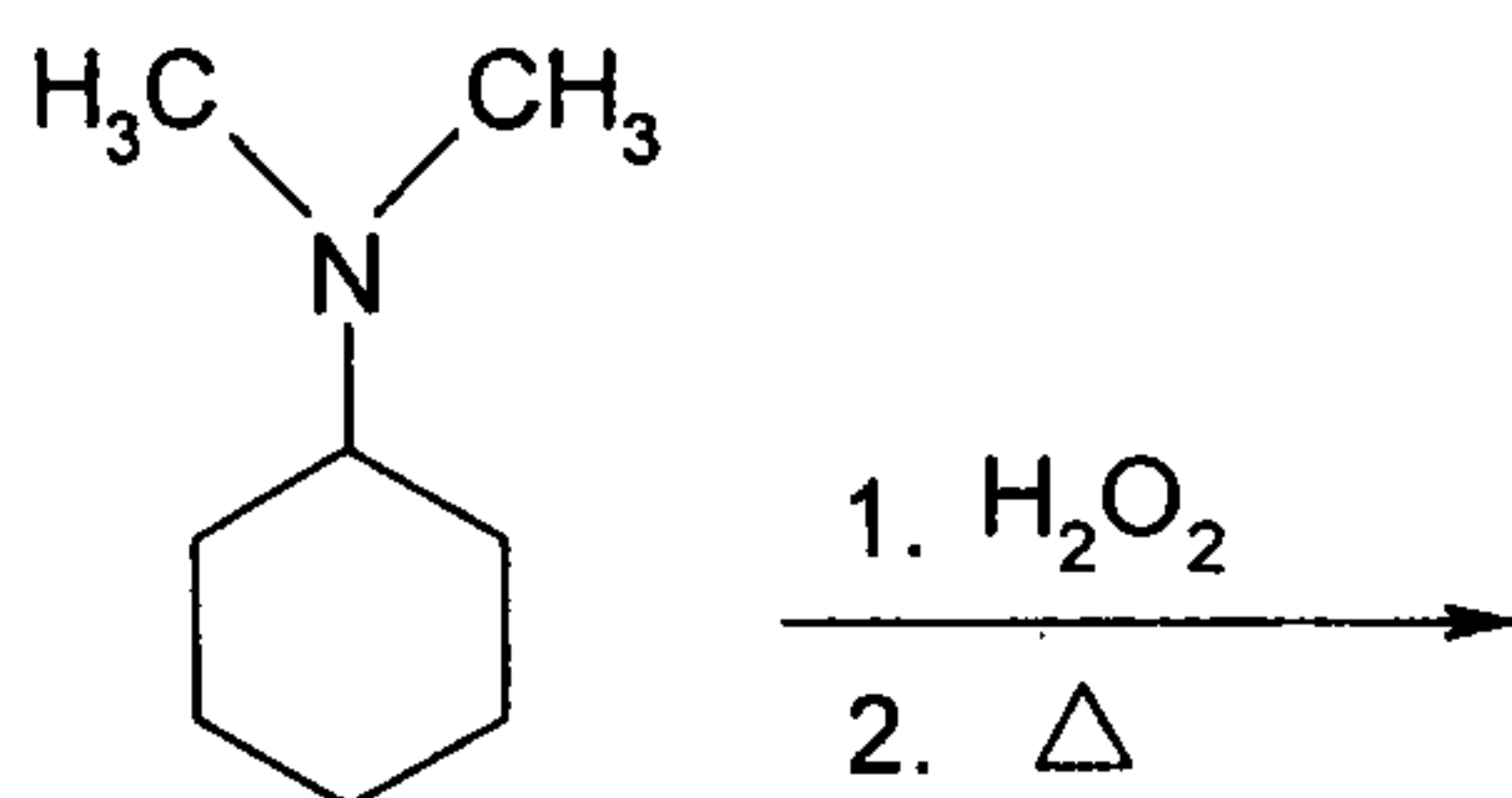
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