2024 CCO Take Home Exam

CANADIAN
CHEMISTRY
OLYMPIAD

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DE CHIMIE
DU CANADA

Due Date: Thursday, April 4th, 2024 (midnight)
Name:
School:

1. Adiabatic Reactor

A constant-volume adiabatic reactor is primarily a theoretical construct that helps in understanding the concepts of thermodynamics. In a reactor like this no heat exchange is possible with the environment, and the overall volume is constant, so if chemical reactions occur, other parameters like temperature and pressure change in response. This reactor also helps to some extent imagine what happens during gas explosions.

Imagine the burning of carbon monoxide in a constant-volume adiabatic reactor. The fixed volume is 1.00 m^3, 50.0 mol carbon monoxide and 50.0 mol oxygen is fed into the reactor at the beginning, the initial temperature is 298K.

You can assume that all gases and their mixture follow the ideal gas law. Note, that the molar entropy of an ideal gas has the following temperature and pressure dependence:

$$S_m(p,T) = S_m(p_0,T_0) + C_p \ln\frac{T}{T_0} - R\ln\frac{p}{p_0}$$

Use the following data:

	C_p (Jmol^{-1}K^{-1})	S^o_{298} (Jmol^{-1}K^{-1})	$\Delta_f H^o_{298}$ (kJ mol^{-1})
O_2(g)	29.4	205.2	
CO(g)	29.1	197.7	−110.5
CO_2(g)	37.1	213.8	−393.5

The constant pressure molar heat capacities are independent of temperature above 298K.

1.1 **Give** the balanced chemical equation of the reaction and its standard enthalpy ($\Delta_r H°$).

The amount of carbon dioxide formed in the reaction is n_{CO2} mol.

1.2 **Give** the stoichiometrically possible maximum value of n_{CO2}?

1.3 Using n_{CO2} as an independent variable **derive** expressions that give certain thermodynamic properties of the system. Where it is not possible to **give** an expression for the property itself, give the expression for the change in the property relative to the initial conditions.

a) the internal energy (*U*) of the system

b) the temperature (*T*) of the system

c) the pressure (*p*) of the system

d) the reaction quotient (*Q*)

e) the enthalpy of the system (*H*)

f) the entropy of the system (*S*)

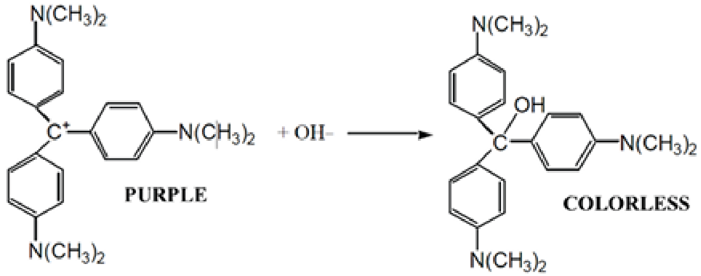
g) the Gibbs free energy of the system (*G*)

h) the equilibrium constant of the reaction (*K*) at the given temperature (already obtained as *T*)

1.4 **Use** spreadsheet software to calculate each property for n_{CO2} = 1 mol, 2 mol, 3 mol, On the spreadsheet, **find** the n_{CO2} value at which the system is in equilibrium. **Which** of the previously listed properties has an extremum in the equilibrium?

2. Crystal Violet

Crystal violet (or gentian violet or methyl violet 10B), is known for its antiseptic and fungicide effects and is commonly used for staining Gram positive bacteria. In aqueous solution crystal violet (CV) dissociates into the cation shown in the figure and chloride ions. The compound has a vivid violet color. In the presence of NaOH, crystal violet forms a colorless carbinol product.



The reaction is represented by the following simple equation:

