PREPARATORY PROBLEMS

Solutions

54th IChO 2022

International Chemistry Olympiad

TIANJIN, CHINA

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Problem 1. The Past and Present of Bronze Ware

1-1 (d)

1-2 $2CuFeS_2 + 2SiO_2 + 5\ O_2 \rightarrow 2Cu + 2\ FeSiO_3 + 4SO_2$

1-3 reaction 1: $4CuCl + 4H_2O + O_2 = 2Cu_2(OH)_3Cl + 2HCl$
reaction 2: $4Cu + 4HCl + O_2 = 4CuCl + 2H_2O$

1-4 reaction 3: $2CuCl + Na_2CO_3 \rightarrow Cu + CuCO_3 + 2\ NaCl$
reaction 4: $Ag_2O + 2CuCl \rightarrow 2AgCl + Cu_2O$

1-5-1 **A:** NO_2 **C:** SnO_2 **E:** $PbSO_4$ **F:** $CuSO_4{\cdot}5H_2O$

1-5-2 **B:** Cu^{2+}, NO_3^- (H^+) **D:** Cu^{2+}, SO_4^{2-} (NO_3^-, H^+)

1-6-1 reaction 5: $2Cu^{2+} + 4\ I^- \rightarrow 2CuI + I_2$
reaction 6: $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ I^-$

1-6-2 $2CuSO_4{\cdot}5H_2O \sim 2Cu^{2+} \sim I_2 \sim 2S_2O_3^{2-}$

$M_w\,(CuSO_4{\cdot}5H_2O) = 249.69\ g\ mol^{-1}$

$$\text{Purity} = \frac{0.05036 \times \left(20.80 \times 10^{-3}\right) \times 249.69}{0.2765} \times 100\% = 94.59\%$$

1-7 249.69 × 15.09% = 37.68

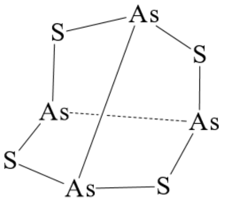
249.69×13.58%=33.91

249.69×7.08%=17.68

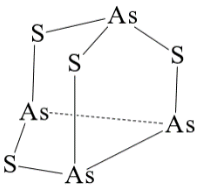
H_2O, 2:2:1

Problem 2. The Chemical Element in Mysterious Elixir

2-1



realgar



2-2 Realgar is difficult to dissolve in ammonium carbonate solution, and orpiment is easy to dissolve:

$As_4S_4 + NH_4HCO_3 \rightarrow \times$

$As_2S_3 + 6NH_4HCO_3 \rightarrow (NH_4)_3AsS_3 + (NH_4)_3AsO_3 + 6CO_2\uparrow + 3H_2O$

2-3-1 $Al_2O_3 + 6Zn + 12HCl \rightarrow 2AsH_3\uparrow + 6ZnCl_2 + 3H_2O$

$$2AsH_3 \xrightarrow{\triangle} 2As + 3H_2$$

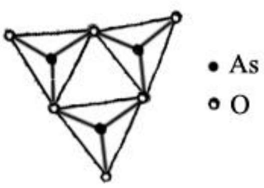
$$2As + 5NaClO + 3H_2O \rightarrow 2H_3AsO_4 + 5NaCl$$

2-3-2 $2AsH_3\uparrow + 12AgNO_3 + 3H_2O \rightarrow 12Ag\downarrow + As_2O_3 + 12HNO_3$

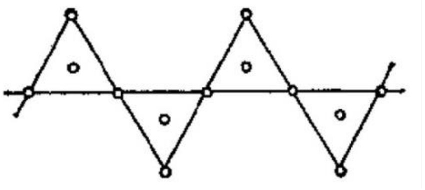
2-3-3 ${}^{75}As + {}^{1}_{0}n \rightarrow {}^{76}As + \gamma$

2-3-4 $(CH_3)_3As$, or other reasonable volatile liquids.

2-3-5



AsO_2^-



AsO_3^-

2-3-6 CuS

2-3-7 three / tri-

2-3-8 $Na_3AsSO_3\cdot7H_2O$

As_2O_3 is an amphoteric oxide and has strong reducibility in alkaline medium. It can react with sulfur to form $AsSO_3^{3-}$, $AsS_2O_2^{3-}$, AsS_3O^{3-}, AsS_4^{3-}. In 5.00 g As_2O_3, $n(As) = 2\times5/197.84 = 0.0505$ mol. Since 1.44g sulfur, $n(S) = 0.0449$ mol, react completely, the amount of As_2O_3 is excess slightly. It can be deduced that the As:S ratio in product is 1:1. So the product is $0.0449 \times (1 - 13.3\%) = 0.0389$ mol Na_3AsSO_3 (sodium mono-thioarsenate, $M_r = 223.95$). According to the weight of product, we known the crystal contains 7 water:

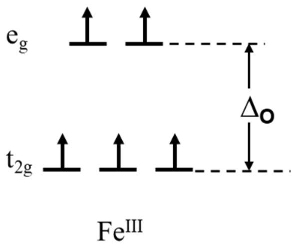
$$[13.66 - (0.0389 \times 223.95)] / 18.02 \times 0.0389 \approx 7$$

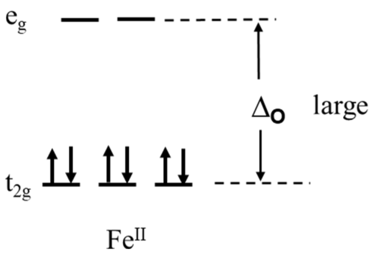
	$4H_2O$ +	$6NaOH$ +	As_2O_3 +	$2S \rightarrow$	$2Na_3AsSO_3\cdot7H_2O$
M_r				32.06	350.09
n				0.0389	0.0389

Problem 3. Cyanotype, Prussian blue and related compounds

3-1 **A** $Fe_4[Fe(CN)_6]_3$; **B** $Fe_3[Fe(CN)_6]_2$; **C** $Fe[Fe(CN)_6]$; **D** $K_2Fe[Fe(CN)_6]$

3.2





3.3 In each unit cell, there are 4 Fe^{III}; 3 Fe^{II} and 1 [Fe^{II}] vacancy; 18 CN^- groups and 6 [CN^-] vacancies.

3.4 Formation of Prussian Blue:

$$2\,Fe^{3+} + 2\,K^+ + 2\,[Fe(CN)_6]^{3-} + C_6H_5O_7^{3-} \rightarrow 2\,KFe[Fe(CN)_6] + CO_2 + C_5H_4O_5^{2-} + H^+$$

Formation of William White:

$$2\,KFe[Fe(CN)_6] + 2K^+ + C_6H_5O_7^{3-} \rightarrow 2\,K_2Fe[Fe(CN)_6] + CO_2 + C_5H_4O_5^{2-} + H^+$$

3-5-1 (**G**) $KCo[Fe(CN)_6]$

3-5-2 (b) (c) (f)

3-6-1 $Na_2FeCo(CN)_6$

3-6-2

Charge: $Na_2FeCo(CN)_6 \rightarrow 2Na + FeCo(CN)_6$

Discharge: $2Na + FeCo(CN)_6 \rightarrow Na_2FeCo(CN)_6$

Problem 4. Tianjin Painted Clay Figure Zhang

4-1-1 $MgO + NH_4H_2PO_4 + 5H_2O \rightarrow NH_4MgPO_4\cdot 6H_2O$

4-1-2 $$\rho = \frac{245.1\times 2}{6.02\times 10^{23}\times(691.4\times 613.7\times 1119.9)\times 10^{-30}} = 1.709\ \mathrm{g\ cm^{-3}}$$

4-2 $SiO_2\cdot\, xH_2O$ $\frac{7y}{15x}$

4-3 **B:** Li_3N; **D:** Li_2O; **E:** $LiOH$; **F:** NH_3

4-4 $\Delta H = -393.5 - 601.6 + 1095.8 = 100.7\ \mathrm{kJ\ mol^{-1}}$

$\Delta S = 213.8 + 27 - 65.7 = 175.1\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$\Delta G = \Delta H - T\Delta S = 100.7 - T \times 175.1\times 10^{-3} < 0$

$T > 575.1\ \mathrm{K}$

Problem 5 Chinese Cloisonné

5-1 (1) $Co^{2+} + 2OH^- \rightarrow Co(OH)_2\downarrow$

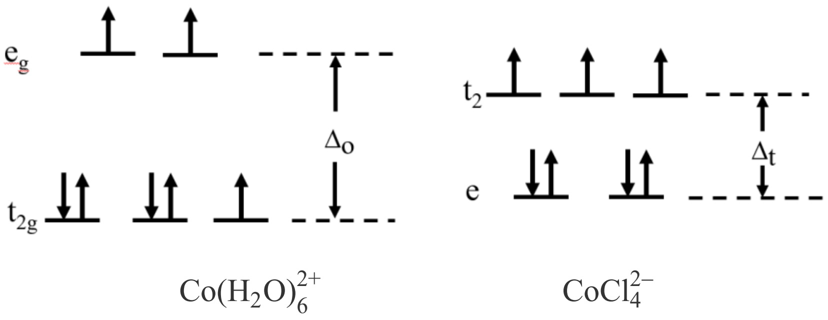
(2) $4Co(OH)_2 + O_2 + 2H_2O \rightarrow 4Co(OH)_3$

(3) $2Co(OH)_3 + 6HCl \rightarrow 2CoCl_2 + Cl_2\uparrow + 6H_2O$

5-2 **A**. $[Co(NH_3)_6]Cl_3$ **B**. $[CoCl(NH_3)_5]Cl_2$ **C**. $[CoCl_2(NH_3)_4]Cl$ **D**. $[Co(NH_3)_3Cl_3]$

5-3-1 (b)II

5-3-2



5-3-3 $\mu=[n(n+2)]^{1/2}=[3(3+2)]^{1/2}=3.87\mu_B$

5-4 (a), (d)

Problem 6. "Titanium" is awesome

6-1-1 TiO^{2+} SO_4^{2-} Fe^{2+} H^+

6-1-2 $FeSO_4\cdot7H_2O$

6-1-3 $TiOSO_4 + 2H_2O \rightarrow H_2TiO_3\downarrow + H_2SO_4$

6-2 $2FeTiO_3 + 3Cl_2 + C \rightarrow 2TiO_2 + 2FeCl_3 + CO_2$

6-3-1

$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$

$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$

6-3-2 Without adding carbon: $TiO_2 + Cl_2 \rightarrow TiCl_4 + O_2$

$\Delta_r H_m^{\ominus} = -804.2 - (-944.0) = 139.8\ kJ\ mol^{-1}$

$\Delta_r S_m^{\ominus} = 205.2 + 252.3 - 50.6 - 223.1\times2 = -39.3\ J\ K^{-1}\ mol^{-1}$

$\Delta_r G_m^{\ominus}$ It is always positive. The reaction cannot proceed. The direct chlorination reaction of TiO_2 is thermodynamically impossible.

With carbon: $TiO_2(s) + 2Cl_2(g) + 2C \rightarrow TiCl_4(l) + 2CO(g)$

$\Delta_r H_m^{\ominus} = -81.2\ kJ\ mol^{-1}$, $\Delta_r S_m^{\ominus} = 139.5\ J\ K^{-1}\ mol^{-1}$

$\Delta_r G_m^{\ominus}$ is negative. Any temperature can be spontaneous. Adding carbon powder and using coupling reaction make the reaction possible.