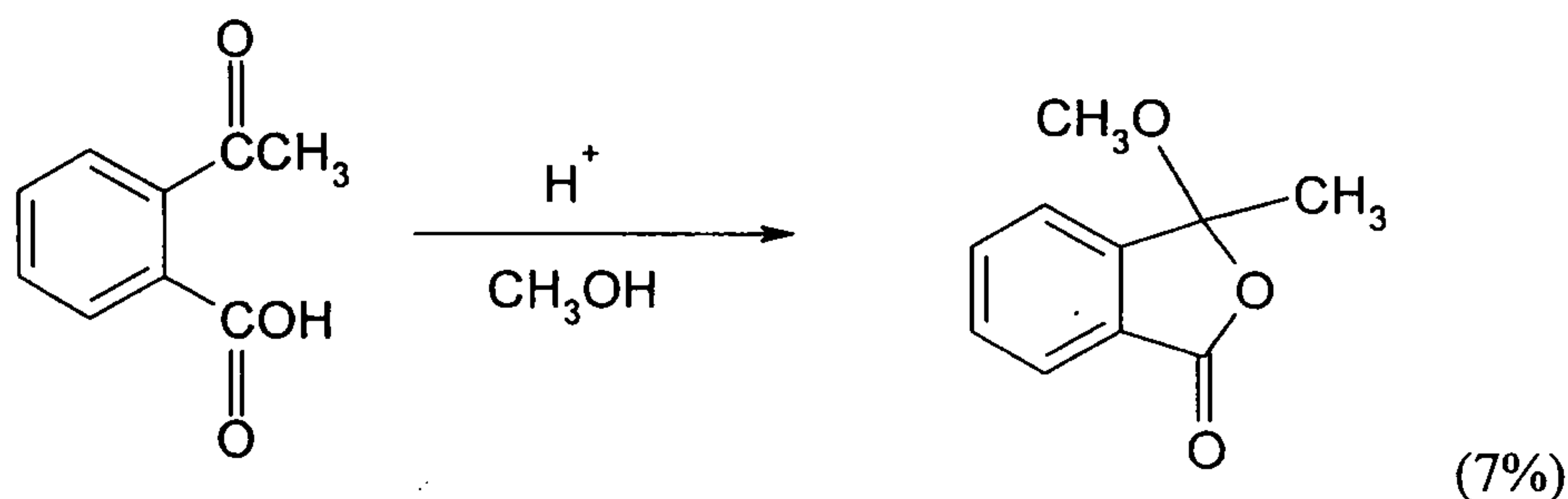
共 5 頁，第 2 頁 *請在【答案卷、卡】作答