$$\mathrm{CV^+ + OH^- = CVOH}$$

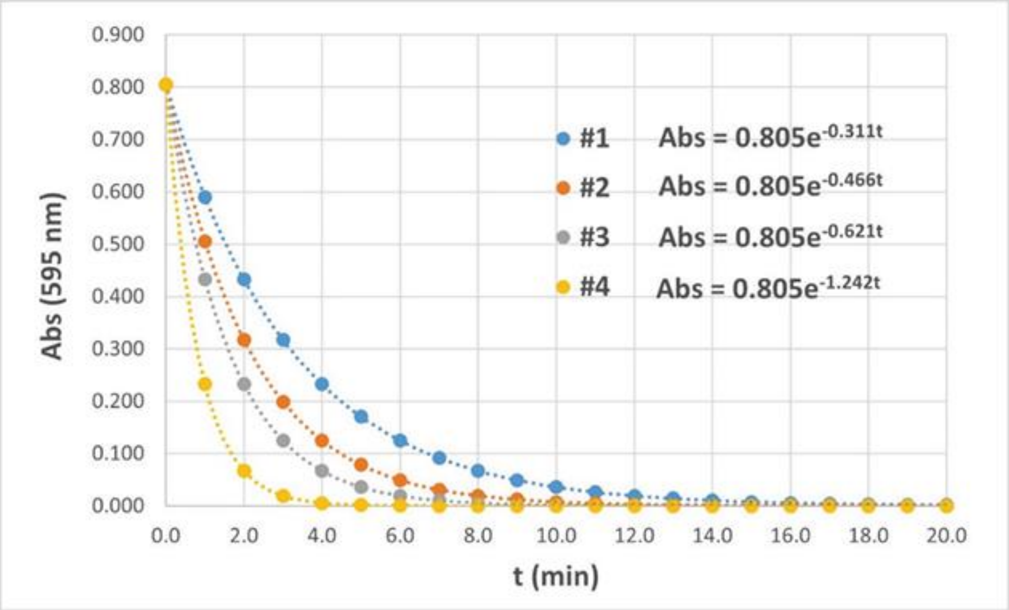
Due to the compound's intense color, the kinetic study of this reaction can be carried out by spectrophotometry at 595 nm. The rate law can be written:

$$v = k[\mathrm{CV}]^a[\mathrm{OH^-}]^b$$

A set of experiments was carried out at 30.0°C using the following mixtures:

Exp. no.	c(CV), mol/dm³	V(CV), cm³	c(NaOH), mol/dm³	V(NaOH), cm³
#1	$1.82\cdot10^{-5}$	5	0.08	5
#2	$1.82\cdot10^{-5}$	5	0.12	5
#3	$1.82\cdot10^{-5}$	5	0.16	5
#4	$1.82\cdot10^{-5}$	5	0.32	5

Performing the measurements in a 1.000 cm pathlength cuvette, the following kinetic curves were recorded:



2.1 **Calculate** the initial concentrations of the reactants in each reaction mixture.

2.2 **Calculate** the molar absorption coefficient of CV at 595 nm (you can assume that the products do not absorb at this wavelength).

2.3 **Determine** *a* and *b* (the partial orders of the reactants) and **give** the rate law of the reaction. **Calculate** the rate constant (k), using the same units as the chart and the table.

2.4 **Calculate** the concentration of CV in experiment #3 at 6 minutes.

The k rate constant follows the Arrhenius law in this temperature range and its numeric value is 22.78 at 45°C, in the same unit as calculated in Part 3.

2.5 **Calculate** the Arrhenius parameters (pre-exponential factor (A) and activation energy (E_a)).

6 cm^3 of $2.75 \cdot 10^{-5}$ mol/dm^3 crystal violet solution is mixed with 14 cm^3 of $3.86 \cdot 10^{-4}$ mol/dm^3 $KMnO_4$ solution. The optical pathlength of the cell is 0.6 cm, $\varepsilon_{595}(KMnO_4) = 1875\ M^{-1} \cdot cm^{-1}$. Assume that the volumes are additive, no chemical reaction takes place in the cell and the solution is completely homogenized.

2.6 **Calculate** the absorbance of the mixture at 595 nm and the corresponding percentage light absorption.

Crystal violet belongs to the family of triphenyl-methyl dyes. A study revealed that triphenyl-methyl (trityl) radicals react with thiophenol producing triphenyl methane and phenyl trityl thioether according to the scheme below: ('I': hexaphenyl ethane).

$$\mathrm{I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,(\mathrm{C_6H_5})_3\mathrm{C}\cdot \qquad (1)$$

$$(\mathrm{C_6H_5})_3\mathrm{C}\cdot + \mathrm{C_6H_5SH} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\mathrm{C_6H_5})_3\mathrm{CH} + \mathrm{C_6H_5S}\cdot \qquad (2)$$

$$(\mathrm{C_6H_5})_3\mathrm{C}\cdot + \mathrm{C_6H_5S}\cdot \xrightarrow{k_3} \mathrm{C_6H_5SC(C_6H_5)_3} \qquad (3)$$

2.7 **Which** elementary step is expected to be most affected by the described isotope exchange? **What** is expected to happen with the overall reaction rate when one of the carbon atoms in the aromatic ring of thiophenol is changed to 13C?