6-4-1 $3TiO^{2+} + Al + 6H^{+} \rightarrow 3Ti^{3+} + Al^{3+} + 3H_2O$；

6-4-2 $w(TiO_2) = \dfrac{28.30 \times 0.08770 \times 79.88}{0.2022 \times 1000} = 98.05\%$

6-5-1 $BaCl_2 + TiCl_4 + 2H_2C_2O_4 + 5H_2O \rightarrow BaTiO(C_2O_4)_2{\cdot}4H_2O \downarrow + 6HCl$

$BaTiO(C_2O_4)_2{\cdot}4H_2O \xrightarrow{\triangle} BaTiO_3 + 2CO_2 \uparrow + 2CO \uparrow + 4H_2O$

6-5-2 (b), (c)

Problem 7. Kaolinite and Sodalite

7-1 $K_2Al_2Si_6O_{16} + 2\ H_2O + CO_2 \rightarrow Al_2Si_2O_5(OH)_4 \cdot + 4\ SiO_2 + K_2CO_3$

7-2 $Mg_3Si_2O_5(OH)_4$

7-3-1 $Si_3Al_4O_{12}$

Tips for solving the problem: According to the information, the detective chemical formula can be written as $[Si_{0.75}□_{0.25}]_T[Al_{1.33}□_{0.67}]_OO_4$ here □ represents empty, T for tetrahedral, and O for Octahedral positions, then the corresponding stoichiometric presentation is $Si_3Al_4O_{12}$.

7-3-2

stage 1: $Al_2Si_2O_5(OH)_4 \rightarrow \cdot Al_2Si_2O_7 + 2\ H_2O$
stage 2: $2\ Al_2Si_2O_7 \rightarrow Si_3Al_4O_{12} + SiO_2$
stage 3: $3\ Si_3Al_4O_{12} \rightarrow 2\ Si_2Al_6O_{13} + 5SiO_2$

7-4-1 $[Si_{24}O_{60}]^{24-}$

Tips for solving the problem: There are 14 faces, 24 corners and 36 edges (14 + 24 −2 = 36) in the β-cage, so there are 24 silicon atoms (at the corners). Since the SiO_4 tetrahedra are linked by vertex-sharing, the number of the oxygen atoms is 36 + 24 = 60.

7-4-2 $Na_6Al_6Si_6O_{24}$

Tips for solving the problem: let see the content of the unit cell: it can be seen that there is a cage inside the cell and six squares are just on the six plane faces, and each is shared by two cells. Therefore, there are 24/2=12 T (Si, Al) atoms each cell. Since the chemical formula is $NaAlSiO_4$, there should be 6 Al and 6 Si in the framework with the composition $Al_6Si_6O_{24}^{6-}$, and 6 Na^+ are needed to compensate the negative charge. Then the composition of the unit cell should be $Na_6Al_6Si_6O_{24}$.

Problem 8. Mars Chemistry

8-1 $6Fe_2SiO_4 + 2H_2O + CO_2 \rightarrow 4Fe_3O_4 + 6SiO_2 + CH_4$

8-2 2.51×10^{13} g

$$V_{\mathrm{CH_4}} = \frac{4}{3}\pi\left[\left(6.996\times10^{6}\right)^{3} - \left(6.796\times10^{6}\right)^{3}\right]\times 0.4\times10^{-9} = 4.78\times10^{10}\ \mathrm{m^3}$$

$$n_{\mathrm{CH_4}} = \frac{pV_{\mathrm{CH_4}}}{RT} = \frac{750\times4.78\times10^{10}}{8.314\times210} = 2.05\times10^{10}\ \mathrm{mol}$$

$6Fe_2SiO_4 + 2H_2O + CO_2 \rightarrow 4Fe_3O_4 + 6SiO_2 + CH_4$

$$n_{\mathrm{Fe_2SiO_4}} = 6n_{\mathrm{CH_4}} = 1.23\times10^{11}\ \mathrm{mol}$$

$$m_{\mathrm{Fe_2SiO_4}} = m_{\mathrm{Fe_2SiO_4}} Mr_{\mathrm{Fe_2SiO_4}} = 1.23\times10^{11}\times\left(55.85\times2+28.09+16.00\times4\right) = 2.51\times10^{13}\ \mathrm{g}$$

8-3-1 $KMnO_4$; Fe^{2+}; magnetite; hematite.

8-3-2 2CO (g) + $2H_2$ (g); +247 kJ mol^{-1}

8-3-3 $H_2+CO_3^{2-}-2e^{-}\rightarrow H_2O+CO_2$

$CO+CO_3^{2-}-2e^{-}\rightarrow 2CO_2$

Problem 9. Greenhouse gas and carbon neutrality

9-1-1 $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2\uparrow + H_2O$

9-1-2 (b)

9-1-3 (a) (b)

9-2-1 $4Na^{+} + 3CO_2 + 4e^{-} \rightarrow 2Na_2CO_3 + C$

9-2-2 (c)

9-2-3 2.35

9-3-1 cathode reaction: $2CO_2 + 12e^{-} + 12H^{+} \rightarrow C_2H_4 + 4H_2O$

anode reaction: $4OH^{-} \rightarrow O_2 + 2H_2O + 4e^{-}$

9-3-2 Total moles of ethylene = (90.0 mL ÷ 1000) × 5.19% ÷ 22.4 mol/L = 0.0000209 mol

The charge required to generate ethylene = 0.0000209 mol × 12 × 96485 C/mol = 24.2 C

Total charge = 3600 s × 0.0100 A =36.0 C

Faraday efficiency = 24.2 ÷ 36.0 × 100% = 67.2%

Total mass of generated ethylene = 0.0000209 mol × 28.06 g/mol × 1000 = 0.586 mg

Ethylene production rate = 0. 586 mg ÷ 1 h = 0.586 mg h^{-1}.

9-4-1 Known W = 5.230 kJ,

Since $\Delta T = 0$, we have

$\Delta U = 0$, $Q_r = W = 5.230$ kJ

$\Delta S = Q_r/T = 19.14\ \mathrm{J\cdot K^{-1}}$

$\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta nRT = 0$

$\Delta G = \Delta H - \mathrm{T}\Delta S = -5.230$ kJ

9-4-2 (b)

9-4-3

(1) From Langmuir isotherm equation

$$\theta = \frac{V}{V_\mathrm{m}} = \frac{\alpha P}{1+\alpha P}$$

With values of $V_1 = 0.0692\ \mathrm{m^3\ kg^{-1}}$, $P_1 = 5.2$ kPa, and $V_2 = 0.0826\ \mathrm{m^3\ kg^{-1}}$, $P_2 = 13.5$ kPa we can solve $\alpha = 54.34$, $V_\mathrm{m} = 0.0940\ \mathrm{m^3\ kg^{-1}}$

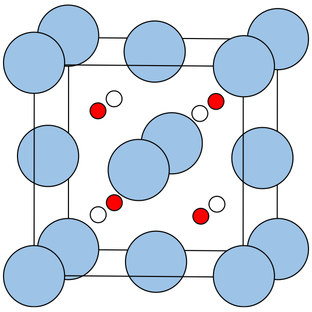
(2) Specific surface area

$$S = (0.0940\ \mathrm{dm^3\ g^{-1}}) \div (22.4\ \mathrm{dm^3\ mol^{-1}}) \times (6.02 \times 10^{23}\ \mathrm{mol^{-1}}) \times (0.32 \times 10^{-18}\ \mathrm{m^2})$$

$$= 808\ \mathrm{m^2\ g^{-1}}$$

Problem 10. Packing of binary crystals

10-1



$$d(\mathrm{Ag-I}) = \frac{\sqrt{3}}{4}a = 280.3\ \mathrm{pm}$$

$$\rho = \frac{4M}{N_\mathrm{A}a^3} = \frac{4*(107.9+126.9)}{6.022\times10^{23}*(6.473\times10^{-8})^3} = 5.75\ \mathrm{g\ cm^{-3}}$$

10-2

NaCl type:

$$a = \frac{\lambda\sqrt{h^2+k^2+l^2}}{2\sin\theta} = \frac{154.2*\sqrt{4}}{2*\sin(14.7°)} = 607.7\ \mathrm{pm}\ ; \quad d(\mathrm{Ag-I}) = \frac{a}{2} = 303.9\ \mathrm{pm}$$

CsCl type:

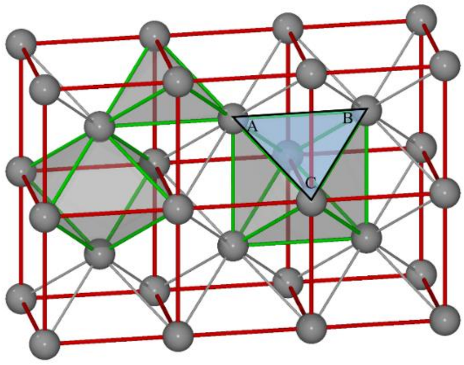
$$a = \frac{154.2*\sqrt{4}}{2*\sin(21.0°)} = 430.3\ \mathrm{pm}\ ; \quad d(\mathrm{Ag-I}) = \frac{\sqrt{3}a}{2} = 372.7\ \mathrm{pm}$$

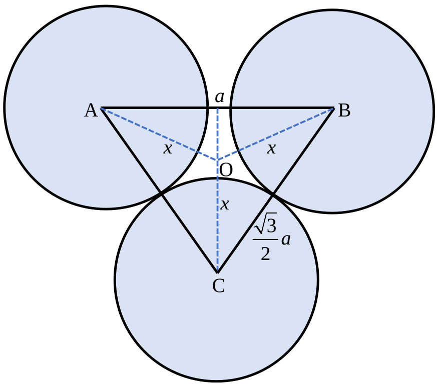
10-3

Assuming $\mathrm{I^-}$ anions are in contact with each other

$$r(\mathrm{I^-}) = \frac{\sqrt{3}}{4}a = 218\ \mathrm{pm}\quad (bcc)$$

$\mathrm{I^-}$ anions form trigonal holes, and AB = a; BC = AC = $\frac{\sqrt{3}}{2}a$, Assume AO = BO =CO = x,





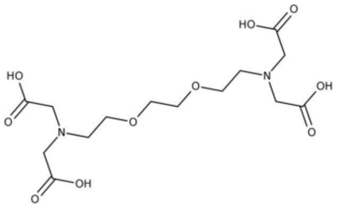
$$\left(\frac{\sqrt{2}}{2}a - x\right)^2 + \left(\frac{a}{2}\right)^2 = x^2$$

$$x = \frac{3\sqrt{2}}{8}a = 267\ \text{pm}$$

$r_{\max}(\mathrm{Ag}^+) = 267 - 218 = 49$ pm

Problem 11. Determination of Calcium Ions by Titration with Ethylene Bis(oxyethylenenitrilo) Tetraacetic Acid (EGTA)

11-1. EGTA is a hexabasic acid, insoluble in water. If using distilled water to dissolve the EGTA, 0.020 mol L^{-1} solution can not be obtained. EGTA can be dissolved in the dilute basic solution as a weak acid.



