

IChO 2022

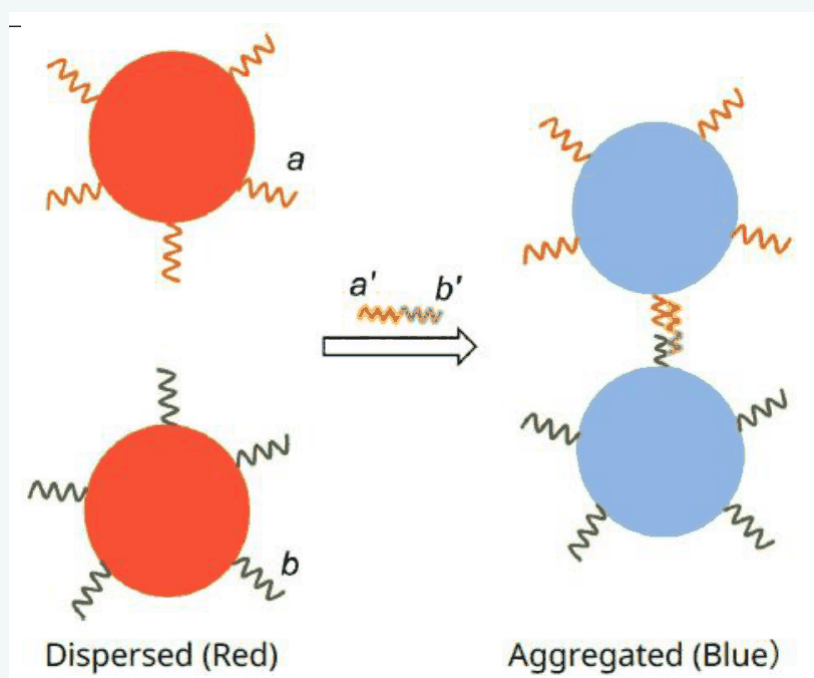
Theory problems and solutions · Tianjin, China (held remotely) · 9 theory problems with complete solutions

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Problem 1: Rapid and Visual Nucleic Acid Testing for COVID-19

Fast and simple methods for early detection of COVID-19 are urgently needed. Gold nanoparticles-aided detection is one of the promising methods. Gold nanoparticles are widely used as a visible readout for test strips due to their high molar extinction coefficients (molar absorptivity). The color appearance of gold nanoparticles is closely associated with their sizes and dispersity. Generally, the larger the gold nanoparticles, the more reddish the color is. Once the nanoparticles are aggregated, the color shifts from red to blue.

When the surface of gold nanoparticles is modified with two kinds of single-stranded nucleic acid fragments a and b , the gold nanoparticles would aggregate in the presence of the target nucleic acid ($a'b'$), causing the color change of the solution from red to blue in several minutes (as indicated below). Based on this principle, the target nucleic acids collected from the coronavirus in a sample can be detected.



1.1 Indicate the absorption band region of the dispersed gold nanoparticles with an appropriate letter (a-f in the color wheel of **Figure 0.1** in **General Instructions**).

The Color Wheel

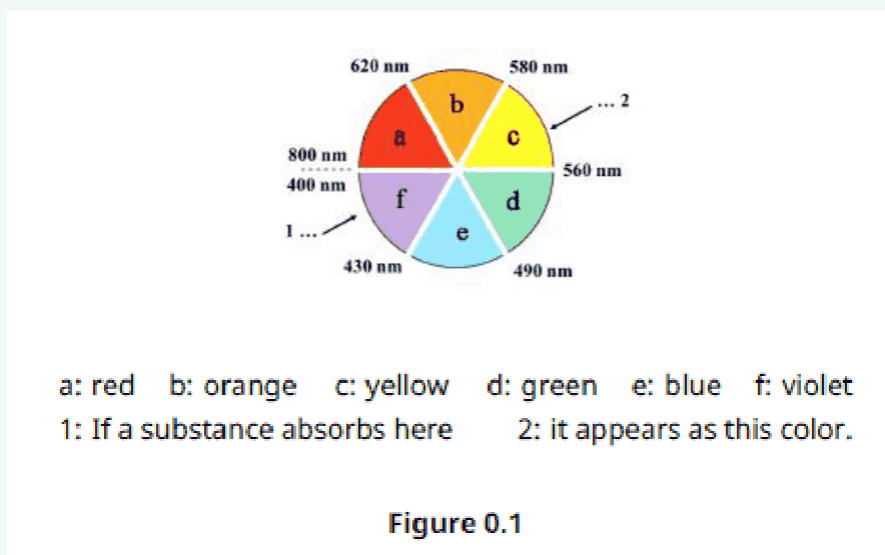


Figure 0.1

1.2 Indicate the change in the absorption spectrum of the gold nanoparticles once they are aggregated. Compared to the absorption wavelength of the dispersed gold nanoparticles, the wavelength of the aggregated nanoparticles

- (a) becomes longer
- (b) becomes shorter
- (c) does not change

Gold nanoparticles are composed of gold atoms that are closely packed as solid gold (density $\rho = 19.3 \text{ g cm}^{-3}$).

1.3 Calculate how many gold atoms (N) are there in a spherical gold nanoparticle with a diameter of 30.0 nm.

The synthesis of gold nanoparticles depends on the redox reaction between hydrogen tetrachloroaurate(III) ($\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$, $MW = 394$) and reducing substances (such as sodium citrate). 5.2 mg of $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ was completely converted into uniform spherical gold nanoparticles with a diameter of 30.0 nm in a 100.0 mL reaction solution. The absorbance of the resulting red solution was 0.800 measured at 530 nm by a UV-Vis spectrometer.

1.4 Calculate the molar extinction coefficient (molar absorptivity) of the resulting gold nanoparticles solution at 530 nm per mol of gold nanoparticles. The optical path of the cuvette used is 1 cm. If you failed to get the number of gold atoms (N) in 1.3, use $N = 1.00 \times 10^5$.

The standard addition method was used for colorimetric detection of the target nucleic acid. The original throat swab sample was collected and divided equally into two portions. After addition of the probe solutions and water (as indicated below), the absorbance of the two resulting solutions was measured at 600 nm separately.

No.	Volume of throat swab sample (mL)	Volume of solution of gold nanoparticles modified with nucleic acid fragments (mL)	Volume of standard solution containing $2.0 \mu\text{g mL}^{-1}$ target nucleic acid (mL)	Volume of water (mL)	Absorbance
1	0.10	0.80	0.00	0.10	0.400
2	0.10	0.80	0.10	0.00	0.900

1.5 Calculate the concentration of the viral nucleic acids in the original throat swab sample.

Official English text of the problem.

Answers

- **1.1:** **d**, the green region, approximately 490–560 nm.
- **1.2:** **(a) becomes longer**: the absorption band undergoes a red shift.
- **1.3:** $N = 8.34 \times 10^5$ gold atoms per nanoparticle.
- **1.4:** $\varepsilon_{530} = 5.1 \times 10^9 \text{ L mol}^{-1} \text{ cm}^{-1}$, per mole of nanoparticles.
- **1.5:** $C_{\text{original}} = 1.6 \mu\text{g mL}^{-1}$.

Solution

1.1

The observed color is complementary to the absorbed color. On the supplied color wheel, red lies opposite green. Therefore, the dispersed nanoparticles, which appear red, absorb in the **green region, d**, approximately 490–560 nm. The stated measurement wavelength of 530 nm lies in this region.

1.2

The aggregated nanoparticles appear blue. On the supplied wheel, blue is complementary to orange, corresponding to approximately 580–620 nm.

Thus, aggregation shifts the absorption from the green region toward longer wavelengths:

$$\lambda_{\text{aggregated}} > \lambda_{\text{dispersed}}.$$

The answer is **(a) becomes longer**.

1.3

Use the standard constants

$$M(\text{Au}) = 197.0 \text{ g mol}^{-1}, \quad N_{\text{A}} = 6.022 \times 10^{23} \text{ mol}^{-1}.$$

The nanoparticle radius is

$$r = \frac{30.0}{2} \text{ nm} = 15.0 \text{ nm} = 1.50 \times 10^{-6} \text{ cm}.$$

Its volume and mass are

$$V_{\text{p}} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(1.50 \times 10^{-6} \text{ cm})^3 = 1.4137 \times 10^{-17} \text{ cm}^3,$$

$$m_p = \rho V_p = (19.3 \text{ g cm}^{-3})(1.4137 \times 10^{-17} \text{ cm}^3) = 2.7285 \times 10^{-16} \text{ g}.$$

Therefore, the number of gold atoms in one nanoparticle is

$$N = \frac{m_p}{M(\text{Au})} N_A = \frac{2.7285 \times 10^{-16} \text{ g}}{197.0 \text{ g mol}^{-1}} (6.022 \times 10^{23} \text{ mol}^{-1}).$$

$$N = 8.34 \times 10^5 \text{ atoms per nanoparticle}.$$

1.4

Each formula unit of the precursor contains one gold atom. Complete conversion therefore gives

$$n_{\text{Au}} = \frac{5.2 \times 10^{-3} \text{ g}}{394 \text{ g mol}^{-1}} = 1.3198 \times 10^{-5} \text{ mol}.$$

Because each nanoparticle contains N gold atoms, the amount of nanoparticles is

$$n_{\text{NP}} = \frac{n_{\text{Au}}}{N} = \frac{1.3198 \times 10^{-5}}{8.34 \times 10^5} \approx 1.582 \times 10^{-11} \text{ mol}.$$

Their molar concentration in 100.0 mL is consequently

$$c_{\text{NP}} = \frac{1.582 \times 10^{-11} \text{ mol}}{0.1000 \text{ L}} = 1.582 \times 10^{-10} \text{ mol L}^{-1}.$$

Using the Beer–Lambert law,

$$A = \varepsilon c_{\text{NP}} l,$$

$$\varepsilon_{530} = \frac{0.800}{(1.582 \times 10^{-10} \text{ mol L}^{-1})(1 \text{ cm})} \approx 5.06 \times 10^9 \text{ L mol}^{-1} \text{ cm}^{-1}.$$

Rounding to two significant figures, consistent with the supplied precursor mass,

$$\varepsilon_{530} = 5.1 \times 10^9 \text{ L mol}^{-1} \text{ cm}^{-1}.$$

This coefficient is expressed per mole of **nanoparticles**, so the concentration used must count particles.

1.5

Both measured solutions have the same final volume:

$$V_f = 1.00 \text{ mL}.$$

Let C_x be the concentration in the original sample. Each solution contains $V_x = 0.10 \text{ mL}$ of that sample. The second solution additionally contains $V_s = 0.10 \text{ mL}$ of standard with concentration $C_s = 2.0 \mu\text{g mL}^{-1}$.

Using the linear absorbance response assumed in this standard-addition determination, with a common proportionality constant k ,

$$A_1 = k \frac{C_x V_x}{V_f}, \quad A_2 = k \frac{C_x V_x + C_s V_s}{V_f}.$$

Subtracting and taking a ratio eliminates both k and V_f :

$$\frac{A_1}{A_2 - A_1} = \frac{C_x V_x}{C_s V_s}.$$

Hence,

$$C_x = \frac{A_1}{A_2 - A_1} \frac{C_s V_s}{V_x} = \frac{0.400}{0.900 - 0.400} \frac{(2.0 \mu\text{g mL}^{-1})(0.10 \text{ mL})}{0.10 \text{ mL}}.$$

$$\boxed{C_x = 1.6 \mu\text{g mL}^{-1}}.$$

The solution was checked against the official solution.

Problem 2: Chromium in Ancient and Modern Times



(The photo is from the website of Palace Museum)

Black glazed porcelain is a special Chinese porcelain and was popular in the Tang and Song dynasties (ca. 1000 years ago). The ceramic ware contained iron oxides as the main color rendering agent, which was mixed with other transition metal oxides to exhibit different color appearance such as auburn, dark brown or black. Currently, the black glazed porcelain is still popular in China.

The typical black glaze is composed of Fe-containing oxides with a spinel structure. Spinel oxides have the general formula AB_2O_4 and the structure consists of a cubic close packing array of O^{2-} ions in which the **A** cations occupy one-eighth of the tetrahedral vacancies and the **B** cations occupy half of the octahedral vacancies, as shown in Figure 2.1(a) for a unit cell.

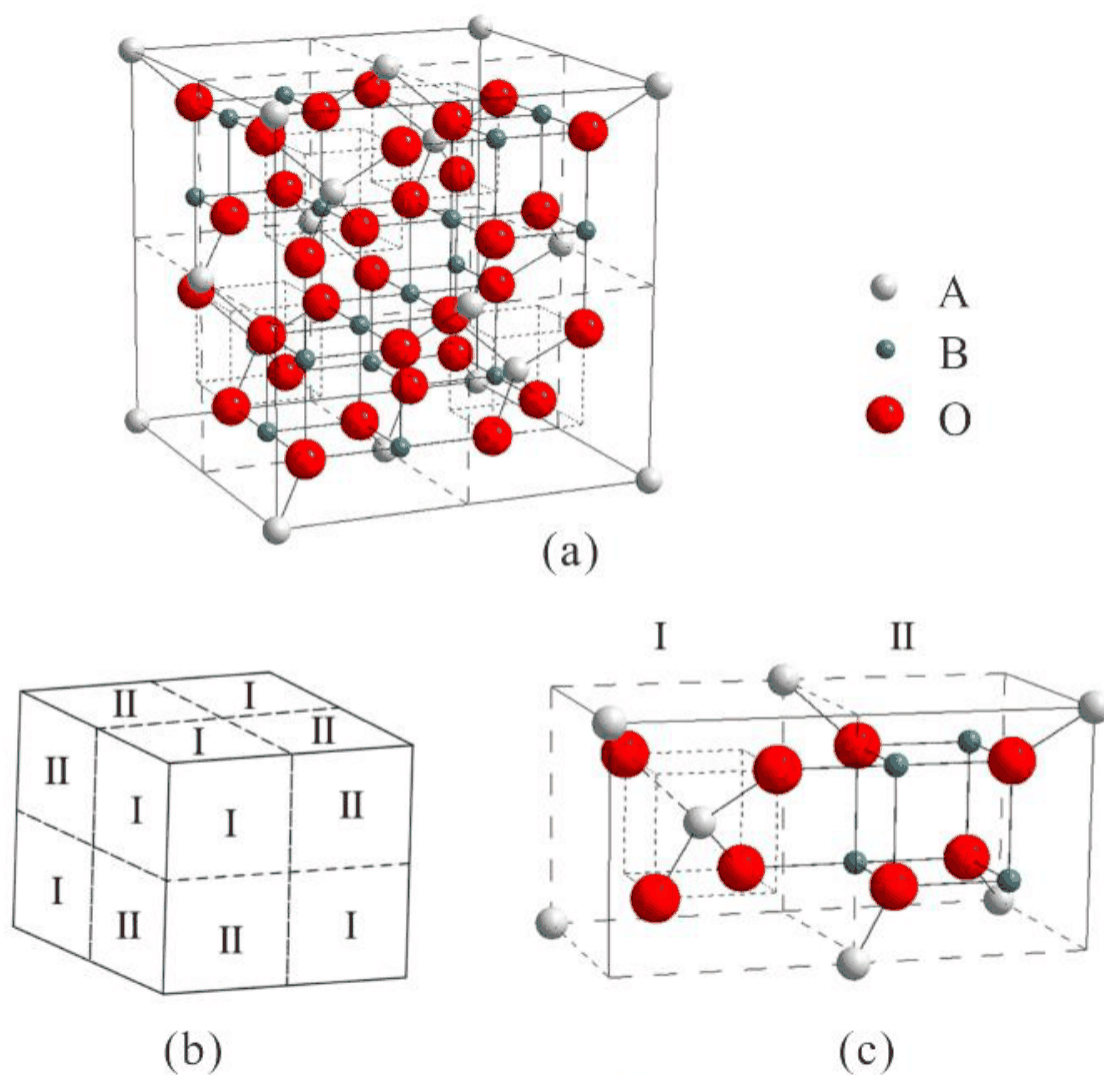


Figure 2.1 Illustration of spinel structure

Figure 2.1 Illustration of spinel structure

The cubic unit cell of a spinel structure can be divided into 8 cubic subunits, and the dashed lines represent the internal edges of the subunits. 4 of the subunits belong to type I, and the other 4 subunits are type II (Figure 2.1(b)). The details of adjacent subunits of type I and type II are shown in Figure 2.1(c).

2.1 How many cations of type **A** and **B** are there in a unit cell?

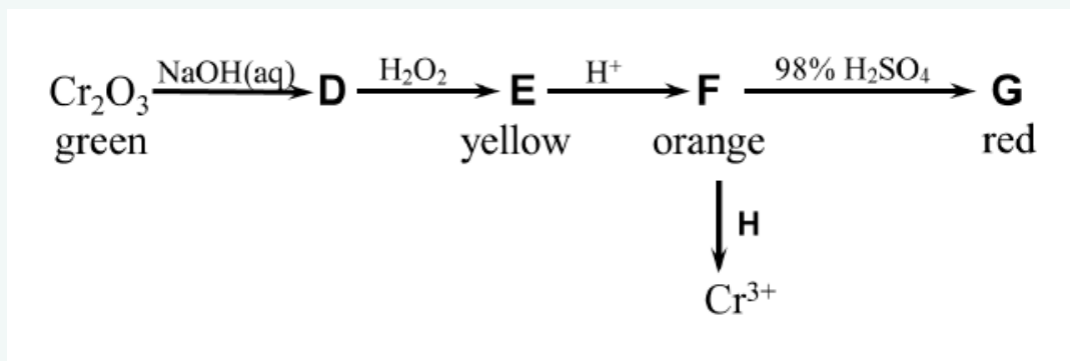
The black ceramic glaze with spinel structure can be produced by roasting Fe_2O_3 and Cr_2O_3 in a certain proportion in a reducing atmosphere (reaction (I)). When Fe_2O_3 and Cr_2O_3 are reacted with the mass ratio of 63.6 : 36.4, they completely transform into a pure stoichiometric compound. The product has a spinel structure, in which the tetrahedral **A** sites are occupied by iron cations only.

2.2 In reaction (I), which element is reduced?

2.3 Calculate the numbers of Fe^{3+} and Cr^{3+} in the **B** sites of one unit cell.

Besides doping in black ceramic glaze, chromium-containing pigments are used in painting and printing due to the abundant color originating from chromium with different oxidation states, such as +2, +3 and +6. The pigment, chrome green (Cr_2O_3) can be converted into a series of other

compounds (**D-G**) in the following process, where **E**, **F**, **G** are yellow, orange and red respectively.



2.4 Write the chemical formula of **E**.

2.5 Write the reaction equation of **F** $\rightarrow$ **G**.

2.6 Choose the agent which could be **H**.

- (A) FeSO_4
- (B) FeCl_3
- (C) ZnSO_4
- (D) CuSO_4

The variable valence of chromium is not only important for the production of pigments, but also useful for catalysis. For example, a typical Phillips catalyst for the polymerization of ethylene consists of chromium oxide species grafted onto a porous support material such as amorphous silica. The tetracoordinated Cr(VI) species is the core in the pre-catalyst (**1**), which is proposed to be reduced quickly into a six-coordinated Cr(II) species (**2**) by the ethylene molecules at the beginning. **2** is proposed to further catalyze polymerization of ethylene molecules.

2.7 The reaction of **1** with ethylene can be traced by UV-vis spectra, which show the light absorption of **1** at 21500 cm^{-1} and the light absorption of **2** at 16700 cm^{-1} in the visible region, respectively. Choose the appropriate combination of colors of **1** and **2**.

- (A) orange and white, respectively
- (B) orange and blue, respectively
- (C) blue and orange, respectively
- (D) blue and white, respectively

2.8 Assuming that the Cr(II) ion in **2** is located in a regular octahedral crystal field with a splitting energy Δ_o of 16000 cm^{-1} , draw the configurations of d electrons of the Cr(II) ion in **2**, and calculate the crystal field stabilization energy (CFSE) for the Cr(II) ion in **2**. (Note: The pairing energy P for Cr(II) in **2** is 23500 cm^{-1} .)

2.9 Coordination compounds/ions exhibit paramagnetism when containing unpaired electrons, and the corresponding magnetic moment (μ) of transition metal cations is calculated by the function $\mu = \sqrt{n(n+2)}\mu_B$ where n is the number of unpaired electrons. Calculate the magnetic moment in term of μ_B for the Cr(II) ion in **2**.

Answers

- **2.1: 8 A cations and 16 B cations** per unit cell.
- **2.2: Iron**, reduced from Fe^{3+} to Fe^{2+} .
- **2.3: 7 Fe^{3+} and 9 Cr^{3+} ions** in the B sites, using the normal-spinel assignment.
- **2.4: Sodium chromate**, Na_2CrO_4 ; its yellow ion is chromate, CrO_4^{2-} .
- **2.5:** $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \longrightarrow 2 \text{CrO}_3 (\text{s}) + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$, using 98% sulfuric acid.
G is chromium(VI) oxide.
- **2.6: (A) FeSO_4** , iron(II) sulfate.
- **2.7: (B): 1 is orange; 2 is blue.**
- **2.8: High-spin d^4 , $t_{2g}^3 e_g^1$** , with four unpaired electrons. $\text{CFSE} = -9600 \text{ cm}^{-1}$, corresponding to a stabilization magnitude of 9600 cm^{-1} .
- **2.9:** $\mu = \sqrt{24} \mu_B \approx 4.90 \mu_B$.

Names, SMILES, and structural qualifications are supplied with the identifications below.

Solution

2.1 — Cation counts

The conventional spinel cell contains eight subunits of the cubic close-packed oxide array. Each accounts for four oxide ions, giving

$$N_{\text{O}} = 8 \times 4 = 32.$$

The oxide ion is O^{2-} , SMILES [O-2].

A close-packed array containing N anions has $2N$ tetrahedral holes and N octahedral holes. Therefore,

$$N_{\text{A}} = \frac{1}{8}(2 \times 32) = \boxed{8}, \quad N_{\text{B}} = \frac{1}{2}(32) = \boxed{16}.$$

Thus the cell contains eight AB_2O_4 formula units. Spinel is an extended crystal; a molecular SMILES cannot represent its periodic unit-cell geometry.

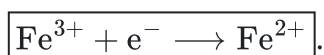
2.2 — Element reduced

Initially, both metals have oxidation state +3 in Fe_2O_3 and Cr_2O_3 .

For the normal-spinel assignment intended here, the B-site ions are trivalent. Charge neutrality of AB_2O_4 then requires

$$q_{\text{A}} + 2(+3) + 4(-2) = 0,$$

so $q_{\text{A}} = +2$. Because the A sites contain only iron, iron must undergo reduction:



The species are the **iron(III) ion**, [Fe+3], and the **iron(II) ion**, [Fe+2].

2.3 — Iron(III) and chromium(III) in the B sites

Take a 100.0 g mixture. Using approximate molar masses

$$M(\text{Fe}_2\text{O}_3) = 159.7 \text{ g mol}^{-1}, \quad M(\text{Cr}_2\text{O}_3) = 152.0 \text{ g mol}^{-1},$$

the amounts of metal atoms are

$$n(\text{Fe}) = 2 \frac{63.6 \text{ g}}{159.7 \text{ g mol}^{-1}} \approx 0.796 \text{ mol},$$

$$n(\text{Cr}) = 2 \frac{36.4 \text{ g}}{152.0 \text{ g mol}^{-1}} \approx 0.479 \text{ mol}.$$

Hence,

$$n(\text{Fe}) : n(\text{Cr}) \approx 1.66 : 1 \approx 5 : 3.$$

There are $8 + 16 = 24$ metal ions per unit cell, so the corresponding integer populations are

$$N_{\text{Fe}} = 24 \frac{5}{8} = 15, \quad N_{\text{Cr}} = 24 \frac{3}{8} = 9.$$

All nine chromium ions must occupy B sites because A sites contain only iron. Chromium remains trivalent: the **chromium(III) ion** has SMILES `[Cr+3]`.

Under the normal-spinel assignment, the eight A-site ions are Fe^{2+} . The remaining seven iron ions occupy B sites as Fe^{3+} :

$$\boxed{N_B(\text{Fe}^{3+}) = 15 - 8 = 7}, \quad \boxed{N_B(\text{Cr}^{3+}) = 9}.$$

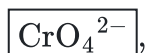
Both the site count and charge balance agree:

$$7 + 9 = 16,$$

$$8(+2) + 7(+3) + 9(+3) + 32(-2) = 0.$$

2.4 — Identification of E

Hydrogen peroxide, H_2O_2 , SMILES `oo`, oxidizes chromium(III) to chromium(VI) in alkaline solution. The yellow chromium(VI) species is the **chromate ion**:



SMILES `[O-][Cr](=O)(=O)[O-]`.

Because the solution contains sodium ions from sodium hydroxide, **E is sodium chromate**:

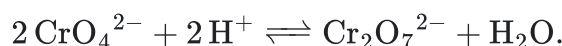


SMILES `[Na+] . [Na+] . [O-][Cr](=O)(=O)[O-]`.

Chromate has tetrahedral coordination around chromium. The SMILES gives a formal bonding representation; it does not explicitly show the tetrahedral geometry or the delocalization of bonding among the oxygen atoms.

2.5 — Conversion of F into G

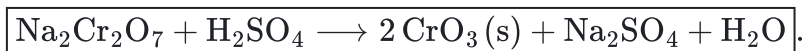
Acidification shifts chromate toward the orange **dichromate ion**, $\text{Cr}_2\text{O}_7^{2-}$:



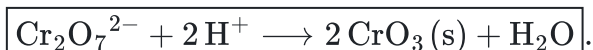
Dichromate has SMILES [O-][Cr](=O)(=O)O[Cr](=O)(=O)[O-]; structurally, it contains two chromium–oxygen tetrahedra sharing one oxygen atom.

Thus **F is sodium dichromate**, $\text{Na}_2\text{Cr}_2\text{O}_7$, SMILES [Na+].[Na+].[O-][Cr](=O)(=O)O[Cr](=O)(=O)[O-].

Treatment with 98% sulfuric acid produces red **chromium(VI) oxide**, also called **chromium trioxide**, CrO_3 :



The corresponding net ionic equation is



Chromium remains in oxidation state +6. Concentrated sulfuric acid promotes formation of the oxide through acidification and dehydration.

A formula-unit SMILES for chromium trioxide is O=[Cr](=O)=O. This representation does not show the polymeric solid structure, which contains linked chromium–oxygen tetrahedra.

The other species in these equations are:

- **Sulfuric acid**, H_2SO_4 : OS(=O)(=O)O.
- **Sodium sulfate**, Na_2SO_4 : [Na+].[Na+].[O-]S(=O)(=O)[O-].
- **Hydrogen ion**, H^+ : [H+].
- **Water**, H_2O : O.

2.6 — Identification of H

Dichromate must be reduced from chromium(VI) to chromium(III). Iron(II) supplies electrons by being oxidized to iron(III), so the suitable reagent is **iron(II) sulfate**, FeSO_4 , SMILES [Fe+2].[O-]S(=O)(=O)[O-].

