

Chemistry 210
“Organic Chemistry I”
Fall Semester 2000
Dr. Rainer Glaser

Examination #5
“Reactions of Alcohols and Related Reactions”

The Final Learning Experience

Wednesday, December 20, 2000, 1:00 - 3:00

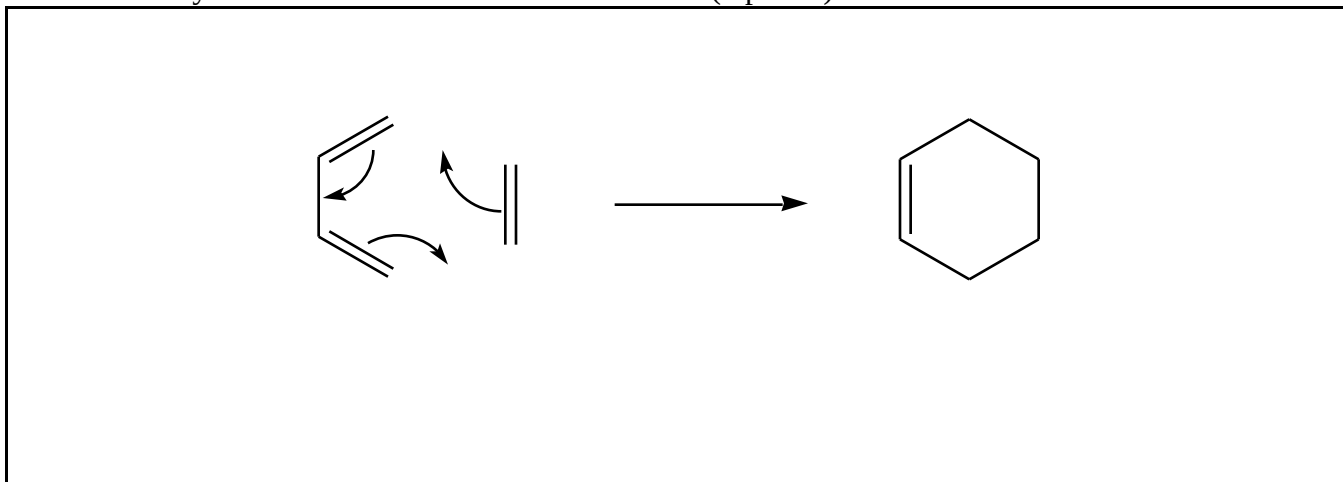
Name:

Answer Key

Question 1. Diels-Alder Reactions.	20	
Question 2. Halogenation of Cyclohexene. Stereochemistry.	40	
Question 3. Halogenation of Cyclohexane & Elimination.	15	
Question 4. Reactions of Cyclohexene.	15	
Question 5. Syntheses of Alcohols: Grignard Reactions & Reductions.	25	
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Question 7: Reactions of Alcohols: Ethers.	20	
Question 8. Physical Properties of Dioxin. (News #14)	25	
Total	200	

Question 1. Diels-Alder Reactions. (20 points)

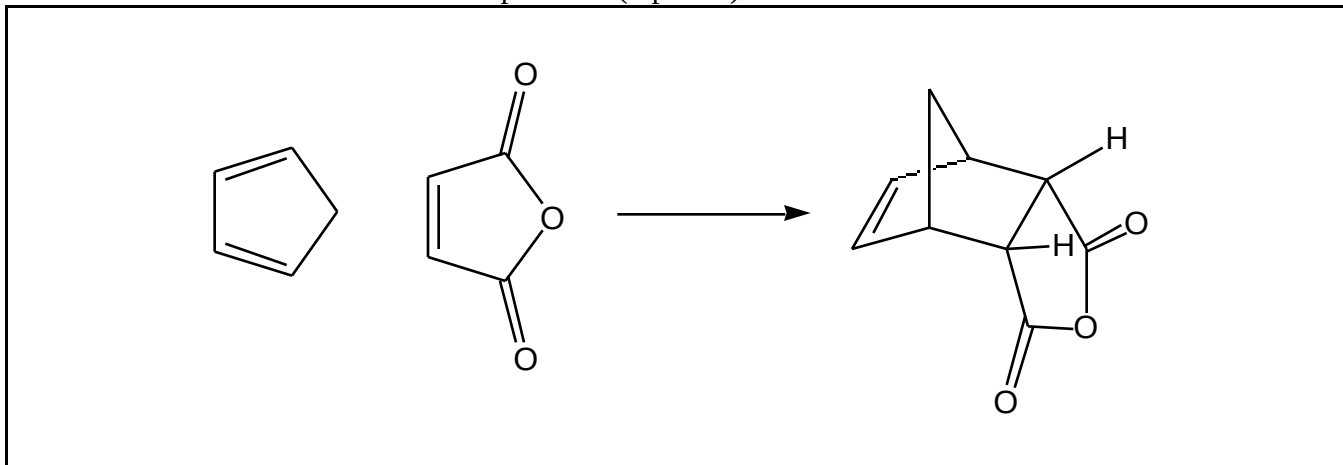
(a) The Diels-Alder reaction is the best reaction to prepare six-membered rings. The simplest Diels-Alder reaction is that between **butadiene and ethene**. The reaction involves the shifting of 3 (how many?) electron pairs simultaneously to convert 3 (how many?) π bonds in the substrates into 2 (how many?) new σ bonds and 1 (how many?) new π bond. Use “curved arrows” to show the formation of cyclohexene from butadiene and ethene. (8 points)



(b) The Diels-Alder reaction reaction can be accelerated by the presence of electron-_____ (**donating**, withdrawing) groups in the diene. (2 points)

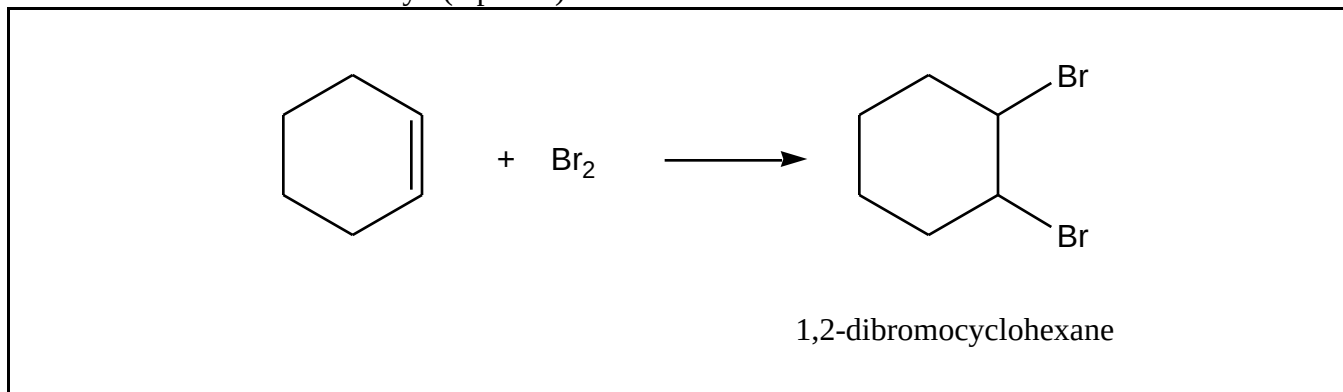
(c) The Diels-Alder reaction reaction can be accelerated by the presence of electron-_____ (donating, **withdrawing**) groups in the dienophile. (2 points)