11-2. At pH=10,

$\alpha_{E(H)} = 1 + [H^+] / K_{a6} + [H^+]^2 / K_{a6}\cdot K_{a5} + [H^+]^3 / K_{a6}\cdot K_{a5}\cdot K_{a4} + [H^+]^4 / K_{a6}\cdot K_{a5}\cdot K_{a4}\cdot K_{a3}$

$= 1 + 10^{-10} / 10^{-9.53} + 10^{-10\times 2} / 10^{-(9.53+8.93)} + 10^{-10\times 3} / 10^{-(9.53+8.93+2.73)} + 10^{-10\times 4} / 10^{-(9.53+8.93+2.73+2.08)}$

$= 10^{0.14}$

11-3. In the presence of Mg^{2+} ions,

$\alpha_{E(Mg)} = 1 + K_{MgE}\cdot c_{Mg}^{sp} = 1 + 10^{5.21} \times 0.010 / 2 = 10^{2.91}$

$\alpha_E = 10^{0.14} + 10^{2.91} - 1 = 10^{2.91}$

$\lg K'_{CaE} = 10.97 - 2.91 = 8.06$

$pCa^{sp} = (8.06 - \lg 0.010 / 2) / 2 = 5.18, \quad pCa_t = 3.8$

$\Delta pCa' = 3.8 - 5.18 = -1.38$

$$E_t = \frac{10^{-1.38} - 10^{1.38}}{\sqrt{10^{8.06} \times 0.010/2}} \times 100\% = -3.2\%$$

11-4. At pH12,

$[OH^-] = 10^{-2}$, $[Mg^{2+}]^{sp} = K_{sp} / [OH^-]^2 = 10^{-10.74} / 10^{-2\times2} = 10^{-6.74}$

$\alpha_{E(Mg)} = 1 + K_{MgE}\cdot[Mg^{2+}]^{sp} = 1 + 10^{5.21} \times 10^{-6.74} = 1$

$\lg K'_{CaE} = 10.97$, $pCa^{sp} = (10.97 - \lg 0.010 / 2) / 2 = 6.64$, $pCa_t = 5.6$

$\Delta pCa' = 5.6 - 6.64 = -1.04$

$$E_t = \frac{10^{-1.04} - 10^{1.04}}{\sqrt{10^{10.97} \times 0.010/2}} \times 100\% = -0.05\%。$$

11-5.

$c(Ca^{2+}) = (2.4907 \times 1 / 10) / 100.09 = 2.488 \times 10^{-3}$ (mol L^{-1})

$c(H_4E) = 2.488\times10^{-3} \times 25.00 / 25.85 = 2.406 \times 10^{-3}$ (mol L^{-1})

content of calcium = $2.406 \times 10^{-3} \times (0.83 - 0.20 / 10) \times 1000 / 0.80 = 2.4$ (mmol L^{-1})

Problem 12. Fast Determination of Vitamin C by Gold Colloids

12-1. (b)

12-2.

The volume of AuNP (V_{AuNP}) is calculated by Eq.(12-1), where D is the diameter of gold colloid:

$$V_{AuNP} = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 \tag{12-1}$$

The volume of one gold atom (V_{Au}) is calculated by Eq.(12-2), where m is the mass of each gold atom, and NA is the Avogadro's constant:

$$V_{Au} = \frac{m}{\rho} = \frac{M/N_A}{\rho} = \frac{M}{\rho N_A} \tag{12-2}$$

Accordingly, the number of gold atoms (N) is calculated by Eq. (12-3):

$$N = \frac{V_{AuNP}}{V_{Au}} = \frac{\pi\rho N_A D^3}{6M} \tag{12-3}$$

$$N = \frac{\pi\rho N_A D^3}{6M} = \frac{3.14\times19.3\times6.02\times10^{23}\times\left(10\times10^{-7}\right)^3}{6\times197} = 30865$$

The molar concentration of the gold colloidal solution is calculated by dividing the total number of gold atoms (N_{total}, equivalent to the initial amount of gold salt added to the reaction solution) over the average number of gold atoms per nanosphere (N) according to Eq.(12-3), where V is the volume of the reaction solution in liter:

$$C=\frac{N_{\text{Total}}}{NVN_{\text{A}}} \tag{12-4}$$

The extinction coefficient of the colloid gold is determined according to Lambert-Beer law, Eq.(12-5):

$$A=\varepsilon lC \tag{12-5}$$

$$C=\frac{N_{\text{Total}}}{NVN_{\text{A}}}=\frac{\dfrac{41\times10^{-3}}{394}\times6.02\times10^{23}}{30865\times100\times10^{-3}\times6.02\times10^{23}}=3.37\times10^{-8}\ \text{mol L}^{-1}$$

$$\varepsilon=\frac{A}{lC}=\frac{0.8}{1\times3.37\times10^{-8}}=2.37\times10^{7}\ \text{L mol}^{-1}\ \text{cm}^{-1}$$

12-3. According to Lambert-Beer law:

$$A=\varepsilon lC$$

Since the amount of chloroauric acid is excess, the concentration of gold colloid is proportional to that of vitamin C.

$$A_1=\varepsilon lC_x \qquad A_2=\varepsilon l\left(C_0+C_x\right)$$

$$\frac{A_1}{A_2}=\frac{C_x}{C_0+C_x}$$

$$0.3=\frac{C_x}{5+C_x}$$

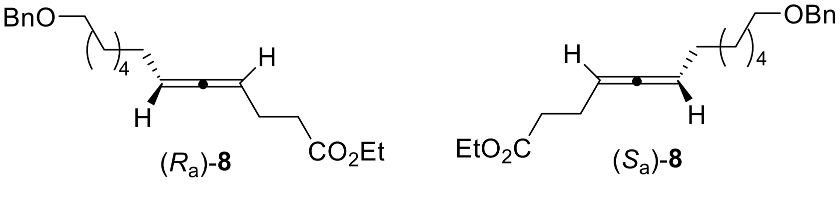
$C_x = 2.14$ μg mL^{-1}

Problem 13. Allenes

13-1-1 *S*a

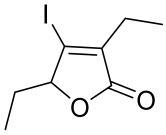
13-1-2 (a) MeMgBr is a nucleophile; (b) MeMgBr is a base.

13-2



(R_a)-**8** (S_a)-**8**

13-3-1



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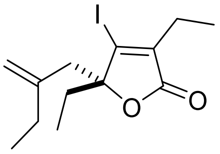
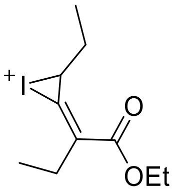
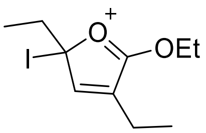


(±)-**12**

13-3-2





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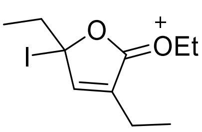
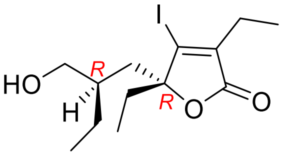
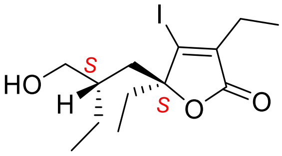


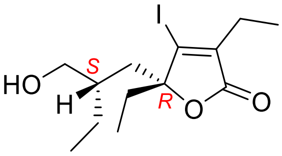
13-3-3



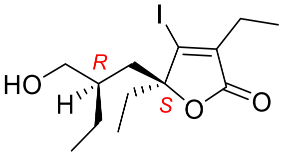
13a



13b

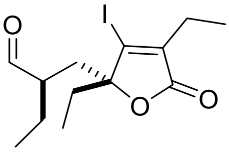


13c

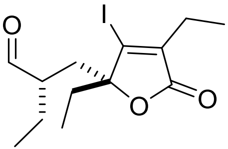


13d

13-3-4

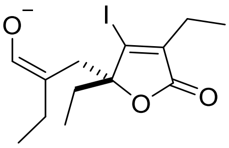


(±)-**14a**



(±)-**14b**

13-3-5



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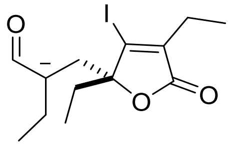
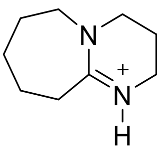


13-3-6



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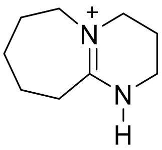
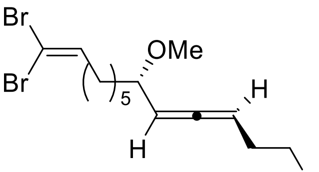
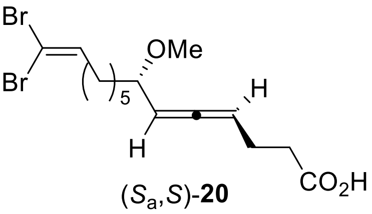


13-4-1



(S_a,S)-**19**



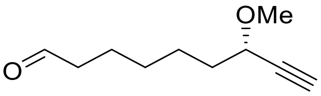
(S_a,S)-**20**

13-4-2 (a) i) ethynylmagnesium bromide, THF; ii) NH_4Cl(aq.)

13-4-3 (c) i) NaH, THF; ii) MeI; iii) 3 M HCl

13-4-4 (d) Nucleophilic addition

13-4-5



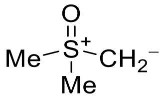
(S)-**25**

Problem 14. Cyclopropanes

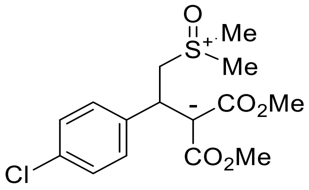
14-1 (a).

14-2-1

A



B



14-2-2

7.23 (2H, d, $J = 8.0$ Hz): a

7.19 (2H, d, $J = 8.0$ Hz): b

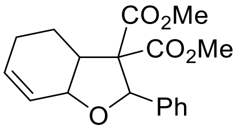
3.77 (3H, s), 3.39 (3H, s): f, g

3.14 (1H, dd, $J = 9.0$ and 8.1 Hz): c

2.12 (1H, dd, $J = 8.1$, 5.1 Hz), 1.74 (1H, dd, $J = 9.0$, 5.1 Hz): d, e

14-3.

2



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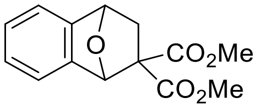

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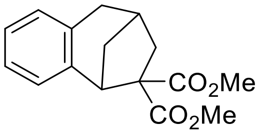

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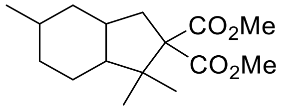
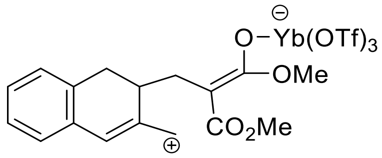
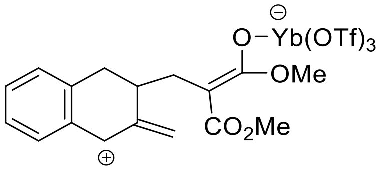


14-4

C

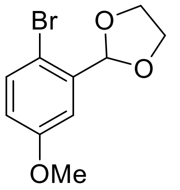


C'



14-5

8



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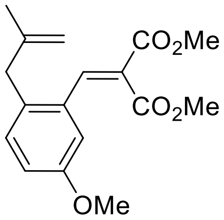

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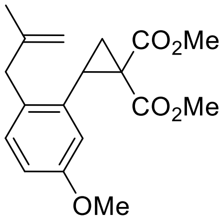

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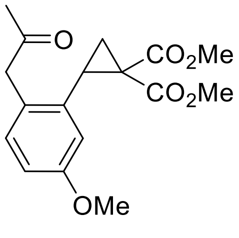

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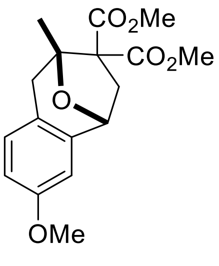
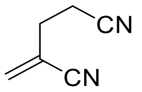


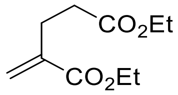
Problem 15. Lewis base catalysis

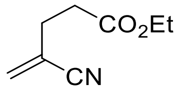
15-1 (b), (c), (d)

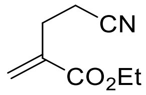
15-2 (c)