[F]



2. Please propose a step-by-step reaction mechanism for the following reactions (14%)

[A]



[B] Benzene reacts with sulfur dichloride in the presence of AlCl₃ to give diphenyl sulfide (C₆H₅-S-C₆H₅). Please propose a mechanism for this process. (7%)

3. For each of the following questions, assume that all measurements are made in 10-cm polarimeter sample container. (6%)

[A] A 10-cm solution of 0.4 g of optically active 2-butanol in water displays an optical rotation of -0.56°. What is its specific rotation? (3%)

[B] A solution of pure (S)-2-bromobutane in ethanol is found to have an observed $[\alpha_D^{25}] = +57.3$. If $[\alpha]$ for (S)-2-bromobutane is 23.1, what is the concentration of the solution? (3%)

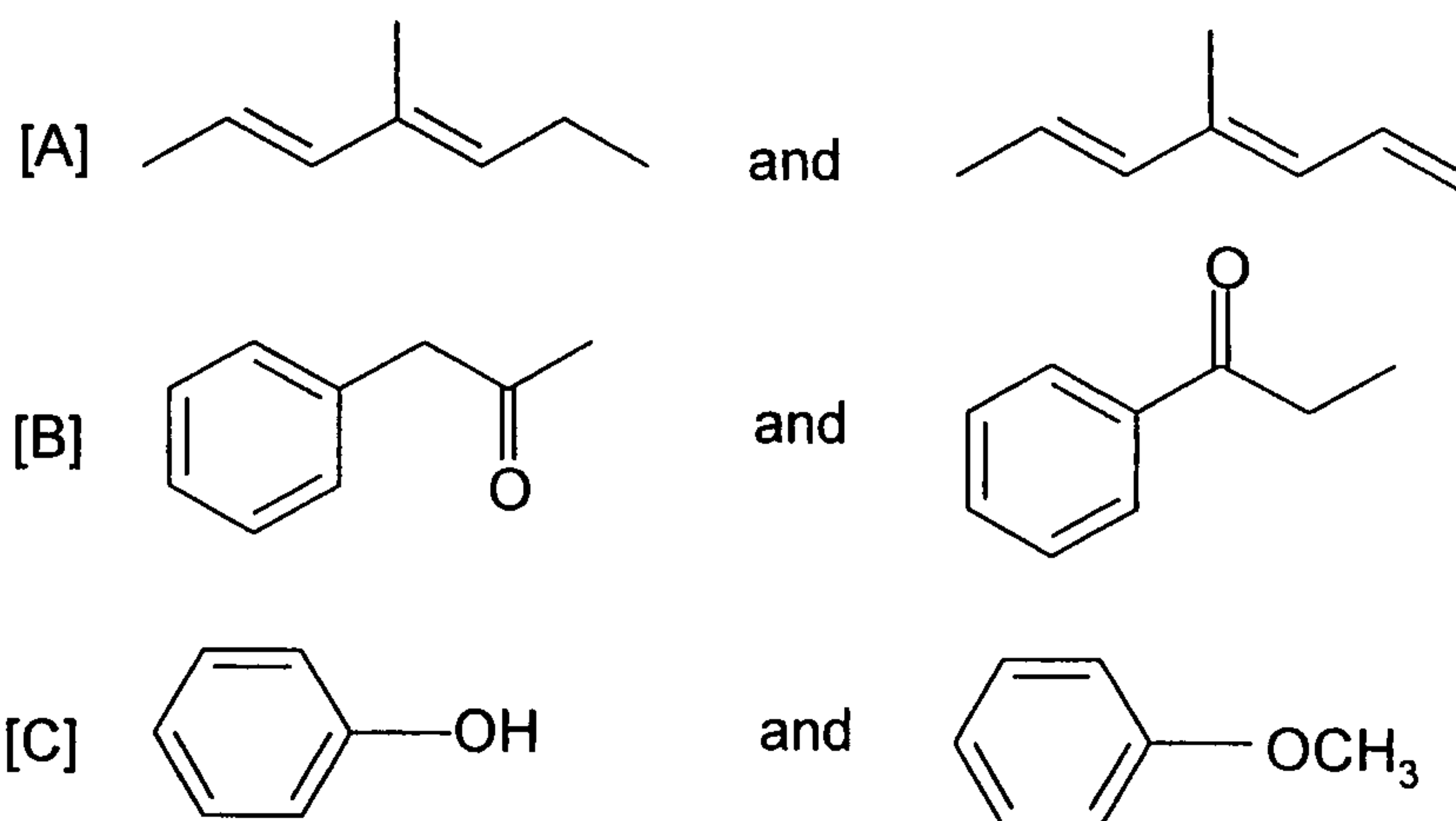
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共 5 頁，第 3 頁 *請在【答案卷、卡】作答

4. How could you distinguish between the compounds in each of the following pairs using UV spectroscopy? (6%)



5. When compound A ($C_5H_{12}O$) is treated with HBr, it forms compound B ($C_5H_{11}Br$). The 1H NMR spectrum of compound A has one singlet (1), two doublets (3, 6), and two multiplets (both 1) (number in parentheses are the relative areas of the signals). The 1H NMR spectrum of compound B has a singlet (6), a triplet (3), and a quartet (2). Please identify compounds A and B. (6%)

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(二) 物理化學 (50%；務必作答於答案卷內)

Fundamental constants

$c = 3.0 \times 10^8$ m/s, $e = 1.6 \times 10^{-19}$ C, $N_A = 6.02 \times 10^{23}$ mol⁻¹, $R = 8.3145$ J/(K mol),
 $k = 1.38 \times 10^{-23}$ J/K, $h = 6.626 \times 10^{-34}$ Js, $m_e = 9.11 \times 10^{-31}$ kg

