

Last Name: \_\_\_\_\_ First Name: \_\_\_\_\_

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CANADIAN  
CHEMISTRY  
OLYMPIAD



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DU CANADA

2022 Take Home Exam

**Deadline:**

12 noon EST on Thursday, April 14<sup>th</sup>, 2022

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### **Introduction:**

The purposes of the Canadian Chemistry Olympiad program is to provide high school students with the opportunity to study and test themselves on advanced Chemistry topics and to prepare students for competition at the International Chemistry Olympiad. The questions on the take-home exam are questions from the advanced topics identified by the IChO hosts. For IChO 2022, China will be hosting. There are 37 problems posted on the [IChO 2022 website](#), seven of these problems are part of the Take home exam.

Please note that CCO participants should tackle these problems **independently**. Your ability to use critical thinking and advanced problem solving techniques will be essential if the CCO selection committee selects you for the IChO team. After completing and submitting the Take home exam, you should continue to solve the rest of the 37 problems.

All of the reference material you need to solve the questions precedes the questions on this exam.

The take home problems are due Thursday, April 14<sup>th</sup> at 12 noon Eastern Standard Time (EST). The CCO will not accept late submissions. Please ensure that all of your answers are legible and clearly organized. The CCO evaluators may not evaluate illegible or disorganized answers. Please ensure that you print your name is clearly at the top of every page. Scan your test, put CCO Take Home Exam – your name (First and Last) in the subject line and send the exam as one pdf file to both [jpittlainsbury@utschools.ca](mailto:jpittlainsbury@utschools.ca) and [bussierg@chem.ubc.ca](mailto:bussierg@chem.ubc.ca) (in the same email).

The CCO gratefully acknowledges the authors of these questions:

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## Physical constants and equations

Avogadro Constant:	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant:	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Standard pressure:	$p^\ominus = 1 \text{ bar} = 10^5 \text{ Pa}$
Standard atmospheric pressure:	$P_{\text{atm}} = 1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ Pa}$
Zero of the Celsius scale:	$273.15 \text{ K}$
Faraday constant:	$F = 9.6485 \times 10^4 \text{ C mol}^{-1}$
Planck's constant:	$h = 6.626 \times 10^{-34} \text{ J s}$
Mass of electron:	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Speed of light:	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
Energy of a photon:	$E = hc/\lambda$
Ideal gas equation:	$pV = nRT$
The first law of thermodynamics:	$\Delta U = q + w$
Enthalpy $H$ :	$H = U + PV$
Entropy $S$ :	$S = k_B \ln W$
The change of entropy:	$\Delta S = q_{\text{rev}}/T$
Gibbs free energy:	$G = H - TS$
	$\Delta G^\ominus = -RT \ln K^\ominus$
	$\Delta G^\ominus = -zFE_{\text{cell}}^\ominus$
	$\Delta G = \Delta G^\ominus + RT \ln Q$
Reaction quotient:	$Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$
For a reaction $a \text{ A} + b \text{ B} \rightleftharpoons c \text{ C} + d \text{ D}$	
Variation of the enthalpy with temperature:	$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \Delta_r C_p^\ominus(T_2 - T_1)$
Variation of the entropy with temperature:	$\Delta_r S^\ominus(T_2) = \Delta_r S^\ominus(T_1) + \Delta_r C_p^\ominus \ln(T_2/T_1)$
Nernst equation:	$E = E^\ominus - \frac{RT}{zF} \ln \frac{c_{\text{red}}}{c_{\text{ox}}}$
Clausius-Clapeyron equation:	$\ln \frac{p_2}{p_1} = \frac{\Delta_{\text{vap}} H^\ominus}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$
Kelvin equation:	$\ln \frac{p}{p_0} = \frac{2\sigma M}{\rho R T r}$
Temperature coefficient of standard cell potential:	$\frac{dE_{\text{cell}}^\ominus}{dT} = \frac{\Delta_r S^\ominus}{zF}$
Langmuir isotherm equation:	$\theta = aP/(1 + aP)$
Arrhenius equation:	$\ln k = \ln A - E_a/RT$
Integrated rate law:	
Zero order:	$[A] = [A]_0 - kt$
First order:	$\ln [A] = \ln [A]_0 - kt$
Second order:	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Half-life for a first order process:

$$t_{1/2} = \ln 2/k$$

Half-life for a second order process:

$$t_{1/2} = \frac{1}{k[A]_0}$$

Temperature dependence of the rate constant:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Lambert–Beer equation:

$$A = \epsilon lc$$

Acidic effective coefficient

$$\alpha_{Y(H)} = 1 + [H^+] \beta_1^H + [H^+]^2 \beta_2^H + \dots + [H^+]^6 \beta_6^H$$

Coexisting ion effect coefficient

$$\alpha_{Y(N)} = 1 + [N] K_{NY}$$

Concentration of metal ion at stoichiometric point

$$pM'_{sp} = 1/2(\lg K'_{MY} - \lg c_M^{sp})$$

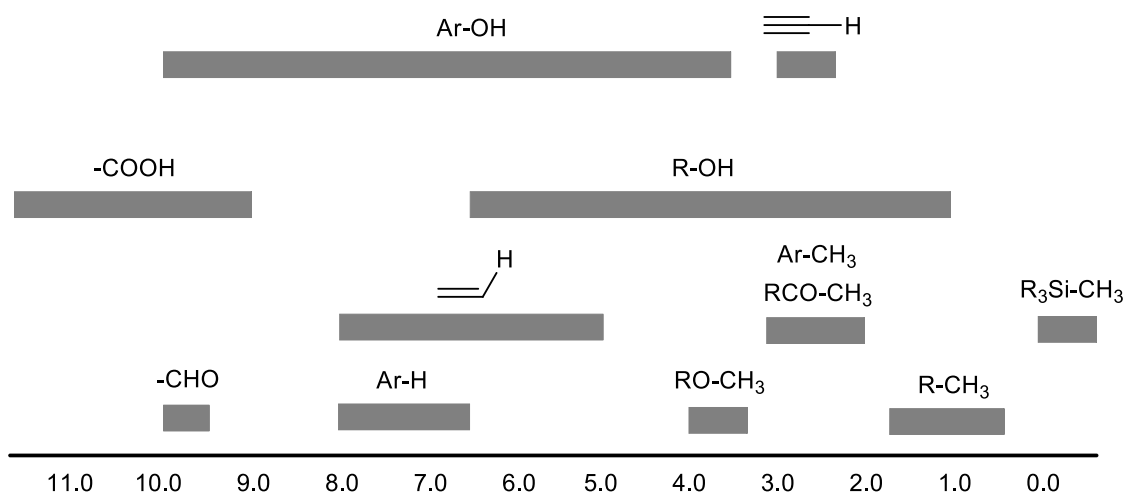
# Periodic table of the Elements

1 H 1.008																	18 He 4.003
3 Li 6.941	2 4 Be 9.012											13 5 B 10.81	14 6 C 12.01	15 7 N 14.01	16 8 O 16.00	17 9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 63.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	38 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 120.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