15-3

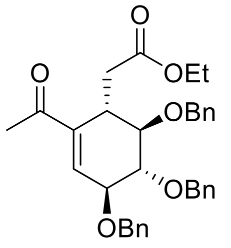








15-4



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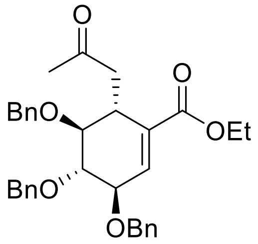
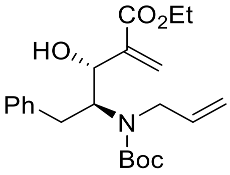
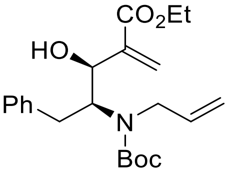


F

15-5



H



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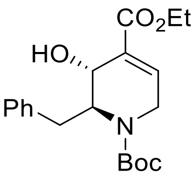

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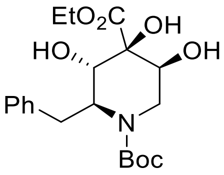
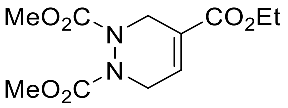


M

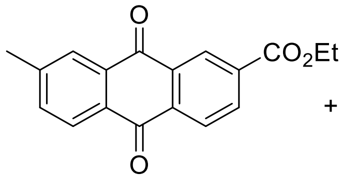
15-6 (b), (e)

15-7



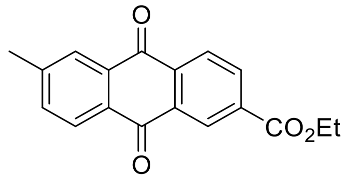
S

15-8



W

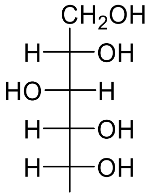
+



isomer

Problem 16. Isosorbitol

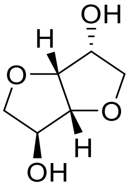
16-1



2

16-2 (b) Pd-C, H_2

16-3



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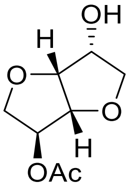

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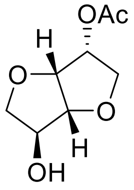
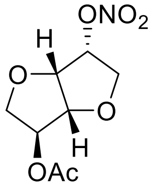


5

16-4 Steric effect

16-5 (b) $-2H_2O$

16-6



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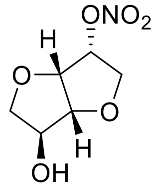
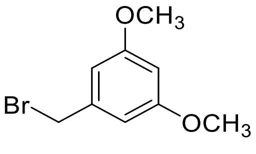


7

Problem 17. Total Synthesis of Hopeanol

17-1



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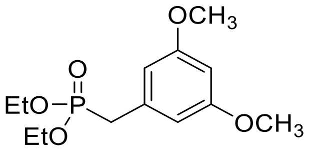
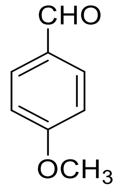


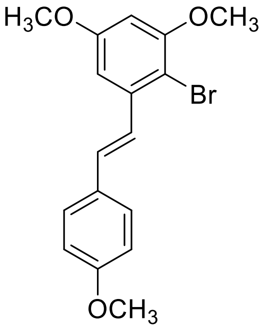
3

17-2

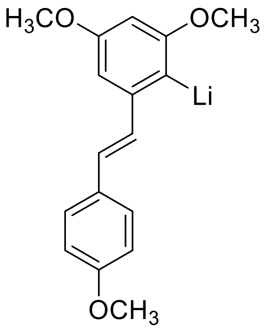


4

17-3

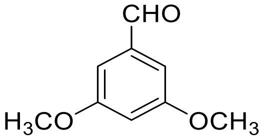


6



[7]

17-4



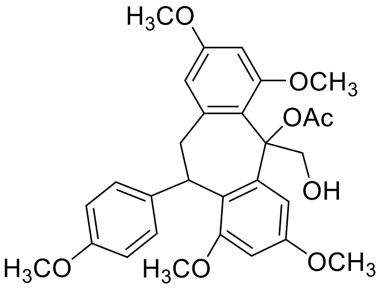
8

17-5 (b) Dess-Martin periodinane (1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one)

17-6 (a) **11a**

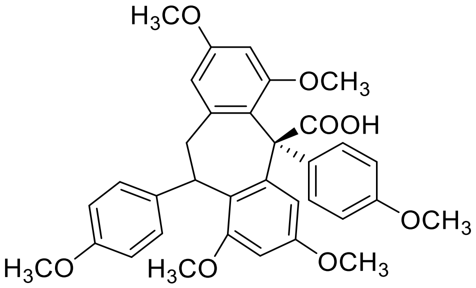
17-7 (c) $Me_2S=CH_2$

17-8



15

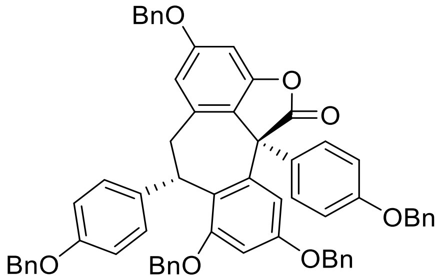
17-9



18

17-10 (a) BBr_3, CH_2Cl_2

17-11

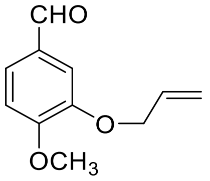


21

17-12 (a) oxidant

Problem 18. Total Synthesis of Lithospermic acid

18-1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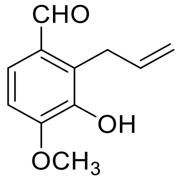
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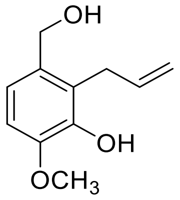
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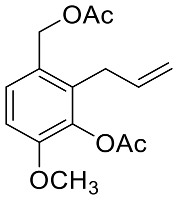
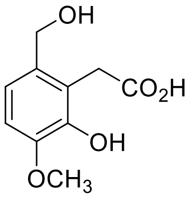

5

HCHO

7

18-2 (c) H_2CrO_4

18-3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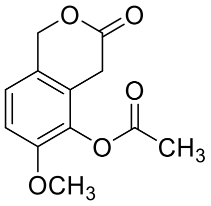
18-4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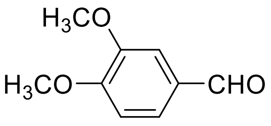
18-5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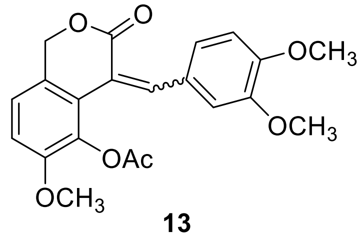
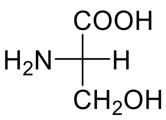

13

18-6 (b) $(COCl)_2$, Me_2SO

18-7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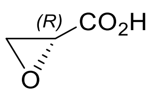
18-8



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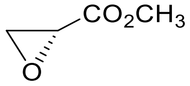
18-9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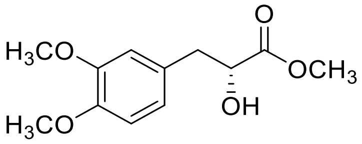

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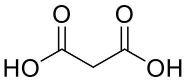
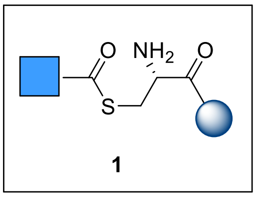


22

18-11

Problem 19. Reaction of peptides

19-1



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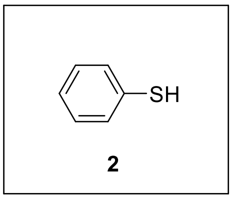

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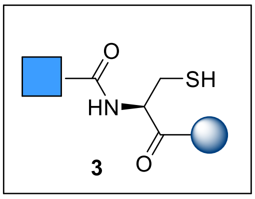

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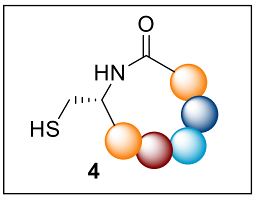

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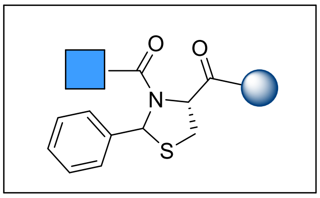

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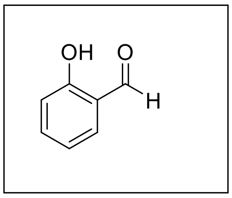

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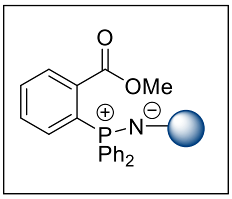

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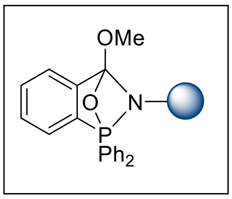

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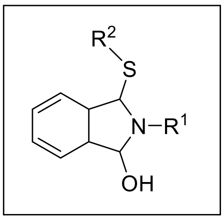

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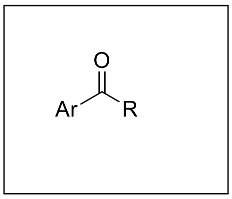
19-6



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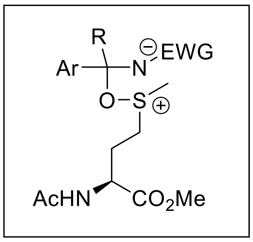

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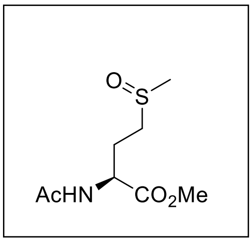


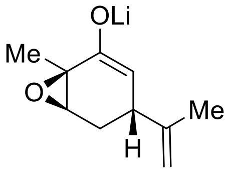
12

Problem 20. Total Synthesis of Hapalindole-Type Natural Products

20-1 (e)

20-2 (b)

20-3



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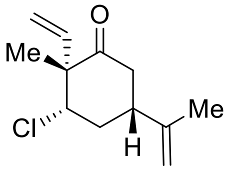

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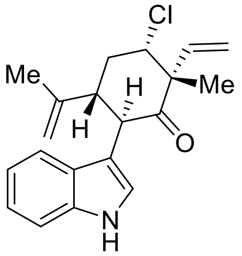

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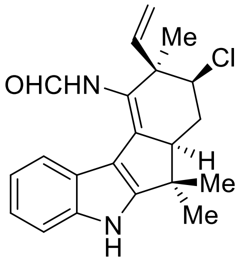

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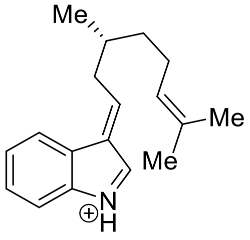
20-4



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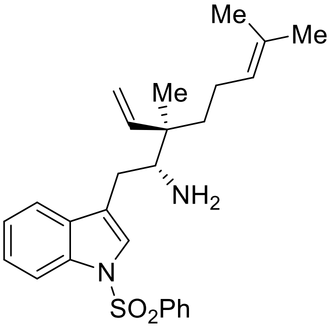

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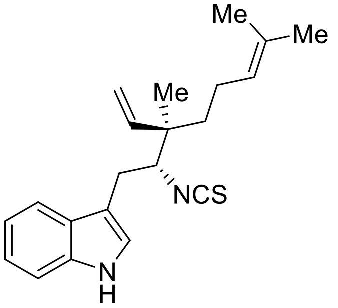