Each of the two chromium atoms gains three electrons, requiring six iron(II) ions:



Therefore,

H is option (A), FeSO_4 .

2.7 — Colors of 1 and 2

Wavelength and wavenumber are related by

$$\lambda(\text{nm}) = \frac{10^7}{\tilde{\nu}(\text{cm}^{-1})}.$$

For **1**,

$$\lambda_1 = \frac{10^7}{21500} \text{ nm} \approx 465 \text{ nm}.$$

This lies in the blue region. Absorption of blue light gives the complementary observed color, **orange**.

For **2**,

$$\lambda_2 = \frac{10^7}{16700} \text{ nm} \approx 599 \text{ nm}.$$

This lies in the orange region, giving the complementary observed color, **blue**.

Thus,

Option (B): 1 is orange and 2 is blue.

2.8 — Electron configuration and CFSE

The **chromium(II) ion**, Cr^{2+} , SMILES `[Cr+2]`, has a $3d^4$ electron configuration. This SMILES represents the metal ion alone; the stipulated octahedral coordination must be specified separately because the ligands of the supported site are not given.

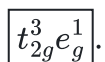
In an octahedral field:

$$E(t_{2g}) = -0.4\Delta_o, \quad E(e_g) = +0.6\Delta_o.$$

Since

$$\Delta_o = 16000 \text{ cm}^{-1} < P = 23500 \text{ cm}^{-1},$$

placing the fourth electron in an e_g orbital costs less energy than pairing it in a t_{2g} orbital. The configuration is therefore **high-spin**:



For the requested drawing: draw three degenerate lower t_{2g} orbitals, each containing one electron with the same spin. Above them, draw two degenerate e_g orbitals, with one containing a single electron of that same spin and the other empty. The separation between the levels is Δ_o .

There are no electron pairs, so

$$\begin{aligned} \text{CFSE} &= 3(-0.4\Delta_o) + 1(+0.6\Delta_o) \\ &= -0.6\Delta_o \\ &= -0.6(16000 \text{ cm}^{-1}). \end{aligned}$$

Thus,

$$\text{CFSE} = -9600 \text{ cm}^{-1}.$$

The stabilization magnitude is 9600 cm^{-1} .

As a check, the alternative low-spin configuration t_{2g}^4 would have one electron pair and total energy

$$-1.6\Delta_o + P = -25600 + 23500 = -2100 \text{ cm}^{-1},$$

which is higher than the high-spin energy by 7500 cm^{-1} .

2.9 — Magnetic moment

The high-spin $t_{2g}^3 e_g^1$ configuration has four unpaired electrons. Substitution into the supplied expression gives

$$\mu = \sqrt{n(n+2)} \mu_B = \sqrt{4(4+2)} \mu_B = \sqrt{24} \mu_B.$$

Therefore,

$$\mu \approx 4.90 \mu_B.$$

The solution was checked against the official solution.

Problem 3: Capture and Transformation of Carbon Dioxide

Climate change is one of the most critical global challenges nowadays. The increase of CO_2 concentration in the atmosphere has been recognized as the primary driver of global warming. The study of the capture and transformation of CO_2 has attracted considerable attention.

Direct air capture (DAC) technology which aims to extract CO_2 directly from ambient air is promising. The conventional method of DAC is wet scrubbing with alkaline hydroxide solutions (typically NaOH), where CO_2 in air is absorbed till $\text{pH} \approx 10$ (step 1). The spent sorbent is regenerated by dosing calcium hydroxide into the system (step 2). The white precipitate **A** received in step 2 decomposes at 700°C , giving rise to CO_2 and another white compound **B** (step 3). Finally, calcium hydroxide can be generated by the hydration of **B**. This process is highly energy-demanding. (H_2CO_3 : $K_{a1} = 4.5 \times 10^{-7}$, $K_{a2} = 4.7 \times 10^{-11}$).

3.1 Write the formulas for **A** and **B** respectively.

3.2 Write the balanced equations of all possible reactions in steps 1-3. NaOH solution is used as sorbent.

Recently, an electrochemical process was developed for regenerating the alkaline solution in the wet scrubbing process for DAC application, and pure CO_2 gas could be recovered that is suitable for storage or utilization. The process is based on a H_2 -recycling electrochemical system (HRES), as shown in Figure 3.1.

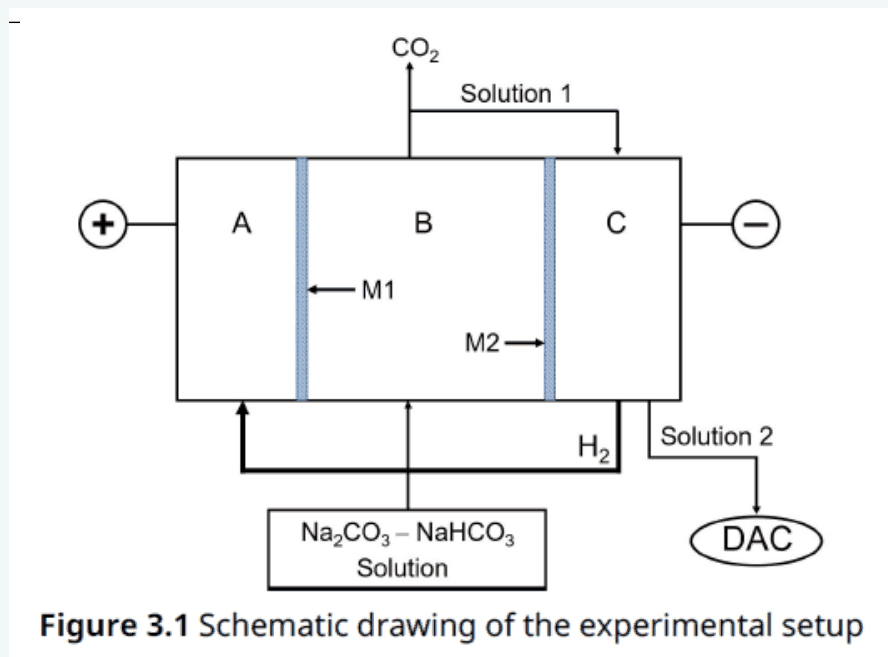


Figure 3.1 Schematic drawing of the experimental setup

The electrochemical cell contains three compartments: an anode region (A), an acidifying region (B), and a cathode region (C). They are separated by ion-selective permeable membranes M1 and M2. During the operation, protons produced from H_2 oxidation at the anode are transported to the acidifying compartment where the spent solution ($\text{Na}_2\text{CO}_3\text{-NaHCO}_3$) coming from the air contactor is fed. The decreasing pH of the solution leads to the conversions of carbonate to hydrocarbonate (reaction 1) and hydrocarbonate to carbonic acid (reaction 2). When the solution is saturated by dissolved CO_2 (solubility: 0.033 mol L^{-1}), a further pH decrease leads to the release of CO_2 gas (reaction 3). H_2 generated in the cathode is introduced to the anode and the solution from the cathode can be reused as a DAC absorbent.

3.3 Write the electrode reactions in the anode (A) and the cathode (C) respectively.

3.4 Write the balanced equations for the reactions **1–3** in the acidifying region (B).

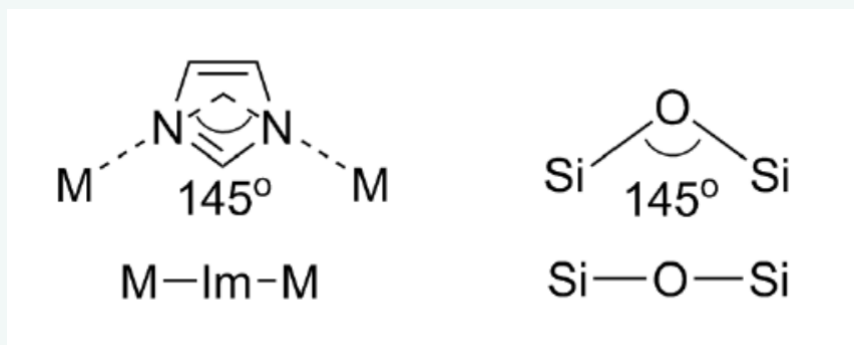
3.5 Check all that correctly describe the movement of cations during the system operation.

- (a) H^+ ions permeate through M1 from A to B.
- (b) H^+ ions permeate through M2 from B to C.
- (c) Na^+ ions permeate through M1 from B to A.
- (d) Na^+ ions permeate through M2 from B to C.
- (e) Both H^+ and Na^+ ions can permeate through M1 and M2.

The cell works at a steady state when the current passing through the cell is 2.00 A and the flow rate of the solution ($0.050 \text{ mol L}^{-1} \text{ Na}_2\text{CO}_3 - 0.10 \text{ mol L}^{-1} \text{ NaHCO}_3$) into the region B is 10.0 mL min^{-1} . The pH in the anode compartment is maintained at 1 in the steady state.

3.6 Calculate the generation rate of CO_2 gas (in mmol min^{-1}).

Zeolitic imidazolate frameworks (ZIFs), a sub-class of metal–organic frameworks (MOFs) are promising materials for the capture and utilization of CO_2 . The structures of ZIFs resemble zeolites. They form 3D frameworks with tetrahedrally coordinated metal ions (e.g. Zn^{2+} , Co^{2+}) bridged by imidazolate (Im^-) and its derivatives. As the conjugated base of imidazole (HIm), imidazolate anion binds to metal cations (M) by its two N atoms. The fact that the M-Im-M angle is similar to the Si-O-Si angle (145°) preferred in zeolites (as shown below) has led to the synthesis of a large number of ZIFs with zeolite-type tetrahedral topologies.



ZIF-8 is one of the representative ZIFs, which adopts a sodalite framework (SOD), as shown in Figure 3.2. ZIF-8 was firstly synthesized by Chinese scientists Xiao-Ming Chen et al. (they named it as MAF-4) by the reaction of Zn^{2+} with 2-methylimidazole ($\text{CH}_3(\text{C}_3\text{N}_2\text{H}_3)$, HmIm). It

crystallizes in the cubic system with the cell parameter $a = 1.632 \text{ nm}$ for a solvent-free phase with the effective pore diameter (shown by the inside virtual sphere in Figure 3.2d) of 1.16 nm .

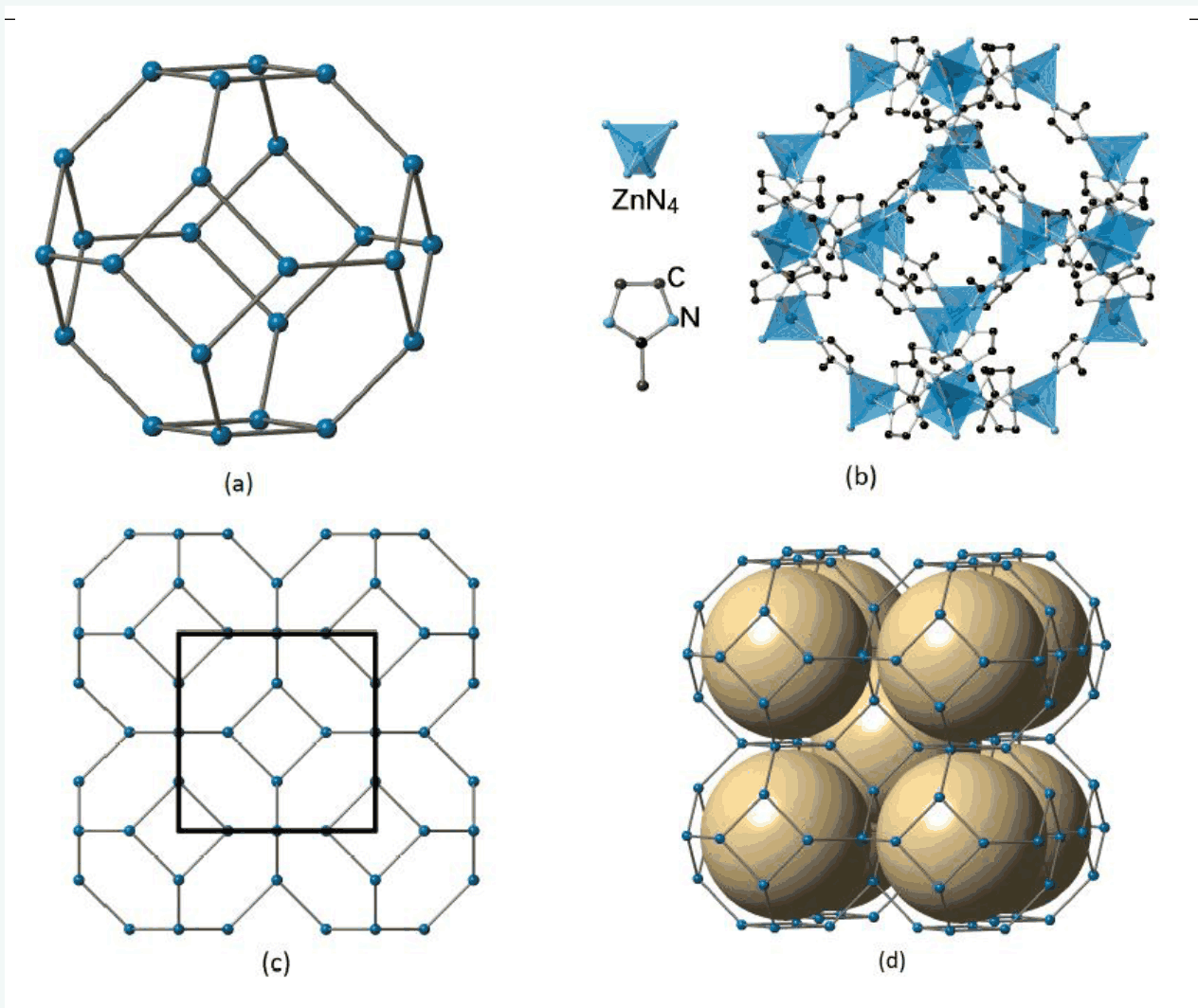


Figure 3.2 Topology of SOD and structure of ZIF-8

(a) Topology of SOD cage;

(b) SOD cage in ZIF-8 formed by Zn^{2+} (at the centers of the tetrahedra) and imidazolate (H atoms are omitted for clarity);

(c) Framework of SOD with the unit cell shown by the square box;

(d) Some of the pores are highlighted by virtual spheres in ZIF-8.

Note: If you wish, you may use the symbol "HmIm" and "mIm" representing 2-methylimidazole and 2-methylimidazolate respectively in solving the following questions.

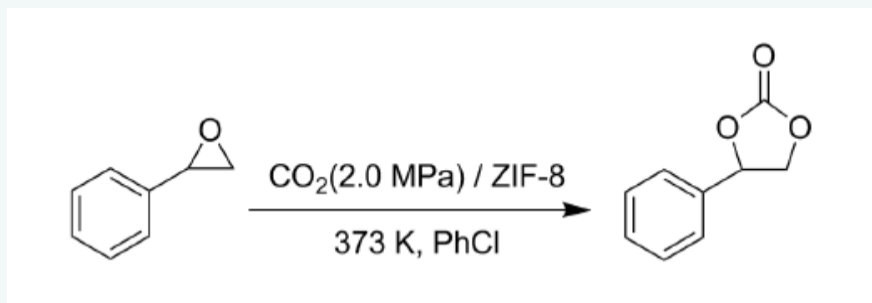
3.7 Write the formula of the single sodalite cage.

3.8 Write the composition of the unit cell of ZIF-8.

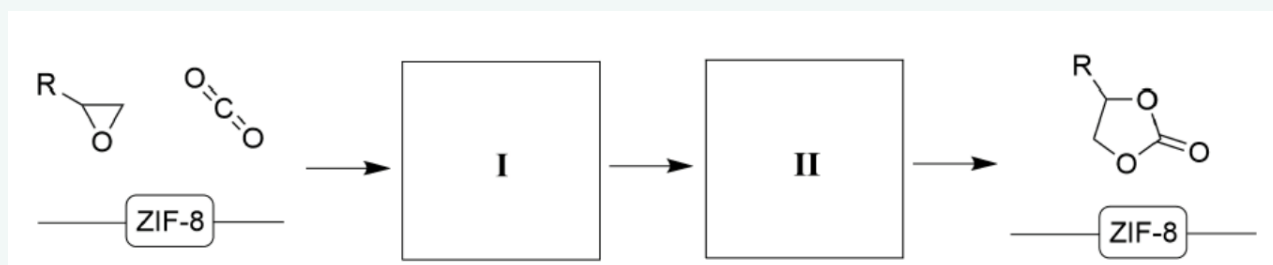
3.9 Calculate the inner surface area (S) of the pores (modeled by the virtual spheres) of 1 g ZIF-8 (in m^2). If you failed to get the composition of the unit cell, use 3500 as the formula weight of the unit cell.

3.10 Calculate the porosity R of ZIF-8 (R is the ratio of pore volume to the actual volume of the material) and the pore volume of 1 g ZIF-8 (V_p , in cm^3).

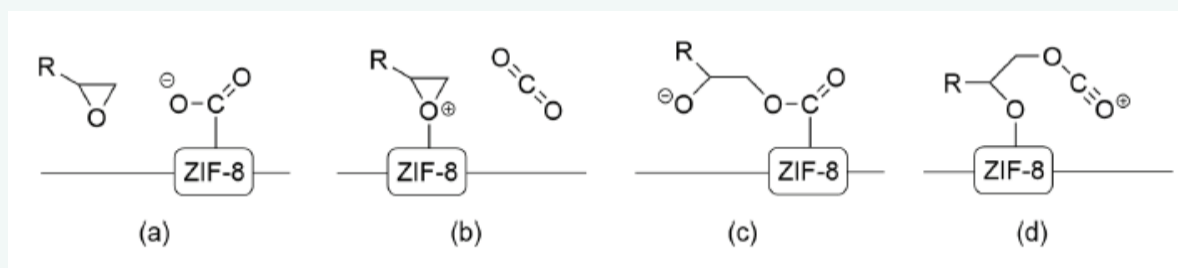
ZIF-8 can also act as a catalyst to promote the conversion of CO_2 to high value-added chemicals. One of the most promising routes for CO_2 fixation is the preparation of cyclic carbonates via CO_2 cycloaddition. An example is shown as below:



A mechanism of catalytic conversion of CO_2 to cyclic carbonate over ZIF-8 catalyst is proposed:



3.11 If ZIF-8 provides acid sites in the above catalytic process, complete the mechanism by choosing the reasonable intermediates from the following species:



Choose the intermediates corresponding to I and II respectively.

ZIF-8 shows a relatively high thermal stability. However, a recent study revealed that its structure would be destroyed if applied in a wet acidic environment. The co-existence of CO_2 and H_2O with ZIF-8 resulted in the formation of ZnCO_3 .

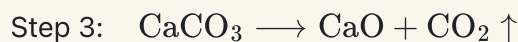
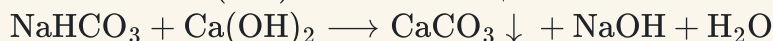
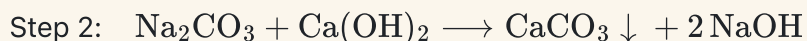
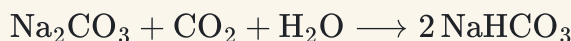
3.12 Write the balanced equation of ZIF-8 with CO_2 and H_2O .

Official English text of the problem.

Answers

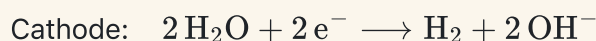
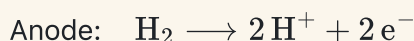
- 3.1 A:** calcium carbonate, CaCO_3 , $[\text{Ca}+2] \cdot [\text{O}-]\text{C}(=\text{O})[\text{O}-]$. **B:** calcium oxide, CaO , $[\text{Ca}+2] \cdot [\text{O}-2]$.

- **3.2** The principal reactions are:

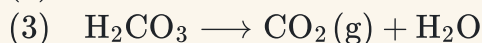
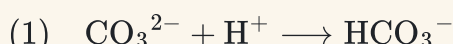


Equivalent net reactions and the final hydration are included in the solution.

- **3.3**



- **3.4**



- **3.5 (a) and (d)** under the intended ideal transport model.

- **3.6** $\dot{n}_{\text{CO}_2(\text{g})} \approx 0.41 \text{ mmol min}^{-1}$, with an unrounded stoichiometric result of $0.4137 \text{ mmol min}^{-1}$.

- **3.7** One geometric cage contains $[\text{Zn}_{24}(\text{C}_4\text{H}_5\text{N}_2)_{36}]^{12+}$, conventionally written $[\text{Zn}_{24}(m \text{ Im})_{36}]^{12+}$.

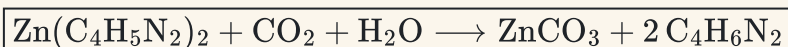
- **3.8** $[\text{Zn}_{12}(\text{C}_4\text{H}_5\text{N}_2)_{24}]$, or $\text{Zn}_{12}\text{C}_{96}\text{H}_{120}\text{N}_{48}$, per unit cell.

- **3.9** $S = 1.86 \times 10^3 \text{ m}^2$ for 1 g.

- **3.10** $R = 0.376 = 37.6\%$ and $V_p = 0.360 \text{ cm}^3$ for 1 g.

- **3.11** $\text{I} = (b)$, $\text{II} = (d)$. Names and schematic SMILES are given below.

- **3.12**



The released organic compound is 2-methylimidazole, Cc1ncc[nH]1.

Solution

The following names and SMILES identify the species used throughout the equations. Dot-separated SMILES for salts specify their constituent ions; they do not describe the crystal lattice.

Species	SMILES
Carbon dioxide, CO_2	<chem>O=C=O</chem>
Water, H_2O	<chem>O</chem>
Sodium hydroxide, NaOH	<chem>[Na+].[OH-]</chem>

Species	SMILES
Sodium carbonate, Na_2CO_3	[Na+] . [Na+] . [O-]C(=O)[O-]
Sodium hydrogencarbonate, NaHCO_3	[Na+] . O=C(O)[O-]
Calcium hydroxide, $\text{Ca}(\text{OH})_2$	[Ca+2] . [OH-] . [OH-]
Calcium carbonate, CaCO_3	[Ca+2] . [O-]C(=O)[O-]
Calcium oxide, CaO	[Ca+2] . [O-2]
Hydrogen, H_2	[H][H]
Proton, H^+	[H+]
Hydroxide ion, OH^-	[OH-]
Carbonate ion, CO_3^{2-}	[O-]C(=O)[O-]
Hydrogencarbonate ion, HCO_3^-	O=C(O)[O-]
Carbonic acid, H_2CO_3	O=C(O)O
Sodium ion, Na^+	[Na+]
Zinc(II) ion, Zn^{2+}	[Zn+2]
2-Methylimidazolate, $\text{C}_4\text{H}_5\text{N}_2^-$, abbreviated <i>m Im</i> ⁻	Cc1ncc[n-]1
2-Methylimidazole, $\text{C}_4\text{H}_6\text{N}_2$, abbreviated <i>HmIm</i>	Cc1ncc[nH]1
Zinc carbonate, ZnCO_3	[Zn+2] . [O-]C(=O)[O-]

3.1

The precipitate contains calcium supplied by calcium hydroxide and carbonate obtained from absorbed carbon dioxide. Thus **A is calcium carbonate**, CaCO_3 .

Its thermal decomposition releases carbon dioxide and leaves **calcium oxide**, CaO , as **B**. Hydration of this oxide regenerates calcium hydroxide.

3.2

At pH 10,

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{K_{a2}}{[\text{H}^+]} = \frac{4.7 \times 10^{-11}}{10^{-10}} = 0.47.$$

Both carbonate and hydrogencarbonate must therefore be included.

In **step 1**, carbon dioxide initially reacts with strongly alkaline solution:



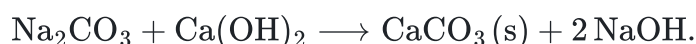
Further absorption produces hydrogencarbonate:



The corresponding overall equation for hydrogencarbonate formation is



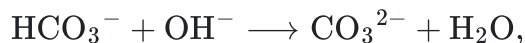
In **step 2**, calcium carbonate precipitates, regenerating sodium hydroxide:



Hydrogencarbonate also reacts:



Here hydroxide first removes the hydrogencarbonate proton,



and the resulting carbonate precipitates with calcium.

For partial regeneration with less calcium hydroxide, an equivalent possible net reaction is

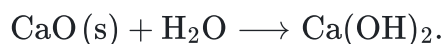


The remaining sodium carbonate can subsequently undergo the first step-2 reaction.

In **step 3**, heating causes calcination:



Finally, the stated hydration closes the calcium cycle:

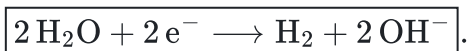


3.3

Hydrogen is oxidized at the anode, producing one proton per electron transferred:

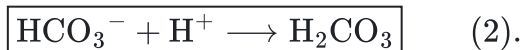
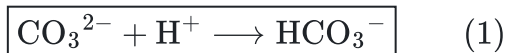


Water is reduced at the cathode, producing hydrogen for recycling and hydroxide for regeneration of the alkaline absorbent:

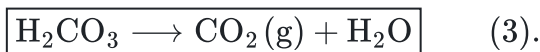


3.4

Successive protonation in B gives:



Carbonic acid supplies dissolved carbon dioxide; once saturation is reached, carbon dioxide escapes as gas:



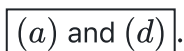
These reactions represent the acid–base and gas-release processes using the carbonic-acid convention of the problem.

3.5

The productive ion flows are:

- Protons travel through M1 from **A to B**, providing the acid needed for reactions 1 and 2.
- Sodium ions travel through M2 from **B to C**, carrying positive charge toward the cathode and balancing the hydroxide generated there.

Thus the intended selections are



3.6

Use $F = 96485 \text{ C mol}^{-1}$. The proton-generation rate is

$$\dot{n}_{\text{H}^+} = \frac{I}{F} = \frac{(2.00 \text{ C s}^{-1})(60 \text{ s min}^{-1})}{96485 \text{ C mol}^{-1}} = 1.2437 \text{ mmol min}^{-1}.$$

The incoming carbonate and hydrogencarbonate rates are

$$\begin{aligned}\dot{n}_{\text{CO}_3^{2-},\text{in}} &= (0.050)(0.0100) = 0.500 \text{ mmol min}^{-1}, \\ \dot{n}_{\text{HCO}_3^-, \text{in}} &= (0.10)(0.0100) = 1.00 \text{ mmol min}^{-1}.\end{aligned}$$

First, approximately $0.500 \text{ mmol min}^{-1}$ of protons converts carbonate to hydrogencarbonate. The remaining proton supply converts hydrogencarbonate into the carbonic-acid/dissolved-carbon-dioxide pool:

$$\dot{n}_{\text{converted to CO}_2} = 1.2437 - 0.500 = 0.7437 \text{ mmol min}^{-1}.$$

The saturated liquid leaving B carries dissolved carbon dioxide at

$$\dot{n}_{\text{CO}_2(\text{aq}),\text{out}} = (0.033 \text{ mol L}^{-1})(0.0100 \text{ L min}^{-1}) = 0.330 \text{ mmol min}^{-1}.$$

Consequently,

$$\begin{aligned}\dot{n}_{\text{CO}_2(\text{g})} &= 0.7437 - 0.330 \\ &= 0.4137 \text{ mmol min}^{-1}.\end{aligned}$$

Thus, to sensible precision,

$$\boxed{\dot{n}_{\text{CO}_2(\text{g})} \approx 0.41 \text{ mmol min}^{-1}}.$$

As a consistency check, the residual hydrogencarbonate rate is

$$0.500 + 1.00 - 0.7437 = 0.7563 \text{ mmol min}^{-1},$$

corresponding to about $0.0756 \text{ mol L}^{-1}$. The supplied acid constant then gives

$$[\text{H}^+]_{\text{B}} \approx K_{\text{a1}} \frac{0.033}{0.0756} = 1.96 \times 10^{-7} \text{ mol L}^{-1},$$

or $\text{pH}_{\text{B}} \approx 6.71$. At this pH,

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \approx 2.4 \times 10^{-4},$$

so neglecting residual carbonate is justified. The specified pH 1 pertains to the anode compartment A.