# <sup>1</sup>H NMR

## Chemical shifts of hydrogen (in ppm/TMS)



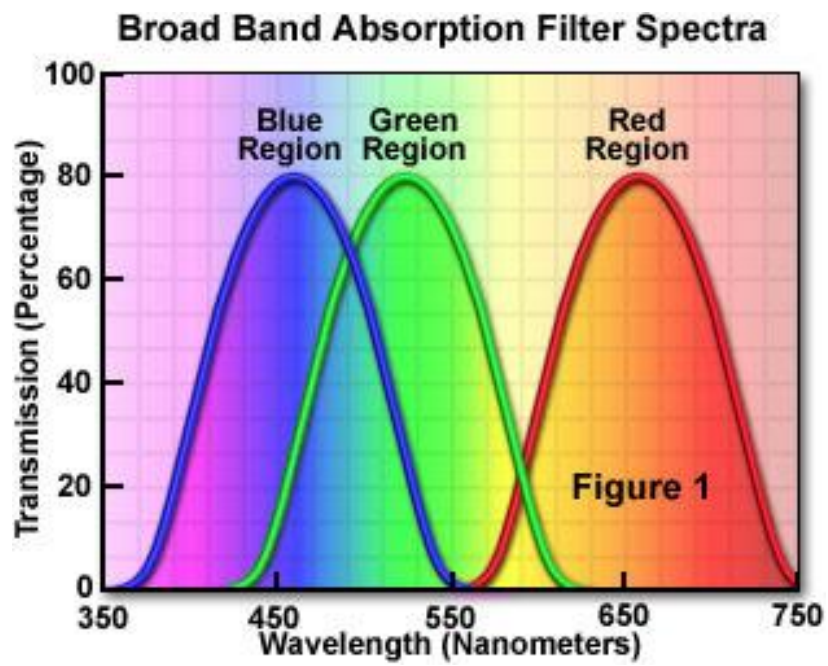
## H-H coupling constants (in Hz)

Hydrogen type	$ J_{ab} $ (Hz)
$R_2CH_aH_b$	4-20
$R_2H_aC-CR_2H_b$	2-12
$RH_aC=CRH_b$	cis: 7-12; trans:12-18
$R_2C=CH_aH_b$	0.5-3
$H_a(CO)-CR_2H_b$	1-3
$RH_aC=CR-CR_2H_b$	0.5-2.5

## IR spectroscopy table

Vibrational mode	$\sigma$ (cm <sup>-1</sup> )	Intensity
alcohol O—H (stretching)	3600-3200	strong
N—H (stretching)	3500-3350	strong
$\equiv C-H$ (stretching)	3300	strong
$=C-H$ (stretching)	3100-3000	weak
C—H (stretching)	2950-2840	weak
C $\equiv$ N (stretching)	2250	strong
C $\equiv$ C (stretching)	2260-2100	variable
C=O (stretching)	1850-1690	strong
alkene C=C (stretching)	1680-1600	weak
aromatic C=C (stretching)	1600-1400	weak
CH <sub>2</sub> (bending)	1480-1440	medium
CH <sub>3</sub> (bending)	1465-1440;1390-1365	medium
C—O—C (stretching)	1250-1050 (several)	strong
C—OH (stretching)	1200-1020	strong

# Visible Light Spectrum



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School: \_\_\_\_\_

Province: \_\_\_\_\_

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School: \_\_\_\_\_

Province: \_\_\_\_\_

Reference Material: Please note that all of the reference material for the 38 questions on the preparatory problems is part of this take home exam. You may not need to use all of the reference materials to solve the problems on this CCO take home exam.

### Physical Constants and Equations:

Speed of light in vacuum,  $c = 2.99792458 \times 10^8 \text{ m s}^{-1}$

Planck constant,  $h = 6.62607015 \times 10^{-34} \text{ J s}$

Elementary charge,  $e = 1.602176634 \times 10^{-19} \text{ C}$

Electron mass,  $m_e = 9.10938370 \times 10^{-31} \text{ kg}$

Electric constant (permittivity of vacuum),  $\epsilon_0 = 8.85418781 \times 10^{-12} \text{ F m}^{-1}$

Avogadro constant,  $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant,  $k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}$

Faraday constant,  $F = N_A \times e = 9.64853321233100184 \times 10^4 \text{ C mol}^{-1}$

Gas constant,  $R = N_A \times k_B = 8.31446261815324 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $= 8.2057366081 \times 10^{-2} \text{ L atm K}^{-1}$

$\text{mol}^{-1}$  Unified atomic mass unit,  $u = 1 \text{ Da} = 1.66053907 \times 10^{-27} \text{ kg}$

Standard pressure,  $p = 1 \text{ bar} = 10^5 \text{ Pa}$  Atmospheric pressure,  $p_{\text{atm}} =$

$1.01325 \times 10^5 \text{ Pa}$

Zero degree Celsius,  $0 \text{ }^\circ\text{C} = 273.15 \text{ K}$

Ångström,  $1 \text{ \AA} = 10^{-10} \text{ m}$

Picometer,  $1 \text{ pm} = 10^{-12} \text{ m}$

Electronvolt,  $1 \text{ eV} = 1.602176634 \times 10^{-19} \text{ J}$

Part-per-million,  $1 \text{ ppm} = 10^{-6}$

Part-per-billion,  $1 \text{ ppb} = 10^{-9}$

Part-per-trillion,  $1 \text{ ppt} = 10^{-12}$

pi,  $\pi = 3.141592653589793$

The base of the natural logarithm (Euler's number),  $e = 2.718281828459045$

Last Name: \_\_\_\_\_ First Name: \_\_\_\_\_

School: \_\_\_\_\_

Province: \_\_\_\_\_

## Question 1: Chinese Cloisonné

Chinese Cloisonné has been known as a treasure of Chinese art for more than 600 years since Ming Dynasty. Chinese cloisonné enamelware is made by covering thin layers of enamel on metal objects such as brass or bronze vases, kettles, or other objects. The enamel layer is colored with metal oxides (mainly cobalt oxide), which exhibits brilliant colors such as blue, which originate from the cobalt compounds.



**1-1**  $\text{Co}^{2+}$  reacts with alkali to form a blue precipitate (1), which is easily oxidized (2). The oxidation product reacts with hydrochloric acid to release yellow-green gas (3). **Write** the equations of reactions (1) to (3).

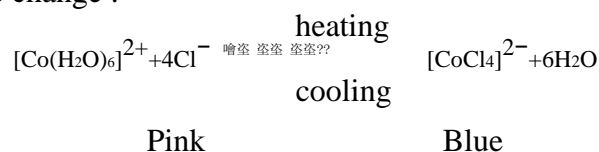
**1-2** Cobalt dichloride can react with ammonia under different conditions to produce four complexes with different colors: **A.**  $\text{CoCl}_3 \cdot 6\text{NH}_3$ (orange), **B.**  $\text{CoCl}_3 \cdot 5\text{NH}_3$ (red purple), **C.**  $\text{CoCl}_3 \cdot 4\text{NH}_3$ (violet), **D.**  $\text{CoCl}_3 \cdot 3\text{NH}_3$ (green). When a sufficient amount of  $\text{AgNO}_3$  (aq) is added, the ratio of  $\text{Ag}^+$  consumed by **A**, **B**, and **C** is 3:2:1, and **D** does not react. **Write** the formulas for complexes **A**, **B**, **C**, and **D** based on inner/outer sphere.

Last Name: \_\_\_\_\_ First Name: \_\_\_\_\_

School: \_\_\_\_\_

Province: \_\_\_\_\_

When dissolving  $\text{CoCl}_2$  in a concentrated  $\text{HCl}$  solution, the following color change is observed along with a temperature change :



**1-3-1** Which absorption spectrum shown in Figure 1.1 should be assigned to the solution at high temperature?

(a) I

(b) II

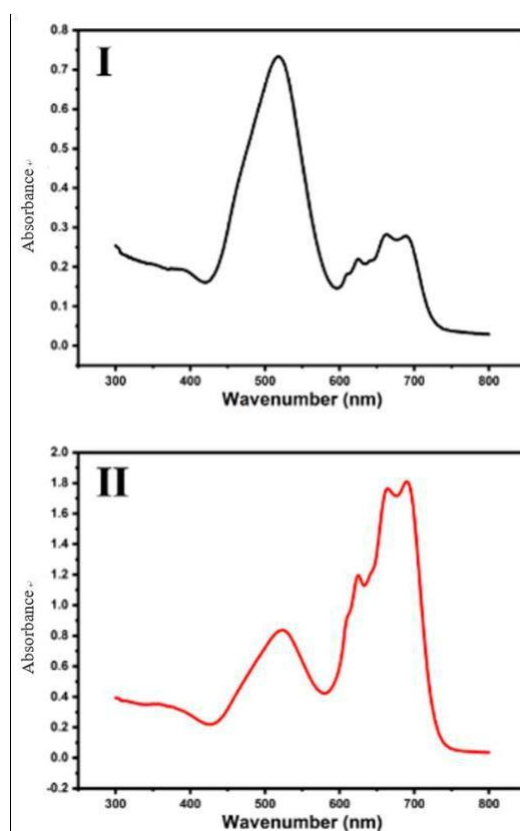


Figure 1.1 Absorption spectra of the solutions of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{CoCl}_4]^{2-}$

**1-3-2** Draw the configurations of  $d$  electrons of the cobalt ion in these two coordination ions with different color, respectively.