(d) Draw the structures of cyclopentadiene and of maleic acid anhydride. Draw the product of the Diels-Alder reaction between these two compounds. (8 points)

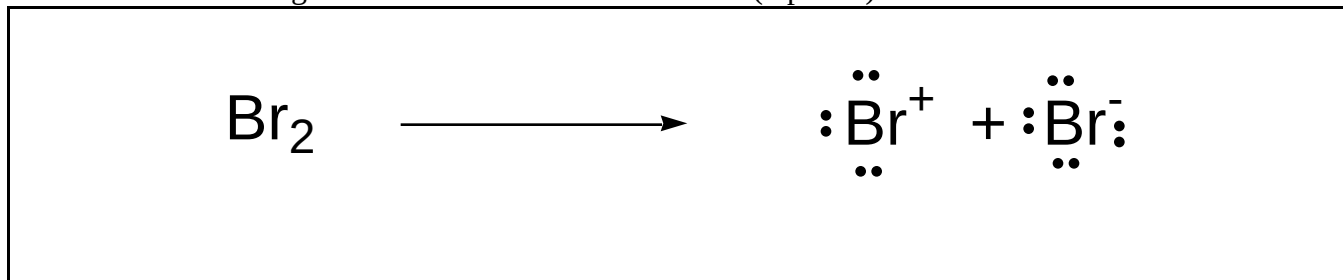


Question 2. Halogenation of Cyclohexene. Stereochemistry. (40 points)

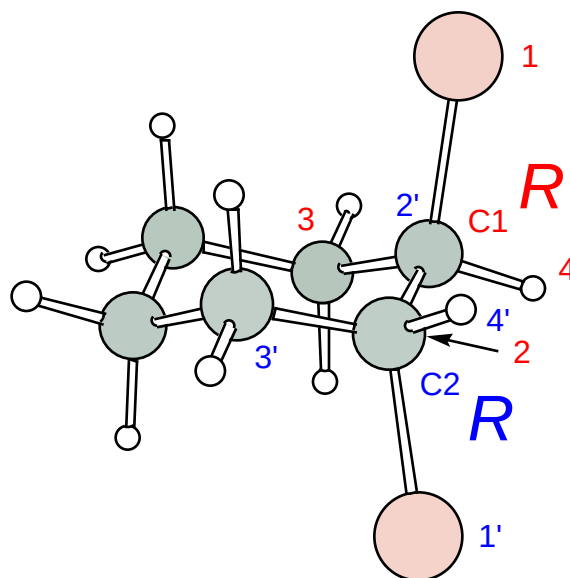
(a) Alkenes react with molecular bromine, Br_2 , to form vicinal dibromides. Write down **the reaction diagram** using complete Lewis structures for the specific example of cyclohexene reacting with bromine, Br_2 . Provide the IUPAC name of the alkyl dibromide formed. At this time, do not be concerned with stereochemistry. (6 points)



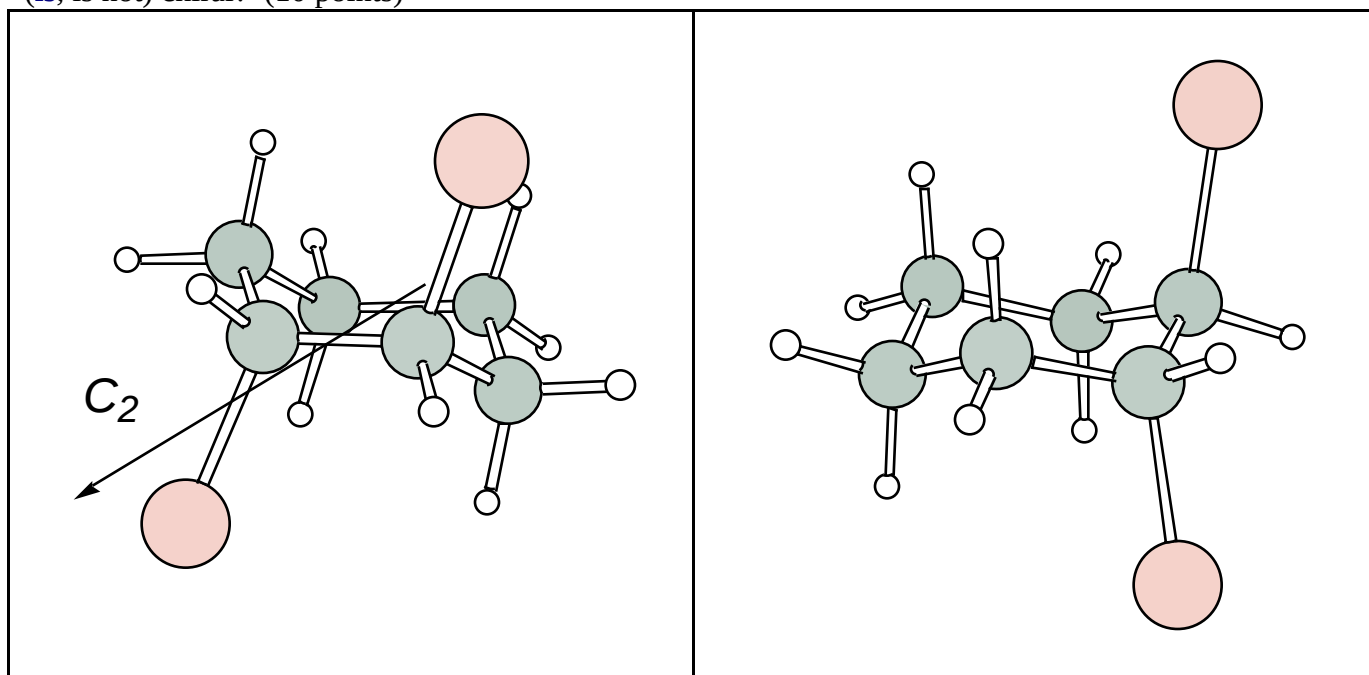
(b) The addition of bromine to alkenes requires **heterolytic dissociation of molecular bromine**. Provide a reaction diagram for this dissociation reaction. (4 points)