3.7

The sodalite cage is a truncated octahedron with six quadrilateral faces and eight hexagonal faces. Every edge belongs to two faces, giving

$$E = \frac{6(4) + 8(6)}{2} = 36.$$

Three cage edges meet at each vertex, so

$$V = \frac{2E}{3} = 24.$$

There is one zinc ion at each vertex and one 2-methylimidazolate linker on each edge. Therefore the geometric cage contains



or $[\text{Zn}_{24}(\text{m Im})_{36}]^{12+}$.

This is a count of the atoms and linkers defining one cage within the extended framework. Each zinc has three connections along that cage and a fourth connection extending into the surrounding network. If only the counted constituents were treated as a separated fragment, their formal charge would be $24(2) - 36 = +12$; the cage is not an isolated neutral molecule.

The constituent-ion SMILES are $[\text{zn}+2]$ and $\text{Cc1ncc}[n-]1$. Their periodic Zn–N coordination and tetrahedral geometry are specified by the framework description, rather than by a disconnected molecular SMILES.

3.8

The cubic unit cell contains two equivalent cage centers:

$$8 \left(\frac{1}{8} \right) + 1 = 2.$$

In the space-filling SOD arrangement, each zinc vertex belongs to four cages, and each linker edge belongs to three cages. Thus the unit-cell contents are

$$N_{\text{Zn}} = \frac{2(24)}{4} = 12, \quad N_{\text{mIm}} = \frac{2(36)}{3} = 24.$$

Hence

$$\boxed{\text{Zn}_{12}(\text{C}_4\text{H}_5\text{N}_2)_{24} = \text{Zn}_{12}\text{C}_{96}\text{H}_{120}\text{N}_{48}}.$$

The empirical formula is $\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2$. Its ionic-composition SMILES is $[\text{zn}+2] \cdot \text{Cc1ncc}[n-]1 \cdot \text{Cc1ncc}[n-]1$; this string does not encode the periodic coordination bonds.

3.9

Using standard atomic masses $C = 12.01$, $H = 1.008$, $N = 14.01$, and $Zn = 65.38$,

$$M_{\text{mIm}} = 4(12.01) + 5(1.008) + 2(14.01) = 81.10 \text{ g mol}^{-1}.$$

The molar mass of unit cells is therefore

$$M_{\text{cell}} = 12(65.38) + 24(81.10) = 2730.96 \text{ g mol}^{-1}.$$

Each cell contains two spherical pores. With

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

the number of pores in 1 g is

$$N_{\text{pores}} = \frac{(1.00 \text{ g})(2N_A)}{M_{\text{cell}}} = 4.4103 \times 10^{20}.$$

The pore radius is

$$r = \frac{1.16}{2} = 0.580 \text{ nm}.$$

Thus

$$\begin{aligned} S &= N_{\text{pores}} 4\pi r^2 \\ &= (4.4103 \times 10^{20}) 4\pi (0.580 \times 10^{-9} \text{ m})^2 \\ &= 1.8644 \times 10^3 \text{ m}^2. \end{aligned}$$

Therefore,

$$S = 1.86 \times 10^3 \text{ m}^2 \text{ for 1 g}.$$

3.10

The volume of one spherical pore is

$$V_{\text{sphere}} = \frac{4}{3}\pi(0.580)^3 = 0.817283 \text{ nm}^3.$$

The unit-cell volume is

$$V_{\text{cell}} = a^3 = (1.632)^3 = 4.346708 \text{ nm}^3.$$

Since there are two pores per cell,

$$R = \frac{2V_{\text{sphere}}}{V_{\text{cell}}} = \frac{2(0.817283)}{4.346708} = 0.376047.$$

Thus

$$R = 0.376 = 37.6\%.$$

Using $1 \text{ nm}^3 = 10^{-21} \text{ cm}^3$, the pore volume in 1 g is

$$\begin{aligned} V_p &= N_{\text{pores}} V_{\text{sphere}} \\ &= (4.4103 \times 10^{20})(0.817283 \times 10^{-21} \text{ cm}^3) \\ &= 0.36044 \text{ cm}^3. \end{aligned}$$

Therefore,

$$V_p = 0.360 \text{ cm}^3 \text{ for 1 g}.$$

3.11

A Lewis acid site accepts an electron pair from the epoxide oxygen. This activates the epoxide toward ring opening, corresponding to **intermediate (b)**.

An oxygen atom of carbon dioxide then attacks the terminal epoxide carbon shown in the scheme. The attacked carbon–epoxide–oxygen bond breaks, giving the ring-opened, catalyst-bound intermediate **(d)**.

Finally, the original epoxide oxygen attacks the carbon dioxide-derived carbon. Ring closure and release from the acid site produce the five-membered cyclic carbonate.

Hence

$$\text{I} = (b), \quad \text{II} = (d).$$

For precise schematic SMILES, let $[*:1]$ denote the catalyst acid site and $[*:2]$ denote the substituent R:

Species	Name	Schematic SMILES
Starting epoxide	R-substituted oxirane	$[*:2]\text{C1CO1}$
I, option (b)	Acid-site-bound epoxide, drawn as an oxonium adduct	$[*:1][\text{O}^+]\text{1C}([*:2])\text{C1}$
II, option (d)	Catalyst-bound, ring-opened alkoxy carbonyl cation	$[*:1]\text{OC}([*:2])\text{COC}\#[\text{O}^+]$
Product	4-R-1,3-dioxolan-2-one	$\text{O=C1OCC}([*:2])\text{O1}$

For II, the carbonyl-cation resonance form can equivalently be written $[*:1]OC([*:2])CO[C+]=O$.

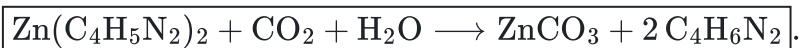
These SMILES encode the schematic connectivity and formal charges. The wildcard for the catalyst does not specify a particular atom, and the drawings do not fully specify the surface coordination geometry. Electron-pair donation, bond cleavage, and ring closure are the electron-flow steps described above.

In the illustrated phenyl-substituted example, the substrate is **styrene oxide (2-phenyloxirane)**, c1ccccc1C1C01, and the product is **4-phenyl-1,3-dioxolan-2-one**, O=C1OCC(c2ccccc2)O1. No absolute stereochemistry is specified in the problem.

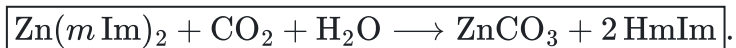
3.12

Each neutral framework formula unit contains one zinc ion and two 2-methylimidazolate anions. Carbon dioxide and water supply the carbonate group and the two protons needed to release two neutral 2-methylimidazole molecules.

Per formula unit,



Equivalently, using the permitted ligand abbreviations,



Zinc carbonate precipitates, while protonation of the coordinating ligands breaks the Zn–N framework connections.

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 4: A New Journey for Ancient Sulfur



Sulfur has been known and used since the ancient times. Nowadays, sulfur is widely used in chemical production and pharmaceutical industry as an inexpensive chemical raw material.

Pyrite (FeS_2) is commonly used as a raw material in the industrial production of elemental sulfur. By heating pyrite in the presence of limited air supply, the theoretical yield of elemental sulfur is 100% and a black magnetic oxide (Fe_3O_4) is the other product.

4.1 Write the balanced reaction equation that describes the above conversion.

In addition to sulfur, a small amount of SO_2 is generated as a by-product during the actual process. This reaction can be monitored by measuring the amount of SO_2 . The following recipe is used for the monitoring:

Raw ore powder is heated in a temperature-controlled tube furnace. The generated SO_2 is absorbed by 2 mol L^{-1} NaOH solution. When the reaction is completed, the solution is transferred to a 500 mL volumetric flask and diluted by distilled water to the mark. 25.00 mL of this diluted solution is then added into an iodine flask containing 50.00 mL $0.05122 \text{ mol L}^{-1}$ I_2 standard solution and 5 mL 20% H_2SO_4 solution. After maintaining the iodine flask in dark for 5 min, the solution is titrated with $0.1012 \text{ mol L}^{-1}$ $\text{Na}_2\text{S}_2\text{O}_3$ standard solution. When the color of the solution turns light brown, 3 mL 0.5% starch indicator is added. Continue the titration until the blue color disappears.

4.2 Write the balanced reaction equations involving I_2 in the above measurement.

4.3 In such a test experiment starting from pyrite, 17.6 g of elemental sulfur was collected. The analysis of the by-product gases according to the above procedure resulted in the consumption of 18.47 mL of $\text{Na}_2\text{S}_2\text{O}_3$ standard solution. Assuming that no other sulfur containing species were produced, calculate what percentage of the sulfur in pyrite was lost as the by-product?

The lithium-sulfur battery is a compelling energy storage system because its high theoretical energy density exceeds conventional Li-ion batteries. The net reaction of a lithium-sulfur battery can be simplified as: $16 \text{ Li} + \text{S}_8 \longrightarrow 8 \text{ Li}_2\text{S}$. Sulfur is the cathode and metallic lithium is the anode active material during discharge.

4.4 Write the balanced equations for reactions that take place at cathode (a) and anode (b) during discharge.

4.5 Calculate the mass ratio of the cathode active material to the anode active material, according to the net battery reaction.

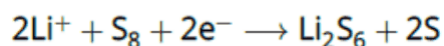
A lithium-ion battery (LIB) that possesses an average operating voltage of 3.8 V and a deliverable capacity of 3110 mAh can provide energy for a mobile phone to play videos continuously for 22 hours upon a full charge.

4.6 If the LIB is replaced by an ideal lithium-sulfur battery pack, which has an average operating voltage of 4.2 V and contains 23 g sulfur as the active electrode material that can react stoichiometrically during discharge, calculate how many hours the new battery pack will provide energy for the phone to play videos continuously after a full charge.

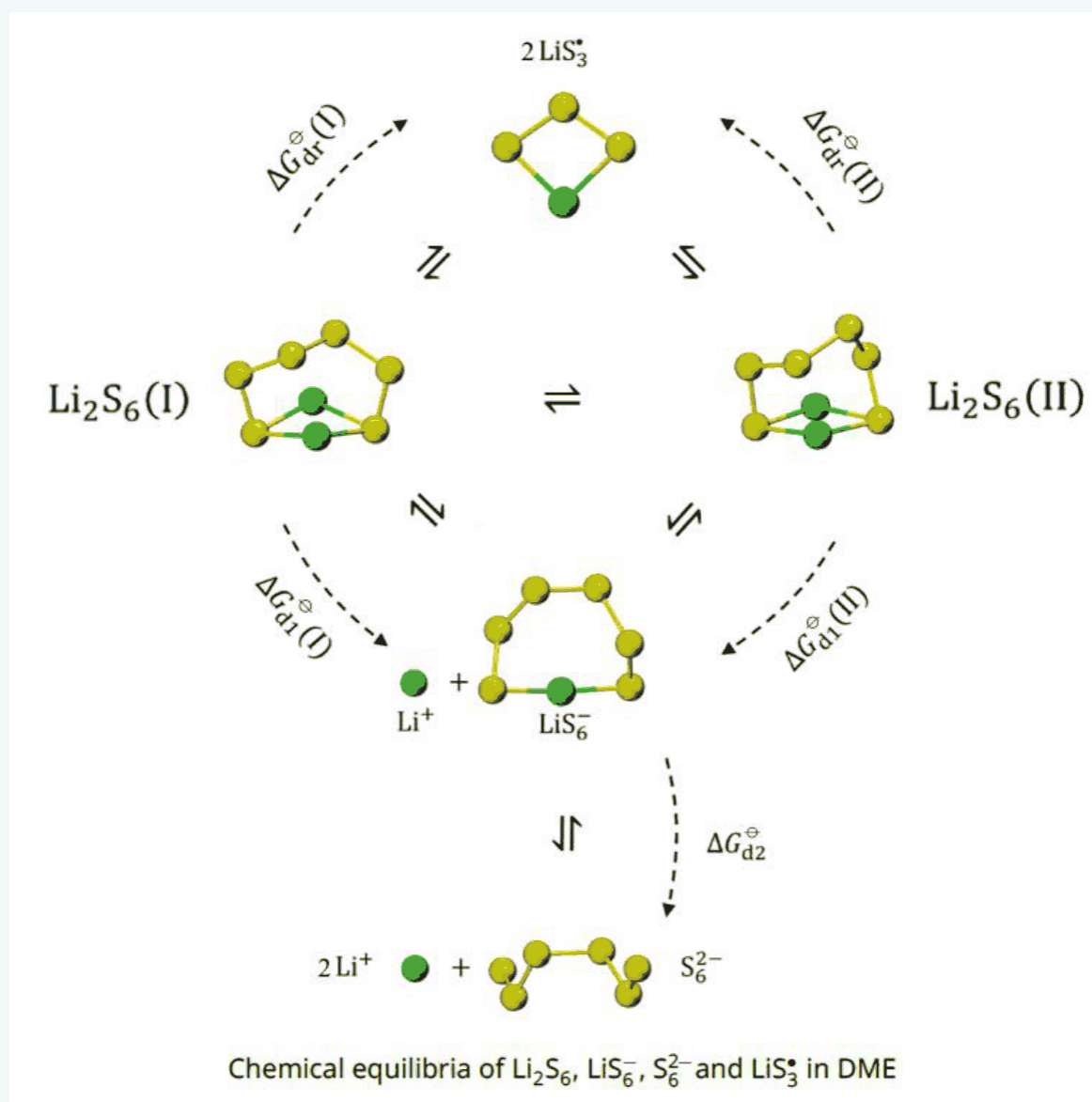
Elemental sulfur generally exists as S_8 molecules. In real lithium-sulfur batteries, S_8 is not directly reduced to Li_2S during discharge, but it undergoes stepwise reactions generating different soluble lithium polysulfides (Li_2S_n , $n = 3-8$). These lithium polysulfides could diffuse to the anode and corrode it, which results in the loss of active electrode materials. This phenomenon is called "shuttle effect".

4.7 Write the balanced reaction equation for the corrosion of anode by soluble lithium polysulfides (Li_2S_n) that produces Li_2S .

In order to suppress the "shuttle effect", the forms of polysulfides in an electrolyte have been extensively studied. Li_2S_6 is one of the most representative intermediate products:



A theoretical study shows that two conformers with comparable energies, $\text{Li}_2\text{S}_6(I)$ and $\text{Li}_2\text{S}_6(II)$ coexist in 1,2-dimethoxyethane (DME), a common electrolyte solvent in lithium-sulfur batteries. The dissociation of Li_2S_6 in DME is shown below:



Chemical equilibria of Li_2S_6 , LiS_6^- , S_6^{2-} and $\text{LiS}_3^\bullet$ in DME

Table 4.1 Dissociation Gibbs energies (kJ mol^{-1}) of different reactions in DME (298.15 K, 1 bar)

$\Delta G_{\text{d1}}^\ominus(I)$	$\Delta G_{\text{d1}}^\ominus(II)$	$\Delta G_{\text{d2}}^\ominus$	$\Delta G_{\text{dr}}^\ominus(I)$	$\Delta G_{\text{dr}}^\ominus(II)$
20.68	18.92	100.55	45.13	43.37

4.8 Using the data from Table 4.1, calculate the equilibrium concentration ratio of two conformers in DME (298.15 K, 1 bar), $\frac{\text{Li}_2\text{S}_6(II)}{\text{Li}_2\text{S}_6(I)}$.

4.9 Using the data from Table 4.1, calculate the apparent dissociation constant of $\text{Li}_2\text{S}_6 \longrightarrow \text{Li}^+ + \text{LiS}_6^-$ in DME (298.15 K, 1 bar).

4.10 Sort the following equilibrium concentrations in decreasing order: $[\text{Li}_2\text{S}_6]$, $[\text{LiS}_6^-]$, $[\text{S}_6^{2-}]$, $[\text{LiS}_3^\bullet]$ in DME.

4.11 The standard reduction potential of metallic lithium in water at 298.15 K and 1 bar is:

$$E^\ominus(\text{Li}^+/\text{Li}) = -3.040 \text{ V}$$

The standard solvation Gibbs energies of gaseous $\text{Li}^+(\text{g})$ to $\text{Li}^+(\text{sol})$ in different solvents.

	$\text{Li}^+(\text{H}_2\text{O})$	$\text{Li}^+(\text{DME})$
$\Delta G^\ominus/\text{kJ mol}^{-1}$	-116.9	-114.6

Calculate the standard reduction potential of metallic lithium electrode in DME.

Studies have shown that electromotive force of a lithium-sulfur battery would be increased by replacing DME with dimethyl sulfoxide (DMSO). Therefore, the forms of polysulfides in DMSO also attract researchers' attention.

In a test, a certain amount of Li_2S and 4.81 mg sulfur powder were added into 10.00 mL DMSO, then heated and stirred until completely dissolved (ignoring the change in volume). Suppose that only the following polysulfides were present in the DMSO: $\text{S}_3^{\bullet-}$, S_4^{2-} , S_5^{2-} , S_6^{2-} , S_7^{2-} , S_8^{2-} . The equilibrium concentration ratio of the sulfur containing species was:

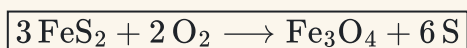
$$[\text{S}_3^{\bullet-}] : [\text{S}_4^{2-}] : [\text{S}_5^{2-}] : [\text{S}_6^{2-}] : [\text{S}_7^{2-}] : [\text{S}_8^{2-}] = 17.50 : 1.00 : 4.50 : 55.00 : 5.00 : 0.75$$

4.12 Calculate the original mass m (in mg) of Li_2S added to DMSO.

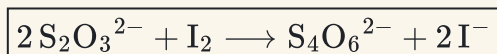
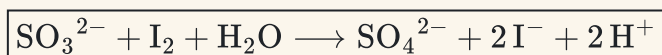
Official English text of the problem.

Answers

• **4.1**

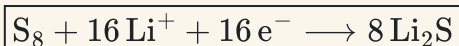


• **4.2**



• **4.3** 5.59% of the original sulfur was lost as SO_2 .

- **4.4** Cathode (a):



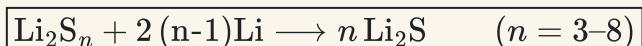
Anode (b):



- **4.5** $m_{\text{cathode}} : m_{\text{anode}} = 2.31 : 1$.

- **4.6** $t \approx 3.0 \times 10^2 \text{ h}$, with an unrounded result of 300.7 h.

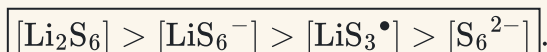
- **4.7**



- **4.8**

$$\frac{[\text{Li}_2\text{S}_6(II)]}{[\text{Li}_2\text{S}_6(I)]} = 0.492$$

- **4.9** $K_{\text{app}} = 1.60 \times 10^{-4}$ using dimensionless activities. The corresponding concentration quotient is $1.60 \times 10^{-4} \text{ mol L}^{-1}$ for $c^\ominus = 1 \text{ mol L}^{-1}$.
- **4.10** The intended ordering at ordinary concentrations is



A concentration-independent ordering is not determined by the supplied data; see the qualification below.

- **4.11** $E_{\text{DME}}^\ominus = -3.016 \text{ V}$, on the same reference scale as the aqueous value.
- **4.12** $m(\text{Li}_2\text{S}) = 1.38 \text{ mg}$.

Names and SMILES for the species in these answers are collected at the end of the Solution.

Solution

The numerical calculations use

$$R = 8.31446 \text{ J mol}^{-1} \text{ K}^{-1}, \quad F = 96485.33 \text{ C mol}^{-1},$$

$$M(\text{S}) = 32.06 \text{ g mol}^{-1}, \quad M(\text{Li}) = 6.94 \text{ g mol}^{-1}.$$

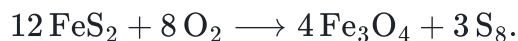
For the equilibrium calculations, activities are approximated by $a_i = [i]/c^\ominus$, where $c^\ominus = 1 \text{ mol L}^{-1}$.

4.1

One formula unit of magnetite contains three iron atoms and four oxygen atoms. It therefore requires three formula units of pyrite and two oxygen molecules. The six sulfur atoms from the pyrite become elemental sulfur:



Here S denotes elemental sulfur counted by sulfur atoms. Written using its common molecular form, cyclooctasulfur, the equivalent equation is

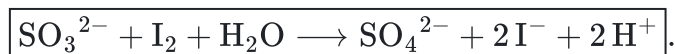


4.2

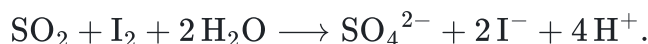
The alkaline absorber converts sulfur dioxide into sulfite:



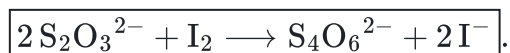
Iodine then oxidizes sulfur from oxidation state +4 in sulfite to +6 in sulfate. Each sulfur atom transfers two electrons, while one iodine molecule accepts two electrons:



Equivalently, expressing the sulfur(IV) species as sulfur dioxide in the acidic solution,



The excess iodine is determined by thiosulfate, which is oxidized to tetrathionate:



Thus one mole of sulfur dioxide consumes one mole of iodine, and each mole of residual iodine consumes two moles of thiosulfate.

4.3

The initial iodine amount in the flask is

$$n_0(\text{I}_2) = (0.05000 \text{ L})(0.05122 \text{ mol L}^{-1}) = 2.5610 \times 10^{-3} \text{ mol}.$$

The thiosulfate amount used is

$$n(\text{S}_2\text{O}_3^{2-}) = (0.01847 \text{ L})(0.1012 \text{ mol L}^{-1}) = 1.869164 \times 10^{-3} \text{ mol}.$$

Therefore, the residual iodine amount is

$$n_{\text{remaining}}(\text{I}_2) = \frac{1}{2} n(\text{S}_2\text{O}_3^{2-}) = 9.34582 \times 10^{-4} \text{ mol}.$$

The iodine consumed by sulfur(IV) in the 25.00 mL aliquot is

$$n_{\text{aliquot}}(\text{SO}_2) = 2.5610 \times 10^{-3} - 9.34582 \times 10^{-4} = 1.626418 \times 10^{-3} \text{ mol}.$$

Scaling to the entire 500 mL solution,

$$n_{\text{total}}(\text{SO}_2) = \frac{500}{25.00} (1.626418 \times 10^{-3}) = 0.03252836 \text{ mol}.$$

The sulfur mass lost in this sulfur dioxide is

$$m_{\text{lost}}(\text{S}) = (0.03252836)(32.06) = 1.04286 \text{ g}.$$

Because the collected elemental sulfur and sulfur dioxide account for all original sulfur,

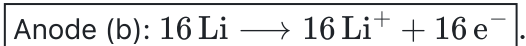
$$\text{percentage lost} = \frac{1.04286}{17.6 + 1.04286} \times 100\% = \boxed{5.59\%}.$$

4.4

During discharge, sulfur is reduced at the cathode. Each sulfur atom gains two electrons, so one S_8 molecule gains sixteen:



Lithium is oxidized at the anode:



Adding these half-reactions cancels the lithium ions and electrons and gives the stated overall reaction.

4.5

The overall reaction consumes one mole of S_8 per sixteen moles of lithium:

$$\frac{m_{\text{cathode}}}{m_{\text{anode}}} = \frac{8M(\text{S})}{16M(\text{Li})} = \frac{32.06}{2(6.94)} = 2.3098.$$

Therefore,

$$\boxed{m_{\text{cathode}} : m_{\text{anode}} = 2.31 : 1}.$$

4.6

The original battery supplies energy

$$E_{\text{LIB}} = (3.8 \text{ V})(3.110 \text{ Ah}) = 11.818 \text{ Wh}.$$

Hence the phone's average power consumption is

$$P = \frac{11.818 \text{ Wh}}{22 \text{ h}} = 0.53718 \text{ W}.$$

Each mole of sulfur atoms accepts two moles of electrons. Complete discharge of 23 g sulfur therefore transfers charge

$$Q = 2F \frac{m(\text{S})}{M(\text{S})} = 2(96485.33) \frac{23}{32.06} = 1.38438 \times 10^5 \text{ C}.$$

Using $1 \text{ Ah} = 3600 \text{ C}$,

$$Q = 38.455 \text{ Ah}.$$

The ideal replacement battery supplies

$$E_{\text{Li-S}} = (4.2 \text{ V})(38.455 \text{ Ah}) = 161.511 \text{ Wh}.$$

At the same phone power consumption,

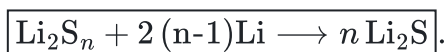
$$t = \frac{161.511 \text{ Wh}}{0.53718 \text{ W}} = 300.66 \text{ h}.$$

Thus, to the precision of the supplied data,

$$\boxed{t \approx 3.0 \times 10^2 \text{ h}}.$$

4.7

The n sulfur atoms in one formula unit of Li_2S_n form n formula units of lithium sulfide. These products contain $2n$ lithium atoms; two are already present in the polysulfide, so $2n - 2$ must come from the lithium anode:



This reaction consumes metallic lithium without delivering its electrons through the external circuit, explaining the loss of active material.

4.8

Both conformers dissociate to the same products, $\text{Li}^+ + \text{LiS}_6^-$. Consequently,

$$G_{II}^{\ominus} - G_I^{\ominus} = \Delta G_{d1}^{\ominus}(I) - \Delta G_{d1}^{\ominus}(II) = 20.68 - 18.92 = 1.76 \text{ kJ mol}^{-1}.$$

The radical dissociation energies give the same difference: $45.13 - 43.37 = 1.76 \text{ kJ mol}^{-1}$.

For conformer interconversion,

$$\frac{[\text{Li}_2\text{S}_6(II)]}{[\text{Li}_2\text{S}_6(I)]} = \exp\left(-\frac{G_{II}^{\ominus} - G_I^{\ominus}}{RT}\right).$$

Therefore,

$$\frac{[\text{Li}_2\text{S}_6(II)]}{[\text{Li}_2\text{S}_6(I)]} = \exp\left[-\frac{1760}{(8.31446)(298.15)}\right] = \boxed{0.492}.$$

Conformer I has the lower standard Gibbs energy and is therefore more abundant.