6. The vapour pressure of each component in a mixture of acetone (A) and chloroform (C) were measured at 35 °C with the following results in Table 1:

Table 1. Vapor Pressures of acetone and chloroform at different mole fractions

x_C	0	0.20	0.40	0.60	0.80	1
P_A /kPa	46.3	33.3	23.3	12.3	4.9	0
P_C /kPa	0	4.7	11	18.9	26.7	36.4

Describe the conditions under which the mixture conforms to Raoult's law and to Henry's law, respectively. Find the Henry's law constants for acetone in chloroform and chloroform in acetone, respectively. (10%)

7. Consider the dissociation reaction of dinitrogen tetroxide: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ with thermodynamic data shown in Table 2.

(a) Calculate the value of ΔG° at 298 K.

(b) Calculate the value of K_p at 298 K.

(c) Calculate the equilibrium pressure of a system that initially consists of 1.0 mol of dinitrogen tetroxide and that is confined in a fixed volume of 24.5 L at 298 K.

(10%)

Table 2. Thermodynamic data at 298 K

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

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8. A particle is in a state described by the wavefunction:

$$\Psi(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha x^2}{2}}$$

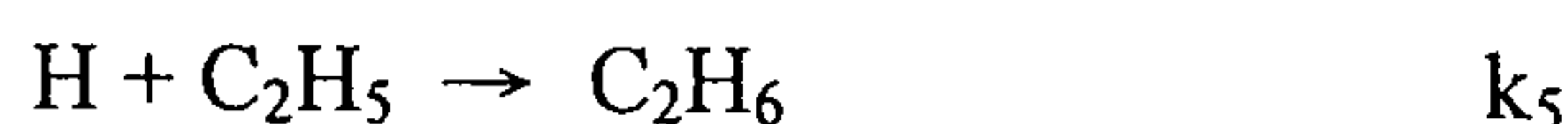
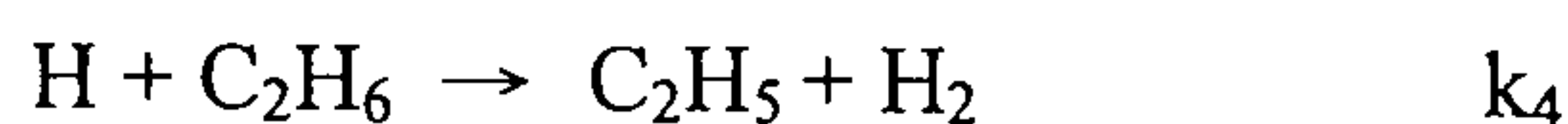
where α is a constant and $-\infty \leq x \leq \infty$. Calculate $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, and $\langle p^2 \rangle$ for the particle in the system, respectively? (The p means momentum.) Determine the value of the product $\Delta x \Delta p$ where $\Delta x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$ and $\Delta p = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2}$ and discuss the quantity with reference to the uncertainty principle. (10%)

9. β -Carotenes are highly conjugated polyenes found in many vegetables. They can be oxidized and used to synthesize pigments that play important roles in the chemistry of mammalian vision. The parent compound, β -carotene, has a maximum absorption of light that occurs at 480 nm. (a) If this transition corresponds to an $n = 11$ to $n = 12$ transition of an electron in a particle-in-a-box system, what is the approximate length of the molecular "box"? (b) Using your results, generate a rule for the prediction of frequency shifts in the absorption spectra of linear polyenes. (10%)

10. The Rice-Herzfeld mechanism for the dehydrogenation of ethane to ethylene and hydrogen showed that it led to first-order kinetics:

$$-\frac{d[C_2H_6]}{dt} = k_{app}[C_2H_6]$$

Given the following possible elementary processes:



Confirm this remark, find the approximations that lead to the rate law quoted there, and express k_{app} in terms of k_1, k_2, k_3, \dots . (10%)