3. Sulfide Minerals

Element substitutions and crystal defects are common in most complex sulfide minerals, resulting in variable compositions in natural samples. However, specimens with relatively pure compositions identifiable as compounds do exist. While not mined in large quantities, many complex sulfide minerals are present in copper ores and are reasonably well-documented due to the significance of copper. These minerals will be discussed in this task.

In minerals of the chalcopyrite group, which are structurally equivalent to chalcopyrite ($CuFeS_2$), iron atom substitution is most prevalent. Some variants with a pure composition in such substitution structures have only been identified in microscopic samples.

Two of these minerals/compounds, which can be derived by complete substitution of iron, have a sulfur content of 32.5% (**A**) and 26.5% (**B**) by weight.

3.1 **Give** the empirical formula of **A** and **B**.

Mineral **C** can be derived from mineral **B** by an additional element substitution and has a sulfur content of 22.4%.

3.2 **Give** the formula of **C**.

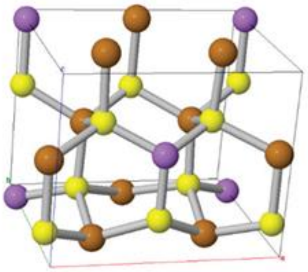
Significant copper ore minerals include enargite (**D**) with a theoretical composition of Cu3AsS4 and bornite (**E**) with a composition of Cu_5FeS_4. Neither structure has an S-S bond, there are no S atoms close to each other in the lattice. Each crystal has chemically equivalent atoms of the same kind (e.g., all Cu atoms in **E** are identical).

3.3 **Give** the conventional oxidation numbers of the elements in **D** and **E**.

3.4 **Write** balanced equations for the reactions of the two minerals if:

- they undergo roasting in air with excess oxygen (resulting in black metal oxides, including magnetite)
- react with an excess of bleach solution.

The figure shows the structure of the elementary cell of enargite.



3.5 **Find** the coordination number of Cu (brown), As (purple) and S (yellow) atoms. **Find** the number of formula units per elementary cell.

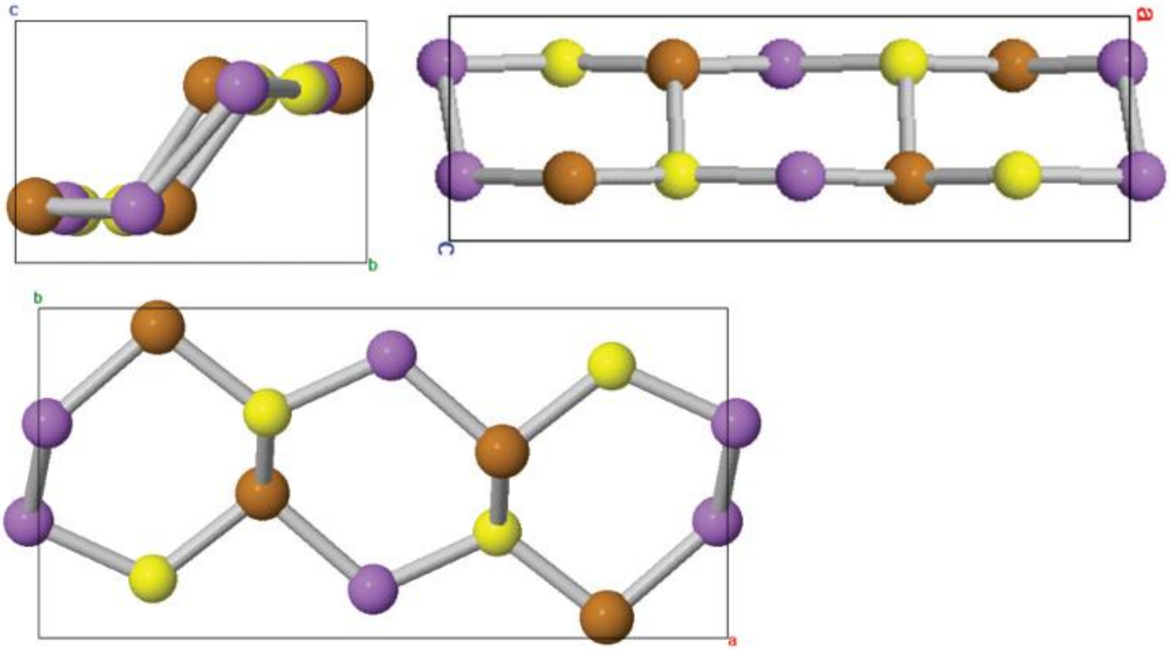
Two additional minerals, **F** and **G**, are derived from the same elements as enargite. Mineral **F** has an ideal composition with a sulfur content of 18.8%, featuring a relatively simple composition. On the other hand, mineral **G** presents challenges in determining the ideal composition due to wide substitution possibilities and a relatively complex structure (its empirical formula mass is close to 1500 g/mol). Its ideal sulfur content is 28.18%. The World Mineralogical Association last fine-tuned the data and classification of this mineral in 2019.