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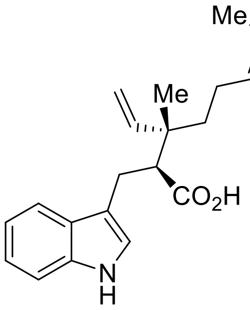
20-6



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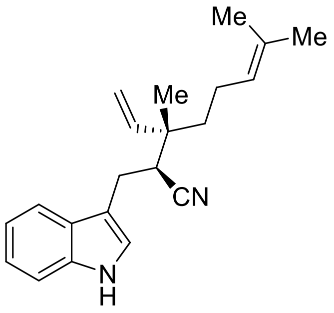
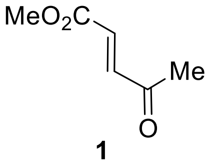


9

Problem 21. Total Synthesis of Schindilactone A

21-1-1



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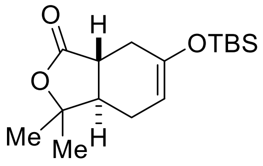

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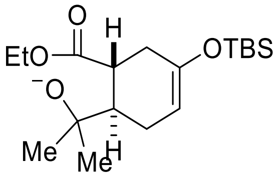
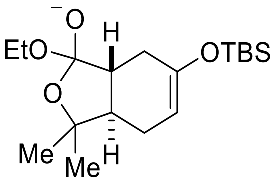
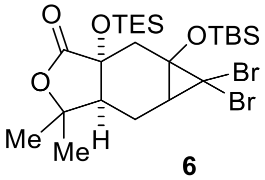
21-1-2



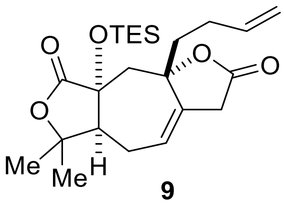


21-1-3



6

21-2 The excellent diastereoselectivity observed in the Grignard reaction presumably could be attributed to the steric bulk of the OTES group in substrate **8**, which might direct the attack of the Grignard reagent on the ketone from the less hindered face.



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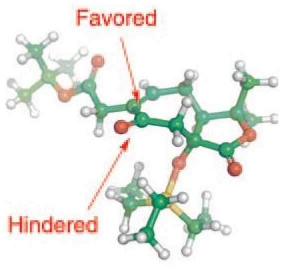
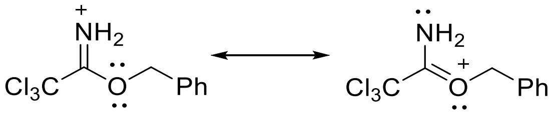
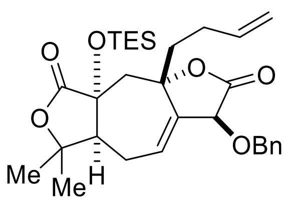


21-3-1



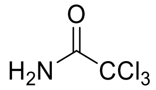
21-3-2



11

21-3-3 (b) S_N1 reaction

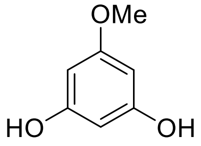
21-3-4



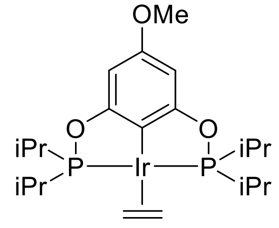
$H_2NC(O)CCl_3$

Problem 22. Recyclable Plastic—Turning Waste into Treasure

22-1



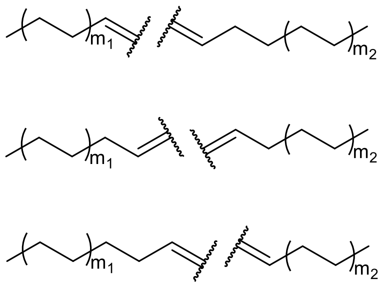
1



2

22-2 69

Since it is 'at most', considering that $m_1 > m_2 >> n_1 > n_2$ and the values are quite different, if there are 3 different kinds of dehydrogenation product **A**, the alkene metathesis may produce at most 6 different kinds of fragments:



Similarly **B** may produce at most 8 different kinds of fragments, and the cross alkene metathesis product contains at most 6×8 = 48 possibilities. However, dehydrogenation product **A** can also form self-recombinant products, at most $C_6^2 + 6 = 21$ possibilities. Therefore the polymer alkene mixture **C** contains at most 48 + 21 = 69 possibilities.

*Notice that mixture **C** is alkene, which allows C=C double bond position isomerism.

22-3 24

When the light alkane added is n-hexane, it can only break into 5 different types of fragments (C_1 ~ C_5 residues), and since hydrogenation erases all the C=C double bond isomers, there are 11 different kinds of cross product (the length of alkane product varies from C_{78} ~ C_{88}), then about self-recombinant of **A**, another 13 possibilities should be considered (the length of alkane product varies from C156 ~ C168). Therefore there are 11 + 13 = 24 kinds of **D** in the ultimate alkane mixture

*Notice that **D** is different from **C**, **D** is the alkane product after hydrogenation, it is not necessary to consider the location of C=C double bonds.

22-4 (a)

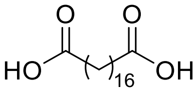
Only PP contains no heteroatom in the polymer main chain, while Phenolic Resin has oxygen, polyamide has nitrogen, and polyurethane has both oxygen and nitrogen in the main chain.

22-5 (d)

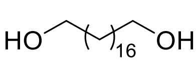
PMMA thermolysis generates stable tertiary carbon free radicals, the decomposed chain mostly undergoes internal disproportionation and MMA monomers are mainly obtained; but PE thermolysis forms carbon radicals with hydrogen on it, which is not that stable and lead to chain transfer easily, therefore preventing further depolymerization.

22-6 (c)

22-7



M1



M2

22-8 The left graph (red) belongs to **P1**, the right graph (blue) belongs to **P2**.

The main difference is the absorption peaks of C-O stretching vibration at 1250cm^{-1}, and apparently the density of C-O structure is higher in **P2**.

22-9 From above to below: **R2**, **R3**, **R1**.

Problem 23. The combustion of water gas

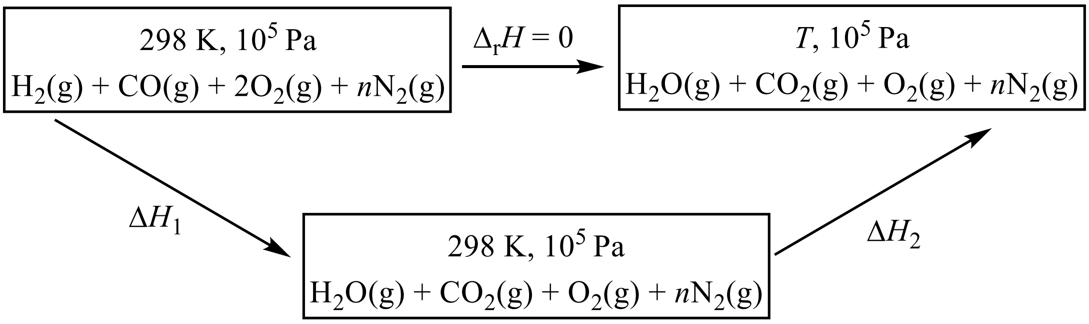
23-1

$$\mathrm{H_2(g)+\frac{1}{2}O_2(g) \rightarrow H_2O(g)}$$

$$\mathrm{CO(g)+\frac{1}{2}O_2(g) \rightarrow CO_2(g)}$$

$$\mathrm{H_2(g)+CO(g)+O_2(g) \rightarrow H_2O(g)+CO_2(g)}$$

Design the following processes:



Assume the initial amounts of substances of $H_2(g)$, $CO(g)$, $O_2(g)$ and $N_2(g)$ 1 mol， 1mol, 2 mol, and *n* mol, respectively.

$n = 79/21 \times 2 = 7.524$ mol

Under constant pressure and adiabatic conditions:

$$\Delta_r H = Q_p = 0 = \Delta H_1 + \Delta H_2$$

$$\Delta H_1 = \Delta_r H_m^\ominus(298\text{K}) = \sum v \Delta_f H_m^\ominus$$
$$= \Delta_f H_m^\ominus(H_2O(g)) + \Delta_f H_m^\ominus(CO_2(g)) - \Delta_f H_m^\ominus(H_2(g)) - \Delta_f H_m^\ominus(CO(g)) - \Delta_f H_m^\ominus(O_2(g))$$
$$= -241.83 - 393.51 - 0 + 110.52 - 0 = -524.82 \text{ kJ mol}^{-1} = -\Delta H_2$$

$$\Delta H_2 = (T - 298)\sum C_p = (T\text{-}298) \times (33.58 + 37.13 + 29.36 + 29.12 \times 7.524)/1000 = 524.82$$
$$T = 1942 \text{ K}$$

23-2 Only consider the combustion of CO:

$$\Delta_r H_m^\ominus(298\text{K}) = -393.51 - (-110.52) - 0 = -282.99 \text{ kJ mol}^{-1}$$
$$\Delta_r G_m^\ominus(298\text{K}) = -394.38 - (-137.27) - 0 = -257.11 \text{ kJ mol}^{-1}$$

$$\Delta_r G_m^\ominus(298) = \Delta_r H_m^\ominus(298) - T\Delta_r S_m^\ominus(298)$$
$$\Delta_r S_m^\ominus(298) = (-282.99 + 257.11)/298 * 1000 = -86.8 \text{ J mol}^{-1} \text{ K}^{-1}$$
$$\Delta C_p = \sum vC_p = 37.13 - 0.5 \times 29.36 - 29.14 = -6.69 \text{ J mol}^{-1} \text{ K}^{-1}$$
$$\Delta_r S_m^\ominus(310) = \Delta_r S_m^\ominus(298) + \Delta C_p \ln(310/298) = -0.0871 \text{ kJ mol}^{-1} \text{ K}^{-1}$$
$$\Delta_r H_m^\ominus(310) = \Delta_r H_m^\ominus(298) + \Delta C_p(310\text{-}298) = -283.07 \text{ kJ mol}^{-1}$$
$$\Delta_r G_m^\ominus(310) = \Delta_r H_m^\ominus(310) - 310\Delta_r S_m^\ominus(310) = -256.08 \text{ kJ mol}^{-1}$$

Problem 24. The thermodynamics of decomposition reactions

24-1 Design the following processes for the decomposition of $Ag_2CO_3(s)$:

$$\begin{tikzcd}
Ag_2CO_3(s,383K) \arrow[r, "\Delta_r G_m^\ominus(383K)"] \arrow[d] & Ag_2O(s,383K) & + & CO_2(g,383K) \\
Ag_2CO_3(s,298K) \arrow[r, "\Delta_r G_m^\ominus(298K)"] & Ag_2O(s,298K) \arrow[u] & + & CO_2(g,298K) \arrow[u]
\end{tikzcd}$$

Then:

$$\Delta_r H_m^\ominus(298\text{K}) = -30.58\text{-}393.51 + 501.66 = 77.57 \text{ kJ mol}^{-1}$$
$$\Delta_r S_m^\ominus(298\text{K}) = 121.8 + 213.8 - 167.4 = 168.2 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta_r G_m^\ominus(298\text{K}) = \Delta_r H_m^\ominus(298\text{K}) - 298 * \Delta_r S_m^\ominus(298\text{K}) = 27.45 \text{ kJ mol}^{-1}$$
$$K_p^\ominus(298\text{K}) = \exp(-\Delta_r G_m^\ominus(298\text{K})/RT) = 1.54 \times 10^{-5}$$

24-2 Further:

$$\Delta_r H_m^\ominus(383\text{K}) = \Delta_r H_m^\ominus(298\text{K}) + \Delta C_p(T_2 - T_1) = 77.57 - 6.3\times(383-298)/1000 = 77.03 \text{ kJ mol}^{-1}$$

$$\Delta_r S_m^\ominus(383\text{K}) = \Delta_r S_m^\ominus(298\text{K}) + \Delta_r C_p \ln\frac{T_2}{T_1} = 168.2 - 6.3\times\ln(383/298) = 166.62 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta_r G_m^\ominus(383\text{K}) = \Delta_r H_m^\ominus - T\Delta_r S_m^\ominus = 77.03 - 383\times 166.62/1000 = 13.21 \text{ kJ mol}^{-1}$$

$$K^\ominus = \exp(-\Delta_r G_m^\ominus / RT) = \exp(13.21\times 1000/8.314/383) = 0.0158 = p(CO_2)/p^\ominus$$

$$p(\text{CO}_2) = K^\ominus p^\ominus = 1.58 \text{ kPa}$$

The minimum partial pressure of CO_2 needed is 1.58 kPa.