4.9

The separate dimensionless dissociation constants are

$$K_I = \exp\left[-\frac{20680}{RT}\right] = 2.3824 \times 10^{-4},$$

$$K_{II} = \exp\left[-\frac{18920}{RT}\right] = 4.8457 \times 10^{-4}.$$

Let a_I and a_{II} denote the conformer activities, and let $p = a_{\text{Li}^+} a_{\text{LiS}_6^-}$. Then

$$K_I = \frac{p}{a_I}, \quad K_{II} = \frac{p}{a_{II}}.$$

The apparent constant uses the total undissociated population:

$$K_{\text{app}} = \frac{p}{a_I + a_{II}} = \frac{1}{K_I^{-1} + K_{II}^{-1}} = \frac{K_I K_{II}}{K_I + K_{II}}.$$

Numerically,

$$\boxed{K_{\text{app}} = 1.5972 \times 10^{-4} \approx 1.60 \times 10^{-4}}.$$

In concentration form,

$$\frac{[\text{Li}^+][\text{LiS}_6^-]}{[\text{Li}_2\text{S}_6(I)] + [\text{Li}_2\text{S}_6(II)]} = K_{\text{app}} c^{\ominus} = \boxed{1.60 \times 10^{-4} \text{ mol L}^{-1}}.$$

4.10

Write

$$C_0 = [\text{Li}_2\text{S}_6(I)] + [\text{Li}_2\text{S}_6(II)].$$

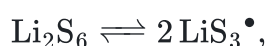
For the second ionic dissociation,

$$\text{LiS}_6^- \rightleftharpoons \text{Li}^+ + \text{S}_6^{2-},$$

$$K_{d2} = \exp\left[-\frac{100550}{RT}\right] = 2.42 \times 10^{-18}.$$

Thus the free hexasulfide dianion is strongly suppressed at ordinary lithium-ion concentrations.

For radical formation,



the apparent constant for the combined conformer pool is

$$K_{r,app} = \frac{\exp[-45130/(RT)]}{1 + 0.491656} = 8.32 \times 10^{-9}.$$

If these dissociations are the only source of free lithium ions, electroneutrality gives

$$[\text{Li}^+] = [\text{LiS}_6^-] + 2[\text{S}_6^{2-}] \approx [\text{LiS}_6^-],$$

because the second dissociation is negligible at ordinary concentrations. Consequently,

$$[\text{LiS}_6^-] \approx \sqrt{K_{app} C_0 c^\ominus},$$

$$[\text{LiS}_3^\bullet] = \sqrt{K_{r,app} C_0 c^\ominus}.$$

Their ratio is approximately

$$\frac{[\text{LiS}_6^-]}{[\text{LiS}_3^\bullet]} \approx \sqrt{\frac{1.5972 \times 10^{-4}}{8.3157 \times 10^{-9}}} = 139.$$

Thus the intended ordering is

$$\boxed{[\text{Li}_2\text{S}_6] > [\text{LiS}_6^-] > [\text{LiS}_3^\bullet] > [\text{S}_6^{2-}]}.$$

However, the first inequality requires approximately

$$C_0 > \sqrt{K_{app} C_0 c^\ominus} \iff C_0 > K_{app} c^\ominus = 1.60 \times 10^{-4} \text{ mol L}^{-1}.$$

At sufficiently low concentration, ionic dissociation becomes extensive and that inequality reverses.

Therefore, the stated ordering is conditional on concentration; it is not a universal consequence of the standard Gibbs energies alone.

4.11

Transfer of a lithium ion from DME to water has standard Gibbs energy

$$\Delta G_{\text{tr}}^\ominus = \Delta G_{\text{solv},\text{H}_2\text{O}}^\ominus - \Delta G_{\text{solv},\text{DME}}^\ominus = -116.9 - (-114.6) = -2.3 \text{ kJ mol}^{-1}.$$

Reduction in DME can be represented by the following thermodynamic cycle:

1. Transfer Li^+ from DME to water.
2. Reduce the aqueous lithium ion to metallic lithium.

Hence

$$\Delta G_{\text{red,DME}}^\ominus = \Delta G_{\text{tr}}^\ominus + \Delta G_{\text{red,H}_2\text{O}}^\ominus.$$

Using $\Delta G^\ominus = -FE^\ominus$ for this one-electron reaction,

$$-FE_{\text{DME}}^\ominus = -2300 - FE_{\text{H}_2\text{O}}^\ominus,$$

so

$$E_{\text{DME}}^\ominus = E_{\text{H}_2\text{O}}^\ominus + \frac{2300}{F} = -3.040 + \frac{2300}{96485.33}.$$

Therefore,

$$\boxed{E_{\text{DME}}^\ominus = -3.016 \text{ V}}.$$

The sign is consistent with the weaker stabilization of the lithium ion in DME: its reduction is slightly more favorable.

4.12

Let the concentrations be the stated numerical ratios multiplied by a common factor x , with units mol L^{-1} .

The relative sulfur-atom concentration is

$$3(17.50) + 4(1.00) + 5(4.50) + 6(55.00) + 7(5.00) + 8(0.75) = 450.00.$$

Thus the total amount of sulfur atoms is $450xV$.

The trisulfur radical anion is singly charged; all the other listed anions are doubly charged. Their total negative-charge concentration is therefore

$$17.50 + 2(1.00 + 4.50 + 55.00 + 5.00 + 0.75) = 150.00.$$

Let n_0 be the initial amount of lithium sulfide. Each mole supplies two moles of lithium ions, so charge balance gives

$$2n_0 = 150xV, \quad n_0 = 75xV.$$

Sulfur balance gives

$$n_0 + n_{\text{powder}} = 450xV.$$

Subtracting the sulfur initially supplied by lithium sulfide,

$$n_{\text{powder}} = (450 - 75)xV = 375xV.$$

Consequently,

$$\frac{n_{\text{powder}}}{n_0} = \frac{375}{75} = 5.$$

The common volume cancels. Therefore,

$$n_0 = \frac{1}{5} \frac{4.81 \text{ mg}}{32.06 \text{ mg mmol}^{-1}} = 0.030006 \text{ mmol}.$$

Since

$$M(\text{Li}_2\text{S}) = 2(6.94) + 32.06 = 45.94 \text{ mg mmol}^{-1},$$

$$m(\text{Li}_2\text{S}) = (0.030006)(45.94) = \boxed{1.38 \text{ mg}}.$$

Species names and SMILES

The salt representations below give formal ionic components. They do not encode crystal lattices, solvent coordination, or lithium–sulfur coordination geometry. In particular, the two Li_2S_6 conformers have the same formula-unit SMILES; their different spatial arrangements are shown in the supplied figure. The S_8 SMILES specifies an eight-membered ring but does not specify its crown conformation.

Species	Name	SMILES
FeS_2	Pyrite; iron(II) disulfide, formal ionic representation	$[\text{Fe}+2] \cdot [\text{S}-] [\text{S}-]$
Fe_3O_4	Magnetite; iron(II,III) oxide, formal ionic representation	$[\text{Fe}+2] \cdot [\text{Fe}+3] \cdot [\text{Fe}+3] \cdot [\text{O}-2] \cdot [\text{O}-2] \cdot [\text{O}-2] \cdot [\text{O}-2]$

Species	Name	SMILES
S ₈	Cyclooctasulfur	S1SSSSSSS1
O ₂	Dioxygen	O=O
SO ₂	Sulfur dioxide	O=S=O
H ₂ O	Water	O
OH ⁻	Hydroxide ion	[OH-]
H ⁺	Hydrogen ion; proton	[H+]
SO ₃ ²⁻	Sulfite ion	[O-]S(=O)[O-]
SO ₄ ²⁻	Sulfate ion	[O-]S(=O)(=O)[O-]
I ₂	Iodine	II
I ⁻	Iodide ion	[I-]
S ₂ O ₃ ²⁻	Thiosulfate ion	[O-]S(=O)(=O)[S-]
S ₄ O ₆ ²⁻	Tetrathionate ion	[O-]S(=O)(=O)SSS(=O)(=O)[O-]
Li	Lithium; atomic representation of the metallic element	[Li]
Li ⁺	Lithium ion	[Li+]
S ²⁻	Sulfide ion	[S-2]
Li ₂ S	Lithium sulfide	[Li+] . [Li+] . [S-2]
LiS ₆ ⁻	Lithium hexasulfide monoanion	[Li+] . [S-]SSSS[S-]
S ₃ ^{•-}	Trisulfur radical anion	[S-]S[S]
LiS ₃ [•]	Lithium trisulfide radical	[Li+] . [S-]S[S]
DME	1,2-Dimethoxyethane	COCCOC
DMSO	Dimethyl sulfoxide	CS(C)=O

The radical SMILES show one localized charge/radical representation; they do not describe the actual delocalization of spin and charge.

The polysulfides in the general corrosion equation and final equilibrium calculation have the following formal representations:

n	S_n^{2-} : name and SMILES	Li_2S_n : name and SMILES
3	Trisulfide ion: [S-]S[S-]	Lithium trisulfide: [Li+] . [Li+] . [S-]S[S-]
4	Tetrasulfide ion: [S-]SS[S-]	Lithium tetrasulfide: [Li+] . [Li+] . [S-]SS[S-]
5	Pentasulfide ion: [S-]SSS[S-]	Lithium pentasulfide: [Li+] . [Li+] . [S-]SSS[S-]
6	Hexasulfide ion: [S-]SSSS[S-]	Lithium hexasulfide: [Li+] . [Li+] . [S-]SSSS[S-]
7	Heptasulfide ion: [S-]SSSSS[S-]	Lithium heptasulfide: [Li+] . [Li+] . [S-]SSSSS[S-]
8	Octasulfide ion: [S-]SSSSSS[S-]	Lithium octasulfide: [Li+] . [Li+] . [S-]SSSSSS[S-]

The solution was checked against the official solution.

Problem 5: Interconversion among Nitrogen Oxides

15% of the total

Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	5.10	Total
Points	4	4	2	4	3	8	4	6	4	6	45
Score											

Nitrogen oxides (including N_2O , NO , NO_2 , N_2O_4 and etc., usually written as NO_x) are one of the main air pollutants that can cause a series of problems such as ozone depletion, acid rain, photochemical smog, and greenhouse effect. Therefore, the emission and conversion of NO_x must be controlled to improve air quality. Here let us investigate the oxidation of NO to NO_2 via the reaction of $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$.

Part A

It is generally accepted that this reaction proceeds through the following mechanism in the atmosphere:



Reaction (1) and (2) and the reverse of reaction (1) are elementary reactions. Reaction (1) is a pre-equilibrium reaction, and its equilibrium constant in terms of concentrations is denoted as K_{c1} . Reaction (2) is the rate-determining step of the overall reaction, and its rate constant is k_2 .

5.1 Deduce the rate expression for the overall reaction of $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ as a function of $[\text{NO}]$, $[\text{O}_2]$, K_{c1} and k_2 . **4.0 pt**

The temperature dependence of K_{c1} could be approximately described as $\ln K_{c1} = M - (N/T)$ (M and N are constants). The change of k_2 with temperature follows the Arrhenius equation with the pre-exponential factor of A_2 and apparent activation energy of $E_{a,2}$. Assume that $E_{a,2}$ and A_2 are independent of the temperature.

5.2 Deduce the expressions for the pre-exponential factor (A_+) and apparent activation energy (E_{a+}) of the reaction of $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ as functions of M , N , A_2 and $E_{a,2}$. **4.0 pt**

The apparent rate constant (k_+) of the overall reaction is $6.63 \times 10^5 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$ at 600 K, and its apparent activation energy is 1.20 kJ mol^{-1} .

5.3 Calculate the rate constant (in $\text{L}^2 \text{ mol}^{-2} \text{ min}^{-1}$) of this reaction at 700 K. **2.0 pt**

The standard enthalpies of formation ($\Delta_f H_m^\ominus$) and standard entropies ($S_m^\ominus$) at 298.15 K are as follows:

	$\text{NO}(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}_2(\text{g})$
$\Delta_f H_m^\ominus (\text{kJ mol}^{-1})$	91.3		33.1
$S_m^\ominus (\text{J K}^{-1} \text{ mol}^{-1})$	210.8	205.2	240.1

The standard reaction enthalpy and entropy changes of $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ can be regarded as temperature independent. All the gases are taken to be ideal for the following questions.

5.4 Calculate the thermodynamic equilibrium constant ($K_p^\ominus$) of this reaction at 600 K. **4.0 pt**

5.5 Calculate the standard internal energy change $\Delta_r U_m^\ominus$ (in kJ mol^{-1}) of this reaction at 600 K. **3.0 pt**

Experimental observation shows that the rate of the reaction of $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$ is independent on the concentration of NO and O_2 .

5.6 Deduce the expression of the rate for this reaction (the apparent rate constant could be directly used as k_-) and **calculate** the value of k_- apparent at 600 K.

(If you failed to find the $K_p^\ominus(600\text{ K})$ in question 5.4, use $K_p^\ominus(600\text{ K}) = 350.0$) **8.0 pt**

NO_2 gas is introduced to a container with a fixed volume which is held at 600 K and allowed to reach equilibrium. 20 percent of the reactant is converted to NO and O_2 . All the gases are taken to be ideal.

5.7 Calculate the total pressure of this reaction system at equilibrium. (If you failed to find the $K_p^\ominus(600\text{ K})$ in question 5.4, use $K_p^\ominus(600\text{ K}) = 350.0$) **4.0 pt**

Part B

Industrial exhaust is a main source of NO_x . One of the approaches to reduce the emission of NO_x is through the oxidation of NO to NO_2 and the subsequent absorption of the formed NO_2 by absorbents. However, because of the low concentration of NO in exhaust, its spontaneous oxidation in the atmosphere is too slow to meet the demand of industry. Generally, solid catalysts are used to accelerate this reaction. The NO oxidation proceeds on the surface of a specific catalyst (**CatX**) through the following mechanism (adsorption site is denoted as Site):



$$r_{S+1} = k_{S+1} [\text{O}_2] \theta_v^2 \quad r_{S-1} = k_{S-1} \theta_{\text{O}}^2$$



$$r_{S+2} = k_{S+2} [\text{NO}] \theta_v \quad r_{S-2} = k_{S-2} \theta_{\text{NO}}$$



$$r_{S+3} = k_{S+3} [\text{NO}] \theta_{\text{O}}$$



$$r_{S+4} = k_{S+4} \theta_{\text{NO}_2} \quad r_{S-4} = k_{S-4} [\text{NO}_2] \theta_v$$

Assume that the adsorptions of NO, NO₂ and O (from the dissociation of O₂) cannot proceed beyond a monolayer coverage, and these species are adsorbed by the same kind of surface sites. Their fractional coverages (θ , defined as the ratio of the number of adsorption sites occupied to the number of total adsorption sites) are denoted as θ_{NO} , θ_{NO_2} and θ_{O} , respectively. Thus, the fraction of unoccupied adsorption sites (θ_v) is $\theta_v = 1 - \theta_{\text{NO}} - \theta_{\text{NO}_2} - \theta_{\text{O}}$. Assume that all the adsorption and desorption processes are much faster than reaction (S3).

5.8 Deduce the expression for θ_v as a function of [NO], [O₂], [NO₂] and the rate constants involved in reactions (S1)–(S4). **6.0 pt**

5.9 Choose the correct expression for the rate of $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g})$ at the beginning of the reaction. Assume that the concentration and adsorption of NO₂ are both negligible. **4.0 pt**

- (A) $r_{S+} = \frac{k_{S+3}(k_{S+1}/k_{S-1})^{0.5}[\text{NO}][\text{O}_2]^{0.5}}{1 + (k_{S+1}[\text{O}_2]/k_{S-1})^{0.5} + k_{S+2}[\text{NO}]/k_{S-2}}$
- (B) $r_{S+} = \frac{0.5k_{S+3}(k_{S+1}/k_{S-1})^{0.5}[\text{NO}][\text{O}_2]^{0.5}}{1 + (k_{S+1}[\text{O}_2]/k_{S-1})^{0.5} + k_{S+2}[\text{NO}]/k_{S-2}}$
- (C) $r_{S+} = \frac{k_{S+3}(k_{S+1}/k_{S-1})[\text{NO}][\text{O}_2]^{0.5}}{1 + k_{S+1}[\text{O}_2]/k_{S-1} + k_{S+2}[\text{NO}]/k_{S-2}}$
- (D) $r_{S+} = \frac{k_{S+4}k_{S+3}(k_{S+1}/k_{S-1})^{0.5}[\text{NO}][\text{O}_2]^{0.5}/k_{S-4}}{1 + k_{S+1}([\text{O}_2]/k_{S-1})^{0.5} + k_{S+2}[\text{NO}]/k_{S-2}}$

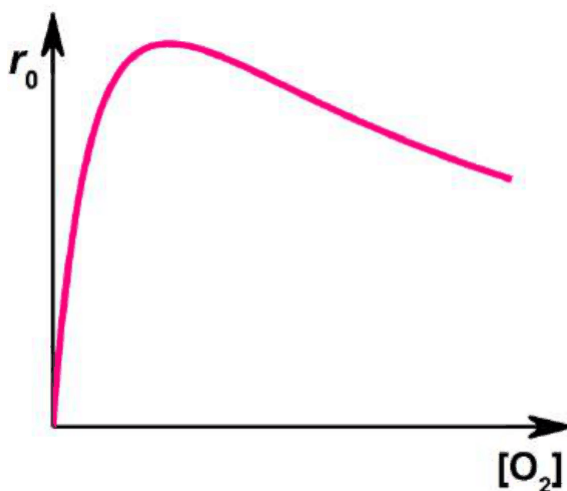
For some catalysts, the surface reaction proceeds via an alternative way instead of reaction (S3):



$$r_{S+5} = k_{S+5} \theta_{\text{NO}} \theta_{\text{O}}$$

This step is also rate-determining for the overall reaction.

A catalyst (**CatY**) is used to promote the reaction of $2 \text{NO} + \text{O}_2 \longrightarrow 2 \text{NO}_2$. When the temperature and NO concentration are constant, the initial reaction rate changes with the concentration of O₂ as follows:



5.10 Choose a mechanism that is consistent with this curve. **6.0 pt**

- (A) S3
- (B) S5
- (C) cannot be determined

Official English text of the problem.

Answers

- **5.1:** $r_+ = k_2 K_{c1} [\text{NO}]^2 [\text{O}_2]$, so $k_+ = k_2 K_{c1}$.
- **5.2:** $A_+ = A_2 e^M$, $E_{a+} = E_{a,2} + RN$.
- **5.3:** $k_+(700 \text{ K}) = 6.86 \times 10^5 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$.
- **5.4:** $K_p^\ominus(600 \text{ K}) = 2.99 \times 10^2$, dimensionless.
- **5.5:** $\Delta_r U_m^\ominus(600 \text{ K}) = -111.4 \text{ kJ mol}^{-1}$.
- **5.6:** $r_- = k_- [\text{NO}_2]^2$, $k_-(600 \text{ K}) = 44.4 \text{ L mol}^{-1} \text{ min}^{-1}$.
- **5.7:** $P_{\text{eq}} = 0.588 \text{ bar} = 58.8 \text{ kPa}$.
- **5.8:**

$$\theta_v = \left[1 + \sqrt{\frac{k_{S+1}[\text{O}_2]}{k_{S-1}}} + \frac{k_{S+2}[\text{NO}]}{k_{S-2}} + \frac{k_{S-4}[\text{NO}_2]}{k_{S+4}} \right]^{-1}$$

- **5.9: (B);** the overall reaction rate is $r_{S+} = \frac{1}{2} r_{S+3}$.
- **5.10: (B), mechanism (S5).**

Solution

Use $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and the standard pressure $p^\ominus = 1 \text{ bar} = 10^5 \text{ Pa}$.

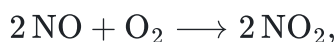
The molecular names and SMILES used in the problem are:

Formula	Name	SMILES
NO	Nitric oxide (nitrogen monoxide)	[N]=O

Formula	Name	SMILES
O ₂	Dioxygen	O=O
NO ₂	Nitrogen dioxide	[N+](=O)[O-]
N ₂ O ₂	Dinitrogen dioxide, the NO dimer	O=NN=O
N ₂ O	Nitrous oxide (dinitrogen monoxide)	N#[N+][O-]
N ₂ O ₄	Dinitrogen tetroxide	[O-][N+](=O)[N+](=O)[O-]

The dimer SMILES gives an N–N-linked connectivity without specifying conformation. The conventional O=O representation does not encode dioxygen's triplet spin state. Surface binding geometries are unspecified, so complete adsorbate–catalyst structures cannot be assigned.

For the overall reaction as written,



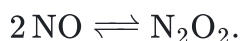
the stoichiometrically normalized rate is

$$r = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}.$$

When both directions operate, $r = r_+ - r_-$.

5.1

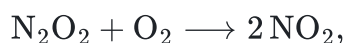
The pre-equilibrium is



Consequently,

$$K_{c1} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}, \quad [\text{N}_2\text{O}_2] = K_{c1}[\text{NO}]^2.$$

The elementary rate-determining step is



with rate

$$r_2 = k_2[\text{N}_2\text{O}_2][\text{O}_2].$$

One occurrence of this step produces two molecules of NO₂, exactly as in the overall equation.

Therefore $r_+ = r_2$, giving

$$r_+ = k_2 K_{c1} [\text{NO}]^2 [\text{O}_2].$$

Thus the apparent rate constant is

$$k_+ = k_2 K_{c1}.$$

5.2

The given temperature dependences give

$$K_{c1} = e^M e^{-N/T}, \quad k_2 = A_2 \exp\left(-\frac{E_{a,2}}{RT}\right).$$

Hence

$$\begin{aligned}
 k_+ &= A_2 e^M \exp\left(-\frac{N}{T} - \frac{E_{a,2}}{RT}\right) \\
 &= A_2 e^M \exp\left[-\frac{E_{a,2} + RN}{RT}\right].
 \end{aligned}$$

Comparison with $k_+ = A_+ \exp[-E_{a+}/(RT)]$ gives

$$\boxed{A_+ = A_2 e^M}, \quad \boxed{E_{a+} = E_{a,2} + RN}.$$

5.3

The two-temperature Arrhenius relation is

$$\ln \frac{k_+(700)}{k_+(600)} = \frac{E_{a+}}{R} \left(\frac{1}{600} - \frac{1}{700} \right).$$

Using $E_{a+} = 1.20 \times 10^3 \text{ J mol}^{-1}$,

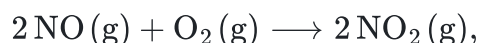
$$\ln \frac{k_+(700)}{6.63 \times 10^5} = \frac{1200}{8.314} \left(\frac{1}{600} - \frac{1}{700} \right) = 0.03437.$$

Therefore,

$$\boxed{k_+(700 \text{ K}) = 6.63 \times 10^5 e^{0.03437} = 6.86 \times 10^5 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}}.$$

5.4

For



the standard formation enthalpy of elemental $\text{O}_2(\text{g})$ is zero. Thus

$$\begin{aligned}
 \Delta_r H_m^\ominus &= 2(33.1) - 2(91.3) - 0 \\
 &= -116.4 \text{ kJ mol}^{-1},
 \end{aligned}$$

and

$$\begin{aligned}
 \Delta_r S_m^\ominus &= 2(240.1) - 2(210.8) - 205.2 \\
 &= -146.6 \text{ J K}^{-1} \text{ mol}^{-1}.
 \end{aligned}$$

At 600 K,

$$\begin{aligned}
 \Delta_r G_m^\ominus &= \Delta_r H_m^\ominus - T \Delta_r S_m^\ominus \\
 &= -116.4 - 600(-0.1466) \\
 &= -28.44 \text{ kJ mol}^{-1}.
 \end{aligned}$$

Since

$$\Delta_r G_m^\ominus = -RT \ln K_p^\ominus,$$

we obtain

$$K_p^\ominus = \exp\left(\frac{28440}{8.314(600)}\right) = 299.234.$$

Therefore,

$$\boxed{K_p^\ominus(600 \text{ K}) = 2.99 \times 10^2}.$$

This thermodynamic equilibrium constant is dimensionless.

5.5

For ideal gases,

$$\Delta_r H_m^\ominus = \Delta_r U_m^\ominus + \Delta n_g RT.$$

The change in gaseous stoichiometric amount is

$$\Delta n_g = 2 - (2 + 1) = -1.$$

Therefore,

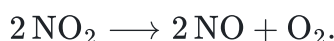
$$\begin{aligned}\Delta_r U_m^\ominus &= \Delta_r H_m^\ominus - \Delta n_g RT \\ &= -116.4 + \frac{8.314(600)}{1000} \\ &= -111.4116 \text{ kJ mol}^{-1}.\end{aligned}$$

Thus,

$$\boxed{\Delta_r U_m^\ominus(600 \text{ K}) = -111.4 \text{ kJ mol}^{-1}}.$$

5.6

The reverse reaction is



Define the concentration equilibrium ratio

$$K_c = \frac{[\text{NO}_2]_{\text{eq}}^2}{[\text{NO}]_{\text{eq}}^2 [\text{O}_2]_{\text{eq}}}.$$

At equilibrium, the forward and reverse rates are equal:

$$r_{-, \text{eq}} = k_+ [\text{NO}]_{\text{eq}}^2 [\text{O}_2]_{\text{eq}} = \frac{k_+}{K_c} [\text{NO}_2]_{\text{eq}}^2.$$

Because the reverse rate depends only on $[\text{NO}_2]$, consistency with this relation for equilibrium mixtures gives

$$\boxed{r_- = k_- [\text{NO}_2]^2}, \quad \boxed{k_- = \frac{k_+}{K_c}}.$$

The dimensionless pressure equilibrium constant is

$$K_p^\ominus = \frac{(p_{\text{NO}_2}/p^\ominus)^2}{(p_{\text{NO}}/p^\ominus)^2 (p_{\text{O}_2}/p^\ominus)}.$$

Substituting $p_i = [i]RT$,

$$K_p^\ominus = \frac{p^\ominus}{RT} K_c, \quad K_c = \frac{RT}{p^\ominus} K_p^\ominus.$$

Using $R = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$,

$$K_c = \frac{(0.08314)(600)}{1} (299.234) = 1.4927 \times 10^4 \text{ L mol}^{-1}.$$

Therefore,

$$\boxed{k_- = \frac{6.63 \times 10^5}{1.4927 \times 10^4} = 44.4 \text{ L mol}^{-1} \text{ min}^{-1}}.$$

For the reverse contribution alone, the corresponding disappearance rate is

$$-\frac{d[\text{NO}_2]}{dt} = 2r_- = 2k_-[\text{NO}_2]^2.$$

5.7

The equilibrium is



Let the initial amount of NO_2 be n_0 . With 20% conversion:

Species	Equilibrium amount	Equilibrium mole fraction
NO_2	$0.80n_0$	$8/11$
NO	$0.20n_0$	$2/11$
O_2	$0.10n_0$	$1/11$

The total amount is $1.10n_0$. With $p_i = y_i P$, the equilibrium constant for the forward oxidation is

$$\begin{aligned} K_p^\ominus &= \frac{y_{\text{NO}_2}^2}{y_{\text{NO}}^2 y_{\text{O}_2}} \frac{p^\ominus}{P} \\ &= \frac{(8/11)^2}{(2/11)^2 (1/11)} \frac{p^\ominus}{P} \\ &= 176 \frac{p^\ominus}{P}. \end{aligned}$$

Hence

$$P = \frac{176 p^\ominus}{K_p^\ominus} = \frac{176}{299.234} \text{ bar} = 0.588 \text{ bar} = 58.8 \text{ kPa}.$$

5.8

Write $*$ for a vacant adsorption site and $\text{O} \cdot$, $\text{NO} \cdot$, and $\text{NO}_2 \cdot$ for occupied sites.