3.6 **Identify** the ideal empirical formulas of **F** and **G**.

In the crystal structure of **G**, Cu(I), Cu(II), thioarsenite (AsS_3^{3-}) and sulfide ions can be identified.

3.7 **Give** the proportions of these ions in **G**.

Lautite is a rare copper arsenosulfide. In it, the coordination number of all atoms is 4. Three projections of the elementary cell:



3.8 **Give** the empirical formula of the mineral. **Identify** the homonuclear bonds found in the crystal. **How many** of these homonuclear bonds are there in an elementary cell?

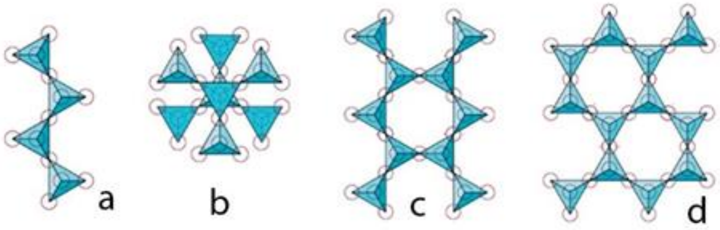
4. Beauty and Infinity

Part I

The largest sand desert on Earth, the Rub'al Khali (ٱلربْع ٱلخَالي) covers the southeastern part of Saudi Arabia. The most common constituents of sand grains are silica (SiO_2) and various silicates. Indeed, silicon and oxygen are the two main elements of Earth's crust in various minerals. Olivine, $(Mg,Fe)_2SiO_4$ and garnet, $(Mg,Fe,Mn)_3Al_2Si_3O_{12}$ or $Ca_3(Al,Cr,Fe)_2Si_3O_{12}$ are only two examples of the many silicate minerals. The bracketed elements signify a variable composition crystal structure with different atoms taking a certain crystal position. For olivine, this means that specimens with any x = 0-1 exist for $(Mg_{1-x}Fe_x)_2SiO_4$.

4.1 **Express** the formula of the garnet variant with the lowest silica content as a combination of oxides.

Several skeletal structures of polysilicate ions are represented on the figure, showing SiO_4 tetrahedra.



4.2 **Find** the corresponding charge for each of the four structures in the Figure. Structures **a** and **c** can be extended to a 1D, structure **d** to a 2D polymeric ion. **Find** the empirical formula for the polymeric ions.

Some silicates are beautiful gemstones, displaying a spectrum of colors. Recent findings in the southwest of Saudi Arabia, in the Bisha area include beryls, belonging to the mineral family of emeralds and aquamarines.

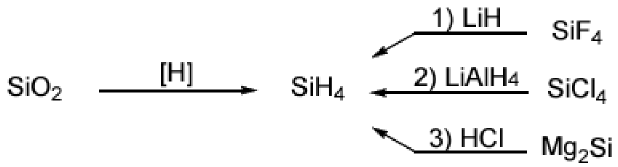
Emerald and aquamarine share the same beryl structure and have specific green and blue colors. Pure beryl is colorless and consists of Si, O, Al and Be. 0.2024 g of beryl contains 0.0635 g of Si and 0.0102 g Be. Another mineral, sky blue bazzite has the same stoichiometry as beryl, but the Al is replaced by another metal. The Si mass fraction in bazzite differs by 6.25% when compared to the Si mass fraction in beryl.

4.3 **Find** the formula of these two minerals: beryl and bazzite.

4.4 **Identify** the color of light absorbed by emerald: a) No absorption in the visible spectrum, b) Green color light, c) Red color light, d) Emerald color light.

Part II

In industrial processes, pure silicon, a primary semiconductor in the electronics industry, is derived from silane (SiH_4), itself obtained through the reduction of SiO_2. Additionally, on a smaller scale, silane can be produced from certain silicon derivatives such as silicon halides (SiF_4, $SiCl_4$) or metal silicides like Mg_2Si.



4.5 **Write** balanced equations for the three numbered reactions of silane formation.

These reactions can yield Si containing byproducts. From the byproducts, let us consider **A**, **B**, and **C**, each unique for one of the three reactions. Their molecular mass increases in order: **B**, **C**, **A**. Compound **A** contains 93.3 % Si by mass. The mass spectrum of compound **B** can be used to obtain an average molar mass of 101 g/mol. Also, **B** possesses two planes of symmetry. Finally, **C** contains 73.1% halogen by mass.