24-3 Assume the initial amount of substance of PCl_5 is 1mol.

$$\begin{array}{cccccc} & \text{PCl}_5(\text{g}) & = & \text{PCl}_3(\text{g}) & + & \text{Cl}_2(\text{g}) \\ t=0 & 1 & & 0 & & 0 \\ eq & 1-x & & x & & x \end{array}$$

The molar mass of PCl_5, M, is 208.5×10^{-3} kg mol^{-1}. Assume PCl_5 is an ideal gas.

$$\rho = M/V$$
$$pV = nRT = (1+x)RT = pM/\rho$$
$$x = pM/\rho RT - 1 = (10^5\times 208.5\times10^{-3})/(4.8\times 8.314\times 440) - 1 = 0.187 \text{ mol}$$

$$\Delta_r G_m^\ominus = -RT\ln K_p^\ominus = -RT\ln\left[\frac{(\frac{x}{1+x}p)^2}{(\frac{1-x}{1+x}p)}\frac{1}{p^\ominus}\right] = -RT\ln\left(\frac{x^2}{1-x^2}\frac{p}{p^\ominus}\right)$$
$$= -8.314\times 440\times\ln(0.187^2/(1-0.187^2)) = 12.14 \text{ kJ mol}^{-1}$$

24-4

$$K_p^\ominus = \frac{x^2}{1-x^2}\frac{p}{p^\ominus} = \frac{y^2}{1-y^2}\frac{0.5p}{p^\ominus}$$
$$\frac{y^2}{1-y^2} = 2\times\frac{x^2}{1-x^2} = 2\times\frac{0.187^2}{1-0.187^2} = 0.073$$

$y = 0.26$ So the percentage of decomposition is 26%.

Problem 25. The condensation of 1-butanol vapor

25-1 According to the Kelvin equation:

$$r = \frac{2\sigma M}{\rho RT\ln\frac{p}{p_0}} = \left(\frac{2\times 0.0261\times 74\times10^{-3}}{0.81\times10^3\times 8.314\times 273\times\ln 4}\right) = 1.52\times10^{-9} \text{ m}$$

25-2 The volume of the droplet: $V = \frac{4}{3}\pi r^3$

The mass of the droplet is ρV, then the total number of the molecules, N, is:

$$N=\frac{\rho V}{M}N_A=\frac{\frac{4}{3}\pi r^3\rho}{M}N_A=96.8\approx 97$$

Problem 26. Chemical kinetics

26-1 For a second order reaction:

$$\begin{array}{llll} & 2\mathrm{A_2B} \xrightarrow{k} & 2\mathrm{A_2} \quad + & \mathrm{B} \\ t=0 & c_0 & 0 & 0 \\ t=t & c & c_0-c & (c_0-c)/2 \end{array}$$

$$\because \quad r=\frac{1}{2}r_{A_2B}=kc_{A_2B}^2 \quad \therefore \quad \frac{1}{c}-\frac{1}{c_0}=2kt=k't$$

$$\therefore \quad t_{1/2}=\frac{1}{2kc_0}=\frac{1}{k'c_0}$$

k' is the consumption rate of A_2B.

$$k(967\mathrm{K})=1/(2c_0t_{1/2})=1/(2\times156.787\times380)=8.392\times10^{-6}\ \mathrm{dm^3\ mmol^{-1}\ s^{-1}}$$

$$k(1030\mathrm{K})=1/(2c_0t_{1/2})=1/(2\times7.066\times1440)=4.914\times10^{-5}\ \mathrm{dm^3\ mmol^{-1}\ s^{-1}}$$

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

$$\therefore E_a=R(\ln\frac{k_2}{k_1})(\frac{T_2T_1}{T_2-T_1})=8.314\times(\ln\frac{4.914\times10^{-6}}{8.392\times10^{-5}})(\frac{1030\times967}{1030-967})=232.34\ \mathrm{kJ\ mol^{-1}}$$

26-2 At time t:

$$c=c_0(1-y)=54\times(1-0.37)=34.02\ \mathrm{mmol\ dm^{-3}}$$

$$t=\frac{1}{k'}(\frac{1}{c}-\frac{1}{c_0})=\frac{1}{2k}(\frac{1}{c}-\frac{1}{c_0})=\frac{1}{2\times4.914\times10^{-5}}(\frac{1}{34.02}-\frac{1}{54.0})=110.7\ \mathrm{s}$$

26-3 The half-life is not related to the initial concentration, then it is a first-order reaction:

$$r_a=k_a[\mathrm{A}]$$

$$k_a(294\mathrm{K})=\ln2/t=0.693/1000=6.93\times10^{-4}\ \mathrm{min^{-1}}$$

$$k_a(340\mathrm{K})=\ln(1/(1-y))/t=\ln(1024)/0.1=69.3\ \mathrm{min^{-1}}$$

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

$$E_{a,a}=208.0\ \mathrm{kJ\ mol^{-1}}$$

By comparing the three activation energies in mechanism b, the first step is fast, but the second step is slow, then:

$$r_2 = k_2\left[\mathrm{A}^*\right]$$

According to equilibrium approximation: $k_1\left[\mathrm{A}\right] = k_{-1}\left[\mathrm{A}^*\right]$

Then $r_2 = k_2\left[\mathrm{A}^*\right] = \left(k_1k_2 / k_{-1}\right)\left[\mathrm{A}\right] = k_b\left[\mathrm{A}\right]$, where $k_b = k_1k_2 / k_{-1}$

So $E_{a,b} = E_{a,1} + E_{a,-1} - E_{a,2} = 172.58\ \mathrm{kJ\ mol^{-1}}$,

and $r_b / r_a = k_b / k_a = \exp\left[\left(E_{aa} - E_{ab}\right) / RT\right] = 5017$

Problem 27: Electrochemistry

27-1 The half-reactions and the overall cell reaction:

$$\begin{array}{ll} (-) & \mathrm{2Hg(l) + 2Br^-(a_{Br^-}) \rightarrow Hg_2Br_2(s) + 2e^-} \\ (+) & \mathrm{Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(a_{Cl^-})} \\ \hline & \mathrm{Hg_2Cl_2(s) + 2Br^-(a_{Br^-}) \rightarrow Hg_2Br_2(s) + 2Cl^-(a_{Cl^-})} \end{array}$$

27-2 $E(298.15\ \mathrm{K}) = 0.1318 - 1.58\times10^{-5}\times298.15 = 0.1271\ \mathrm{V}$

which means the temperature coefficient $k = \dfrac{dE}{dT} = -1.58\times10^{-5}$

$$\Delta_\mathrm{r}S_\mathrm{m} = zF\frac{dE}{dT} = -1.58\times10^{-5}zF\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$\begin{aligned}\Delta_\mathrm{r}H_\mathrm{m} &= -zFE + T\Delta_\mathrm{r}S_\mathrm{m} = -zFE + zFTk \\ &= 2\times96485\times(-1.58\times10^{-5}\times298.15 - 0.1271) = -25436\ \mathrm{J\ mol^{-1}}\end{aligned}$$

27-3

$$E(298.15) = 0.1271 = E_{\mathrm{Cl^-|Hg_2Cl_2|Hg}} - E_{\mathrm{Br^-|Hg_2Br_2|Hg}} = 0.3335 - E_{\mathrm{Br^-|Hg_2Br_2|Hg}}$$

$$\therefore E_{\mathrm{Br^-|Hg_2Br_2|Hg}} = 0.3335 - 0.1271 = E^{\ominus}_{\mathrm{Br^-|Hg_2Br_2|Hg}} - \frac{RT}{zF}\ln a^2_{\mathrm{Br^-}}$$

$$\therefore E^{\ominus}_{\mathrm{Br^-|Hg_2Br_2|Hg}} = 0.2064 + \frac{RT}{zF}\ln(0.1\times0.772)^2 = 0.1406\ \mathrm{V}$$

Given:

$$\mathrm{Hg_2Br_2(s) \rightarrow Hg_2^{2+}}(a_{\mathrm{Hg_2^{2+}}}) + \mathrm{2Br^-}(a_{\mathrm{Br^-}})$$

Design a battery: $\mathrm{Hg(l)|Hg_2^{2+}}(a_{\mathrm{Hg_2^{2+}}})\ \vdots\vdots\ \mathrm{Br^-}(a_{\mathrm{Br^-}})\mathrm{|Hg_2Br_2(s)|Hg(l)}$

$$E^{\ominus} = E^{\ominus}_{\mathrm{Br^-|Hg_2Br_2|Hg}} - E^{\ominus}_{\mathrm{Hg_2^{2+}|Hg}} = 0.1406 - 0.799 = -0.6584\ \mathrm{V}$$

$$\therefore K^{\ominus}_{\mathrm{ap}} = \exp\left(\frac{zE^{\ominus}F}{RT}\right) = 5.46\times10^{-23}$$

$$K_{\mathrm{sp}} \approx K_{\mathrm{ap}} = K^{\ominus}_{\mathrm{ap}}(\mathrm{c}^{\ominus})^3 = 5.46\times10^{-23}\ \mathrm{mol\ dm^{-9}} = c_{\mathrm{Hg_2^{2+}}}(2c_{\mathrm{Br^-}})^2 = 4c^3$$

$$\therefore c = \sqrt[3]{K_{\mathrm{sp}}/4} = 2.39\times10^{-8}\ \mathrm{mol\ dm^{-3}}$$

Problem 28. π-conjugated systems

28-1 $\lambda_{\mathrm{a,max}} < \lambda_{\mathrm{b,max}} < \lambda_{\mathrm{c,max}}$

(a) 1, 3-butadiene, (b) 1, 3, 5-hexatriene, and (c) 1, 3, 5, 7-octatetraene have $2k$ values of 4, 6, and 8, respectively.

$$\Delta E_{\mathrm{a}} = \frac{h^2}{40md^2};\quad \Delta E_{\mathrm{b}} = \frac{h^2}{56md^2};\Delta E_{\mathrm{c}} = \frac{h^2}{72md^2}$$

$$\lambda_{\max} = \frac{hc}{\Delta E} = \frac{8mcd^2}{h}\left(2k+1\right)$$

The order of the absorption spectrum: $\lambda_{\mathrm{a,max}} < \lambda_{\mathrm{b,max}} < \lambda_{\mathrm{c,max}}$

28-2

$$\frac{hc}{\lambda_{\max}} = \Delta E'_{\mathrm{b}} = \frac{h^2}{56md^2} + 3.25\times10^{-19}\left(1-\frac{1}{2k}\right)$$

$d = 135$ pm

28-3 An anthracene molecule has 14 π electrons.