(c) The bromination of cyclohexene resulted in the formation of the dibromide shown. Let's consider the stereochemistry of this molecule. Mark both chiral carbon atoms by a star. For each chiral carbon, number its substituents according to their priorities; use 1 – 4 for one center and 1' – 4' for the other center. Assign the configurations of each chiral carbon atom using the **R/S nomenclature** by Cahn-Ingold-Prelog. (8 points)



(d) Now let's consider the **symmetry elements** of the molecular model. The same model is shown in two perspectives for your convenience. Does the molecule contain a center of inversion? _____ (Yes, **No**). Does the molecule contain a plane of symmetry? _____ (Yes, **No**). If there is a plane of symmetry, then indicate this plane in the molecular model. Does the molecule contain a rotational axis? _____ (**Yes**, No). If there is a rotational axis C_n , then indicate this rotational axis in the molecular model and specify the value of n . Based on this analysis, do you think the molecule shown _____ (**is**, is not) chiral? (10 points)



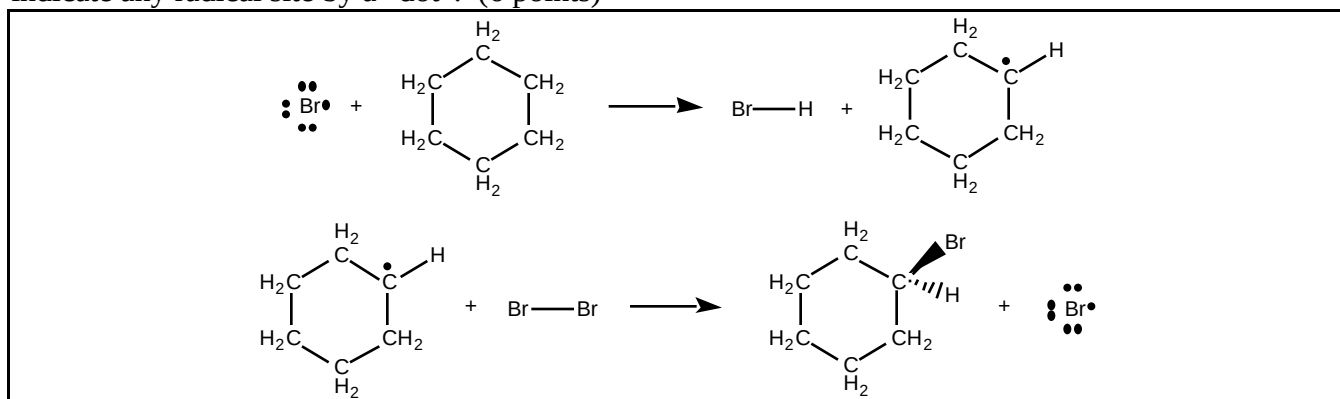
(e) Will the product formed in the bromination of cyclohexene be **optically active**? _____ (Yes, **No**). Briefly explain your answer. (4 points)

Both enantiomers are formed in a racemate.

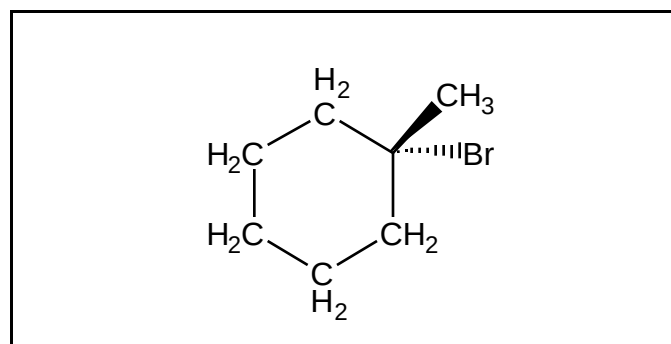
(f) The bromination of an alkene involves an _____ (**electrophilic**, radical, nucleophilic) addition of a bromine _____ (**cation**, radical, anion) to the alkene and leads to the formation of a cyclic **bromonium** ion intermediate. This cyclic intermediate is responsible for the _____ (**trans**, *cis*) addition of the two bromine atoms. (8 points)

Question 3. Halogenation of Cyclohexane & Elimination. (15 points)

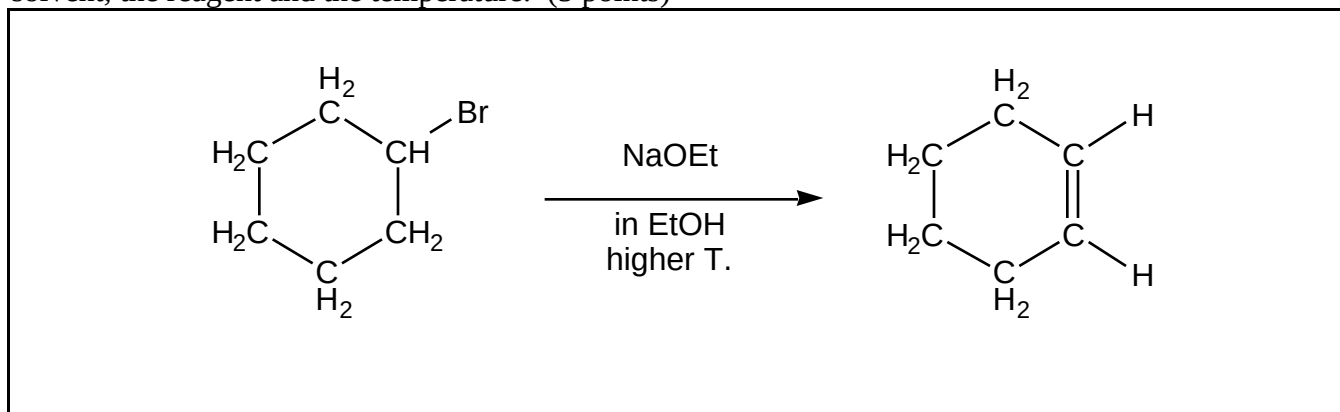
(a) The halogenation of an alkane involves a radical chain mechanism. The radical chains are initiated either by light or by the use of initiators. Once the halogen radicals are formed, the reaction proceeds by way of two propagation reaction steps. In the space below, write down these two propagation steps for the specific example of the bromination of cyclohexane. In your structures, show all atoms and clearly indicate any radical site by a “dot”. (6 points)



(b) Suppose you brominated methylcyclohexane. Draw the structure of the major product. (4 points)



(c) The elimination of HBr from bromocyclohexane affords cyclohexene. Draw the reaction diagram for this elimination reaction. What reaction conditions would be best for this reaction? Specify the solvent, the reagent and the temperature. (5 points)



Question 4. Reactions of Cyclohexene. (15 points)

For each reaction, draw the substrate cyclohexene, provide the structure of the reagent and of any needed catalyst, and provide the structure of the product. If the reactions involve several reaction steps, then draw the intermediate and provide reagents for each reaction step.