The fast adsorption and desorption steps are approximately equilibrated.

For (S1),



so

$$k_{\text{S}+1}[\text{O}_2]\theta_v^2 = k_{\text{S}-1}\theta_{\text{O}}^2.$$

Taking the physically meaningful nonnegative root,

$$\theta_{\text{O}} = \sqrt{\frac{k_{\text{S}+1}[\text{O}_2]}{k_{\text{S}-1}}} \theta_v.$$

For (S2),



so

$$k_{\text{S}+2}[\text{NO}]\theta_v = k_{\text{S}-2}\theta_{\text{NO}},$$

giving

$$\theta_{\text{NO}} = \frac{k_{\text{S}+2}[\text{NO}]}{k_{\text{S}-2}}\theta_v.$$

For (S4),



so

$$k_{\text{S}+4}\theta_{\text{NO}_2} = k_{\text{S}-4}[\text{NO}_2]\theta_v,$$

giving

$$\theta_{\text{NO}_2} = \frac{k_{\text{S}-4}[\text{NO}_2]}{k_{\text{S}+4}}\theta_v.$$

Substitution into the site balance

$$1 = \theta_v + \theta_{\text{O}} + \theta_{\text{NO}} + \theta_{\text{NO}_2}$$

gives

$$\theta_v = \frac{1}{1 + \sqrt{k_{\text{S}+1}[\text{O}_2]/k_{\text{S}-1}} + k_{\text{S}+2}[\text{NO}]/k_{\text{S}-2} + k_{\text{S}-4}[\text{NO}_2]/k_{\text{S}+4}}.$$

5.9

Initially, the NO_2 adsorption term is negligible. Therefore,

$$\theta_{\text{O}} = \frac{\sqrt{k_{\text{S}+1}[\text{O}_2]/k_{\text{S}-1}}}{1 + \sqrt{k_{\text{S}+1}[\text{O}_2]/k_{\text{S}-1}} + k_{\text{S}+2}[\text{NO}]/k_{\text{S}-2}}.$$

The slow step is



with

$$r_{\text{S}+3} = k_{\text{S}+3}[\text{NO}]\theta_{\text{O}}.$$

Each occurrence produces one adsorbed NO_2 , which rapidly desorbs. Two occurrences of (S3) are required per occurrence of the overall reaction



Thus,

$$r_{\text{S}+} = \frac{1}{2}r_{\text{S}+3},$$

and

$$r_{\text{S}+} = \frac{0.5k_{\text{S}+3}(k_{\text{S}+1}/k_{\text{S}-1})^{0.5}[\text{NO}][\text{O}_2]^{0.5}}{1 + (k_{\text{S}+1}[\text{O}_2]/k_{\text{S}-1})^{0.5} + k_{\text{S}+2}[\text{NO}]/k_{\text{S}-2}}.$$

The correct choice is **(B)**.

5.10

For the alternative slow step,



the overall rate is

$$r_{S+} = \frac{1}{2} k_{S+5} \theta_{NO} \theta_O.$$

At fixed temperature and $[NO]$, define

$$b = \frac{k_{S+2}[NO]}{k_{S-2}}, \quad a = 1 + b, \quad x = \sqrt{\frac{k_{S+1}[O_2]}{k_{S-1}}}.$$

Here a and b are constant, while x increases with $[O_2]$.

With negligible initial NO_2 adsorption,

$$\theta_v = \frac{1}{a + x}, \quad \theta_O = \frac{x}{a + x}, \quad \theta_{NO} = \frac{b}{a + x}.$$

For mechanism (S3),

$$r_{S+}^{(S3)} = \frac{1}{2} k_{S+3}[NO] \frac{x}{a + x}.$$

Its derivative is

$$\frac{dr_{S+}^{(S3)}}{dx} = \frac{1}{2} k_{S+3}[NO] \frac{a}{(a + x)^2} > 0.$$

Thus its rate rises monotonically toward a plateau.

For mechanism (S5),

$$r_{S+}^{(S5)} = \frac{1}{2} k_{S+5} \frac{bx}{(a + x)^2},$$

and

$$\frac{dr_{S+}^{(S5)}}{dx} = \frac{1}{2} k_{S+5} b \frac{a - x}{(a + x)^3}.$$

This derivative is positive for $x < a$, zero at $x = a$, and negative for $x > a$. The rate therefore rises to a maximum and then falls, as shown in the figure. The maximum occurs at

$$\sqrt{\frac{k_{S+1}[O_2]}{k_{S-1}}} = 1 + \frac{k_{S+2}[NO]}{k_{S-2}}.$$

At high oxygen concentration, oxygen occupies most sites and suppresses the coverage of adsorbed NO . Since (S5) requires both adsorbed species, its rate decreases.

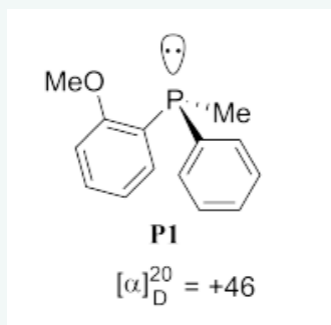
Therefore the consistent choice is

(B), mechanism (S5).

The solution was checked against the official solution.

Problem 6: Enabling Phosphines

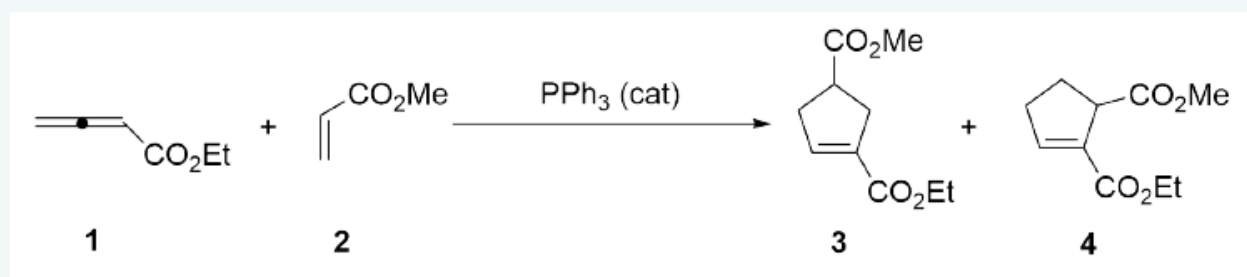
Phosphines are phosphorus analogues of amines. They also carry a lone pair of electrons at the phosphorus atom and thus exhibit Lewis basicity or nucleophilicity. But in contrast with tertiary amines, chiral phosphines like **P1** with three different substituents can be isolated as single enantiomers. Chiral phosphines are often used as chiral ligands in transition metal catalysis.



6.1 Using *R/S* symbol, assign the absolute configuration of **P1**.

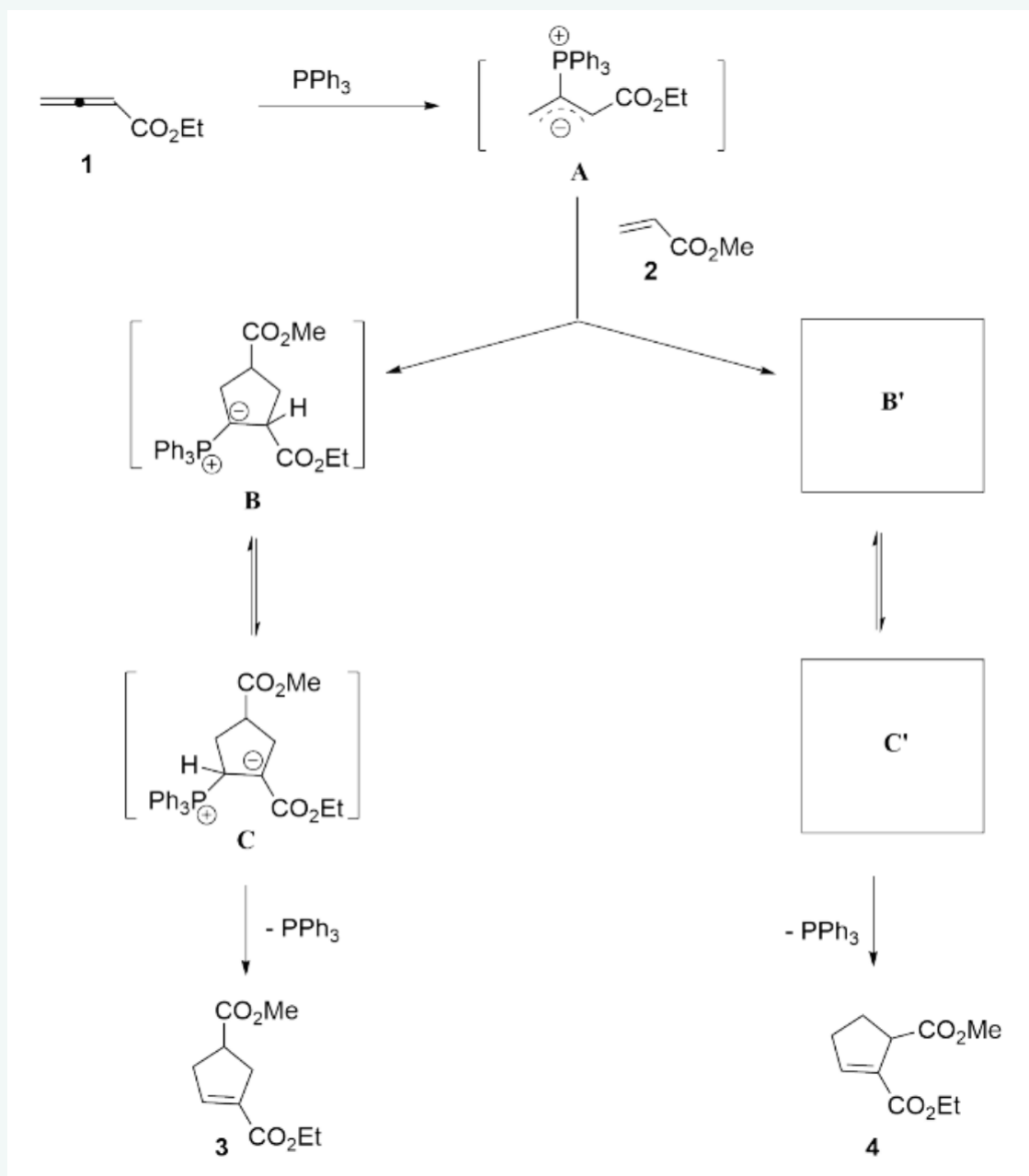
In the past two decades, as organocatalysis grew rapidly, a large number of nucleophilic phosphinecatalyzed synthetic reactions have emerged. Among them, one of the most famous phosphine-catalyzed reactions is the Lu (3+2) cycloaddition reaction, which was first developed by Chinese scientist Xiyan Lu. For instance, under the catalysis of triphenylphosphine, ethyl allenoate **1** and methyl acrylate **2** smoothly produce two cyclopentene derivatives **3** (major) and **4** (minor).

Lu (3+2) cycloaddition:



In a generally accepted mechanism, the Lu (3+2) reaction is a *formal* cycloaddition reaction. Initially, the catalyst triphenylphosphine engages in a nucleophilic addition to ethyl allenoate **1** to generate a zwitterionic intermediate **A**, which subsequently cyclizes with methyl acrylate **2** by two paths. In the path leading to compound **3**, an *in situ* generated phosphorus ylide intermediate **B** reversibly converts into intermediate **C** *via* proton transfer; **C** undergoes an elimination to deliver the major product **3** and release the phosphine catalyst. In the path leading to compound **4**, a phosphorus ylide intermediate **B'** is formed, which also reversibly converts into intermediate **C'** *via* proton transfer; **C'** undergoes an elimination to give the minor product **4** and regenerate the phosphine catalyst.

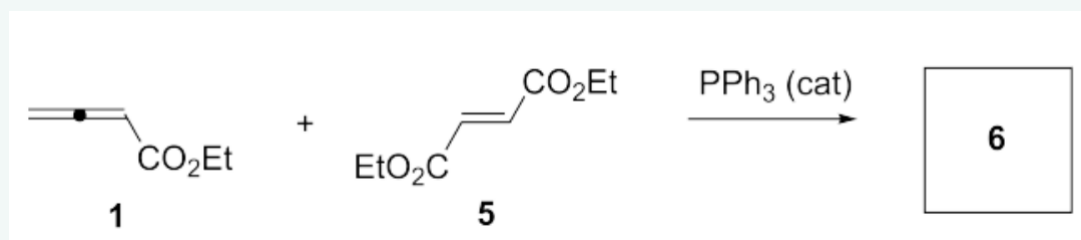
Mechanism:



6.2 Draw the two major resonance structures that make up the shown resonance hybrid **A** (the involvement of ester group is not considered, and stereochemistry is not required).

6.3 Draw the structures of intermediates **B'** and **C'** (stereochemistry is not required).

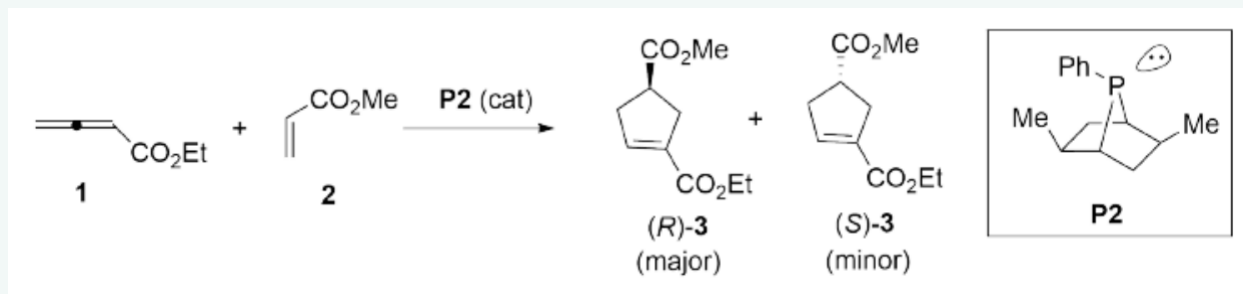
Under similar conditions, ethyl allenoate **1** and diethyl fumarate **5** readily deliver the corresponding cycloaddition product **6**.



6.4 Draw the structure of compound **6** (stereochemistry is not required).

Asymmetric Lu (3+2) cycloaddition reaction can be readily realized by utilizing chiral phosphine catalysts. For example, under the catalysis of a chiral bicyclic phosphine **P2**, ethyl allenoate **1** and methyl acrylate **2** smoothly delivered an enantio-enriched cycloaddition product **3** in 80% ee (enantiomeric excess).

Asymmetric Lu (3+2) cycloaddition:



Calculation equation of ee:

$$ee = \frac{n_{\text{major}} - n_{\text{minor}}}{n_{\text{major}} + n_{\text{minor}}} \times 100\%$$

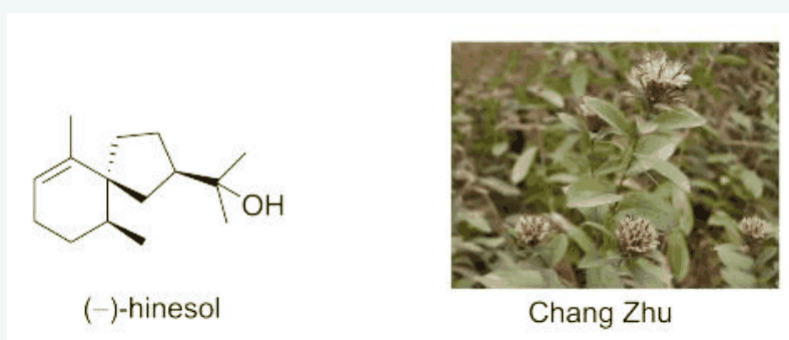
n_{major} = the amount of major enantiomer

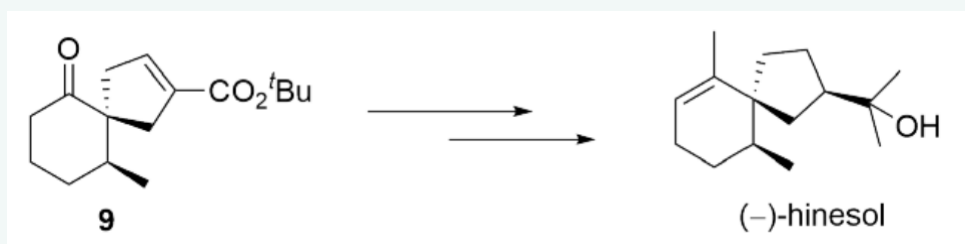
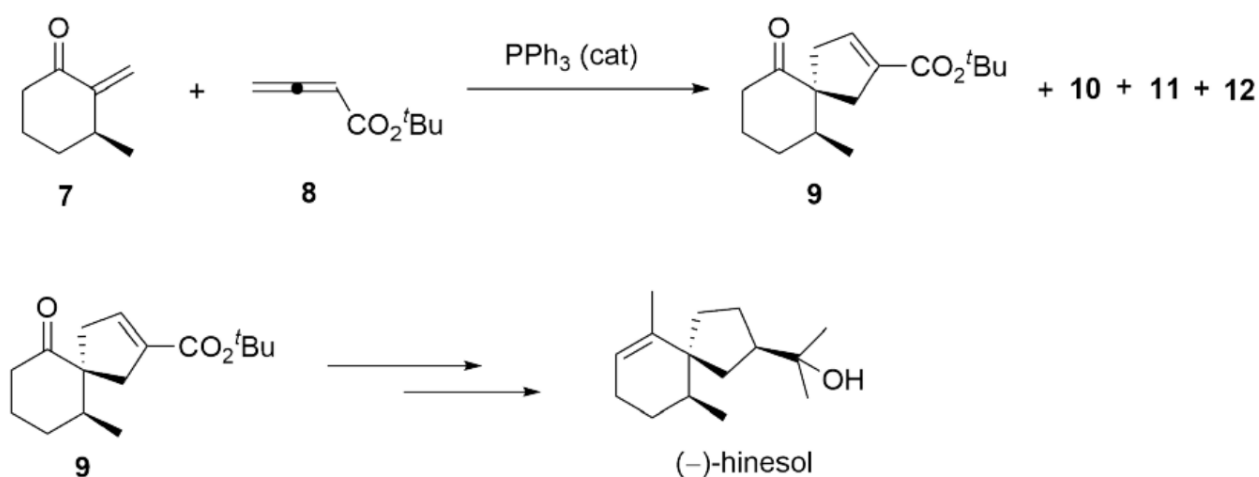
n_{minor} = the amount of minor enantiomer

6.5 Mark the chirality centers in the chiral phosphine **P2** by using asterisks. (Note: points will be deducted for every wrong asterisk until 0 points)

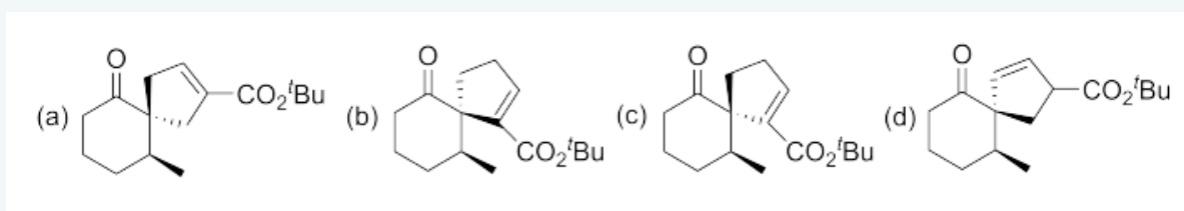
6.6 Give the ratio of $n_{\text{major}}/n_{\text{minor}}$ of product **3**.

Lu (3+2) cycloaddition reaction is a versatile tool in organic synthesis. For example, it was successfully used to synthesize (–)-hinesol, an important component of the Chinese medicinal herb Chang Zhu (*Atractylodes lancea* var *Chinensis*). Under the catalysis of PPh_3 , a chiral cyclohexanone **7** cyclized with tertbutyl allenoate **8**, affording a major product **9** and three minor products **10**, **11** and **12**. Minor products **10–12** are all the isomers of **9**. Compound **9** could be readily transformed into (–)-hinesol by a multistep process.





6.7 In the following compounds, choose which one does not belong to the minor products **10–12**.



Official English text of the problem.

Answers

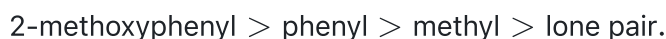
- **6.1:** *R*. **P1** is (*R*)-methyl(2-methoxyphenyl)(phenyl)phosphine: COc1ccccc1[P@](C)(c1ccccc1)c1ccccc1.
- **6.2:** The two contributors to the β -triphenylphosphonium allylic zwitterion **A** are:
 - **α -carbanion contributor:** C=C([P+](c1ccccc1)(c1ccccc1)c1ccccc1)[CH-]C(=O)OCC
 - **γ -carbanion contributor:** [CH2-]C([P+](c1ccccc1)(c1ccccc1)c1ccccc1)=CC(=O)OCC
- **6.3:**
 - **B'**, the cyclic triphenylphosphonium ylide: [C-]1([P+](c2ccccc2)(c2ccccc2)c2ccccc2)C(C(=O)OCC)C(C(=O)OC)CC1
 - **C'**, the proton-transferred phosphonium ester enolate: C1([P+](c2ccccc2)(c2ccccc2)c2ccccc2)[C-](C(=O)OCC)C(C(=O)OC)CC1

- **6.4: 6** is triethyl cyclopent-3-ene-1,2,3-tricarboxylate:
CCOC(=O)C1=CCC(C(=O)OCC)C1C(=O)OCC.
- **6.5:** Mark **four carbon atoms**: both bridgehead carbons bonded to phosphorus and both methyl-bearing ring carbons. These are **C1, C2, C4 and C5** of the 7-phospha-bicyclo[2.2.1]heptane framework. **Do not mark phosphorus.**
P2, 2,5-dimethyl-7-phenyl-7-phospha-bicyclo[2.2.1]heptane: C[C@H]1C[C@@H]2[C@@H](C)C[C@H]1P2c1ccccc1.
- **6.6:** $n_{\text{major}}/n_{\text{minor}} = 9$, or 9 : 1; the mixture contains **90% (*R*)-3 and 10% (*S*)-3.**
- **6.7: (d)** does not belong. It is tert-butyl (5*S*,6*S*)-6-methyl-10-oxospiro[4.5]dec-3-ene-2-carboxylate, with its C2 configuration unspecified: O=C1CCC[C@H](C)[C@]12CC(C(=O)OC(C)(C)C)C=C2.

Solution

6.1

For pyramidal phosphorus, the lone pair is treated as the lowest-priority group. The CIP order is



All three organic groups begin with carbon. The aromatic groups outrank methyl at the next comparison, and the ortho oxygen distinguishes 2-methoxyphenyl from phenyl.

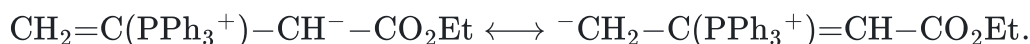
In the drawing, the phenyl bond is a solid wedge toward the observer, while methyl is behind the page. Orienting the lowest-priority lone pair away makes the sequence 1 → 2 → 3 clockwise. Thus **P1 is *R***.

The positive optical rotation shown in the figure does not itself establish an *R* configuration; the assignment follows from the molecular geometry and CIP priorities.

6.2

The starting materials relevant here are ethyl buta-2,3-dienoate, or **ethyl allenolate 1**, C=C=CC(=O)OCC, and **triphenylphosphine**, P(c1ccccc1)(c1ccccc1)c1ccccc1.

Label the allenolate carbon adjacent to the ester **α**, its central allene carbon **β**, and its terminal methylene carbon **γ**. Phosphorus attacks β, and the α–β π electrons move onto α. This gives the first contributor:



To obtain the second contributor, move the α-carbon lone pair into the α–β bond and move the β–γ π electrons onto γ.

Thus, in the requested drawings:

- Phosphorus is positively charged and bonded to β in **both** contributors.
- One contributor has a β–γ double bond and a negative charge on α.
- The other has an α–β double bond and a negative charge on γ.
- The ester group is unchanged.

These are resonance contributors of one zwitterion, not species interconverting by proton transfer.

6.3

The alkene partner is **methyl acrylate 2**, or methyl prop-2-enoate, $C=CC(=O)OC$.

The two products are:

- **3**, ethyl 4-(methoxycarbonyl)cyclopent-1-ene-1-carboxylate: $CCOC(=O)C1=CCC(C(=O)OC)C1$.
- **4**, ethyl 5-(methoxycarbonyl)cyclopent-1-ene-1-carboxylate: $CCOC(=O)C1=CCCC1C(=O)OC$.

For the minor pathway, the γ end of **A** bonds to the terminal carbon of methyl acrylate. The resulting acrylate-derived carbanion closes the ring by bonding to the allenolate α carbon, producing **B'**.

For a precise drawing, number the five-membered ring consecutively as follows:

Ring atom	Origin	Substitution in B'
1	Allenolate β carbon	PPh_3^+ , negative charge on carbon, no hydrogen
2	Allenolate α carbon	CO_2Et and one hydrogen
3	Ester-bearing acrylate carbon	CO_2Me and one hydrogen
4	Terminal acrylate carbon	Methylene
5	Allenolate γ carbon	Methylene

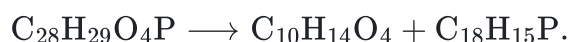
All ring bonds in **B'** are single bonds. The adjacent formal charges on ring carbon 1 and phosphorus identify the phosphorus ylide.

To draw **C'**, transfer the hydrogen from ring carbon 2 to ring carbon 1:

- Carbon 1 becomes neutral and bears hydrogen and PPh_3^+ .
- Carbon 2 bears the negative charge and CO_2Et , with no hydrogen.
- The remaining connectivity is unchanged.

Finally, the lone pair on carbon 2 forms the carbon 1–carbon 2 double bond. The carbon–phosphorus bond breaks with its electrons returning to phosphorus, releasing triphenylphosphine and giving **4**.

The elimination is atom-balanced:



The overall cycloaddition, for either regioisomer, is



6.4

Diethyl fumarate 5, diethyl (*E*)-but-2-enedioate, is $CCOC(=O)/C=C/C(=O)OCC$.

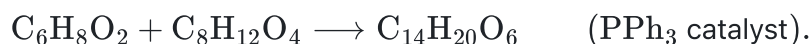
Its two alkene carbons each carry an ethoxycarbonyl group. Both carbons enter the new five-membered ring, retaining those substituents. The allenolate supplies the other three ring carbons and the third ester.