$$E_{n_x,n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}\right) = \frac{h^2}{8m}\left(\frac{n_x^2}{9b^2}+\frac{n_y^2}{b^2}\right) = \frac{h^2}{72mb^2}\left(n_x^2+9n_y^2\right)$$

n_x	1	2	3	4	5	1	2	3	6
n_y	1	1	1	1	1	2	2	2	1
$n_x^2+9n_y^2$	10	13	18	25	34	37	40	45	45
							HOMO	LUMO	LUMO

$$\Delta E = \frac{5h^2}{72mb^2} = \frac{hc}{\lambda_{\max}} \qquad b = 245\mathrm{nm}$$

28-4 1, 3, 5-hexatriene molecule has 6 π electrons that occupy three molecular orbitals. Their energy levels are:

E_1=α+1.802β

E_2=α+1.247β

E_3(HOMO)=α+0.445β

E_4(LUMO)= α−0.445β

28-5 $\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} = -0.828\beta = \dfrac{hc}{\lambda_{\max}}$ $\qquad\beta = -6.72\times10^{-19}$ J

Practical Tasks

P1. Extraction of Berberine and Its Structural Characterization

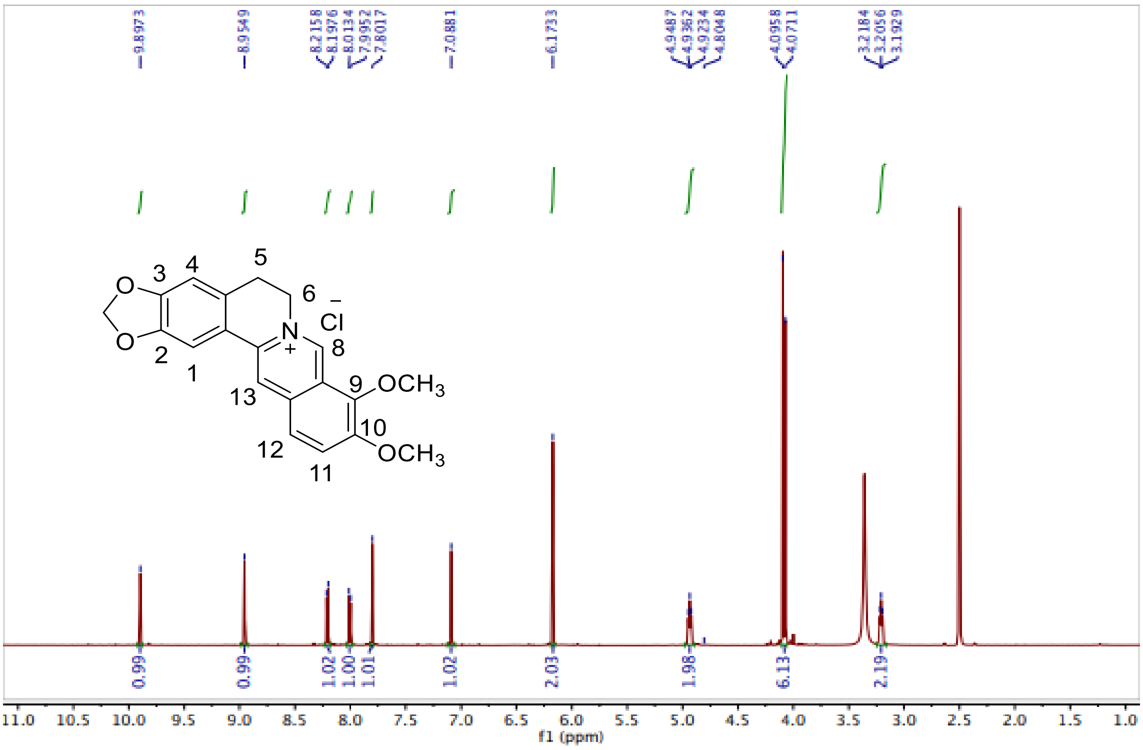
Questions

1. $Y = m_1/m_2$,

Y is the yield of **1b** from Coptis chinensis, m_1 is the weight of **1b**, m_2 (2g) is the weight of Coptis chinensis.

2. Analysis the ^{1}H NMR spectra of the product

The ^{1}H NMR spectra and analysis of **1b** are showed in the following Figure and Table.



(500 MHz, DMSO-d_6)

Atom	1H NMR(DMSO-d_6), δ multiplicity (J in Hz)#
1	7.80, s
4	7.09, s
5	3.21, t (6.4)
6	4.93, t (6.3)
8	9.90, s
11	8.21, d (6.1)
12	8.00 (9.1)
13	8.95, s
OCH_2O	6.17, s
9-OCH_3	4.09, s
10-OCH_3	4.07

The ^{1}H NMR spectra and data are cited from M. D. Clift, et al *Org. Lett.* **2018**, *20*, 4281-4284.

P2. Synthesis of (2,4-Dichlorophenoxy)acetic Acid and Evaluation of Product Purity

Questions

1 The main side reaction is showed as follows

$ClCH_2COONa + NaOH \rightarrow HOCH_2COONa + NaCl$

2.

$$Y = \frac{m_1/M_1}{m_2/M_2} \times 100\% = \frac{m_1/221}{3.3/163} \times 100\%$$

m_1: the weight of **2,4D**, M_1: the molecular weight of **2,4D**;

m_2: the weight of 2,4-dichlorophenol, M_2: the molecular weight of 2,4-dichlorophenol**.**

3. Concentration of NaOH standard solution

$$c(\mathrm{NaOH}) = \frac{m_1}{M_1 \times V_1} \times 1000$$

Where, m_1 is the mass of weighed potassium hydrogen phthalate (g), M_1 is the molar mass of potassium hydrogen phthalate (204.22 g mol^{-1}), V_1 is the volume of NaOH standard solution consumed by titration (mL).

Concentration of HCl standard solution

$$c(\mathrm{HCl}) = \frac{m_2 \times 2}{M_2 \times V_2} \times 1000$$

Where, m_2 is the mass of weighed anhydrous sodium carbonate (g), M_2 is the molar mass of anhydrous sodium carbonate (105.99 g mol^{-1}), V_2 is the volume of HCl standard solution consumed by titration (mL).

Purity of product

$$w(\%) = \frac{m}{G} \times 100 \qquad m = \frac{\left[25.00 \times c(\mathrm{NaOH}) - c(\mathrm{HCl}) \times V(\mathrm{HCl}) \times M\right]}{1000}$$

Where, m is the calculated mass of product (g), M is the molar mass of product (221.04 g mol^{-1}), c(NaOH) is the concentration of NaOH standard solution (mol L^{-1}), c(HCl) is the concentration of HCl standard solution, V(HCl) is the volume of HCl standard solution consumed by titration (mL), G is the weighed mass of product.

4. The product is difficult to dissolve in water.

5. Sodium salt of the product (weak base) is titrated by HCl solution in procedure 11 and the pH at the ending-point is in the alkaline range.

P3. Enzymatic Protein Digestion

1. By following Step 8 in the experiment procedure, the volumes of NaOH consumed in the titration ($\boldsymbol{B}_{\mathbf{n}}$, mL) can be summarized in a table.

Samples	Casein **A**			Casein **B**			Casein **C**		
	1	2	3	1	2	3	1	2	3
Volume of NaOH mL	B_{A1}	B_{A2}	B_{A3}	B_{B1}	B_{B2}	B_{B3}	B_{C1}	B_{C2}	B_{C3}

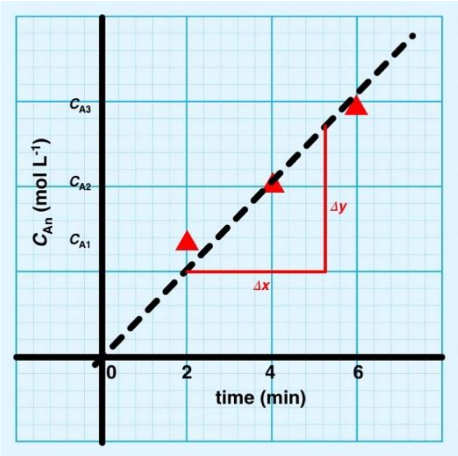
Then the concentration ($\boldsymbol{C}_{\mathbf{n}}$) of amino acid in each sample is given by

$$\boldsymbol{C}_{\mathbf{n}} = 0.1 \times \boldsymbol{B}_{\mathbf{n}} / 15$$

Fill up the table with the concentration calculated

Samples	Casein **A**			Casein **B**			Casein **C**		
	1	2	3	1	2	3	1	2	3
Amino acid concentration mol L^{-1}	C_{A1}	C_{A2}	C_{A3}	C_{B1}	C_{B2}	C_{B3}	C_{C1}	C_{C2}	C_{C3}

2. The initial velocity of the reaction (v_{10}、v_{20}、v_{30}) of enzymatic protein hydrolysis is given by plotting amino acid concentrations against time according to the data in the above table. Take Casein **A** as the example. One should be able to get a plot similar to the following one, where the vertical axis is the amino acid concentration ($\boldsymbol{C}_{\mathbf{An}}$), the horizontal axis is the time of the corresponding sample. Please note the line has to pass through (0,0).



According to the plot, the initial velocity of the reaction of Casein **A** is given by

$$v_{10} = \Delta y / \Delta x / 60$$

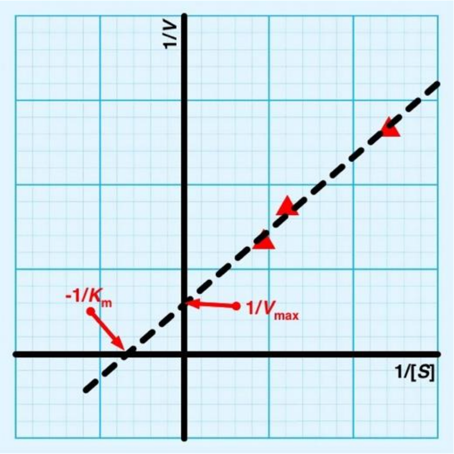
Please note that the unit of v_{10} is mol L^{-1} s^{-1} .

Calculate v_{20}, and v_{30} by following the same method.

3. First, calculate the reciprocal of all the casein concentrations and the initial velocity of the reaction. Summarize the results in a table.

Sample	**Casein A**	**Casein B**	**Casein C**
Casein concentration (g L^{-1}) **[*S*]**	10	20	30
1/[*S*]	0.1	0.05	0.033
Initial velocity of the reaction (mol L^{-1} s^{-1}) ***V***	v_{10}	v_{20}	v_{30}
1/*V*	$1/v_{10}$	$1/v_{20}$	$1/v_{30}$

Plot **1/*V*** (y-axis) over **1/[*S*]** (x-axis)



Read **−1/K_m** and **1/V_{max}** from the plot, calculate **K_m** and **V_{max}**

P4. Synthesis of the Thermochromic Spin-crossover Materials

Results

Complex	Yield	Complex color at room temperature	Spin state of Fe^{2+} at room temperature	SC temperature
$\{[Fe(Htrz)_3](BF_4)_2\}_n$		Purple	low-spin	
$\{[Fe(Htrz)_3](ClO_4)_2\}_n$		Purple	low-spin	

Questions

1. **Write** the reaction equation for procedure I and calculate the yield.

$$n\,Fe(BF_4)_2 + 3n\,Htrz \rightarrow \{[Fe(Htrz)_3](BF_4)_2\}_n\downarrow$$

2. **Write** the reaction equation for procedure II and calculate the yield.