4.6 **Identify** the unknown compounds **A**, **B** and **C** and assign them to their respective reactions.

4.7 Among the SiX4 molecules (SiH4, SiF4, SiCl4), **determine** a) the one with the lowest melting point, and b) the one with the highest Lewis acidity.

Part III

SiH_4 is highly flammable in O_2 containing atmospheres. The final product is SiO_2, however, in a less oxidative atmosphere like N_2O gas, partial oxidation of silane can yield valuable products. Significant elementary reactions of the radical mechanism of this gas phase reaction are below. The 1st and the 6th steps are very slow.

$$N_2O \xrightarrow{k_1} N_2 + O$$
$$O + SiH_4 \xrightarrow{k_2} SiH_3 + OH$$
$$OH + SiH_4 \xrightarrow{k_3} SiH_3 + H_2O$$
$$SiH_3 + N_2O \xrightarrow{k_4} SiH_3O + N_2$$
$$SiH_3O + SiH_4 \xrightarrow{k_5} SiH_3OH + SiH_3$$
$$SiH_3 + SiH_3O \xrightarrow{k_6} H_3SiOSiH_3$$

4.8 **Categorize** steps 1, 4 and 6 with respect to their role in the chain reaction mechanism.

4.9 **Write** the net chemical reaction.

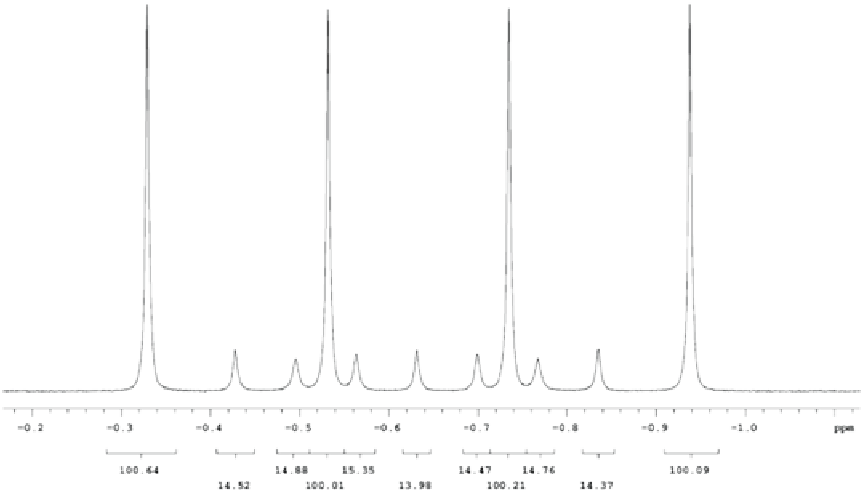
4.10 **Find** the kinetic law and reaction orders for the net reaction when N_2O is in excess. Use the steady-state approximation for the intermediates.

4.11 **Identify** the coordinate system that would result in a linear graph:

a) ln[SiH_4] vs. t, b) log[SiH_4] vs. t, c) 1/[SiH_4] vs. t, d) 1/[SiH_4]^2 vs. t, e) none of these

5. NMR Puzzle

One day Dr. Preping found a sealed container in his lab, filled with a white powder. The label only said has disappeared. He did not want to dispose of it, so he tried to figure out what it was. Upon dissolving the powder in water, he experienced intensive bubbling and the solution turned slightly basic afterwards. When he dissolved the powder in alcohol, he experienced gas evolution again, but less intensive than before. He could not observe melting in the range of his apparatus (up to 300°C). The compound could not be dissolved in ether and was only slightly soluble in THF. He asked for the help of Prof. Speclock, who examined the filtrate of the THF suspension, and found an interesting group of signals in the ^{1}H NMR spectrum. See the figure. (The numbers at the bottom are integrals of the respective signals.)

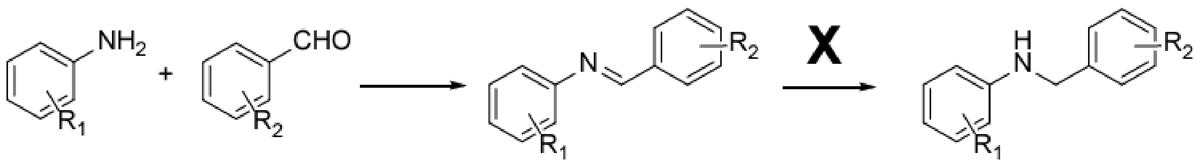


She immediately knew what the unknown compound could be. She showed Dr. Preping the following table.