(a) Hydrogenation of cyclohexene. (3 points)

Reaction with hydrogen gas in the presence of a Pt or Pd catalyst to form cyclohexane.

(b) Epoxidation of cyclohexene. (4 points)

Reaction with peroxycarboxylic acid (e.g. MCPBA) to form the epoxide of cyclohexene.

(c) Ozonolysis of cyclohexene. (4 points)

Step 1: Reaction with O_3 gives ozonide.

Step 2, reduction: Work up with dimethyl sulfide or Zn/acid and obtain $OHC-(CH_2)_4-CHO$.

Step 2, oxidation: Work up with H_2O_2 /acid and obtain $HOOC-(CH_2)_4-COOH$.

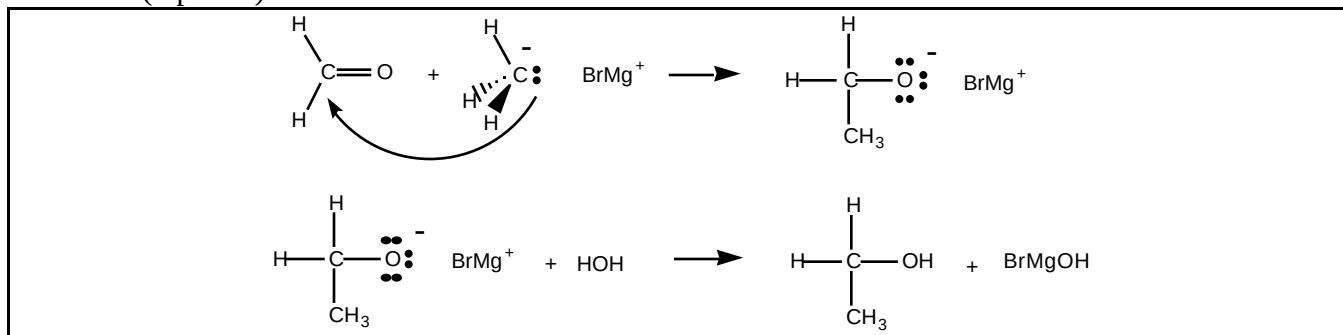
(d) Oxymercuration/demercuration of cyclohexene. (4 points)

Step 1: Reaction with $HgAc_2$ gives the organomercurial alcohol.

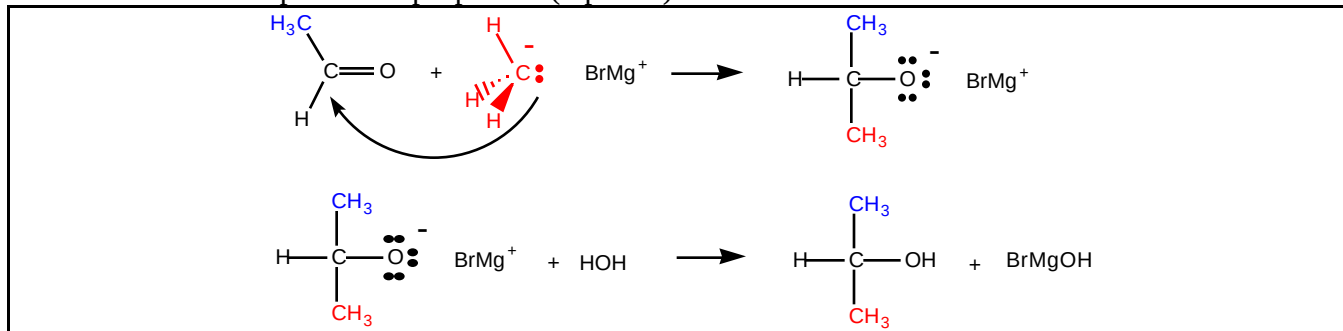
Step 2: Reduction with $NaBH_4$ replaces the $-HgAc$ group by $-H$ to give cyclohexanol.

Question 5. Syntheses of Alcohols: Grignard Reactions and Reductions. (25 points)

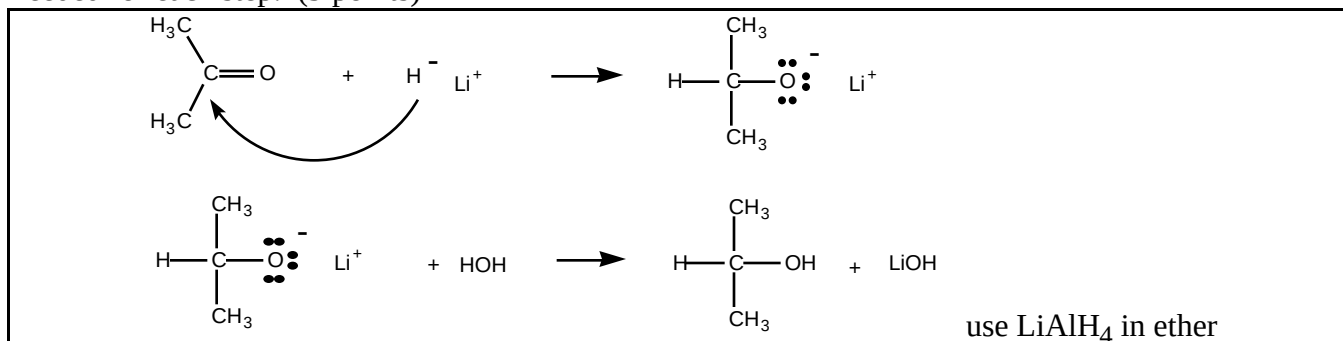
(a) Formaldehyde, $\text{H}_2\text{C}=\text{O}$, is reacted with methyl magnesium bromide, MeMgBr , and the initially formed intermediate is hydrolyzed. Draw the Lewis structures of the substrate, of the intermediate, and of the final product. This reaction provides a synthesis of _____ (**primary**, secondary, tertiary) alcohols. (8 points)



(b) Suggest a synthesis of 2-propanol by way of a Grignard reaction. Draw the Lewis structures of the substrate, specify the Grignard reagent, draw the Lewis structure of the intermediate, and give the structure of the final product 2-propanol. (8 points)



(c) Suppose you wanted to prepare 2-propanol by reduction of a ketone. What ketone would you use? What reducing reagent would you use? What solvent would you use for the reduction reaction? Provide a reaction diagram with complete Lewis structures that shows both steps of the reduction and the reagent needed for each step. (9 points)