**1-3-3** Coordination compounds/ions exhibit paramagnetism when containing unpaired electrons, and the corresponding magnetic moment ( $\mu$ ) is calculated by the function  $\mu = \sqrt{n(n+2)} \text{ B.M.}$  where  $n$  is the number of the unpaired electrons. Calculate the value of  $\mu$  for the coordination ion  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ .

Put an aluminum plate covered by its oxide layer into a dilute cobalt nitrate solution for a while, take out the plate and burn it in the flame of a Bunsen burner for minutes. A blue substance can be observed on the surface. The blue substance, known as cobalt blue, is  $\text{CoAl}_2\text{O}_4$  with a spinel structure. The general formula of spinel is expressed as  $\text{AB}_2\text{O}_4$ , where oxygen ions arrange in a cubic close packing pattern, **A** cations occupy the tetrahedral holes formed by oxygen ions, and **B** cations take the octahedral holes, as shown in Figure 1.2.

Last Name: \_\_\_\_\_ First Name: \_\_\_\_\_

School: \_\_\_\_\_

Province: \_\_\_\_\_

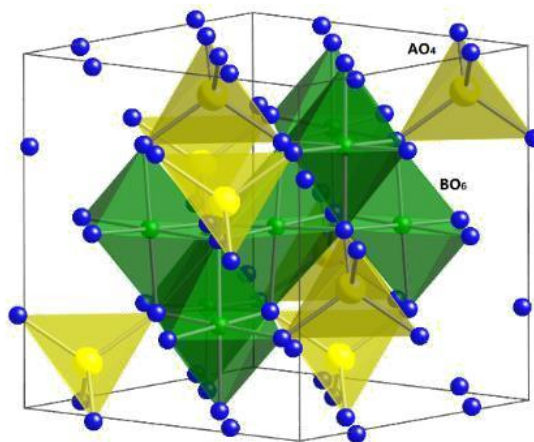


Figure 1.2 Structure of spinel **AB<sub>2</sub>O<sub>4</sub>**

**1-4** Regarding the cations and their position which is responsible for blue color, **choose** all correct statements for cations.

- (a)  $\text{Co}^{2+}$  is in a tetrahedral ligand field.
- (b)  $\text{Co}^{2+}$  is in an octahedral ligand field.
- (c)  $\text{Al}^{3+}$  is in a tetrahedral ligand field.
- (d)  $\text{Al}^{3+}$  is in an octahedral ligand field.

## Question 2: Greenhouse Gas and Carbon Neutrality

The United Nations Assessment Report (the fifth assessment report issued by the United Nations Intergovernmental Panel on Climate Change in 2014) points out that there is a positive correlation between the cumulative emission of greenhouse gases and the increase of global average temperature. To mitigate global warming and climate change that is a common threat to human beings, a direct and effective measure is to control and reduce the concentration of greenhouse gases in the atmosphere. In recent years, worldwide efforts have been put forward to cut carbon dioxide emission. At the 75<sup>th</sup> session of the United Nations General Assembly in 2020, China proposed striving to achieve peak carbon emission before 2030 and carbon neutrality before 2060. Technological strategies for carbon neutralization include planting trees, capturing and storing carbon dioxide, expanding the use of clean power such as in electric vehicles, boosting renewable energy, and so on.

Using CO<sub>2</sub> as a chemical raw material can increase its value by ‘turning waste into treasure’. In the industrial production of soda, CO<sub>2</sub>, NH<sub>3</sub> and NaCl are raw materials. Debang Hou, a famous Chinese scientist and chemical engineer, invented the Hou’s Process that improves the Solvay Process. Figure 2.1 shows a simplified flow diagram of Hou’s Process of Soda production.

Last Name: \_\_\_\_\_ First Name: \_\_\_\_\_

School: \_\_\_\_\_

Province: \_\_\_\_\_

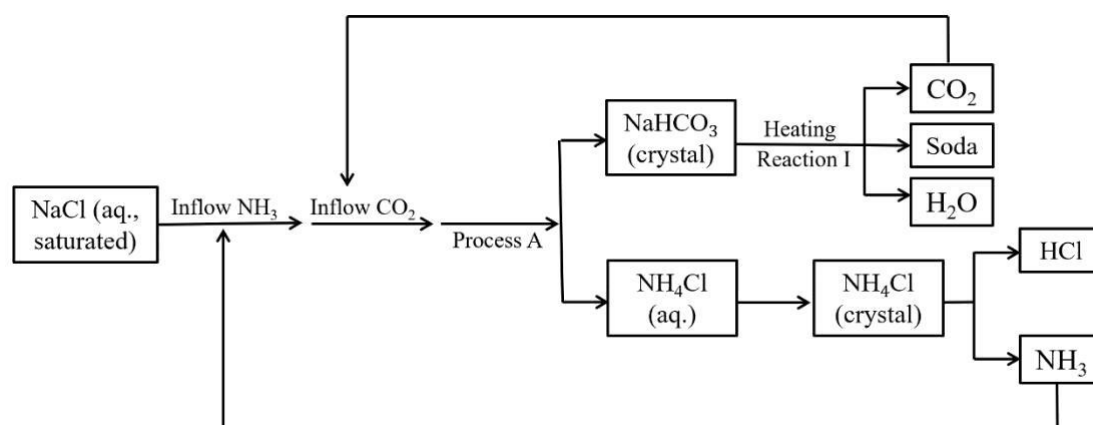
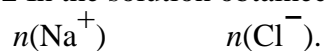


Figure 2.1 Hou's Process of Soda production

**2-1-1 Write** the equation for Reaction I

**2-1-2** In the solution obtained by Process A, **compare** the molar number of ions:



- (a) more than            (b) less than            (c) equal to

**2-1-3** Hou's process features a high utilization ratio of NaCl. The key is that the solubility of  $\text{NH}_4\text{Cl}$  is \_\_\_\_\_ that of NaCl at room temperature but the former is \_\_\_\_\_ the latter at low temperatures.

**Which** of the following words fits into the blank in the above sentence?

- (a) higher than            (b) lower than            (c) equal to

Metal-carbon dioxide batteries, which employ metal and  $\text{CO}_2$  as active materials respectively in the anode and the cathode, are attractive devices, simultaneously fixing/utilizing  $\text{CO}_2$  and generating electricity. Taking Na- $\text{CO}_2$  battery as an example, assuming that the total reaction is:  $4\text{Na} + 3\text{CO}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + \text{C}$  ( $\Delta_r G_m = -905.6 \text{ kJ mol}^{-1}$ ), the Na anode releases electrons during discharge, and the metallic Na is deposited on charging.

**2-2-1 Write** down the reaction equation for the cathode of a Na- $\text{CO}_2$  battery.

**2-2-2 Select** an appropriate solvent from the following items to prepare the electrolyte of the Na- $\text{CO}_2$  battery.

- (a) water            (b) ethanol            (c) tetraethylene glycol dimethyl ether

**2-2-3 Calculate** the standard voltage of this Na- $\text{CO}_2$  battery under standard conditions.

Under mild conditions (room temperature and ambient pressure), electrochemical reduction reaction of carbon dioxide generates high value-added chemicals and fuels ( $\text{CO}_2\text{RR}$ ). This process offers a promising route for efficient conversion and storage of intermittent electricity generated from renewable energy such as solar and wind. The  $\text{CO}_2\text{RR}$  occurs on the catalyst-containing cathode of an electrolytic cell, while oxygen is released from water decomposition in the anode. Extensive research interest has been directed to formulating compatible electrolytes and exploring efficient catalysts to enhance the rate and yield of  $\text{CO}_2$  conversion into target products.