Isotope	Spin quantum number	Natural abundance (%)	Isotope	Spin quantum number	Natural abundance (%)
^{1}H	½	99.99	^{29}Si	−½	4.69
^{2}H	1	0.0115	^{31}P	½	100
^{6}Li	1	7.42	^{32}S	0	99.24
^{7}Li	3/2	92.58	^{33}S	3/2	0.76
^{10}B	3	19.9	^{35}Cl	3/2	75.53
^{11}B	3/2	80.1	^{37}Cl	3/2	24.47
^{12}C	0	98.93	^{47}Ti	5/2	7.28
^{13}C	½	1.07	^{49}Ti	7/2	5.51
^{14}N	1	99.64	^{117}Sn	½	7.61
^{15}N	−½	0.36	^{119}Sn	½	8.58
^{16}O	0	99.96	^{121}Sb	5/2	57.21
^{17}O	−5/2	0.04	^{123}Sb	7/2	42.79
^{19}F	½	100	^{203}Tl	½	29.5
^{27}Al	5/2	100	^{205}Tl	½	70.5

5.1 **Suggest** a formula for the unknown compound **X**. (Give your explanation!)

Dr. Preping was very happy because he wanted to perform the following reactions and he had been looking for the necessary reagent in his lab for a long time. Now he understood that he hadn't been able to find it because it was labelled 'compound **X**' the whole time. When carrying out the reactions, he was again absentminded a bit and could not remember which reactants he used for which flask. He knew only that he used all the amines and aldehydes once (see table). Prof. Speclock helped again. Based on the ^{1}H NMR spectra of the amine products (**A**, **B**, **C**) it was obvious which flask contained which compound.



R1
p-I
p-MeO
p-Me

R2
H
o-Br
p-F

A: ^{1}H NMR δ 2.19 (3H, s), 3.7 (1H, br. s), 4.32 (2H, s), 6.86 (2H, d), 6.92 (1H, t), 7.05 (2H, d), 7.23 (1H, d), 7.28 (1H, t), 7.45 (1H, d) ppm.

B: ^{1}H NMR δ 3.6 (1H, br. s), 3.71 (3H, s), 4.25 (2H, s), 6.59 (2H, d), 6.74 (2H, d), 7.32 (5H, m) ppm.

C: ^{1}H NMR δ 4.31 (2H, s), 4.8 (1H, br, s), 6.41 (2H, d), 7.02 (2H, t), 7.29 (2H, dd), 7.52 (2H, d) ppm.

5.2 **Give** the structures for **A**, **B**, **C**.

The next week he attempted the same synthesis using a new combination of his amines and aldehydes listed above. He obtained a colored compound **D** with totally different characteristics. It gave the ^{1}H NMR spectrum listed below.

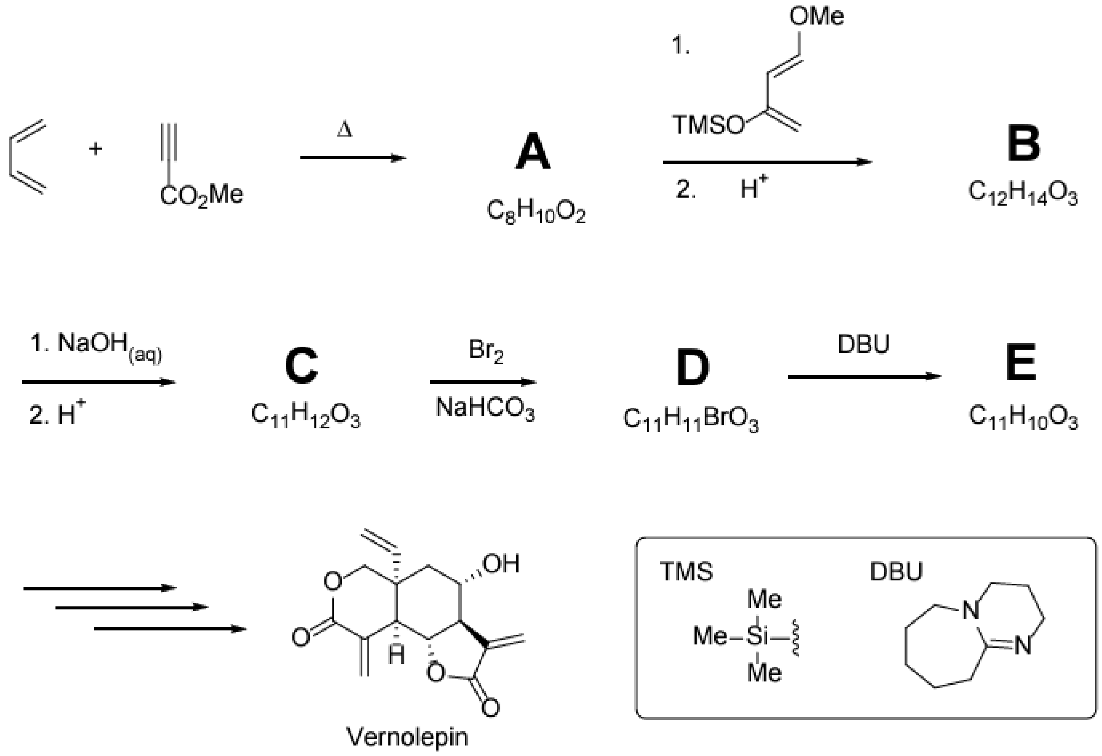
D: ^{1}H NMR δ 2.35 (3H, s), 7.14 (2H, d), 7.23 (2H, d), 7.45 (3H, m), 7.88 (2H, d), 8.44 (1H, s) ppm.