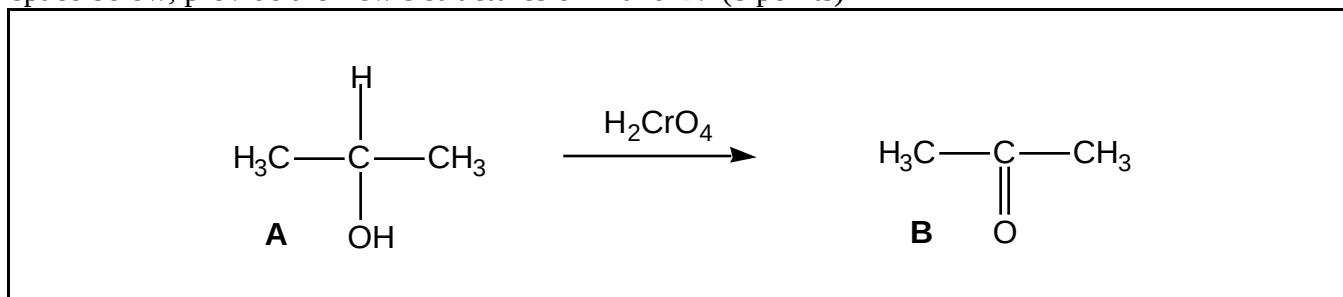


Question 6. Reactions of Alcohols: Oxidations. (40 points)

An oxidation mystery!

An isomer of propanol **A** was oxidized with chromic acid, H_2CrO_4 , and a product **B** was obtained. The H-NMR spectra and the IR-spectra of **A** and **B** are provided on the following pages.

(a) Using the spectra, decide whether **A** is 1-propanol or 2-propanol. Using the spectra, decide whether **B** is the product obtained from 1-propanol or whether **B** is the product of oxidation of 2-propanol. In the space below, provide the Lewis structures of **A** and **B**. (8 points)

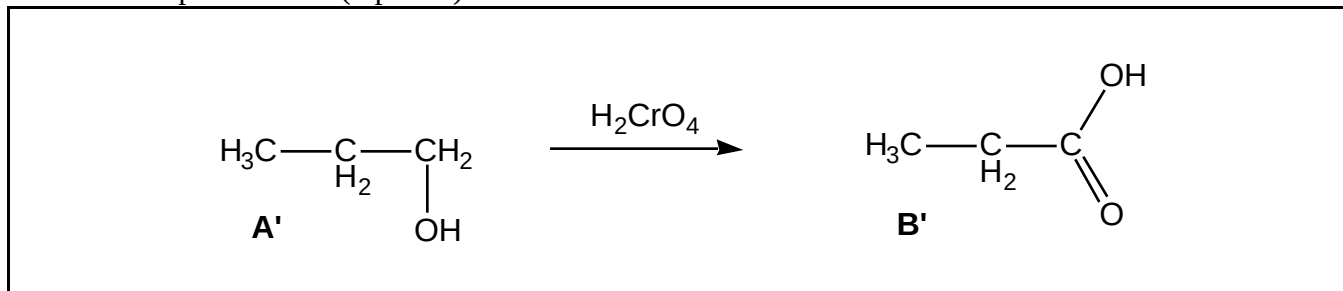


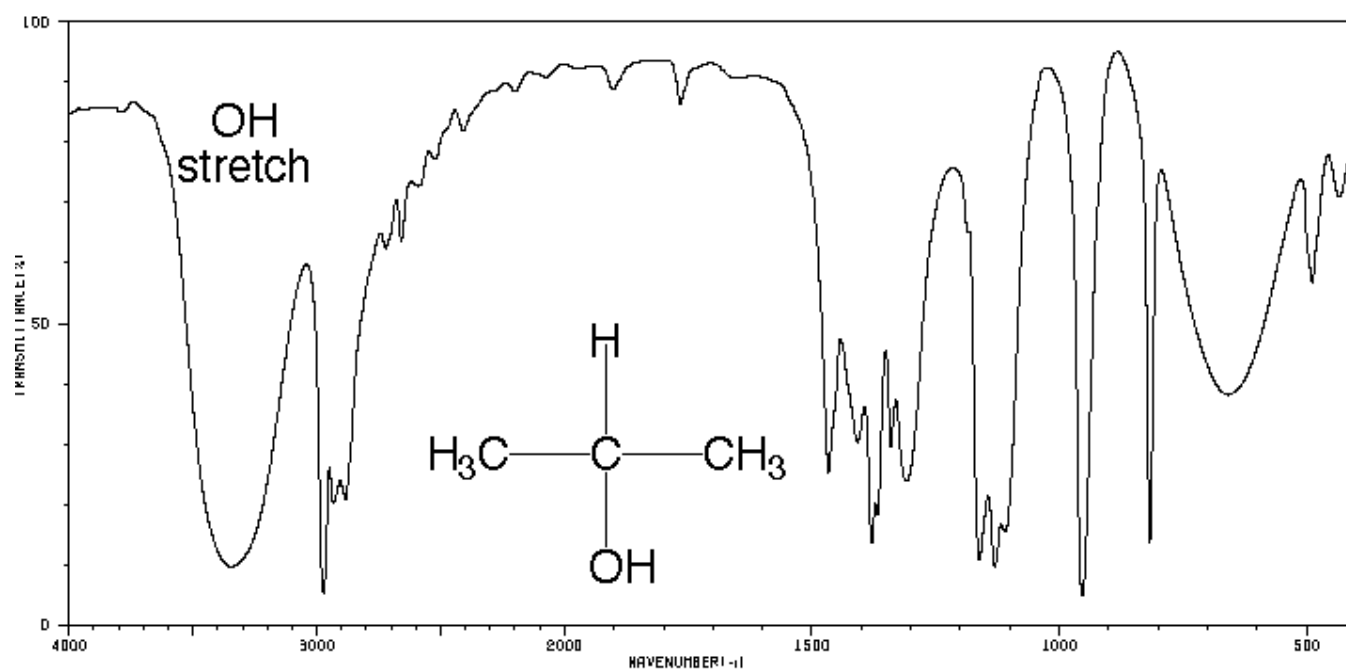
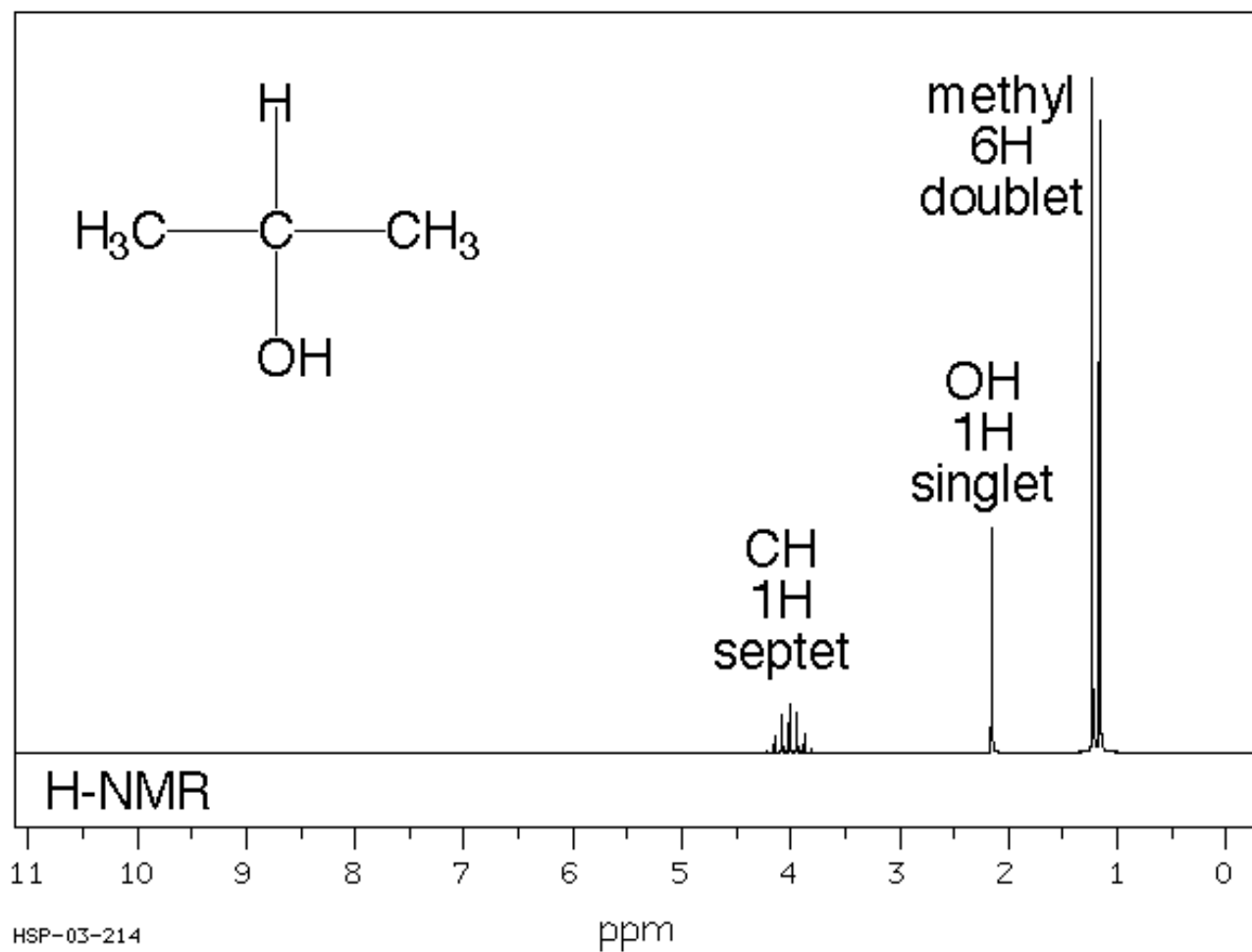
(b) In the four spectra, indicate which ones are the IR spectra and which ones are the H-NMR spectra. The units of the horizontal axis of the NMR spectra is ppm and the units of the horizontal axis of the IR spectra is 1/cm. (6 points)