Last Name: \_\_\_\_\_ First Name: \_\_\_\_\_

School: \_\_\_\_\_

Province: \_\_\_\_\_

**2-3-1** Previous studies indicate that using a weakly alkaline  $\text{KHCO}_3$  aqueous solution as the electrolyte and a Cu-based catalyst can promote the reduction of  $\text{CO}_2$  to generate ethylene. Providing only ethylene as the product from  $\text{CO}_2$ , **write** the cathode and anode reactions of the electrolytic cell.

**2-3-2** In addition to ethylene, there are gaseous products (e.g.,  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$ ) and liquid products (e.g., formic acid and ethanol) generated in the process of  $\text{CO}_2$  reduction. Gas chromatography is often employed to quantitatively detect the distribution of gaseous products. In a  $\text{CO}_2$  reduction experiment, the electrolysis was conducted by applying a constant current of 10.0 mA for 1.00 h. The total amount of gas entering the chromatogram was 90.0 mL as determined from the flowmeter, and the volumetric concentration of detected ethylene was 0.519%. Assuming that all produced gases are ideal gases in standard conditions, **calculate** the Faraday efficiency (defined as the percentage of the actual product in theoretical value) and the rate (unit  $\text{mg h}^{-1}$ ) of ethylene generation.

Carbon dioxide is viewed as the primary greenhouse gas emitted through human activities. One of the important paths to decrease the concentration of greenhouse gas is the capture and storage of  $\text{CO}_2$ .

**2-4-1** Assuming 1 mol of  $\text{CO}_2$  (regarded as an ideal gas) expands isothermally at the temperature ( $T$ ) of 273.15 K, if the expansion process is reversible and known work ( $W$ ) is 5.23 kJ. **Calculate** the heat ( $Q$ ), change of internal energy ( $\Delta U$ ), change of enthalpy ( $\Delta H$ ), change of entropy ( $\Delta S$ ), and change of Gibbs free energy ( $\Delta G$ ) of this process.

**2-4-2**  $\text{CO}_2$  can be captured by physical sorption in porous materials. Generally, the capacity of physical adsorption \_\_\_\_\_ with increasing temperature.

**Which** of the following words fits into the blank in the above sentence?

- (a) increases                      (b) decreases                      (c) does not change

**2-4-3** Assume that the physical adsorption of  $\text{CO}_2$  on activated carbon obeys the Langmuir adsorption isotherm equation:

$$\theta = \frac{P}{P + P_m}$$

where  $\theta$  is coverage of single-layer adsorbate on the surface,  $V$  is adsorbed amount in volume,  $V_m$  is saturated adsorbed amount in volume,  $\alpha$  is a constant, and  $P$  is partial pressure of adsorbate gas.

In two separate tests, the partial pressures of  $\text{CO}_2$  in the adsorption state are 5.2 kPa and 13.5 kPa at 298 K, and the corresponding equilibrium adsorption capacities measured after desorption are  $0.0692 \text{ m}^3 \text{ kg}^{-1}$  and  $0.0826 \text{ m}^3 \text{ kg}^{-1}$  (already converted to standard conditions), respectively.

(1) **Determine** the saturated adsorption capacity of the tested activated carbon;

(2) If the dynamic cross-sectional area of a  $\text{CO}_2$  molecule is  $0.32 \text{ nm}^2$ , **determine** the specific surface area of the tested activated carbon.

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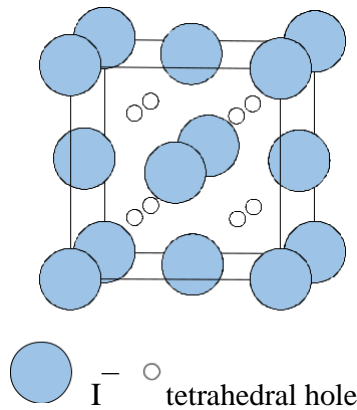
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### Question 3: Packing of binary crystals

The structures of binary crystals can be viewed as the packing of atoms of the first element, and the atoms of second element filling into the holes formed by the first one. In the unit cell of the  $\text{-AgI}$  crystal ( $a = 647.3 \text{ pm}$ ),  $\text{I}^-$  anions are arranged in a face-centered cubic (*fcc*) manner, and  $\text{Ag}^+$  cations fill into half of the tetrahedral holes formed by the array of  $\text{I}^-$  anions.

**3-1 Label** the Ag atoms in the figure below, and **calculate** the Ag-I bond length and the density of the crystal.



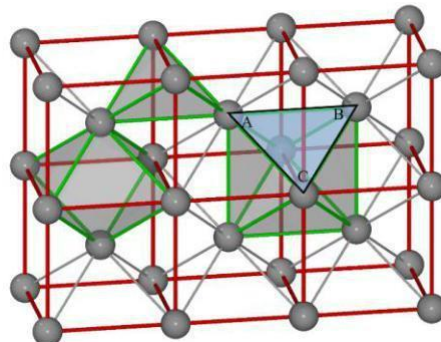
Upon changing temperature and pressure, the crystal of  $\text{AgI}$  can be transformed to the  $\text{NaCl}$  type or the  $\text{CsCl}$  type. when X-rays of wavelength ( )  $154.2 \text{ pm}$  were used, X-ray diffraction measured the glancing angles ( ) of the (200) reflection ( $h = 2, k = 0, l = 0$ ) of the two types of crystals to be  $14.7^\circ$

and  $21.0^\circ$ , respectively. Bragg's law:  $\sin \theta = \frac{1}{2a} \sqrt{h^2 + k^2 + l^2}$

**3-2 Calculate** the unit cell dimensions  $a$  and the Ag-I bond lengths of these two types of crystals.

In the  $\text{-AgI}$  crystal ( $a = 504 \text{ pm}$ ),  $\text{I}^-$  anions are arranged in a body-centered cubic (*bcc*) manner. The tetrahedral and octahedral holes formed by the  $\text{I}^-$  anions are presented below. Under the influence of an external electric field,  $\text{Ag}^+$  cations can move freely across the trigonal holes such as ABC. Assuming that  $\text{I}^-$  anions are in contact with each other and both  $\text{I}^-$  and  $\text{Ag}^+$  are hard spheres.

**3-3 Calculate** the radius of  $\text{I}^-$ ,  $r(\text{I}^-)$ , and the maximum radius of  $\text{Ag}^+$ ,  $r_{\text{max}}(\text{Ag}^+)$ .



Last Name: \_\_\_\_\_ First Name: \_\_\_\_\_

School: \_\_\_\_\_

Province: \_\_\_\_\_

## Question 4: Determination of Calcium Ions by Titration with Ethylene Bis(oxyethylenitrilo) Tetraacetic Acid (EGTA)

Aminocarboxy ligands are a class of reagents with amino groups and carboxylic groups. These reagents, containing oxygen and nitrogen as coordination atoms, can bind to many metal ions to form stable chelates. The reagents are widely used in analytical chemistry and biochemistry as masking agents, separation reagents and titrants. Ethylene bis(oxyethylenitrilo) tetraacetic acid (EGTA, H<sub>4</sub>E) is one such aminocarboxy ligand reagents. Its molecular formula is C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>O<sub>10</sub>. EGTA is a hexaprotic acid when it combines two other protons. The following species can exist: H<sub>6</sub>E<sup>2+</sup>, H<sub>5</sub>E<sup>+</sup>, H<sub>4</sub>E, H<sub>3</sub>E<sup>-</sup>, H<sub>2</sub>E<sup>2-</sup>, HE<sup>3-</sup> and E<sup>4-</sup>. The first two dissociations are those of strong acids and its remaining four dissociation constants pK<sub>a3</sub>-pK<sub>a6</sub> are 2.08, 2.73, 8.93 and 9.53, respectively. EGTA can coordinate with calcium ions and magnesium ions to form chelates. The formation constants of the calcium-EGTA and magnesium-EGTA chelates are lgK<sub>CaE</sub> = 10.97, lgK<sub>MgE</sub> = 5.21, respectively.