5.3 **Identify** compound **D** and **consider** the possible reasons for its formation.

6. Natural Products Syntheses

Part A

Vernolepin is a highly functionalized elemanolide dilactone isolated from sweet bitterleaf (Vernonia hymenolepis) that grows in tropical Africa. Thanks to its platelet antiaggregating and irreversible DNA polymerase inhibiting properties, it may serve as antitumor agent. Compound **E** serves as a key intermediate in the total synthesis of vernolepin. It can be prepared in several steps, starting with a series of cycloaddition reactions as shown below.



6.1 **Draw** the structures of compounds **A**–**E** (stereochemistry is not required).

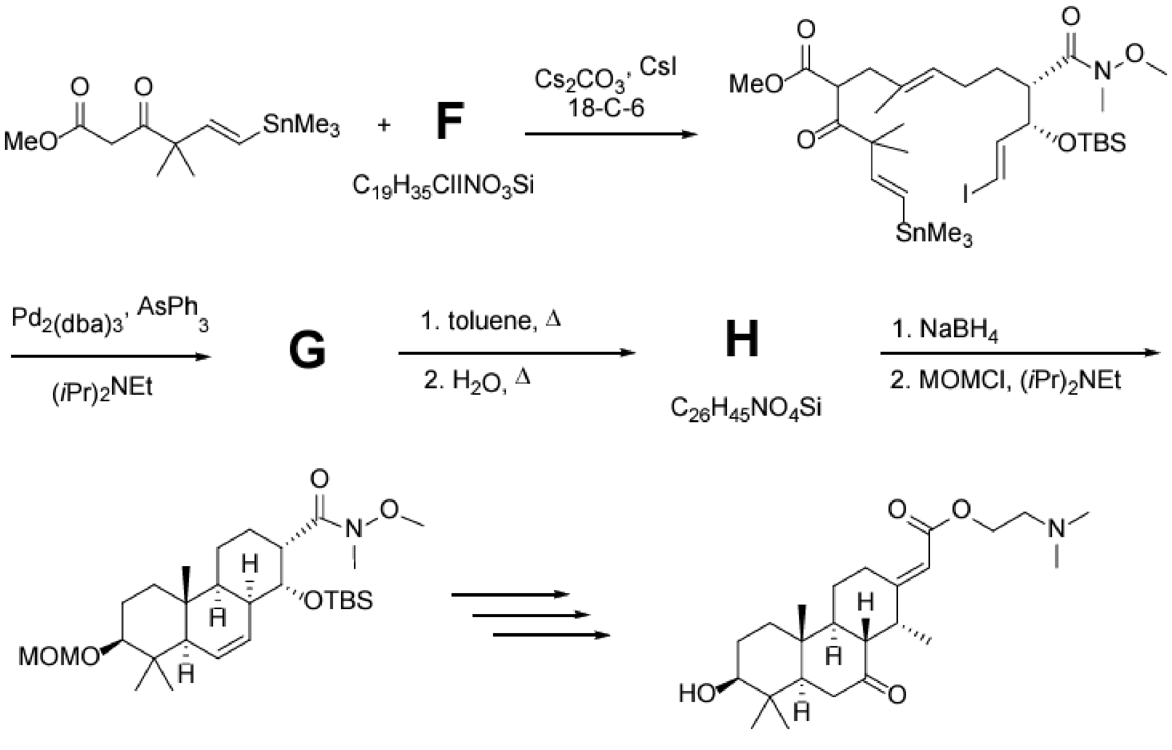
Hints:

1) **B** contains two fused rings and two carbon–carbon double bonds.