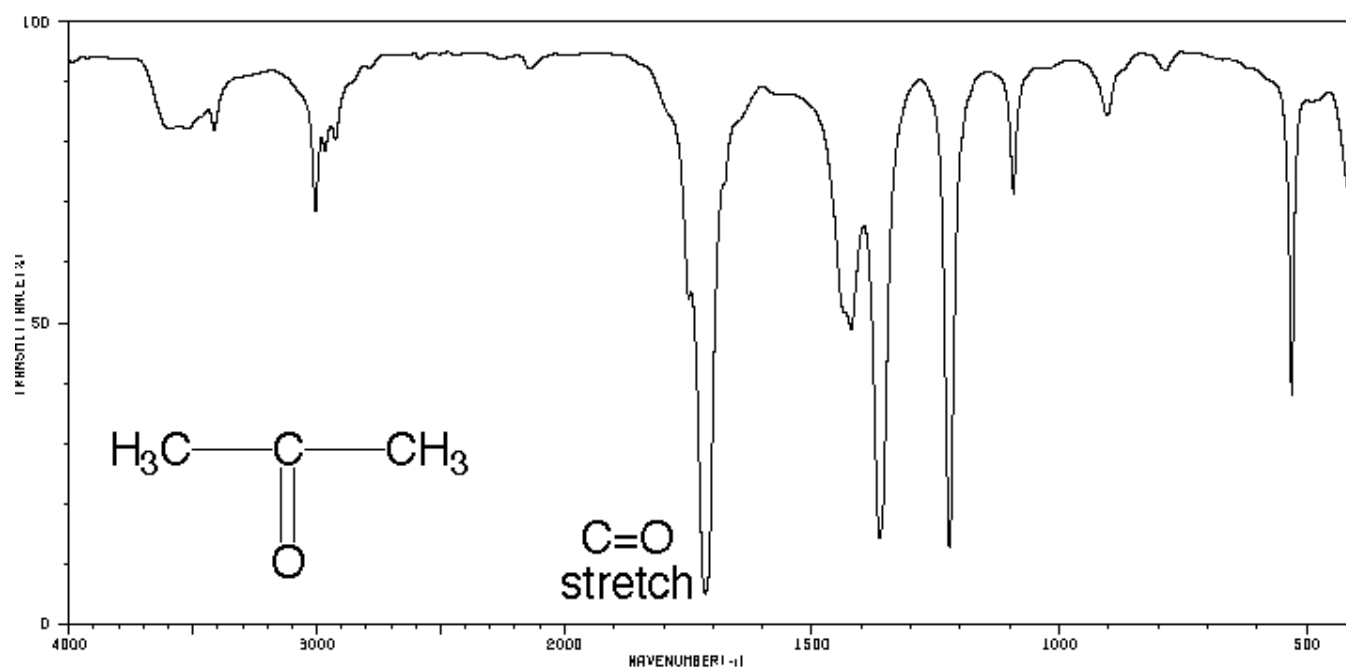
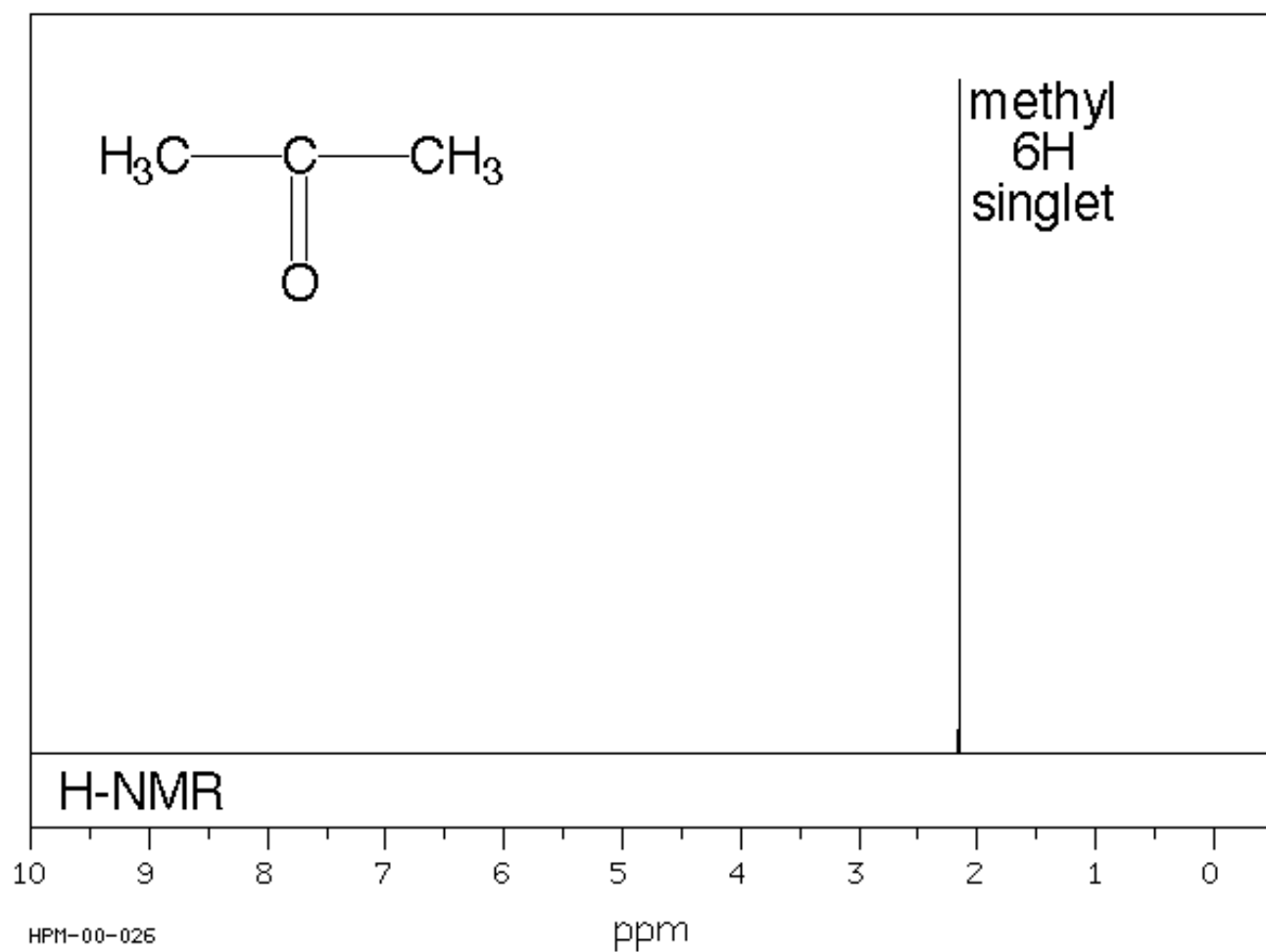
(c) Assign all peaks in the H-NMR spectra, that is, state which H-atom causes the peak, state how many H-atoms cause the peak (write 1H, 2H, 3H, ...), and write next to the peak what its splitting pattern is (e.g. singlet, doublet, triplet, ...). (12 points)