**4-1** H<sub>4</sub>E is dissolved in 0.10 mol L<sup>-1</sup> NaOH solution to prepare EGTA solution of 0.020 mol L<sup>-1</sup>. **Why** it is not dissolved in distilled water directly?

**4-2 Calculate** the coefficient of acid effect α<sub>E(H)</sub> of H<sub>4</sub>E at pH10 in the buffer solution.

**4-3** Titrate 0.01000 mol L<sup>-1</sup> Ca<sup>2+</sup> in the presence of 0.01000 mol L<sup>-1</sup> Mg<sup>2+</sup> with 0.01000 mol L<sup>-1</sup> H<sub>4</sub>E at pH10 in the NH<sub>3</sub>-NH<sub>4</sub>Cl buffer solution. Using Eriochrome Black T (EBT) as indicator, Ca<sup>2+</sup> ions concentration at end-point pCa<sub>t</sub> = 3.8, **calculate** the titration error. Mg<sup>2+</sup> ions can form a colored complex with EBT, and pMg<sub>t</sub> = 5.4.

**4-4** Because of the large error in the above determination, calconcarboxylic acid should be used as indicator. Titrate 0.01000 mol L<sup>-1</sup> Ca<sup>2+</sup> in the presence of 0.01000 mol L<sup>-1</sup> Mg<sup>2+</sup> with 0.01000 mol L<sup>-1</sup> H<sub>4</sub>E at pH12 in the sodium hydroxide solution, using calconcarboxylic acid as indicator, and Ca<sup>2+</sup> concentration at end-point pCa<sub>t</sub>=5.6, **calculate** the titration error. Known Mg(OH)<sub>2</sub>, pK<sub>sp</sub>=10.74, and acid effect of H<sub>4</sub>E is negligible.

**4-5** Standardization of EGTA solution: A 2.4907g of primary standard calcium carbonate is dissolved in 0.1 mol L<sup>-1</sup> hydrochloric acid, and the solution diluted to 1000.00 mL in a volumetric flask. Then the 10.00 mL solution is withdrawn and diluted to 100.00 mL in another volumetric flask to obtain standard solution. A 25.00 mL aliquot standard solution is withdrawn, adding the sodium tetraborate buffer solution and calconcarboxylic acid as indicator, titrated with solution of H<sub>4</sub>E. When the color of solution from red to bright yellow to indicate the end-point, required 25.85 mL of H<sub>4</sub>E solution. **Calculate** the concentration of H<sub>4</sub>E solution. A 0.80 mL aliquot serum sample is withdrawn, adding buffer solution and indicator, titrated with 0.83 mL solution of H<sub>4</sub>E using 5 mL burette, the color of solution from red to bright yellow to indicate the end-point. The blank experiment was carried out with distilled water 10 times the volume of serum sample as the sample, it required 0.20 mL solution of H<sub>4</sub>E to reach the end-point. **Calculate** the content of calcium (mmol L<sup>-1</sup>) in the serum sample.



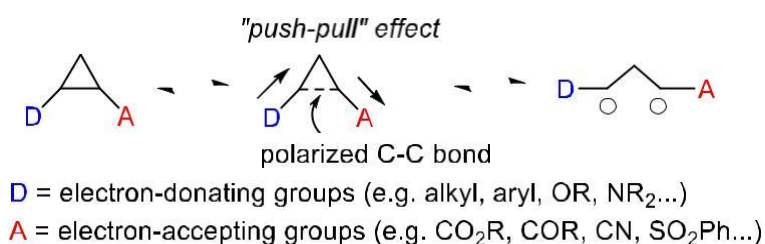
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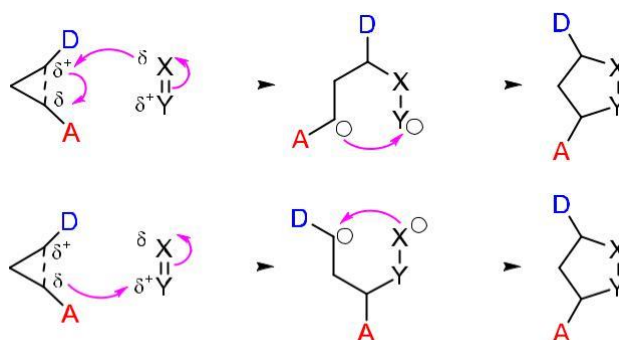
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## Question 5: Cyclopropanes

Cyclopropane is the smallest possible saturated three membered cyclic structure. An unsubstituted cyclopropane, though highly strained, possesses enough kinetic stability with a Baeyer strain energy of  $115 \text{ kJ mol}^{-1}$  and offers limited synthetic potential. Introducing electron-accepting and electron-donating groups to cyclopropanes offers a method for increasing reactivity over their unsubstituted counterparts through C–C bond activation from the ‘push-pull’ effect, leading to the formation of 1,3-dipoles, in which the negative charge is stabilized by the acceptor while the positive charge is stabilized by the donor.



Formal cycloadditions of activated D-A (D, electron-donating group; A, electron-accepting group) cyclopropanes with a variety of electrophilic unsaturated C=C or C=X bonds are a valuable tool for accessing highly functionalized carbocyclic and heterocyclic systems. Because of the dual electrostatic character of the intermediate 1,3-zwitterion, the cyclization can begin with either an electrophilic or nucleophilic reaction with the intermediate 1,3-dipole. Very high regioselectivity is observed in all these reactions, as the partially negatively charged center of the reaction partner preferentially attacks the donor-substituted carbon atom of the three-membered ring. Ring opening is usually triggered by a LUMO-lowering Lewis acid catalyst through coordination of the electron-withdrawing substituent, very often via chelation to a diester, facilitating the attack by a nucleophile.



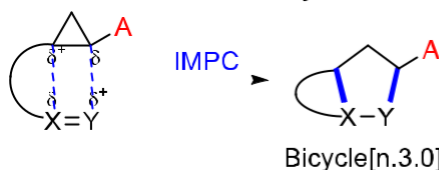
The benefits of intramolecularity for ring-opening cyclization reactions of cyclopropanes include increased reactivity, milder reaction conditions, better control of diastereoselectivity, and rapid formation of polycyclic structures. In the case that the 1,2-dipole (X = Y) is connected to C-2 of cyclopropane, depending on the regioselectivity initiated by the difference of polarities of the internal and external atoms in the 1,2-dipole, the intramolecular [3+2] formal cycloadditions can be classified into two types: ‘Intramolecular Cross-Cycloaddition (IMCC)’ and ‘Intramolecular Parallel-Cycloaddition (IMPC)’.

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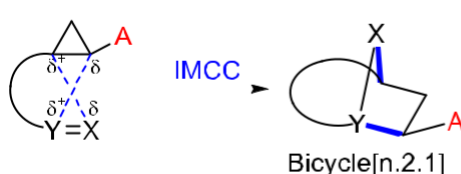
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intramolecular Parallel-Cycloaddition (IMPC)



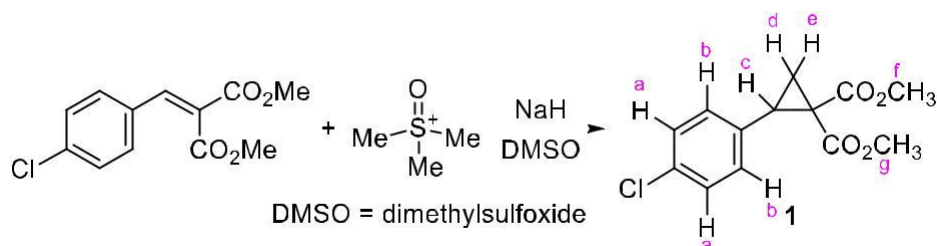
intramolecular Cross-Cycloaddition (IMCC)



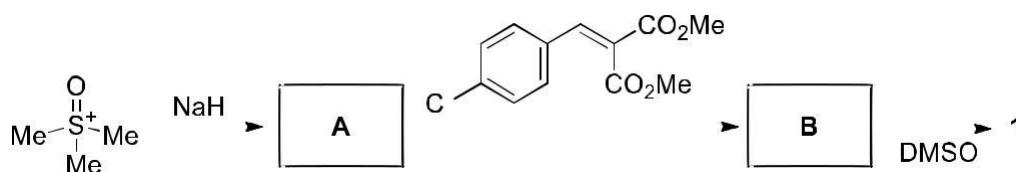
**5-1** The heats of combustion of cyclopropane and cyclohexane are  $697.1$  and  $658.6 \text{ kJ mol}^{-1}$  per  $\text{CH}_2$  unit, respectively. Which one is more thermally stable? Please give a choice based on the structural analysis of cyclopropane and cyclohexane, **which** of the following factors is **not** associated with this difference in thermal stability?