$n\,Fe(ClO_4)_2 + 3n\,Htrz \rightarrow \{[Fe(Htrz)_3](BF_4)_2\}_n\downarrow$

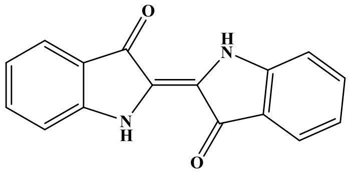
3. According to the experiment results, the calculated magnetic moment (μ) of complexes $\{[Fe(Htrz)_3](BF_4)_2\}_n$ and $\{[Fe(Htrz)_3](ClO_4)_2\}_n$ at room temperature **should be** (a), respectively.

(a) 0, 0 (b) 0, 4.90 (c) 3.87, 3.87 (d) 4.90, 4.90

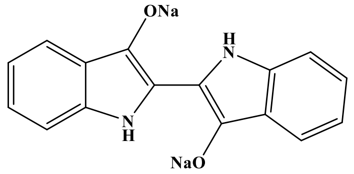
P5. The Extraction of Indigo from Radix Isatidis and its Synthesis for Application in Tie-dyeing

Questions

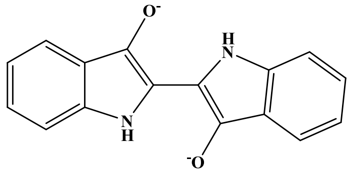
1. Thiourea dioxide is firstly added in the dyeing process to increase the solubility of indigo in water and the firmness of binding fabric fibers , the indigo becomes indigo white, and its structure **is** (**C**); then after NaOH is added, its structure **becomes** (**B**) and after NaCl is added, its structure **is** (**C**). Finally soaked in H2O2 solution, the structure **is** (**A**).



A

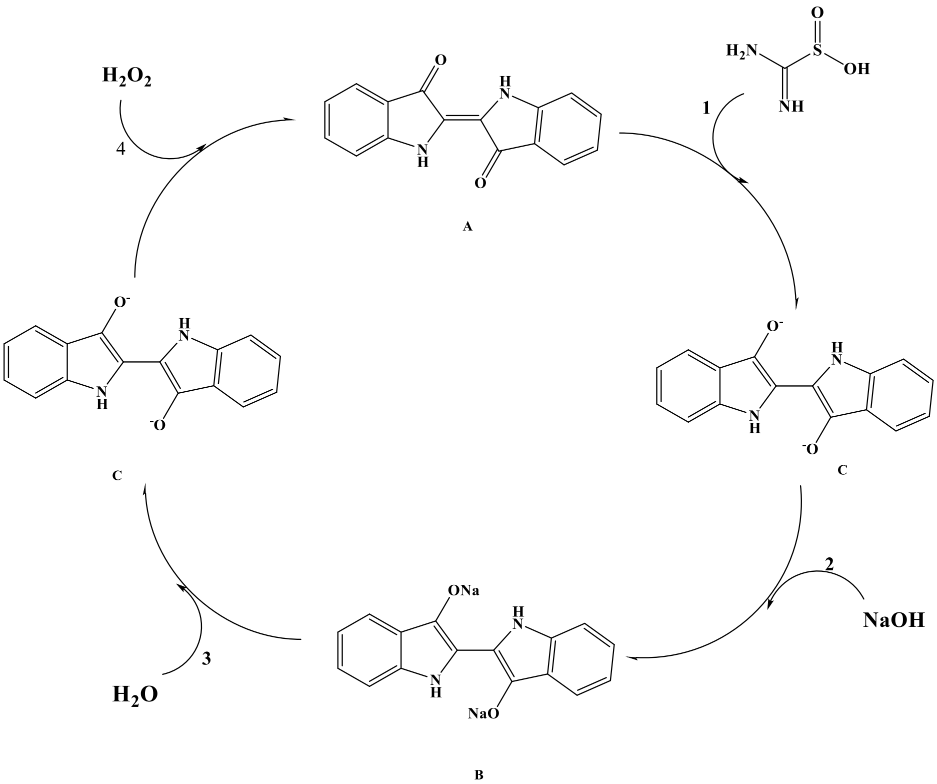


B



C

2.



3. The order of solubility of A, B, C in water is (**A**) < (**C**) < (**B**)

P6. Synthesis of Carbon Dots Made from Kitchen Waste

Questions:

1. Answer: a, b, c, d

There are so much raw materials to be used for preparing carbon dots. Many carbon containing components in plants can be transformed into carbon dots through "top-down" or "bottom-up" approaches.

2. Answer: wrong

There is a partial energy loss when the electron transitions from the excited state to the ground state, resulting in the energy of the emitted light is less than that of the excited light. That is, the wavelength of the emitted light is greater than that of the excited light.

P7. Synthesis and Purity Analysis of N-acetylphenylalanine in Aqueous Phase

Concentration of NaOH standard solution

$$c(\mathrm{NaOH}) = \frac{m}{M \times V(\mathrm{NaOH})} \times 1000$$

Where, *m* is the mass of weighed potassium hydrogen phthalate (g), *M* is the molar mass of potassium hydrogen phthalate (204.22 g mol^{-1}), *V* is the volume of NaOH standard solution consumed by titration (mL).

Purity of product

$$w(\%) = \frac{m}{G} \times 100, \qquad m = \frac{c(\mathrm{NaOH}) \times V(\mathrm{NaOH}) \times M}{1000}$$

Where, *m* is the calculated mass of product (g), *M* is the molar mass of product (207.23 g mol^{-1}), *c*(NaOH) is the concentration of NaOH standard solution (mol L^{-1}), *V*(NaOH) is the volume of NaOH standard solution consumed by titration (mL), *G* is the weighed mass of product.

Questions

1. Using amino and carboxyl protective groups, it can not only prevent side reactions, but also make the reaction oriented; It can not only eliminate the zwitterionic form of amino acids, but also make amino acids more soluble in organic solvents.

2. With phenolphthalein as indicator, the end point color of titration changed from colorless to reddish, which was easy to be observed and recognized by human eyes. When litmus is used as an indicator, the ending-point of titration changes from red to purple and then to blue. The change of color is not easy to be observed by human eyes and it is difficult to determine the ending-point of titration.

3. After 30 seconds, the ending-point color of titration fades due to CO_2 in the air.

P8. Reaction Types and Chemical Logic (Virtual Experiment)

(https://prj15.xnfz.cmet.ustc.edu.cn/）

One group was randomly selected from the following 10 groups as the test questions.

No.	**A**	**B**	**C**	**D**	**E**	**F**	**G**
0	$NaOH$	$BaCl_2$	$Cu(NO_3)_2$	Na_2CO_3	HCl	$CoCl_2$	$CuSO_4$
1	$Cu(NO_3)_2$	$NaOH$	HCl	H_2SO_4	$BaCl_2$	Na_2CO_3	$NaCl$
2	$NaCl$	$CuSO_4$	H_2SO_4	$BaCl_2$	Na_2CO_3	NH_3	$CoCl_2$
3	HCl	$NaCl$	$BaCl_2$	Na_2CO_3	$CoCl_2$	$Cu(NO_3)_2$	NH_3
4	$CuSO_4$	$BaCl_2$	$CoCl_2$	NH_3	Na_2CO_3	HCl	$Cu(NO_3)_2$
5	NH_3	$NaCl$	$CuSO_4$	Na_2CO_3	H_2SO_4	$BaCl_2$	$NaOH$
6	$BaCl_2$	H_2SO_4	Na_2CO_3	HCl	$CoCl_2$	$Cu(NO_3)_2$	$NaOH$
7	$CoCl_2$	NH_3	$NaOH$	$CuSO_4$	HCl	Na_2CO_3	$BaCl_2$
8	Na_2CO_3	$CoCl_2$	NH_3	H_2SO_4	$BaCl_2$	$NaOH$	$CuSO_4$
9	H_2SO_4	Na_2CO_3	$CoCl_2$	NH_3	$BaCl_2$	$NaOH$	$CuSO_4$

P9. Properties and Identification of Heavy Metal Ions (Virtual Experiment)

(https://prj16.xnfz.cmet.ustc.edu.cn/)

One group was randomly selected from the following 10 groups as the test questions.

No.	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**	**M**	**N**	**O**
0	$NaOH$	NaI	Na_2S	NH_3	$NaBr$	$FeCl_3$	$AgNO_3$	$Zn(NO_3)_2$	$SrCl_2$	$Ni(NO_3)_2$	$Cu(NO_3)_2$	$Pb(NO_3)_2$	$CrCl_3$	$FeSO_4$	$MnCl_2$
1	Na_2CO_3	NH_3	$NaCl$	Na_2SO_4	Na_2S	$Hg_2(NO_3)_2$	$CoCl_2$	$MnCl_2$	$CrCl_3$	$Zn(NO_3)_2$	$Hg(NO_3)_2$	$AgNO_3$	$Ni(NO_3)_2$	$SrCl_2$	$Cd(NO_3)_2$
2	NH_3	$NaCl$	Na_2CO_3	$NaOH$	NaI	$FeCl_3$	$Hg_2(NO_3)_2$	$MnCl_2$	$Hg(NO_3)_2$	$CoCl_2$	$AgNO_3$	$Pb(NO_3)_2$	$SrCl_2$	$FeSO_4$	$CrCl_3$
3	$NaCl$	Na_2S	$NaBr$	NH_3	NaI	$Zn(NO_3)_2$	$Pb(NO_3)_2$	$AgNO_3$	$Hg_2(NO_3)_2$	$Cd(NO_3)_2$	$Hg(NO_3)_2$	$MnCl_2$	$FeSO_4$	$CoCl_2$	$FeCl_3$
4	Na_2SO_4	NH_3	NaI	$NaOH$	Na_2CO_3	$AgNO_3$	$Cu(NO_3)_2$	$MnCl_2$	$SrCl_2$	$CoCl_2$	$Pb(NO_3)_2$	$Ni(NO_3)_2$	$FeCl_3$	$CrCl_3$	$FeSO_4$
5	$NaOH$	$NaBr$	Na_2CO_3	NH_3	Na_2S	$Cd(NO_3)_2$	$FeCl_3$	$CoCl_2$	$FeSO_4$	$CrCl_3$	$Pb(NO_3)_2$	$Hg(NO_3)_2$	$Ni(NO_3)_2$	$SrCl_2$	$Zn(NO_3)_2$
6	$NaBr$	NH_3	NaI	$NaOH$	$NaCl$	$Cu(NO_3)_2$	$FeCl_3$	$CoCl_2$	$FeSO_4$	$MnCl_2$	$Pb(NO_3)_2$	$Hg(NO_3)_2$	$Hg_2(NO_3)_2$	$SrCl_2$	$AgNO_3$
7	Na_2SO_4	$NaCl$	Na_2CO_3	NH_3	Na_2S	$Cd(NO_3)_2$	$MnCl_2$	$AgNO_3$	$FeSO_4$	$CrCl_3$	$Cu(NO_3)_2$	$Hg(NO_3)_2$	$Ni(NO_3)_2$	$SrCl_2$	$Zn(NO_3)_2$
8	NH_3	NaI	Na_2CO_3	Na_2SO_4	Na_2S	$CoCl_2$	$MnCl_2$	$AgNO_3$	$FeSO_4$	$CrCl_3$	$FeCl_3$	$Hg_2(NO_3)_2$	$Ni(NO_3)_2$	$SrCl_2$	$Pb(NO_3)_2$
9	$NaBr$	Na_2S	NaI	Na_2SO_4	$NaCl$	$Cu(NO_3)_2$	$FeCl_3$	$CoCl_2$	$Cd(NO_3)_2$	$Zn(NO_3)_2$	$Pb(NO_3)_2$	$Hg(NO_3)_2$	$Hg_2(NO_3)_2$	$SrCl_2$	$AgNO_3$