(d) Assign the important peaks in the IR spectra. Assign only the important peaks. Simply write down on the spectra what bonds cause the important peaks. (6 points)

(e) In the space below, provide the Lewis structures of the isomer of **A'** and write down the structure of its oxidation product **B'**. (8 points)



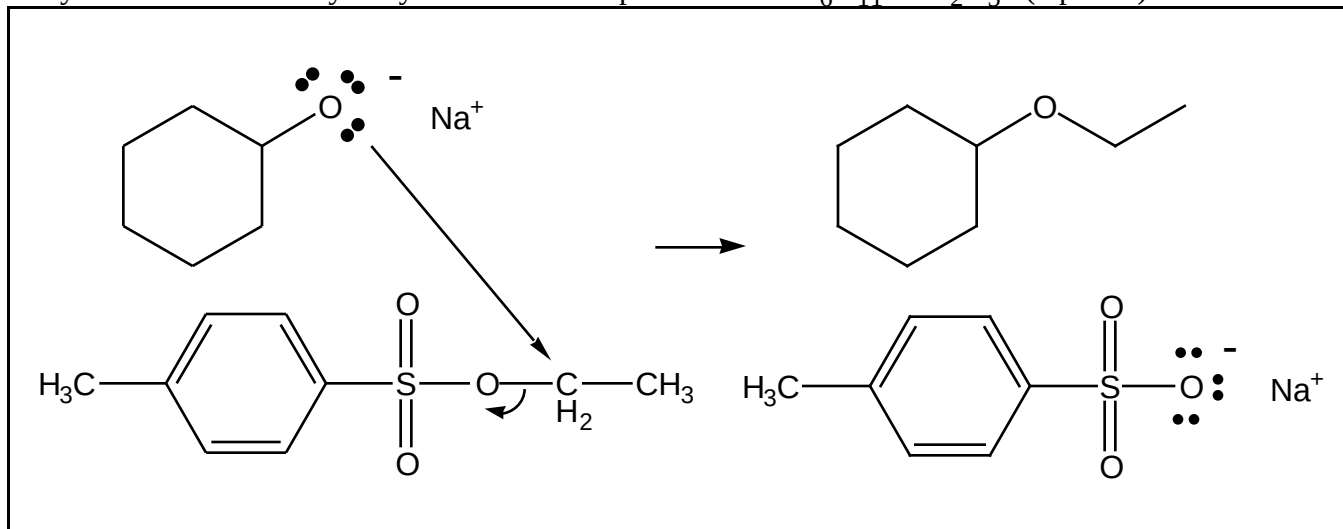




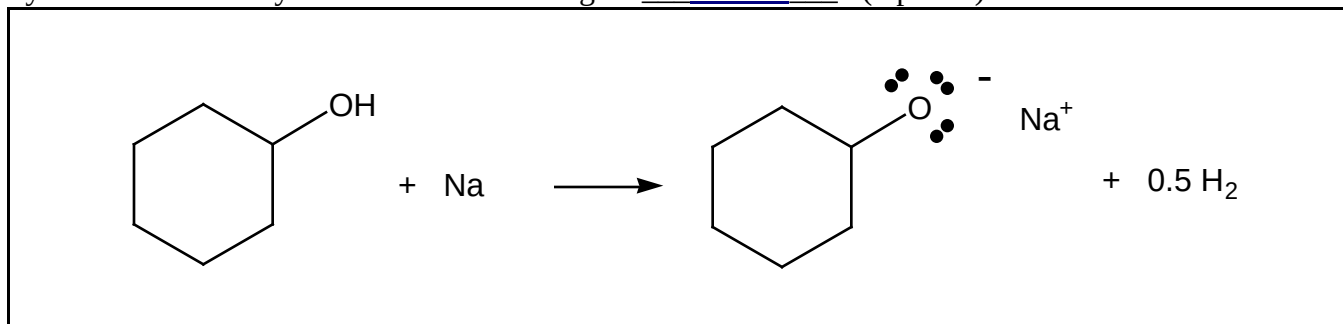
Question 7. Reactions of Alcohols. Ethers. (20 points)

The **Williamson ether synthesis** consists in the reaction of an alkoxide anion with an alkyl halide or alkyl tosylate. Let's look at the Williamson ether synthesis of the ether $C_6H_{11}-O-C_2H_5$. This ether is best made by reaction of the sodium alkoxide of cyclohexanol and ethyl tosylate.

(a) Provide the reaction diagram with complete Lewis structures for the reaction of the sodium alkoxide of cyclohexanol with ethyl tosylate to form the product ether $C_6H_{11}-O-C_2H_5$. (6 points)



(b) Provide a stoichiometric equation for the quantitative formation of the sodium alkoxide of cyclohexanol from cyclohexanol and the reagent sodium. (6 points)



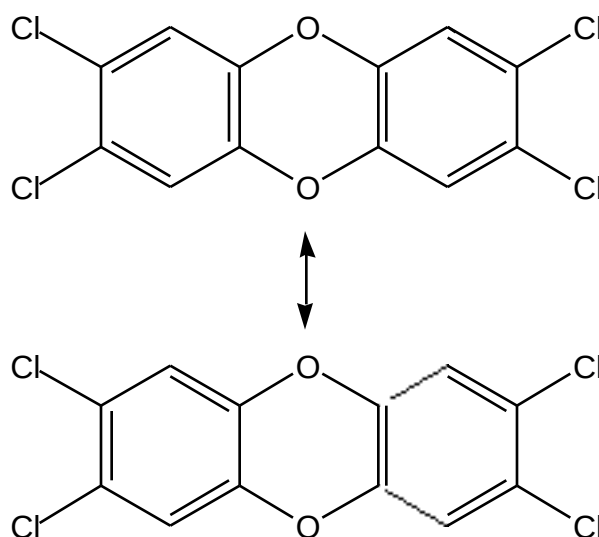
(c) The reaction mechanism of the Williamson ether synthesis is of the SN2 type. This reaction proceeds especially well with _____ (**primary**, secondary, tertiary) substrates. If the ether $C_6H_{11}-O-C_2H_5$ were made by the reaction of sodium ethoxide with the cyclohexyl tosylate, then the nucleophilic substitution reaction would occur at a _____ (primary, **secondary**, tertiary) site and this reaction is expected to be _____ (faster, **slower**). (8 points)

Question 8. Physical Properties of Dioxin. (25 points)

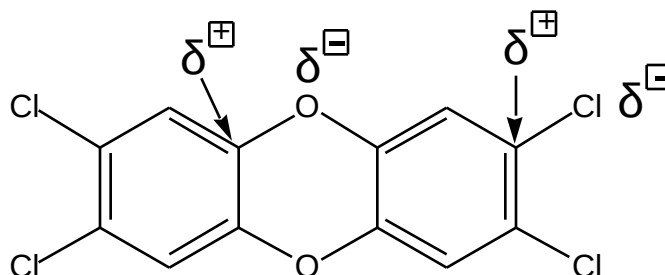
The article “Awakening to a Nightmare of Dioxin”, *Asahi News Service*, November 21, 1997, reported on the adverse health effects of polychlorinated dibenzo-para-dioxins (PCDDs) and specifically talked about the most toxic among them, the compound 2,3,7,8-tetrachlorodibenzo dioxin, TCDD or “dioxin”. Missourians understand this article all too well because a dioxin disaster “hit home” in *Times Beach* about two decades ago. Yet, there is good news at last and dioxin disasters soon will be a thing of the past. Last month, led by the United Nations, representatives from 121 countries drafted a treaty that aims at the elimination of the “dirty dozen” of persistent organic pollutants (POPs) and dioxin is one of them (*The New York Times*, November 28, 2000). The article says the following about the health effects of POPs: “Dr. Thornton and other scientists are concerned about the ability of POP’s to persist in the environment and thus accumulate in fatty tissues of animals and humans. These chemicals can also be moved great distances by air circulation and tend to concentrate in the Arctic. In high doses, they are exceptionally toxic, and even low exposures have caused cancer and damaged reproductive, nervous and immune systems in laboratory animals.”



(a) The Lewis structure of dioxin is shown. Complete the Lewis structure by adding all lone pairs. Dioxin is an aromatic compound and several other resonance forms can be written. Using curved arrows, draw one more resonance form of dioxin using the template provided on the bottom. (8 points)



(b) The electronegativity of oxygen is _____ (give approximate value) and it is _____ (higher, lower) than the electronegativity of _____ (give approximate value) of carbon. The electronegativity of chlorine is _____ (higher, lower) than that of carbon. Provide the partial charges of the indicated atoms, e.g. δ^+ or δ^- . (8 points)



(c) Considering the polarities of the $C\text{---}Cl$ and $C\text{---}O$ bonds in dioxin, what can be said about the molecular dipole moment of dioxin? Address both the magnitude of the dipole moment and, if the molecule has a dipole moment, the direction of the dipole moment. (4 points)

The $C\text{---}Cl$ and $C\text{---}O$ bonds are very polar but all bond dipoles cancel!
The molecule has no permanent dipole moment.

(d) Considering your analysis in (b) and (c), briefly explain why dioxin can “accumulate in fatty tissues of animals and humans.” As much as possible, use the correct terminology for intermolecular interactions (e.g. charge-dipole, dipole-dipole, van der Waals interactions, and so on). (5 points)

The molecule has no permanent dipole moment.
The molecule will mix with other non-polar molecules and not with polar molecules.
Fats contain long non-polar hydrocarbon chains.
Dioxin interacts with fats by way of van der Waals interactions.