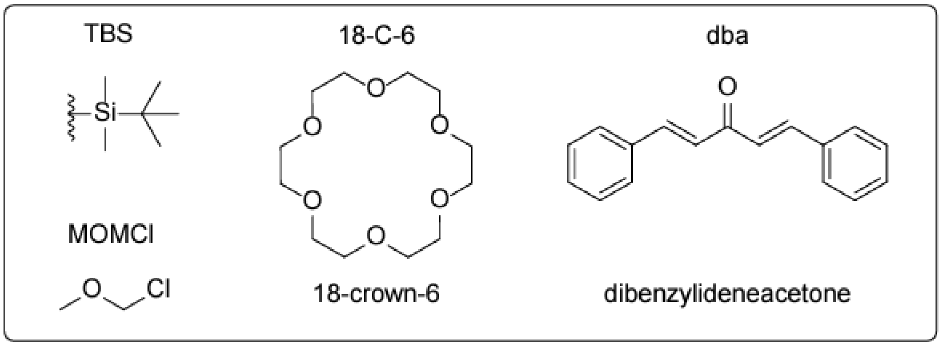
2) **E** contains two carbon–carbon double bonds.

Part B

(+)-Cassaine is a toxic compound which is found in the tree genus Erythrophleum. Since ancient times, it has been used as an ordeal poison by African tribes and as an arrow poison by the Casamance people of Senegal. It inhibits Na^+, K^+-ATPase, thereby changing the force and energy of cardiac muscle contractions. One synthetic route to (+)-cassaine is depicted below.



(+)-Cassaine



6.2 **Draw** the structures of compounds **F**–**H**, including stereochemistry.

Hints:

1) **G** was synthesized by a palladium-catalyzed cross-coupling reaction.

Palladium-catalyzed cross-coupling reaction
(Stille coupling)

$$R^1{-}Sn(Alkyl)_3 \quad + \quad R^2{-}X \xrightarrow[\text{ligand}]{Pd^0\text{ (cat.)}} R^1{-}R^2 \quad + \quad X{-}Sn(Alkyl)_3$$

2) The first reaction from **G** to **H** is a Diels–Alder reaction.

6.3 **Explain** the role of 18-C-6.

6.4 **Identify** all chirality centers in (+)-cassaine. **Label** them with an asterisk and assign R/S configuration to each of them.

7. Polyurethane Network

We aim to create a novel polyurethane network using hexamethylene diisocyanate (HDI, OCN-$(CH_2)_6$-NCO), poly(ethylene glycol) (HO-$(CH_2CH_2O)_n$-H, M_n = 500 g/mol), and a "homemade" polyol crosslinker. Initially, we convert the hydroxyl groups of the crosslinking polyol into acetates using acetic anhydride. Subsequently, the obtained product, i.e., the acetylated polyol, along with the initial polyol, undergoes gel permeation chromatography. The results are as follows:

	M_n / g/mol	M_w / g/mol	I_p
Sample 1	1383	2531	1.83
Sample 2	1240	2232	1.80

For the polyurethane synthesis, we mix 1.6820 g of HDI, 4.0000 g of poly(ethylene glycol), and a sufficient amount of cross-linking polyol to ensure an equal number of hydroxyl and isocyanate groups.

7.1 **Determine** the average number of hydroxyl groups per molecule in the crosslinking polyol.

7.2 **Calculate** the mass of cross-linking polyol required for the polyurethane synthesis?

The reaction between isocyanate and hydroxyl groups is modeled by the following equation. Moving forward, we disregard changes in volume and temperature, and assume equal reactivity between identical groups in different chemical environments:

$$\sim\sim\sim NCO + HO\sim\sim\sim \rightarrow \sim\sim\sim NHCOO\sim\sim\sim$$

You can model the time evolution of the process using a simple kinetic law with an order of 1 for each reactant.

After 3 hours of the reaction, a sample was withdrawn, and the subsequent GPC result is as follows:

	M_n / g/mol	M_w / g/mol	I_p
Sample 3	1227	3288	2.68

7.3 **Calculate** the conversion after 3 hours?

Crosslinking polymers leads to gelation, a sudden increase in viscosity. A simple model predicts that this gel point occurs when M_n becomes infinitely high.

7.4 **Identify** the conversion corresponding to the gel point in this model.

7.5 **Determine** the reaction time at which the reaction reaches the gel point.