- (a) Hydrogen bond (b) Angle strain  
(c) Torsional strain (d) Van der Waal's force

**5-2** Substituted cyclopropanes can be obtained by the reaction of alkenes with a sulfur ylide. For example, D-A cyclopropane **1** can be prepared by the following reaction:



**5-2-1 Draw** the structures of two key intermediates **A** and **B** of this reaction.



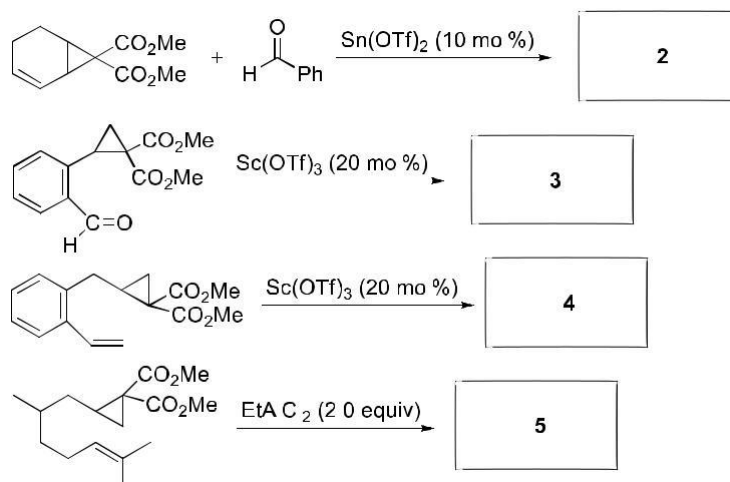
**5-2-2** The  $^1\text{H}$  NMR data of **1** are shown as following:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (2H, d,  $J = 8.0$  Hz), 7.19 (2H, d,  $J = 8.0$  Hz), 3.77 (3H, s), 3.39 (3H, s), 3.14 (1H, dd,  $J = 9.0$  and  $8.1$  Hz), 2.12 (1H, dd,  $J = 8.1, 5.1$  Hz), 1.74 (1H, dd,  $J = 9.0, 5.1$  Hz). Please assign all the peaks to the corresponding hydrogen atoms.

**5-3** The formal cycloaddition reactions of D-A cyclopropanes with unsaturated bonds are highly regioselective. **Draw** the structures of products **2-6** for the following reactions (The stereochemistry is ignored).

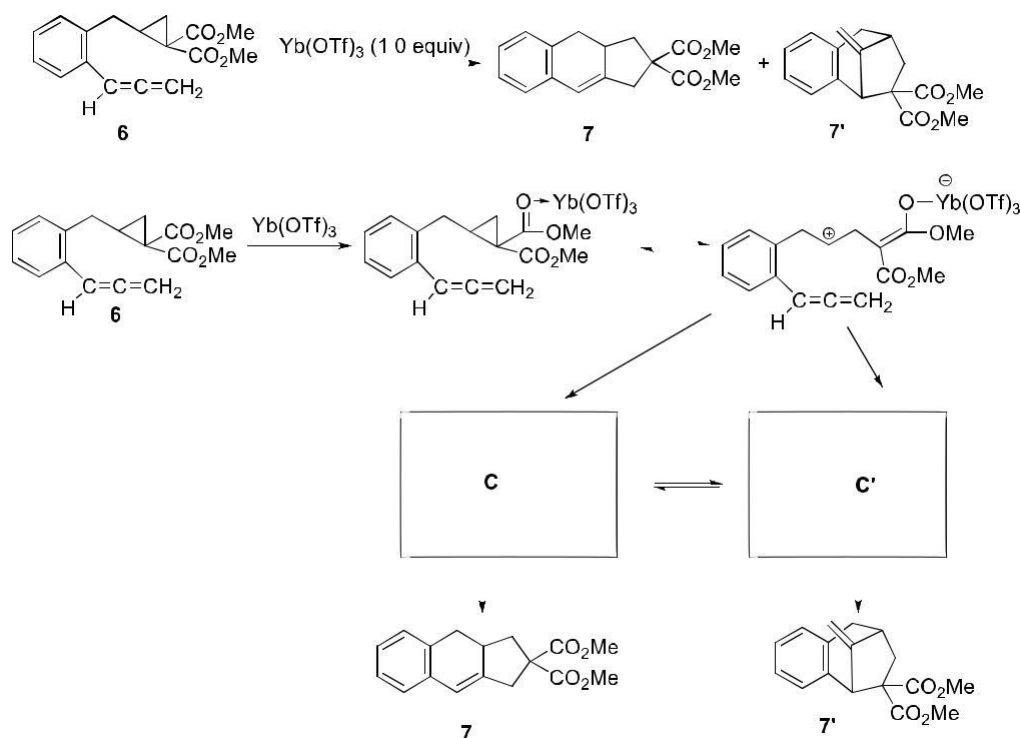
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**5-4** The intramolecular cycloaddition reaction of D-A cyclopropane **6** can be promoted by Lewis acid Yb(OTf)<sub>3</sub>, to form the parallel-cycloaddition (IMPC) product **7** and cross-cycloaddition (IMCC) product **7'**. **Draw** the structures of the two possible intermediates **C** and **C'**.



**5-5** Platensimycin is discovered in 2006 as a metabolite of *Streptomyces platensis*, and acts by efficiently blocking bacterial fatty acid biosynthesis. Because platensimycin has a unique mode of action, no cross-resistances to existing drugs have been observed to date, and no toxic effects have been detected, it has been hailed as a true breakthrough in antibiotic research. This natural product has a unique structure characterized by a 8-oxabicyclo[3.2.1]octane core. With the interesting structural features and potential biological activities, the synthesis of platensimycin began to attract attention from the synthetic community. Lewis acid-catalyzed intramolecular [3+2] cycloaddition of cyclopropane 1,1-diester with carbonyls provided an efficient construction of bridged oxa-[n.2.1] skeletons, and successfully applied it to the formal total synthesis of platensimycin. **Draw** the structures of compounds **8-12**.