Consequently, **6** has:

- One CO_2Et group on an alkene carbon.
- One CO_2Et group on each of two adjacent saturated ring carbons.

The two possible orientations of fumarate give the same constitution because fumarate is symmetric. No stereochemical specification is required.

The balanced overall equation is



6.5

There are **four chirality centers** in **P2**:

1. **The two methyl-bearing ring carbons, C2 and C5.** Each is attached to hydrogen, methyl and two different paths through the bicyclic framework.
2. **The two bridgehead carbons, C1 and C4.** Each is attached to hydrogen, phosphorus and two different carbon paths; one path immediately encounters a methyl-bearing carbon, while the other encounters a methylene carbon.

Place an asterisk on each of these four carbons.

The two carbon ligands attached to phosphorus are equivalent within the stereochemical framework. Phosphorus therefore does not have three distinguishable organic substituents and is **not an additional chirality center**.

The isomeric SMILES in the answer records the four carbon configurations; it does not reproduce the particular perspective used to draw the cage.

6.6

Let

$$r = \frac{n_{\text{major}}}{n_{\text{minor}}}.$$

Using the given 80% ee,

$$\frac{r-1}{r+1} = 0.80,$$

so

$$r - 1 = 0.80r + 0.80, \quad 0.20r = 1.80, \quad \boxed{r = 9}.$$

Equivalently,

$$x_{\text{major}} = \frac{1 + 0.80}{2} = 0.90, \quad x_{\text{minor}} = \frac{1 - 0.80}{2} = 0.10.$$

The ratio is dimensionless. The enantiomers are:

- **Major (*R*)-3:** ethyl (4*R*)-4-(methoxycarbonyl)cyclopent-1-ene-1-carboxylate, CCOC(=O)C1=CC[C@@H](C(=O)OC)C1.
- **Minor (*S*)-3:** ethyl (4*S*)-4-(methoxycarbonyl)cyclopent-1-ene-1-carboxylate, CCOC(=O)C1=CC[C@H](C(=O)OC)C1.

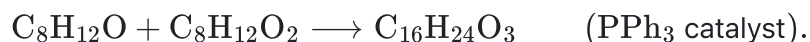
6.7

The starting compounds are:

- **7, (3*S*)-3-methyl-2-methylenecyclohexan-1-one:** C=C1[C@@H](C)CCCC1=O.

- **8**, tert-butyl buta-2,3-dienoate: C=C=CC(=O)OC(C)(C)C.

Their cycloaddition has the balanced molecular equation



The existing methyl-bearing stereocenter is retained. Two regioisomeric connections are possible, and each can give either configuration at the new spiro center. These produce **four products in total**: major product **9** and the three minor products represented by **(a)**, **(b)** and **(c)**.

Their identities are:

Structure	Name	SMILES
9	tert-Butyl (5S,6S)-6-methyl-10-oxospiro[4.5]dec-2-ene-2-carboxylate	<chem>O=C1CCC[C@H](C)[C@]12CC(C(=O)OC(C)(C)C)=CC2</chem>
(a)	tert-Butyl (5R,6S)-6-methyl-10-oxospiro[4.5]dec-2-ene-2-carboxylate	<chem>O=C1CCC[C@H](C)[C@@]12CC(C(=O)OC(C)(C)C)=CC2</chem>
(b)	tert-Butyl (5R,6S)-6-methyl-10-oxospiro[4.5]dec-1-ene-1-carboxylate	<chem>O=C1CCC[C@H](C)[C@]12C(C(=O)OC(C)(C)C)=CCC2</chem>
(c)	tert-Butyl (5S,6S)-6-methyl-10-oxospiro[4.5]dec-1-ene-1-carboxylate	<chem>O=C1CCC[C@H](C)[C@@]12C(C(=O)OC(C)(C)C)=CCC2</chem>

Thus, **(a)** is the spiro epimer of **9**, while **(b)** and **(c)** are the two spiro configurations of the alternative regioisomer.

In every one of these products, elimination of phosphine forms a double bond involving the allenoate's **ester-bearing α carbon**. The ester is consequently conjugated with the ring double bond.

In **(d)**, the ester is attached to a **saturated** ring carbon, and the double bond lies elsewhere. That connectivity does not result from either of the two illustrated cycloaddition/elimination pathways. Therefore,

(d) does not belong to products 10–12.

The configuration of the additional, saturated ester-bearing stereocenter in **(d)** is not specified in the drawing.

The answers were checked against the official answers published by the organisers.

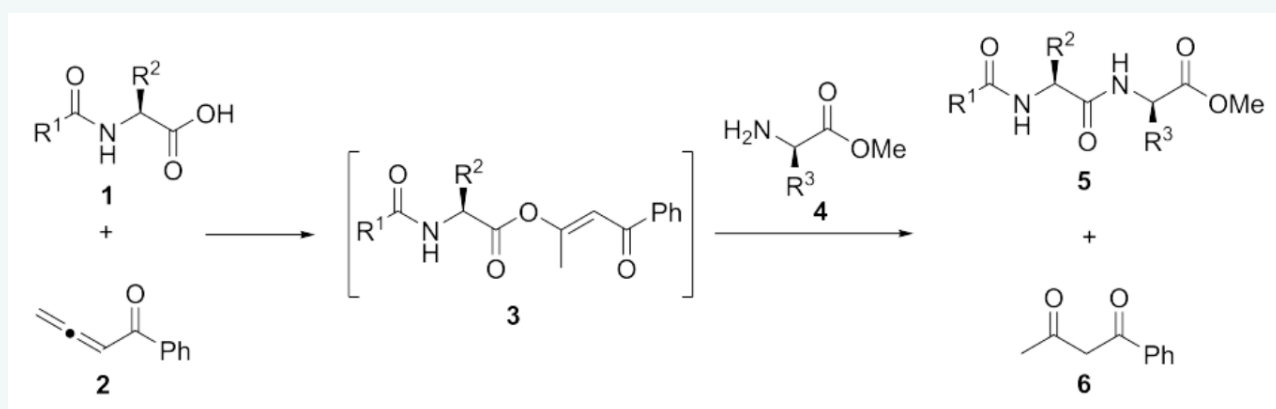
Problem 7: Organic Molecules in Life

The synthesis of complex peptides and proteins is a challenging task. On September 17, 1965, Chinese scientists synthesized crystalline bovine insulin artificially for the first time, marking a crucial step in the journey of exploring the secret of life and opening the era of protein synthesis.

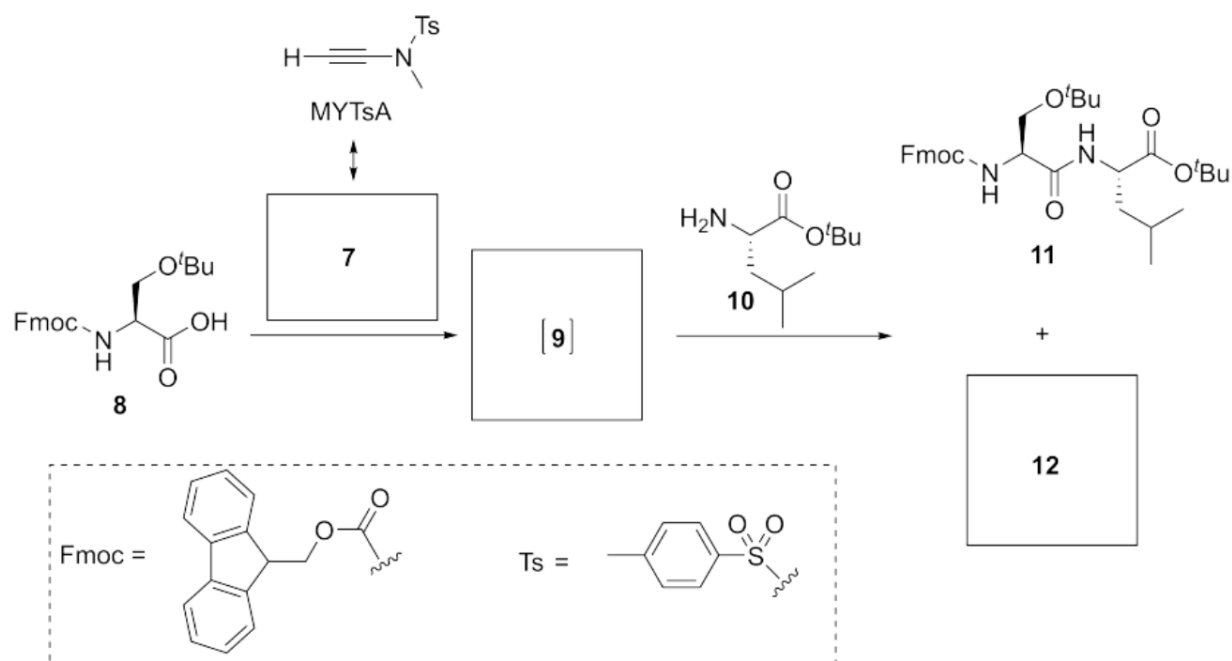


Stamp issued on the 50th anniversary (2015) of the first synthesis of crystalline bovine insulin.

Coupling of carboxylic acid groups with amine groups to forge an amide bond is the most elementary reaction in the synthesis of peptides and proteins. Allenone **2** was reported to be able to activate the carboxylic acid **1** under mild reaction conditions forming the intermediate **3**. Intermediate **3** then reacts with amine **4** to give amide **5** with high yield, along with the byproduct **6**.

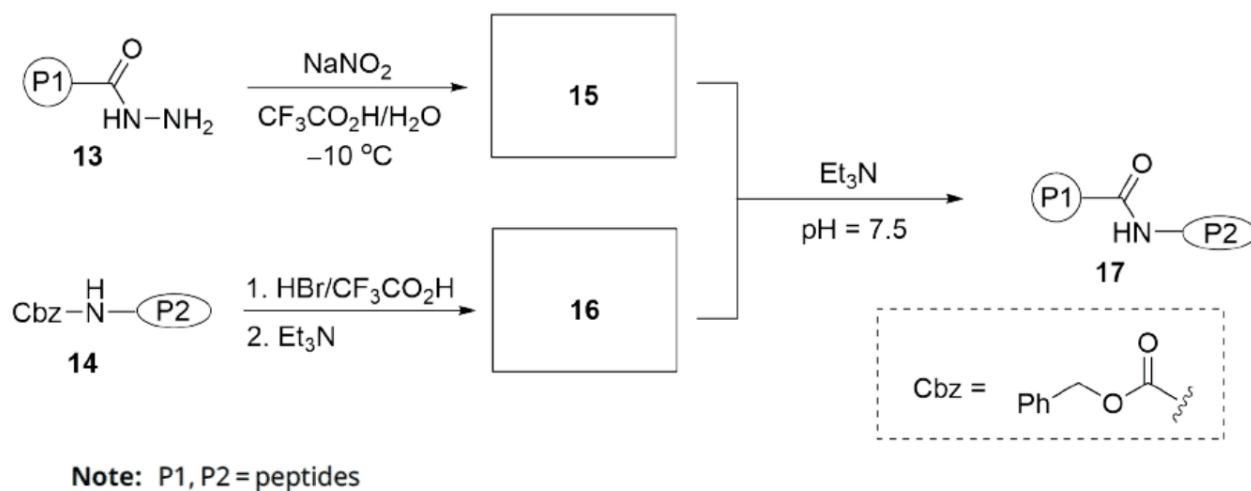


Similarly, *N*-ethynyl-*N*-methyl-*p*-toluenesulfonamide (MYTsA) with its major resonance structure **7** (involvement of Ts group is not considered) can activate carboxylic acid in the same way as allenone **2**.



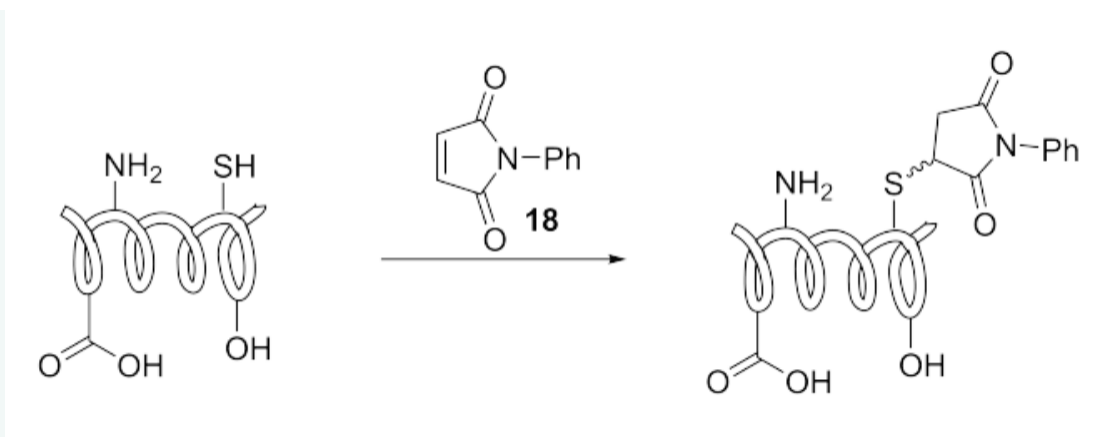
7.1 Draw the structures of **7**, intermediate **9** and compound **12**. Show the stereochemistry of any stereocenters.

As the length of peptide chain grows, formation of amide bonds becomes more difficult, and conventional condensation methods are not applicable in the synthesis of proteins. In the first synthesis of crystalline bovine insulin, a method based on the chemistry of acylhydrazine **13** was developed to achieve the challenging amide coupling between two peptides. As the following equations, compound **15** reacts with **16** smoothly in the presence of triethylamine.

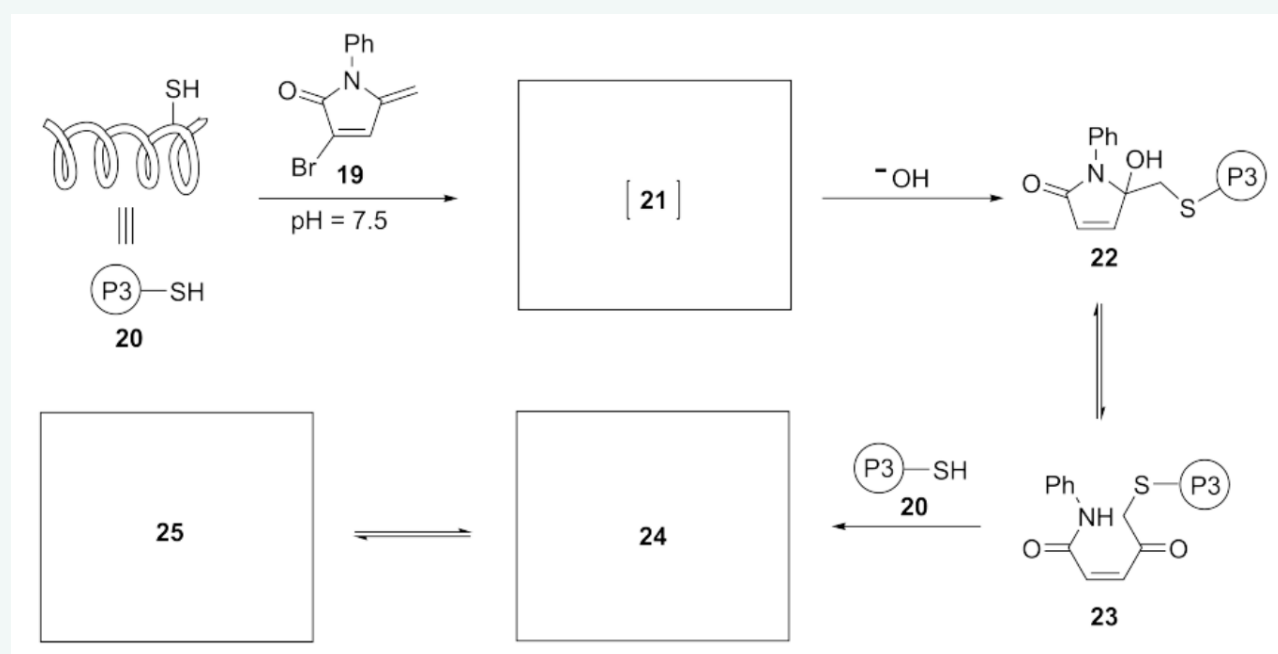


7.2 Draw the structures of compounds **15** and **16**.

In addition to *de novo* synthesis, scientists can modify existing proteins. Although there are multiple reactive sites on the surface of protein, such as amino groups, thiol groups, and carboxyl groups, the most nucleophilic thiol groups are the preferred site when the protein is treated with electrophilic reagents such as *N*-phenyl maleimide **18** via Michael addition.



Under mild basic conditions (pH = 7.5), reagent **19** was proposed to react with the thiol group of protein **20** to give a neutral intermediate **21** which is attacked by hydroxide to give compound **22**. Compound **22** can equilibrate with an acyclic form **23**, and subsequently react with another protein **20**. The resulting major product can exist either in the acyclic form **24** or in the cyclic form **25** in a similar way as the equilibration between **22** and **23**.



7.3 Draw the structures of intermediate **21**, compounds **24** and **25**. Stereochemistry is not required.

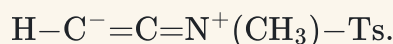
Official English text of the problem.

Answers

In the SMILES below, [*:1] and [*:2] represent the unspecified peptide residues P1 and P2. [*:3] and [*:4] represent **two separate copies** of protein residue P3. Their internal structures are not specified in the problem.

- **7.1**

- **7:** The charge-separated keteniminium–carbanion resonance contributor of MYTsA:



SMILES: [CH-]=C=[N+](C)S(=O)(=O)c1ccc(C)cc1

- **9: 1-[Methyl(tosyl)amino]ethenyl N-Fmoc-O-tert-butyl-L-serinate**, the activated enol ester. The serine stereocenter remains *S*.

SMILES: O=C(OCC1c2ccccc2-c2ccccc21)N[C@@H](COC(C)(C)C(=O)OC(=C)N(C)S(=O)(=O)c1ccc(C)cc1

12: N-Acetyl-N-methyl-4-methylbenzenesulfonamide, also called N-methyl-N-tosylacetamide.

SMILES: CC(=O)N(C)S(=O)(=O)c1ccc(C)cc1

• 7.2

- **15:** The **P1 peptide acyl azide**, $\text{P}_1-\text{C}(=\text{O})-\text{N}_3$.

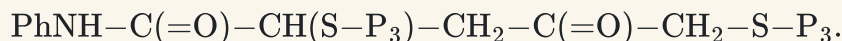
SMILES: [*:1]C(=O)N=[N+]=[N-] - **16:** The **P2 peptide with its free terminal amino group**, $\text{H}_2\text{N}-\text{P}_2$.

SMILES: N[*:2]

• 7.3

- **21: 3-Bromo-1-phenyl-5-[(P3-sulfanyl)methyl]-1,3-dihydro-2H-pyrrol-2-one**, a neutral brominated enamine lactam.

SMILES: O=C1C(Br)C=C(CS[*:3])N1c1ccccc1 - **24: N-Phenyl-4-oxo-2,5-bis(P3-sulfanyl)pentanamide:**



SMILES: O=C(Nc1ccccc1)C(S[*:4])CC(=O)CS[*:3] - **25: 5-Hydroxy-1-phenyl-3-(P3-sulfanyl)-5-[(P3-sulfanyl)methyl]pyrrolidin-2-one**, the cyclic hemiaminal of **24**.

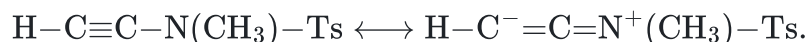
SMILES: O=C1C(S[*:4])CC(O)(CS[*:3])N1c1ccccc1

Solution

7.1 — Activation by MYTsA and peptide-bond formation

MYTsA is **N-ethynyl-N-methyl-4-methylbenzenesulfonamide**, SMILES C#CN(C)S(=O)(=O)c1ccc(C)cc1.

Donation of the nitrogen lone pair into the adjacent alkyne, accompanied by movement of one alkyne π -electron pair onto the terminal carbon, gives resonance contributor **7**:



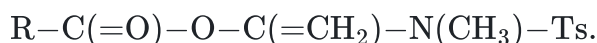
Thus, the terminal carbon carries the negative formal charge, and nitrogen carries the positive formal charge. This is a resonance relationship, not an equilibrium between separate compounds.

Acid **8** is **N-Fmoc-O-tert-butyl-L-serine**, SMILES O=C(OCC1c2ccccc2-c2ccccc21)N[C@@H](COC(C)(C)C(=O)O.

Write it as RCO_2H , with its existing stereochemistry understood. Addition across the ynamide places the acid's proton on the terminal carbon and its carboxylate oxygen on the carbon adjacent to nitrogen:



The product is **9**. Its newly formed ester linkage is specifically



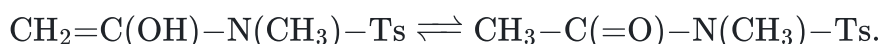
The double bond terminates in a methylene group, so it has no *E/Z* stereochemistry.

At the serine stereocenter, the priority order is amino nitrogen, carboxyl carbon, side-chain carbon, then hydrogen. The configuration shown in **8** is *S*, and it is retained in **9** because no bond at that stereocenter is broken. A drawing should therefore preserve the solid wedge to the serine side chain when using the same orientation as **8**.

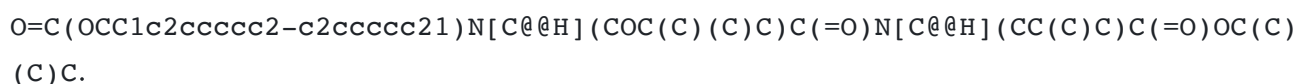
Amine **10** is **tert-butyl L-leucinate**, SMILES N[C@@H](CC(C)C)C(=O)OC(C)(C)C. Writing it as $\text{H}_2\text{N}-\text{R}'$, its nitrogen attacks the **amino-acid acyl carbonyl** of **9**. Collapse of the tetrahedral intermediate gives the peptide bond:



The leaving fragment is initially protonated to **1-[methyl(tosyl)amino]ethen-1-ol**, SMILES C=C(O)N(C)S(=O)(=O)c1ccc(C)cc1. It tautomerizes to **12**:



Product **11** is **N-Fmoc-O-tert-butyl-L-seryl-L-leucine tert-butyl ester**, SMILES



Both amino-acid stereocenters retain their *S* configurations. The two coupling equations above are atom-balanced; no separate water molecule is released in these steps.

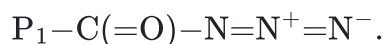
7.2 — Acyl-azide coupling of peptide fragments

Compound **13** is the **P1 peptide acyl hydrazide**, SMILES [*:1]C(=O)NN.

Acidified nitrite converts its hydrazide group into an acyl azide through nitrosation and dehydration. The balanced net ionic equation is



Thus, **15** is the acyl azide identified above. One valid charge-explicit representation of its azide group is



The low temperature, -10°C , allows the acyl azide to be used for the subsequent coupling.

Compound **14** is the **N-Cbz-protected P2 peptide**, SMILES O=C(OCc1ccccc1)N[*:2].

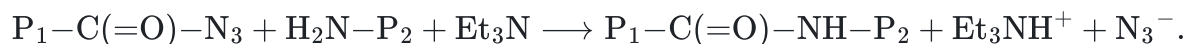
Hydrogen bromide cleaves the benzyl protecting group, and the remaining carbamate decarboxylates. Written with bromide as the ammonium counterion, the balanced reaction is



The initially formed **P2 peptide ammonium ion** has SMILES [NH3+][*:2]. Triethylamine liberates the free amine **16**:



Amine **16** then attacks the acyl carbonyl of **15**. Elimination of azide and removal of a proton give the new peptide bond. Including the base, the balanced coupling is



The product, **17**, is the **amide-linked P1–P2 peptide**, SMILES [*:1]C(=O)N[*:2].

The small species used in these equations are nitrite, [O-]N=O; proton, [H+]; water, O; hydrogen bromide, [H]Br; bromide, [Br-]; benzyl bromide, BrCc1ccccc1; carbon dioxide, O=C=O; triethylamine, CCN(CC)CC; triethylammonium, CC[NH+](CC)CC; and azide, [N-]=[N+]=[N-].

7.3 — Formation of the two-protein conjugate

For the five-membered ring, number the nitrogen **1**, the carbonyl carbon **2**, and the remaining ring carbons **3**, **4**, and **5** in sequence.

Reagent **19** is **3-bromo-5-methylene-1-phenyl-1,5-dihydro-2H-pyrrol-2-one**, SMILES C=C1C=C(Br)C(=O)N1c1ccccc1.

Protein **20** is the **P3 thiol**, SMILES [*:3]S; its reactive **thiolate** form has SMILES [*:3][S-].

The thiolate attacks the terminal exocyclic methylene carbon in a **1,6-conjugate addition**. Electron displacement through the conjugated system gives an enolate, and protonation at ring position 3 produces neutral **21**. Using bold-numbered compounds as the molecular labels, the stoichiometry is



A precise drawing of **21** has:

- an N-phenyl nitrogen at position 1;
- a carbonyl at position 2;
- a **CHBr** group at position 3;
- a double bond between positions 4 and 5;
- a **–CH₂–S–P₃** substituent at position 5.

In particular, **bromine remains attached in 21**.

Hydroxide then gives an allylic substitution with double-bond migration: oxygen bonds to position 5, the double bond shifts to positions 3–4, and bromide leaves position 3. The balanced equation is



Hydroxide has SMILES [OH-]. Product **22** is **5-hydroxy-1-phenyl-5-[(P3-sulfanyl)methyl]-1,5-dihydro-2H-pyrrol-2-one**, SMILES O=C1C=CC(O)(CS[*:3])N1c1ccccc1.

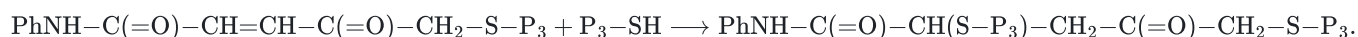
Compound **22** is a cyclic hemiaminal. Breaking its bond between nitrogen and position 5, forming a carbonyl at position 5, and transferring the hydroxyl proton to nitrogen give **23**. No water is gained or lost:



Compound **23** is **N-phenyl-4-oxo-5-(P3-sulfanyl)pent-2-enamide**, SMILES O=C(Nc1ccccc1)C=CC(=O)CS[*:3]. Its connectivity is

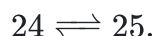


The alkene is conjugated with both an amide carbonyl and a ketone carbonyl. The ketone provides the stronger Michael-acceptor activation because nitrogen donation reduces the electron-withdrawing effect of the amide carbonyl. Consequently, the second thiol adds predominantly at the alkene carbon **beta to the ketone**, which is the carbon next to the amide carbonyl:



This identifies **24**, with the second protein attached through sulfur at the carbon adjacent to the amide carbonyl.

Finally, the amide nitrogen attacks the ketone intramolecularly. Proton transfer gives the cyclic hemiaminal **25**:

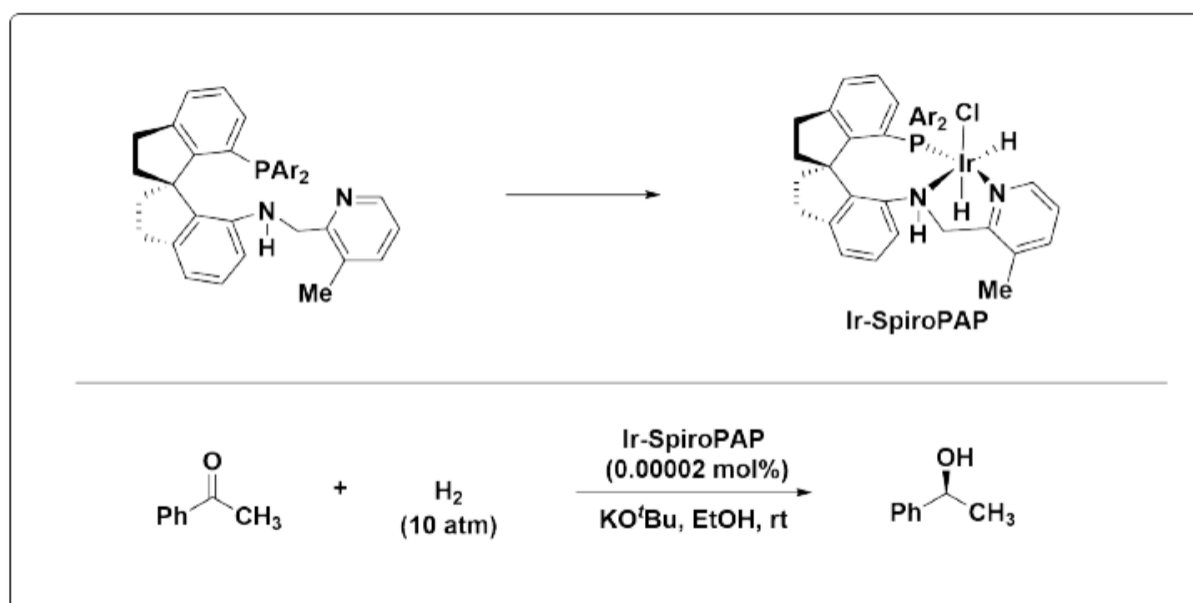


A precise drawing of **25** is a five-membered ring containing an N-phenyl nitrogen at position 1, a carbonyl at position 2, $\text{CH}(\text{S}-\text{P}_3)$ at position 3, methylene at position 4, and a carbon bearing both $-\text{OH}$ and $-\text{CH}_2-\text{S}-\text{P}_3$ at position 5. The two P_3 groups are separate protein molecules. No water is eliminated during this ring closure, and stereochemistry need not be specified.

The answers were checked against the official answers published by the organisers.

Problem 8: Amazing Chiral Spiro Catalyst

Chiral compounds are important for human health, for example, more than 50% of the medicines currently in clinical use are single enantiomers of chiral molecules. However, synthesizing chiral molecules in enantio-enriched form is a great challenge. Professor Qilin Zhou's team in Nankai University in China developed a series of chiral spiro catalysts with high activity, raising the efficiency of asymmetric synthesis to a new height, and being widely used in the pharmaceutical industry. These catalysts can give up to (reach up to) 99.9% ee and can be used down to 0.00002 mol% loading. This research result won the first prize of the 2019 National Natural Science Award of China.

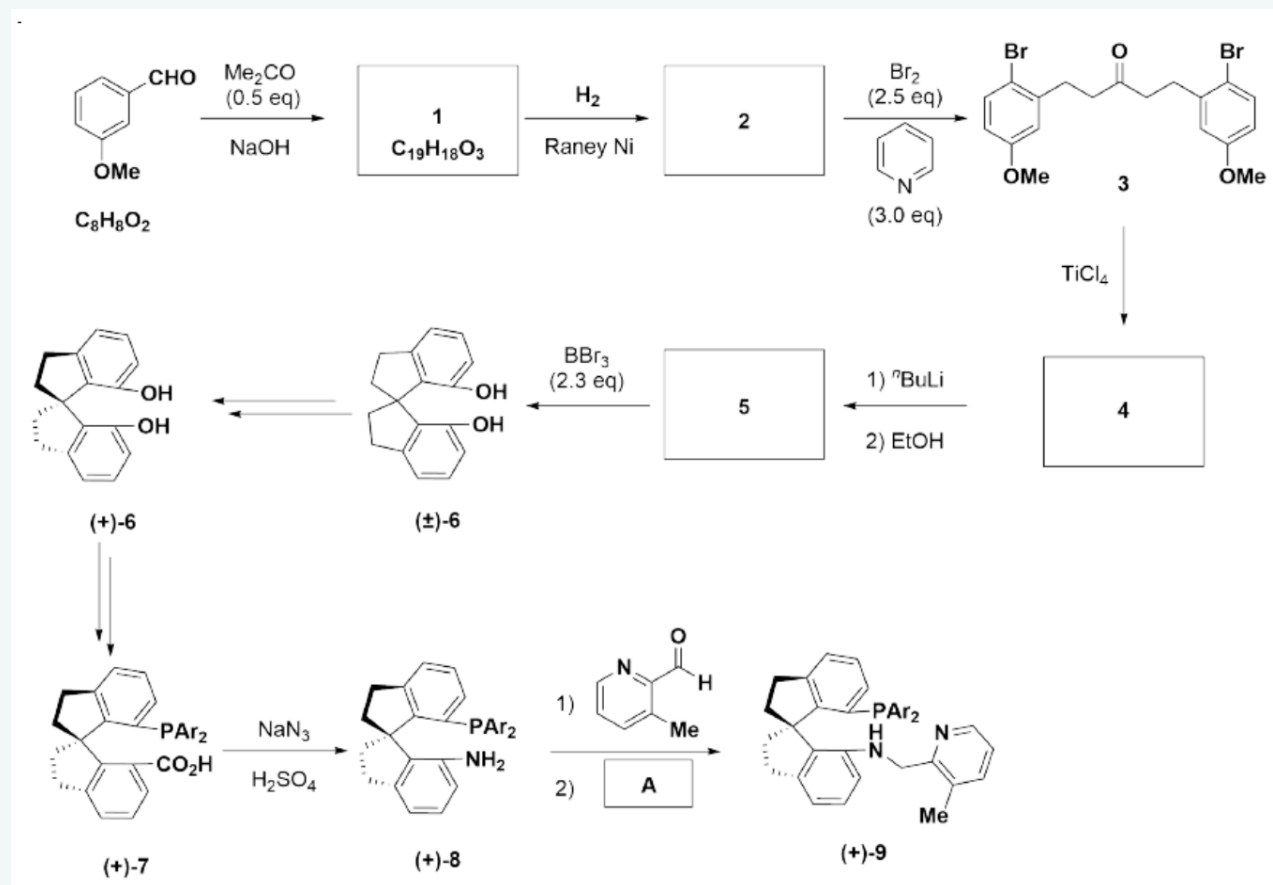


Note:

Ar = 3, 5- $(^t\text{Bu})_2\text{C}_6\text{H}_3$

Part A

The synthetic route of the chiral ligand SpiroPAP is shown in the following scheme.

**Note:**

eq = equivalent

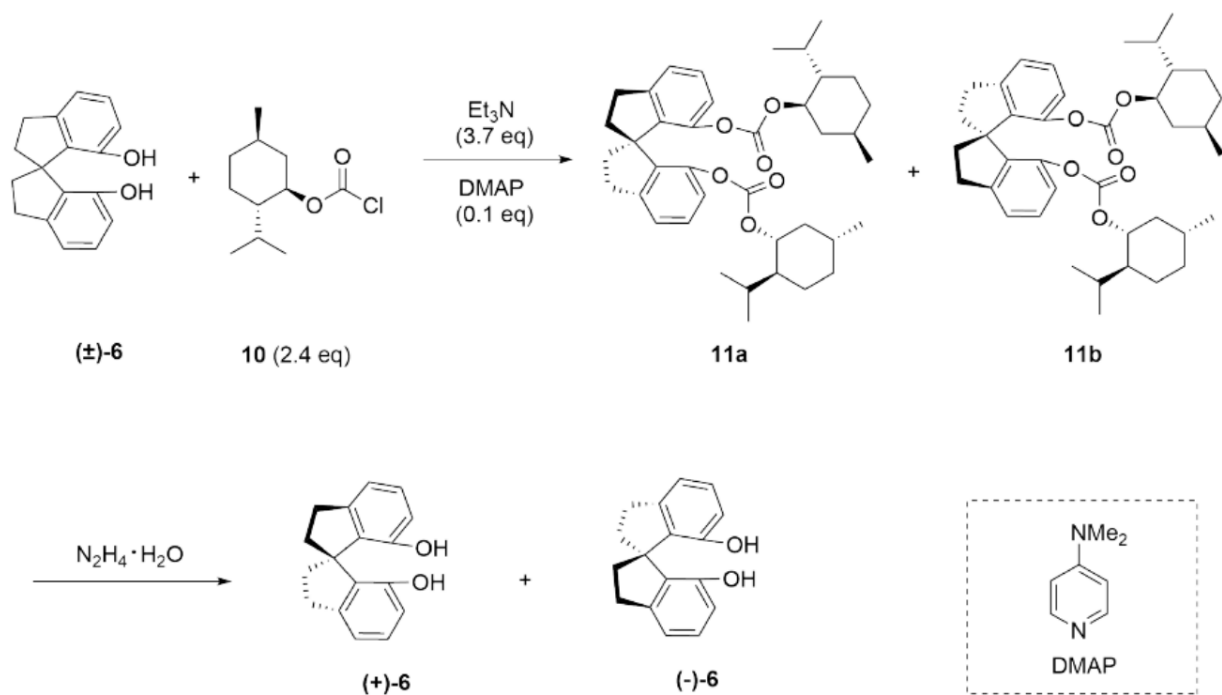
Ar = 3, 5- $(^t\text{Bu})_2\text{C}_6\text{H}_3$

8.1 Draw the structures of **1**, **2**, **4**, **5**. (Stereochemistry is not considered).

8.2 From the following reagents, which reagent **A** can NOT be used for the transformation of **8** to **9**?

- (a) $\text{NaBH}(\text{OAc})_3$
- (b) NaBH_3CN
- (c) NH_2NH_2 , NaOH
- (d) NaBH_4

The racemic spiro compound **6** reacts with (–)-menthyl chloroformate (**10**) to generate compounds **11a** and **11b**, which can be separated by column chromatography, followed by hydrazinolysis to obtain optically pure (+)-**6** and (–)-**6**.



Note:

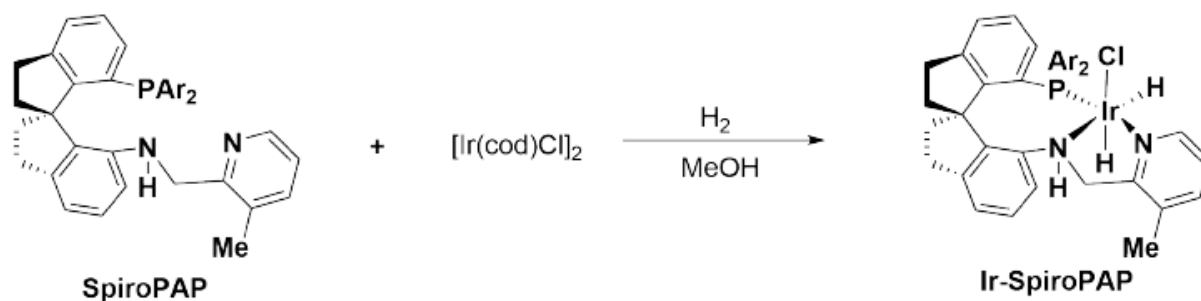
eq = equivalent

8.3 Choose the correct statement below.

- (a) Compounds **11a** and **11b** are a pair of enantiomers.
- (b) Compounds **11a** and **11b** are a pair of diastereomers.
- (c) Compounds **11a** and **11b** are a pair of *cis-trans* isomers.
- (d) Compounds **11a** and **11b** are a pair of conformational isomers.

Part B

The Ir-SpiroPAP was prepared by reaction of SpiroPAP with $[\text{Ir}(\text{cod})\text{Cl}]_2$ (cod is cycloocta-1,5-diene) in MeOH under hydrogen as shown below.



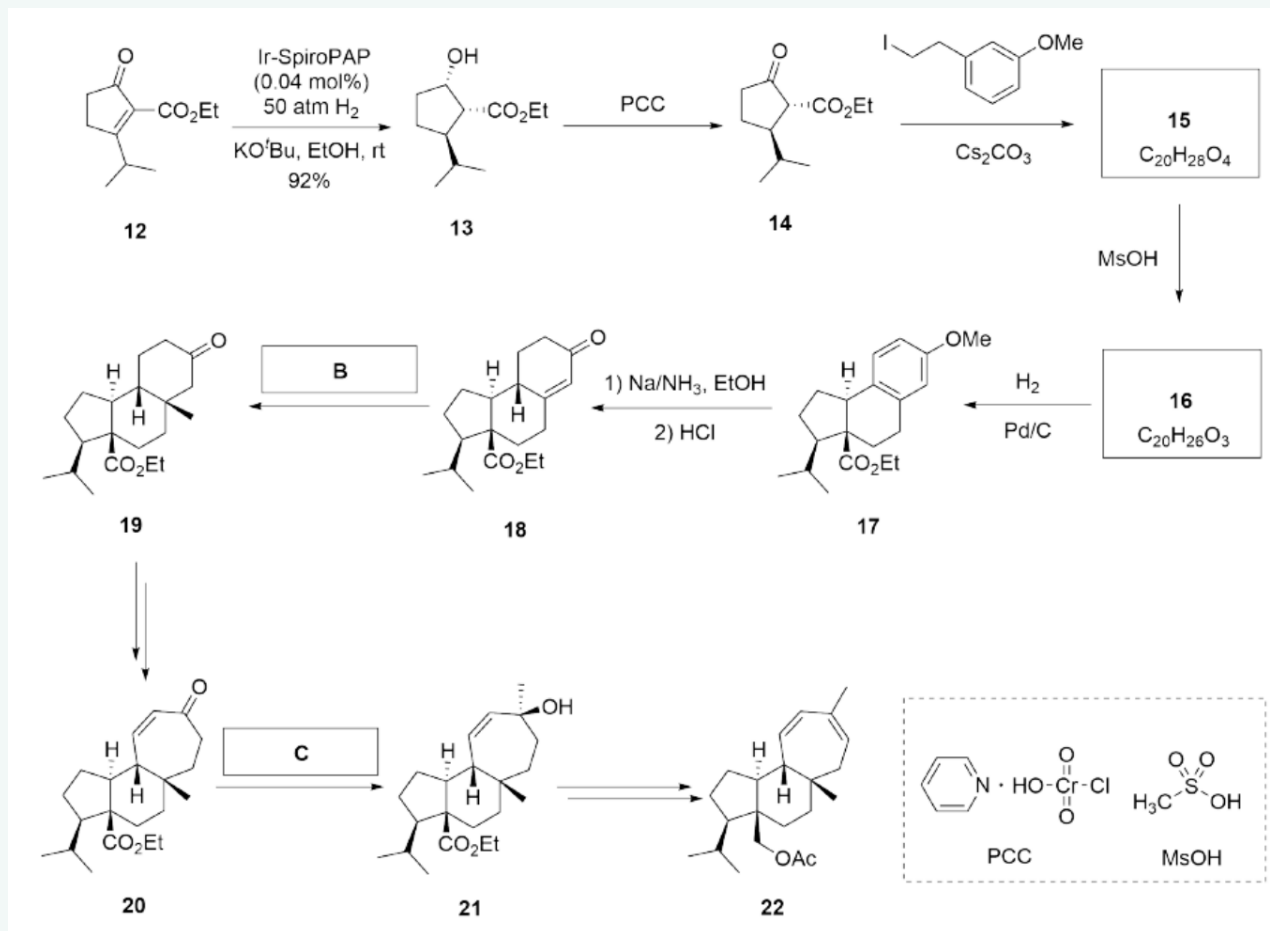
Note:

$\text{Ar} = 3, 5\text{-(}^t\text{Bu)}_2\text{C}_6\text{H}_3$

8.4 Write the oxidation number of Ir in the catalyst Ir-SpiroPAP.

8.5 Write the number of valence electrons of d orbitals for metal Ir in the catalyst Ir-SpiroPAP.

The chiral spiro catalyst Ir-SpiroPAP was used for the asymmetric total synthesis of Mulinane-type diterpene **22** as shown below.



8.6 Draw the structures of **15** and **16**, including the appropriate stereochemistry.

8.7 From the following reagents, choose the best for **B**.

- (a) MeLi/CeCl₃
- (b) MeLi/CuI
- (c) MePh₃P⁺ I⁻, ⁿBuLi
- (d) Me₃S⁺ I⁻, NaH

8.8 From the following reagents, choose the best for **C**.

- (a) MeLi/CeCl₃
- (b) MeLi/CuI
- (c) MePh₃P⁺ I⁻, ⁿBuLi
- (d) Me₃S⁺ I⁻, NaH

Official English text of the problem.

Answers

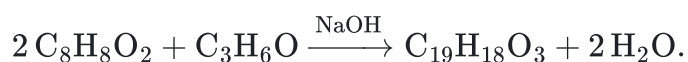
- **8.1**
- **1:** 1,5-Bis(3-methoxyphenyl)penta-1,4-dien-3-one.
SMILES: COc1cccc(C=CC(=O)C=Cc2cccc(OC)c2)c1
- **2:** 1,5-Bis(3-methoxyphenyl)pentan-3-one.
SMILES: COc1cccc(CCC(=O)CCc2cccc(OC)c2)c1
- **4:** 4,4'-Dibromo-7,7'-dimethoxy-1,1'-spirobiindane.
SMILES: COc1ccc(Br)c2c1C1(CCc3c(Br)ccc(OC)c31)CC2
- **5:** 7,7'-Dimethoxy-1,1'-spirobiindane.
SMILES: COc1cccc2c1C1(CCc3cccc(OC)c31)CC2
- **8.2: (c)** Hydrazine, NN , with sodium hydroxide, $[\text{Na}^+] \cdot [\text{OH}^-]$.
- **8.3: (b)** Diastereomers.
- **8.4:** The oxidation number of Ir is +3.
- **8.5: Six d electrons**, i.e. $5d^6$.
- **8.6**
- **15:** Ethyl (1S,5R)-1-[2-(3-methoxyphenyl)ethyl]-2-oxo-5-(propan-2-yl)cyclopentane-1-carboxylate.
SMILES: CCOC(=O)[C@]1(CCc2cccc(OC)c2)C(=O)CC[C@@H]1C(C)C
- **16:** Ethyl (3R,3aS)-7-methoxy-3-(propan-2-yl)-2,3,4,5-tetrahydro-3aH-cyclopenta[a]naphthalene-3a-carboxylate.
SMILES: CCOC(=O)[C@]12CCC3cc(OC)ccc3C1=CC[C@@H]2C(C)C
In both **15** and **16**, the ethoxycarbonyl and isopropyl groups are **cis**. In **16**, the nonaromatic double bond lies in the five-membered ring.
- **8.7: (b)** Methyllithium, $[\text{Li}^+] \cdot [\text{CH}_3^-]$, with copper(I) iodide, $[\text{Cu}^+] \cdot [\text{I}^-]$.
- **8.8: (a)** Methyllithium, $[\text{Li}^+] \cdot [\text{CH}_3^-]$, with cerium(III) chloride, $[\text{Ce}^{+3}] \cdot [\text{Cl}^-] \cdot [\text{Cl}^-] \cdot [\text{Cl}^-]$.

Solution

8.1 — Structures of 1, 2, 4 and 5

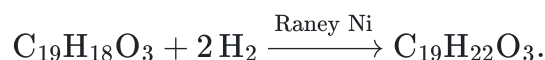
The starting aldehyde is **3-methoxybenzaldehyde**, COc1cccc(C=O)c1, and the ketone reagent is **acetone**, CC(=O)C.

Formation of 1. Acetone has two enolizable methyl groups. The stated 0.5 equivalent of acetone therefore allows two aldehyde molecules to condense with one acetone molecule. Two aldol additions, each followed by dehydration, give the conjugated dienone **1**:



Thus, draw a central ketone bearing a $-\text{CH}=\text{CH}-$ (3-methoxyphenyl) group on each side. Its formula agrees with the supplied $\text{C}_{19}\text{H}_{18}\text{O}_3$. Alkene stereochemistry is omitted as instructed.

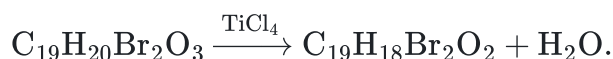
Formation of 2. Hydrogenation reduces both carbon–carbon double bonds. The ketone remains, as confirmed by the structure of **3**:



Thus, **2** has a central ketone bearing two $-\text{CH}_2\text{CH}_2-(3\text{-methoxyphenyl})$ groups.

Formation of 4. In the supplied dibrominated ketone **3**, bromine blocks one ortho position of each aryl ring. Titanium tetrachloride activates the carbonyl group, permitting successive intramolecular Friedel–Crafts cyclizations at the two unblocked ortho positions.

The original carbonyl carbon becomes the common spiro carbon of two five-membered rings. The net organic balance is:



Draw two indane units sharing only their C1 atom. Each aromatic ring carries bromine at C4 and methoxy at C7. This gives **4**, 4,4'-dibromo-7,7'-dimethoxy-1,1'-spirobiindane.

Formation of 5. Butyllithium effects bromine–lithium exchange at both aryl bromides. Ethanol then protonates the two carbon–lithium sites, replacing both bromines with hydrogen. An overall balanced equation is:

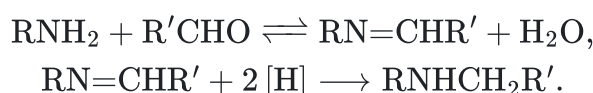


The spiro skeleton and both methoxy groups remain intact, giving **5**. Subsequent boron tribromide cleavage of its methyl ethers produces the two phenolic groups of **6**, confirming the methoxy positions.

8.2 — Reagent A that cannot be used

The transformation is **reductive amination**. The primary amino group of **8** first condenses with **3-methylpyridine-2-carbaldehyde**, Cc1cccnc1C=O, forming an imine. Reduction then gives the secondary amine **9**.

Writing R for the spiroaryl portion and R' for the 3-methylpyridin-2-yl group:



Here, $2[\text{H}]$ denotes the formal hydrogen equivalents supplied by reduction and protonation.

The following reagents can reduce the imine:

- **Sodium triacetoxyborohydride:** $[\text{Na}^+] \cdot [\text{BH}^-] (\text{OC}(\text{C})=\text{O}) (\text{OC}(\text{C})=\text{O}) \text{OC}(\text{C})=\text{O}$
- **Sodium cyanoborohydride:** $[\text{Na}^+] \cdot [\text{BH}_3^-] \text{C}\equiv\text{N}$
- **Sodium borohydride:** $[\text{Na}^+] \cdot [\text{BH}_4^-]$

Sodium borohydride is suitable because the scheme specifies condensation first and reduction second.

Hydrazine with sodium hydroxide supplies **Wolff–Kishner conditions**. These convert a carbonyl group into a methylene group through a hydrazone; they do not perform the required reduction of the imine while retaining the linkage to the amino group of **8**.

Therefore, **A cannot be (c)**.

8.3 — Relationship between 11a and 11b

The two derivatives have:

- Opposite configurations of the spiro framework.
- The same configurations at every stereocentre of their menthyl groups.

A mirror image would invert both the spiro configuration and all the menthyl stereocentres. Since only the spiro configuration differs, **11a and 11b are diastereomers**.

Their different physical properties allow chromatographic separation. Removal of the menthyl-derived carbonate groups then releases the separate enantiomers of **6**.

Thus, **(b)** is correct.

8.4 — Oxidation number of Ir

The depicted complex is neutral. Its ligands comprise:

- One neutral tridentate phosphine–amine–pyridine ligand.
- One **chloride ligand**, [Cl[−]], of charge −1.
- Two **hydride ligands**, [H[−]], each of charge −1.

The hydrogen attached to the amine nitrogen belongs to the neutral amine; it is not an additional hydride ligand.

If the oxidation number of Ir is x ,

$$x + 0 - 1 - 1 - 1 = 0,$$

so

$$\boxed{x = +3}.$$

The three donor atoms of SpiroPAP, chloride and two hydrides give a six-coordinate, approximately octahedral complex.

8.5 — Number of metal d electrons

Iridium belongs to group 9. The formal d -electron count is therefore

$$n_d = 9 - \text{oxidation number} = 9 - 3 = 6.$$

Hence the metal has the configuration

$$\boxed{5d^6}.$$

As a consistency check, the six d electrons plus twelve electrons donated by the six donor sites give an 18-electron complex.

8.6 — Structures and stereochemistry of 15 and 16

For tracing the atoms, number the cyclopentanone ring of **14** as follows:

- **C1**: the carbon bearing the ethoxycarbonyl group.
- **C2**: the ketone carbonyl carbon.
- **C3 and C4**: the two methylene carbons.

- **C5**: the carbon bearing the isopropyl group.

For the incoming aromatic ring, let C1' bear the ethyl tether and C3' bear methoxy.

Formation of 15. The alkylating reagent is **1-(2-iodoethyl)-3-methoxybenzene**, COc1cccc(CCI)c1.

The hydrogen at C1 of **14** lies between the ketone and ester carbonyl groups. Carbonate-assisted enolate formation followed by S_N2 alkylation introduces a $-\text{CH}_2\text{CH}_2-(3\text{-methoxyphenyl})$ group at C1.

An overall balance including carbonate neutralization is:



The resulting formula is the supplied $\text{C}_{20}\text{H}_{28}\text{O}_4$.

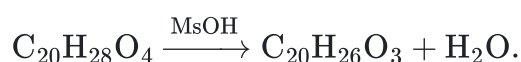
Stereochemistry of 15. Enolate formation removes the original configuration at C1; that stereocentre is established again during alkylation. The configuration at C5 is retained.

The subsequent structure **17** fixes the required relative configuration: its ethoxycarbonyl and isopropyl groups are both shown as solid wedges. Therefore, these groups must already be **cis** in **15**. The new phenethyl substituent is **trans** to the isopropyl group.

To draw **15** in the orientation of **14**, retain the solid-wedge isopropyl group and show the ethoxycarbonyl group on the same face, with the new phenethyl group on the opposite face. The absolute configuration is **(1S,5R)**, as encoded in the answer SMILES.

Formation of 16. Methanesulfonic acid activates the ketone for intramolecular Friedel–Crafts attack. Aromatic C6' attacks carbonyl carbon C2, forming a new six-membered ring. C6' is ortho to the tether and para to methoxy.

The resulting alcohol loses water. C1 has no hydrogen after alkylation, so dehydration forms the **C2=C3 double bond in the five-membered ring**:



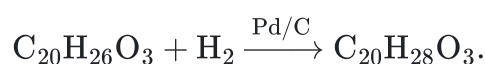
This matches the formula supplied for **16**.