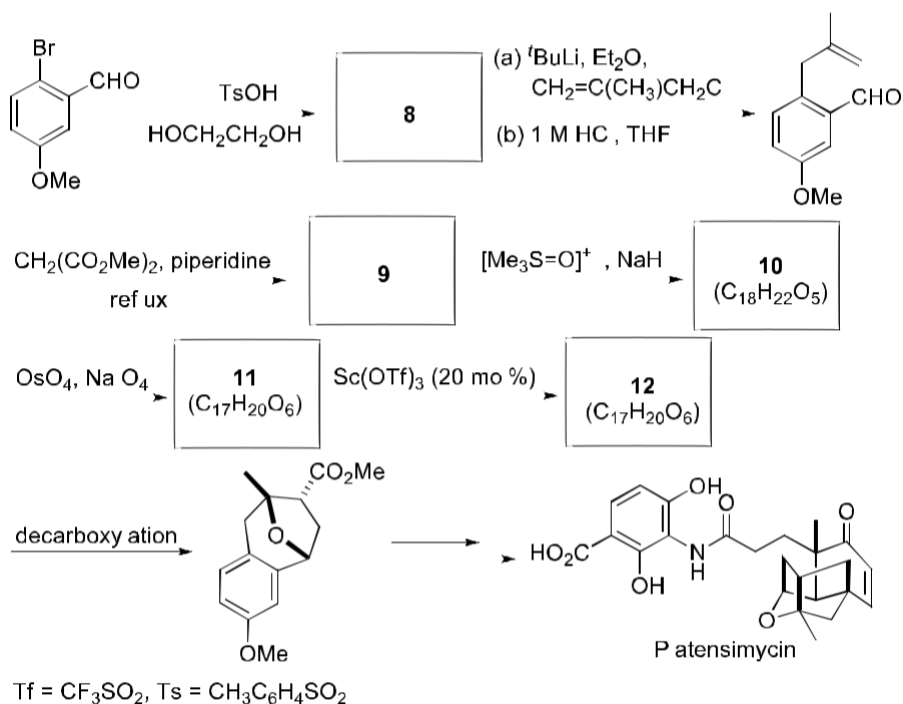
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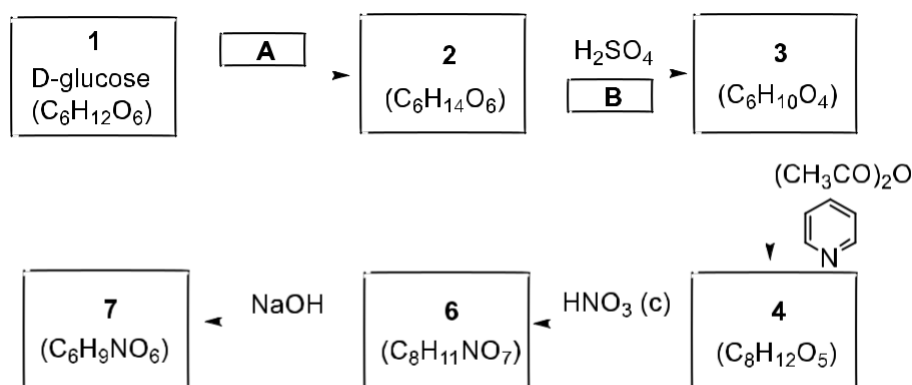
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## Question 6: Isosorbitol

In recent years, with the rising price of crude oil and the depletion of non renewable resources, the research on renewable resources - biomass and its derivatives has attracted more and more attention. Sorbitol **2**, the hydrogenation product of glucose, has become an important biomass conversion platform compound. As shown in the figure below, chiral compound **3** is produced by intramolecular dehydration of sorbitol **2**. Compound **7**, a drug for the treatment of angina pectoris, is produced by multi-step transformation.



**6-1 Draw** the structure of sorbitol **2** (Fisher projection)

**6-2** From the following conditions, **choose** the best for **A**

- (a)  $Al(Oi-Pr)_3$ , *i*-PrOH (b) Pd-C,  $H_2$  (c) Na,  $NH_3(l)$

**6-3** Theoretically, compound **3** can be transformed into diastereomers **4** and **5** in the presence of acetic anhydride and pyridine. In practice, the main product is compound **4**. **Draw** the structures of compounds **3**, **4** and **5**. *Hint: compound 3 is a bicyclic compound.*

**6-4** To explain the reason for the selective formation of compound **4** from compound **3**, **Choose** the most appropriate option from the following reasons

- (a) Electronic effect (b) Steric effect (c) Field effect

**6-5** Choose the correct answer for **B** from the following options

- (a)  $-H_2O$  (b)  $-2H_2O$  (c)  $-3H_2O$

**6-6 Draw** the structures of compounds **6** and **7**.

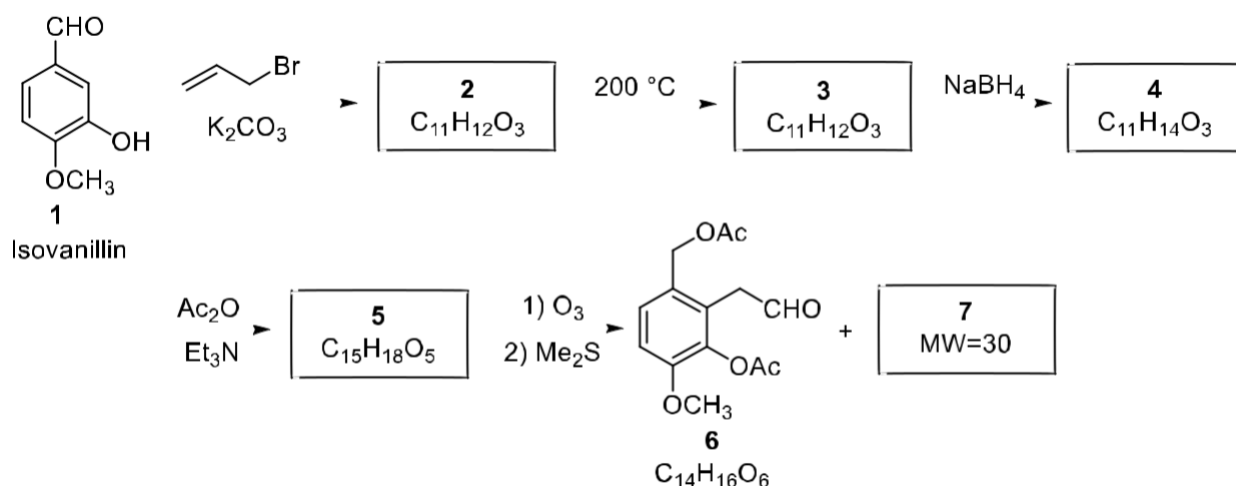
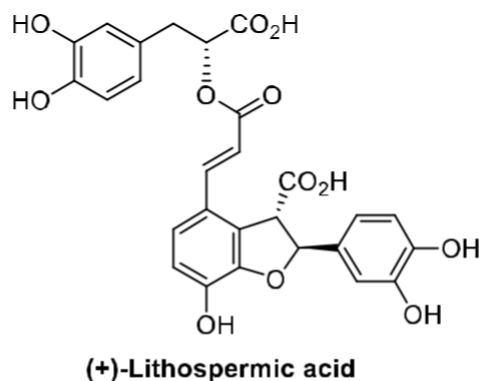
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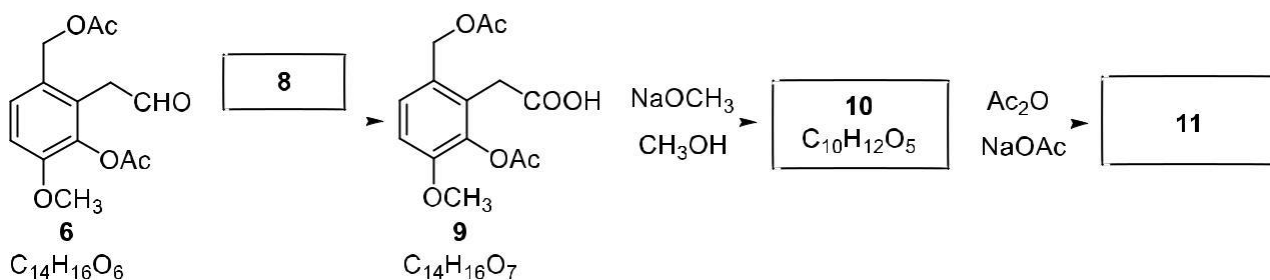
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## Question 7: Total Synthesis of Lithospermic acid

Lithospermic acid was first isolated from the root of *Lithospermum ruderales* in 1963 by Johnson and co-workers. Lithospermic acid is an active ingredient of the Chinese herb *Danshen* and shows important biological properties. Herein, a total synthesis route of Lithospermic acid is described.