The configurations at the original C1 and C5 remain unchanged. In the fused-ring nomenclature used in the answer, these correspond to **3aS** and **3R**, respectively.

A precise way to draw **16** is to start from the supplied structure **17**:

1. Retain its complete carbon skeleton, methoxy group, ester and isopropyl group.
2. Retain the solid-wedge ester and isopropyl substituents.
3. Remove the dashed-wedge hydrogen from the upper five-/six-membered-ring junction.
4. Make the bond from that junction to the adjacent nonjunction carbon of the five-membered ring a double bond.

Hydrogenation of this alkene then gives **17**:



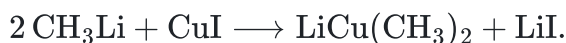
8.7 — Best reagent for B

Comparing **18** with **19**, the required transformation:

- Adds a methyl group to the **β-carbon** of the enone.
- Consumes the enone carbon–carbon double bond.
- Retains the ketone.

This is **1,4-conjugate addition**.

Methyl lithium with copper(I) iodide supplies an organocopper methyl reagent. A representative species is **lithium dimethylcuprate**, $[\text{Li}^+]\cdot\text{C}[\text{Cu}^-]\text{C}$, formed formally by:



The formal conjugate-addition balance, including protonation, is:



Organocuprates favour this conjugate addition, producing the methyl-substituted saturated ketone **19**.

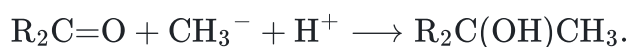
Therefore, **B is (b)**, MeLi/CuI .

8.8 — Best reagent for C

Comparing **20** with **21**, the required transformation:

- Adds methyl directly to the ketone carbonyl carbon.
- Converts that carbonyl into a tertiary alcohol.
- Retains the pre-existing carbon–carbon double bond.

This is **1,2-addition to the carbonyl**, with the formal balance:



Methyl lithium with cerium(III) chloride generates an organocerium reagent that favours carbonyl addition and reduces competing strongly basic behaviour. Protonation of the alkoxide gives **21**.

The copper-containing reagent instead favours conjugate addition. The phosphorus- and sulfur-ylide options do not give the required methyl-substituted tertiary alcohol.

Therefore, **C is (a)**, $\text{MeLi}/\text{CeCl}_3$.

The answers were checked against the official answers published by the organisers.

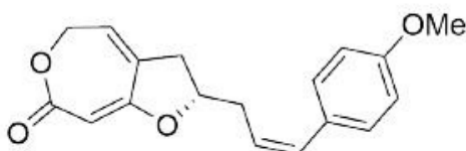
Problem 9: Total Synthesis of Capitulactone

The plant of *Curculigo capitulata* grows in the Southern China and has long been used in traditional Chinese herbal medicine for the treatment of many diseases. Capitulactone (**1**) was isolated from the roots of *Curculigo capitulata*. Its structure with absolute configuration was unambiguously established by a combination of spectroscopic data and total synthesis.



Curculigo capitulata

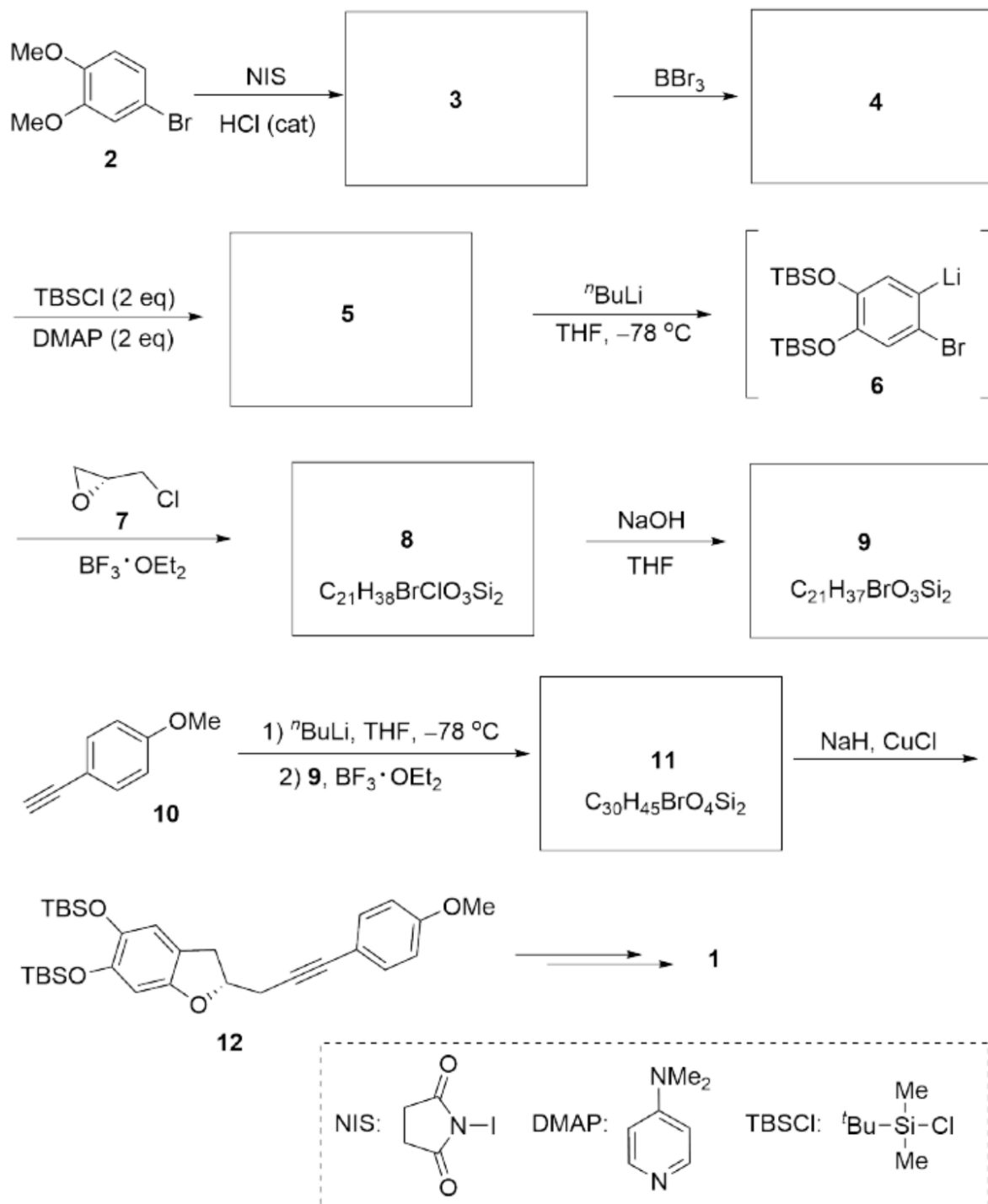
Curculigo capitulata



Capitulactone (**1**)

Capitulactone (**1**)

The total synthesis of **1** began with the iodination of commercially available 4-bromoveratrole **2** through a key intermediate **12** as shown in the following scheme.



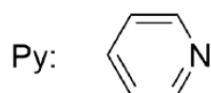
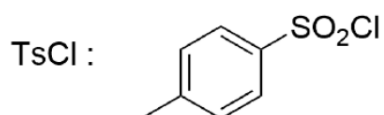
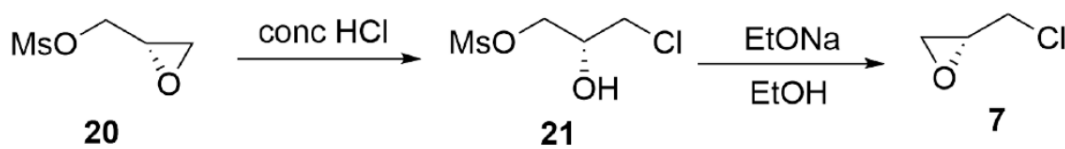
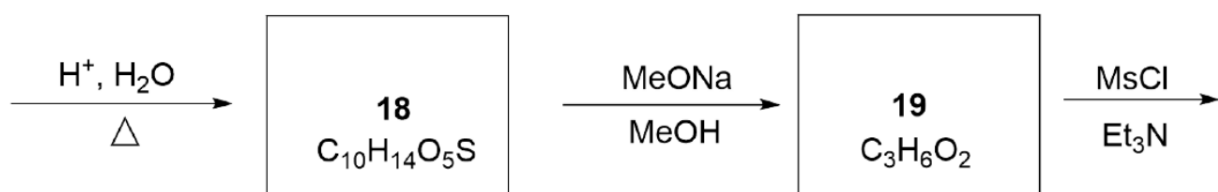
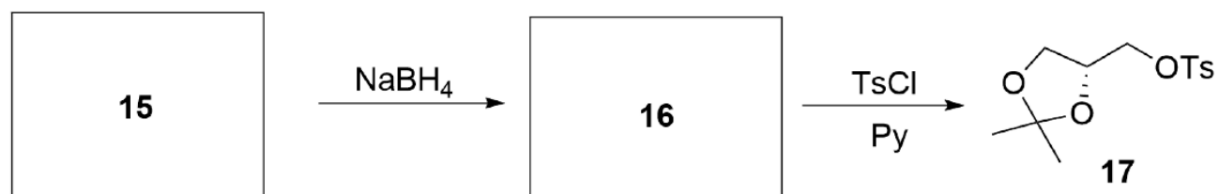
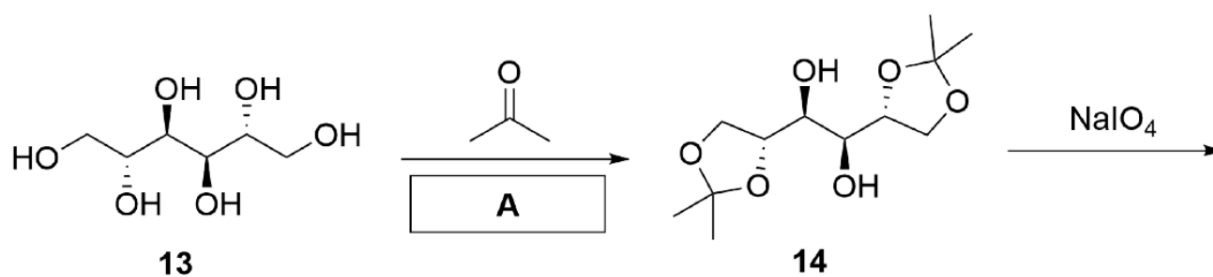
Note:

cat = catalyst

eq = equivalent

9.1 Draw the structures of compounds **3-5**, **8**, **9** and **11** and show the stereochemistry of any stereocenters.

(*R*)-Epichlorohydrin (**7**) was prepared from (+)-mannitol (**13**) through a route as shown below.



Note:

eq = equivalent

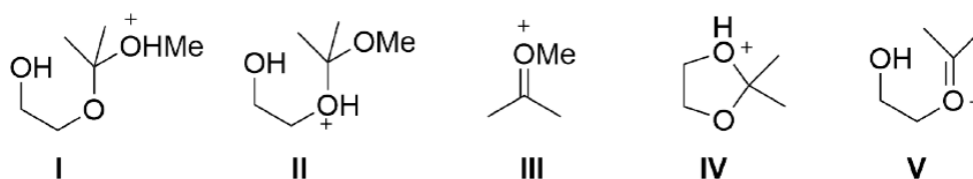
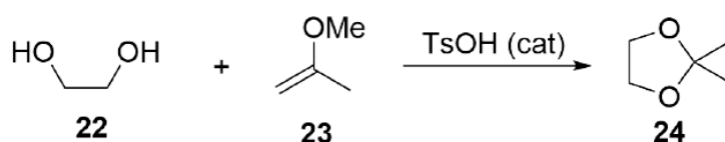
conc = concentrated

9.2 From the following conditions, choose the best for **A**.

- (a) Pyridine
- (b) 5% KOH/H₂O
- (c) 1% HCl/H₂O
- (d) Anhydrous ZnCl₂

9.3 Draw the structures of intermediate products **15**, **16**, **18** and **19** and show the stereochemistry of any stereocenters.

The diketal **14** can also be prepared by treating (+)-mannitol (**13**) with 2-methoxypropene (**23**) in the presence of catalytic amount of toluenesulfonic acid (TsOH) in anhydrous toluene. The model reaction is shown below.



9.4 The proposed mechanism for this reaction involves key intermediates (**I-V**) as shown above, choose the correct order of the formation of the key intermediates during the reaction process.

- (a) **I, II, III, IV, V**
- (b) **III, II, I, V, IV**
- (c) **III, I, II, IV, V**
- (d) **III, I, II, V, IV**

Official English text of the problem.

Answers

- **9.1.** The structures are:

Compound	Name and absolute configuration	SMILES
3	4-Bromo-5-iodo-1,2-dimethoxybenzene	<chem>COc1cc(I)c(Br)cc1OC</chem>
4	4-Bromo-5-iodobenzene-1,2-diol	<chem>Oc1cc(I)c(Br)cc1O</chem>
5	1-Bromo-2-iodo-4,5-bis[(tert-butyl)dimethylsilyl]oxy]benzene	<chem>CC(C)(C)[Si](C)(C)Oc1cc(I)c(Br)cc1O[Si](C)(C)C(C)(C)C</chem>
8	(2R)-1-Chloro-3-{2-bromo-4,5-bis[(tert-butyl)dimethylsilyl]oxy]phenyl}propan-2-ol	<chem>CC(C)(C)[Si](C)(C)Oc1cc(C[C@H](O)CCl)c(Br)cc1O[Si](C)(C)C(C)(C)C</chem>
9	(2R)-2-[(2-Bromo-4,5-bis[(tert-butyl)dimethylsilyl]oxy]phenyl)methyl]oxirane	<chem>CC(C)(C)[Si](C)(C)Oc1cc(C[C@H]2CO2)c(Br)cc1O[Si](C)(C)C(C)(C)C</chem>
11	(2S)-1-{2-Bromo-4,5-bis[(tert-butyl)dimethylsilyl]oxy]phenyl}-5-(4-methoxyphenyl)pent-4-yn-2-ol	<chem>CC(C)(C)[Si](C)(C)Oc1cc(C[C@H](O)CC#Cc2ccc(OC)cc2)c(Br)cc1O[Si](C)(C)C(C)(C)C</chem>

Compounds **3–5** have no stereocenters. Compounds **8, 9**, and **11** each have one.

- **9.2. (d) Anhydrous zinc chloride, ZnCl_2 , $[\text{Zn}^{+2}] \cdot [\text{Cl}^-] \cdot [\text{Cl}^-]$.**
- **9.3.** The structures are:

Compound	Name and absolute configuration	SMILES
15	(4R)-2,2-Dimethyl-1,3-dioxolane-4-carbaldehyde	<chem>CC1(C)OC[C@H](C=O)O1</chem>
16	[(4S)-2,2-Dimethyl-1,3-dioxolan-4-yl]methanol, also called (S)-solketal	<chem>CC1(C)OC[C@H](CO)O1</chem>
18	(2R)-2,3-Dihydroxypropyl 4-methylbenzenesulfonate	<chem>OC[C@H](O)COS(=O)(=O)c1ccc(C)cc1</chem>
19	[(2R)-Oxiran-2-yl]methanol, also called (R)-glycidol	<chem>OC[C@H]1CO1</chem>

- **9.4. (b): III → II → I → V → IV.**

Solution

9.1 — Identification of compounds 3–5, 8, 9, and 11

For the explanations below, let:

- Ar denote the **2-bromo-4,5-bis[(tert-butyldimethylsilyl)oxy]phenyl** group.
- An denote the **4-methoxyphenyl** group.

The complete molecular structures, including all protecting groups, are specified by the SMILES in the Answers section.

Formation of 3: electrophilic aromatic iodination.

The starting material, 4-bromoveratrole (**2**), is 4-bromo-1,2-dimethoxybenzene, COc1ccc(Br)cc1OC.

The methoxy groups activate the ring toward electrophilic aromatic substitution. N-Iodosuccinimide supplies electrophilic iodine. Iodination occurs at the position adjacent to bromine and para to one methoxy group. This position is also fixed unambiguously by the carbon bearing lithium in the supplied structure of **6**.

Thus **3** is **4-bromo-5-iodo-1,2-dimethoxybenzene**.

N-Iodosuccinimide, O=C1CCC(=O)N1I, becomes succinimide, O=C1CCC(=O)N1. The balanced net equation is



Formation of 4: cleavage of both methyl ethers.

Boron tribromide coordinates to the ether oxygens and promotes cleavage of the oxygen–methyl bonds. Hydrolytic work-up gives the two phenolic groups. The aryl–oxygen bonds and both aryl–halogen bonds remain intact.

Therefore **4** is **4-bromo-5-iodobenzene-1,2-diol**.

One balanced representation including hydrolytic work-up is

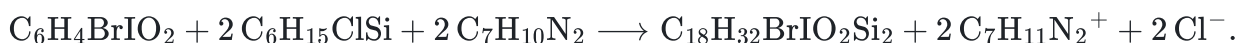


Formation of 5: protection of both phenolic groups.

The two equivalents of tert-butyldimethylsilyl chloride convert both phenolic groups into TBS ethers. DMAP assists silylation and accepts the released protons.

Consequently, **5** has the same substituted aromatic ring as **4**, with each OH replaced by $\text{O}-\text{Si}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_3$.

Using the molecular formulas of TBSCl and DMAP, the balanced net equation is



Formation of **8**: opening of (R)-epichlorohydrin.

Iodine–lithium exchange converts **5** into the drawn aryllithium **6**, while retaining the aryl bromide.

The electrophile **7** is **(R)-epichlorohydrin**, or (2R)-2-(chloromethyl)oxirane, ClC[C@H]1CO1.

The aryl nucleophile attacks the **less substituted epoxide carbon**, the terminal ring CH_2 . The carbon–oxygen bond at the stereogenic carbon is not broken. Protonation of the resulting alkoxide gives



This is **8**, with **R** configuration. Its priorities at the stereocenter are



A balanced net equation combining lithium–iodine exchange, epoxide opening, and aqueous work-up is



The product formula matches the supplied $\text{C}_{21}\text{H}_{38}\text{BrClO}_3\text{Si}_2$.

Formation of **9**: intramolecular epoxide formation.

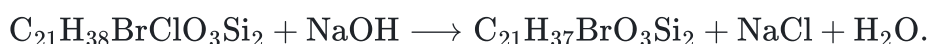
Hydroxide converts the alcohol into an alkoxide. The alkoxide attacks the neighboring primary carbon bearing chlorine by an intramolecular S_N2 reaction.

The new epoxide therefore contains the original alcohol-bearing carbon and the carbon that previously belonged to CH_2Cl . Its substituent is $\text{Ar}-\text{CH}_2-$.

The attacked carbon is not the stereocenter, so the existing spatial arrangement is retained. The configuration of **9** is **R**:



The balanced equation is

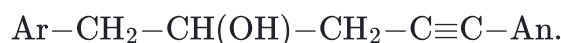


Thus the formula changes by loss of HCl , exactly as shown in the problem.

Formation of **11**: acetylide opening of epoxide **9**.

Compound **10** is **1-ethynyl-4-methoxybenzene**, COc1ccc(C#C)cc1.

Its terminal alkyne is deprotonated by *n*-butyllithium. The resulting acetylide attacks the less substituted carbon of epoxide **9**, giving, after protonation,



This identifies **11**.

Again, the carbon–oxygen bond at the existing stereocenter is retained. Nevertheless, its descriptor becomes **S**, because the priorities now are



The two carbon chains initially tie in the CIP comparison; the path through the ortho-brominated aromatic ring eventually reaches bromine and takes priority over the alkynyl chain.

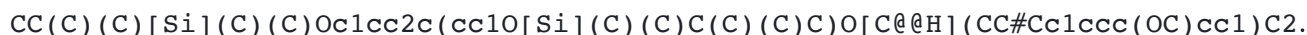
The balanced net equation, including deprotonation and aqueous work-up, is



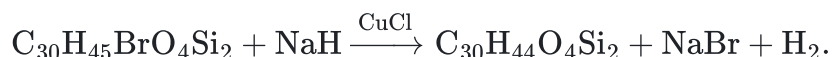
This gives the stated formula $\text{C}_{30}\text{H}_{45}\text{BrO}_4\text{Si}_2$.

As a structural check, the alcohol of **11** can undergo the supplied NaH/CuCl-mediated intramolecular aryl ether formation at the adjacent aryl bromide. This produces the five-membered ring of **12**:

(2S)-5,6-bis[(tert-butyldimethylsilyl)oxy]-2-[3-(4-methoxyphenyl)prop-2-yn-1-yl]-2,3-dihydrobenzofuran,

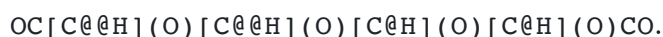


The net cyclization is



9.2 — Selection of condition A

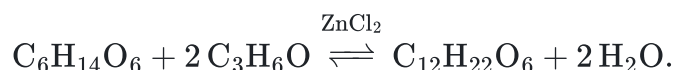
The starting material **13** is **D-(+)-mannitol**,



Reaction with acetone, $\text{CC}(=\text{O})\text{C}$, protects the terminal **1,2- and 5,6-diol pairs** as cyclic ketals. The product **14** is **1,2:5,6-di-O-isopropylidene-D-mannitol**,



The balanced equilibrium is



Anhydrous ZnCl_2 , option (d), is the best condition. It acts as a Lewis acid to activate acetone, and anhydrous conditions favor ketal formation.

Pyridine and aqueous KOH do not provide the required acid activation. Aqueous HCl supplies acid, but the large amount of water opposes ketal formation and favors ketal hydrolysis.

9.3 — Identification of 15, 16, 18, and 19

Formation of 15: periodate cleavage of the central diol.

In **14**, the two terminal diols are protected, leaving only the hydroxyl groups at the original mannitol carbons 3 and 4 available for periodate oxidation.

Periodate forms a cyclic intermediate with this vicinal diol and cleaves the bond between those two carbons. Each becomes an aldehyde carbon. The two halves are identical and give **two molecules of (R)-glyceraldehyde acetone, 15**.

The balanced equation is



To draw **15**, retain the acetonide ring and stereochemical arrangement shown in **17**, but replace its CH_2OT s substituent by CHO. The ring stereocenter is **R**.

Formation of 16: aldehyde reduction.

Sodium borohydride reduces the aldehyde group of **15** to a primary alcohol. It does not alter the existing stereocenter or the acetonide.

Thus **16** is **(S)-solketal**. To draw it, replace the CH₂OTs group of **17** by CH₂OH, keeping the depicted geometry.

A balanced formal reduction equation including aqueous work-up is



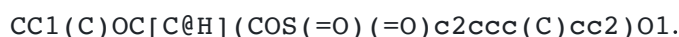
The change from **R** in **15** to **S** in **16** is a priority change, not an inversion:

Compound	CIP priority order at the existing stereocenter
15	Ring O > CHO > ring CH ₂ O > H
16	Ring O > ring CH ₂ O > CH ₂ OH > H

In **15**, the aldehyde carbon is compared as (O, O, H), which outranks the ring methylene carbon's (O, H, H). After reduction, the two methylene branches initially tie, but the ring oxygen is attached to carbon whereas the hydroxyl oxygen is attached to hydrogen.

Formation of **18**: tosylation followed by acetonide hydrolysis.

Tosylation of the only free alcohol in **16** gives the supplied **17**, [(4R)-2,2-dimethyl-1,3-dioxolan-4-yl]methyl 4-methylbenzenesulfonate,

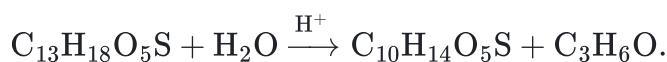


Acidic hydrolysis removes the acetonide, regenerating the primary and secondary hydroxyl groups while retaining the terminal tosylate. Hence **18** has the connectivity



and **R** configuration.

The balanced hydrolysis is



Its formula is therefore C₁₀H₁₄O₅S, as required.

Formation of **19**: intramolecular displacement of tosylate.

Methoxide deprotonates the secondary alcohol of **18**. The resulting alkoxide attacks the adjacent primary CH₂OTs carbon, expelling tosylate and forming an epoxide.

The product is **(R)-glycidol**, **19**: an epoxide bearing a hydroxymethyl substituent. The substitution occurs at a primary carbon, so the existing stereocenter retains its spatial arrangement.

The balanced net equation is



To draw **19**, use the epoxide geometry shown for **20**, replacing MsO by HO. This gives the required formula C₃H₆O₂.

The subsequent supplied transformations provide a consistency check:

- **20**, [(2S)-oxiran-2-yl]methyl methanesulfonate, CS(=O)(=O)OC[C@H]1CO1, results from mesylating the primary alcohol.
- Terminal epoxide opening gives **21**, (2R)-3-chloro-2-hydroxypropyl methanesulfonate, CS(=O)(=O)OC[C@H](O)CC1.
- Intramolecular displacement of mesylate then gives the supplied **(R)-epichlorohydrin**, **7**.

These steps preserve the stereogenic carbon's geometry; changes in descriptors arise from changes in substituent priorities.

9.4 — Ordering the ketalization intermediates

The reactants are **ethylene glycol (22)**, OCCO, and **2-methoxyprop-1-ene (23)**, C=C(C)OC.

The correct sequence is **III** → **II** → **I** → **V** → **IV**, for the following reasons.

1. **III: methoxy-stabilized isopropyl oxocarbenium ion**, C[O+]=C(C)C.

The alkene is protonated at its terminal carbon, converting that carbon into a methyl group. Donation from the methoxy oxygen stabilizes the resulting cation. The drawing represents its oxygen-positive, carbon–oxygen double-bond resonance contributor.

2. **II: the mixed ketal protonated on the incoming ethylene-glycol oxygen**, COC(C)(C)[OH+CCO].

One hydroxyl oxygen of ethylene glycol attacks the electrophilic carbon of **III**. The carbon–oxygen π electrons move onto the methoxy oxygen. The attacking oxygen now has three bonds and bears the positive charge.

3. **I: the mixed ketal protonated on the methoxy oxygen**, C[OH+](C)(C)OCCO.

Proton transfer, which may be mediated by other molecules in the reaction mixture, moves the proton from the incoming glycol oxygen to the methoxy oxygen. This converts the methoxy group into a suitable neutral leaving group upon bond cleavage.

4. **V: 2-hydroxyethoxy-stabilized isopropyl oxocarbenium ion**, CC(C)=[O+CCO].

Methanol, CO, leaves. Donation from the remaining ether oxygen produces the oxocarbenium resonance form shown as **V**.

5. **IV: O-protonated 2,2-dimethyl-1,3-dioxolane**, CC1(C)OCC[OH+]1.

The remaining hydroxyl group attacks the electrophilic carbon intramolecularly. This closes the five-membered ring, while the carbon–oxygen π electrons move onto the other oxygen.

Finally, deprotonation of **IV** regenerates the acid catalyst and gives **2,2-dimethyl-1,3-dioxolane (24)**, CC1(C)OCCO1.

The balanced overall reaction is



The SMILES for **III** and **V** encode the resonance contributors drawn in the question; the actual positive charge is delocalized over the oxygen–carbon unit.

The answers were checked against the official answers published by the organisers.