**7-1 Draw** the structures of compounds **2**, **3**, **4**, **5** and **7**.



**7-2** From the following conditions, **choose** the correct condition for **8**.

- (a)  $Ce(NH_4)_2(NO_3)_6$       (b)  $CrO_3(Pyridine)_2$   
 (c)  $H_2CrO_4$                 (d)  $CH_3COCH_3, Al[O\text{Pr}]_3$

**7-3 Draw** the structure of compound **10**.

**7-4** Compound **11** contains a benzo-fused six-membered heterocycle structure. The  $^1H$  NMR spectrum of compound **11** gives the following data. **Draw** the structure of compound **11**.

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School: \_\_\_\_\_

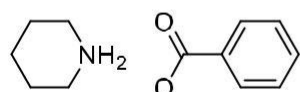
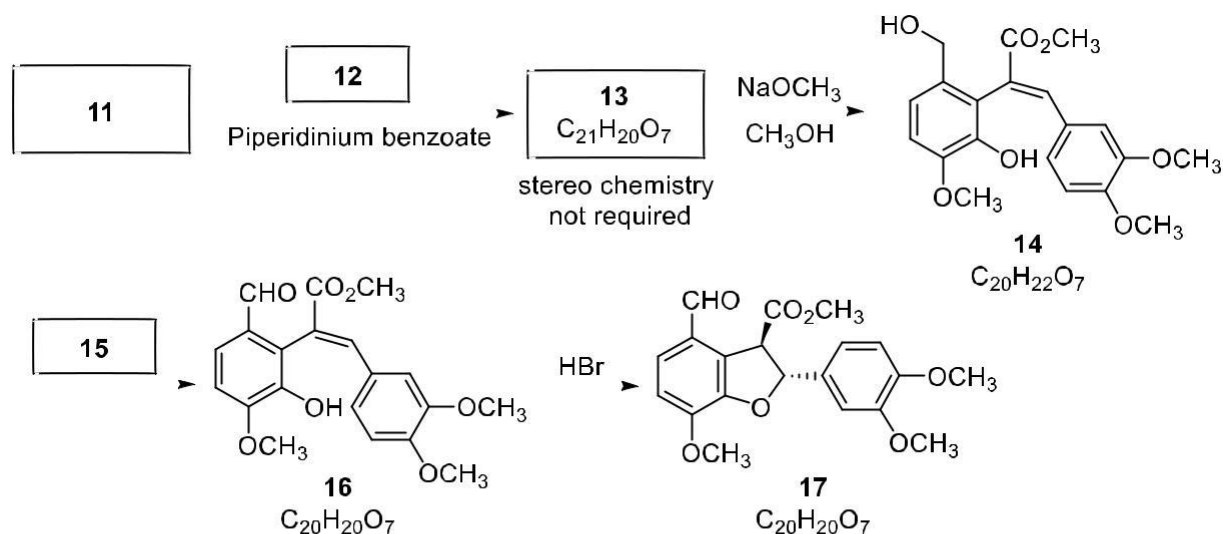
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$^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 2.32 (s, 3H), 3.54 (s, 2H), 3.79 (s, 3H), 5.23 (s, 2H), 6.84 (d,  $J = 9$  Hz, 1H), 7.04 (d,  $J = 9$  Hz, 1H).

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School: \_\_\_\_\_

Province: \_\_\_\_\_

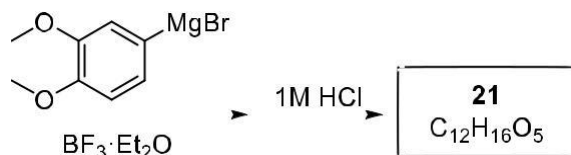
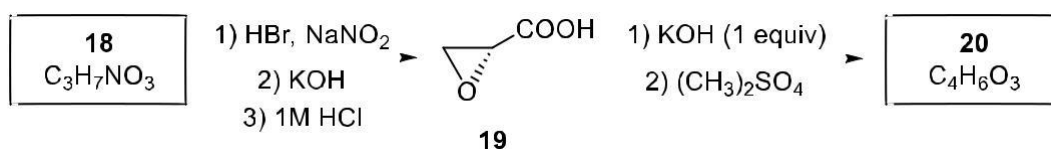


Piperidinium benzoate

7-5 **Draw** the structures of compounds **12** and **13**.

7-6 From the following conditions, **choose** the correct condition for **15**.

- (a)  $\text{I}_2, \text{NaOH}$  (b)  $(\text{COCl})_2, \text{Me}_2\text{SO}$  (c)  $\text{Ag}(\text{NH}_3)_2\text{OH}$  (d)  $\text{CrO}_3, \text{H}_2\text{SO}_4$



7-7 Compound **18** is an  $\alpha$ -amino acid. **Draw** Fischer projection for compound **18** (Notice that the stereochemical configuration of the asymmetric carbon is inverted by the opposite-side substitution reaction from **18** to **19**).

7-8 **Assign** the absolute configuration of the center of chirality in compound **19** using the *R/S* nomenclature.

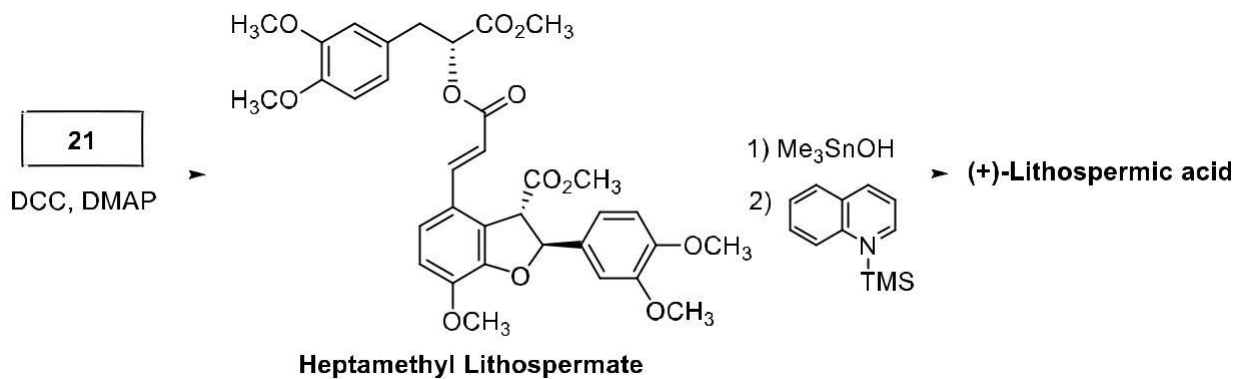
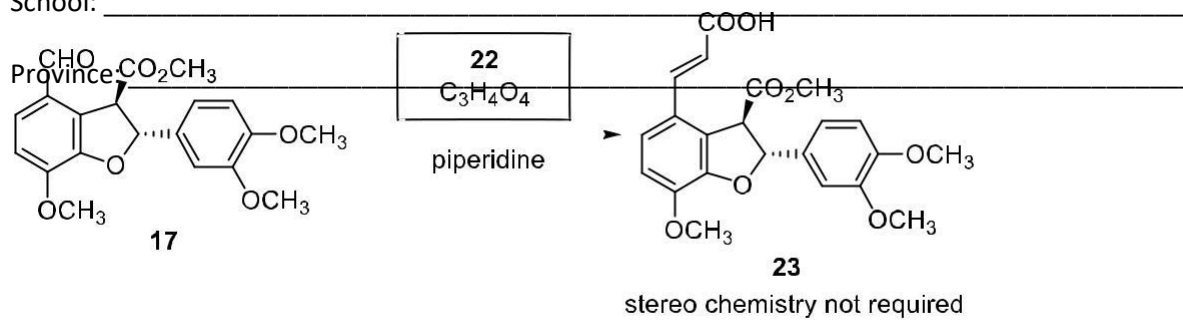
7-9 **Draw** the structure of compound **20** and clearly identify the stereochemistry.

7-10 **Draw** the structure of compound **21** and clearly identify the stereochemistry.



Last Name: \_\_\_\_\_ First Name: \_\_\_\_\_

School: \_\_\_\_\_



7-11 **Draw** the structure of compound 22.