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Final Exam – CHM 1321D

Date: April 20, 2012 **Length: 3 hours**

Professor: Mathieu Frenette

First name : _____ Last name : _____

Student # : _____ Seat number : _____

Instructions:

- Molecular models are permitted
- The exam can be written in pen or in pencil
- Please ask questions if you find anything unclear
- Lone pairs and hydrogens are often implied
    - Formal charges will always be shown if present
- Attempt all questions; partial marks will be given on most questions
- Approximate total number of points: 94 (+ 4 bonus)
    - The marks are given as a guide and are subject to changes
- Total number of pages: 14

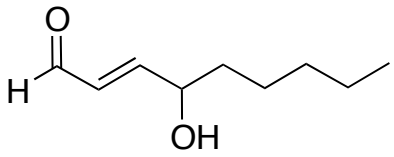
GOOD LUCK!!

Question	1	2	3	4	5	6	7	8	9	10	11	12
Mark												
Question	13	14	15	16	17	18	19	20	21	22	23	Bonus
Mark												

TOTAL:	

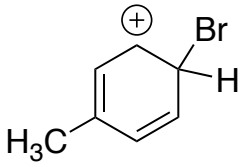
1) Draw the structure of *Z*-3,4-diethylhept-3-en-2-one. **(2 points)**

2) Give the IUPAC name for this lipid oxidation product: **(2 points)**

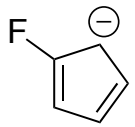


3) Draw the <u>important resonance forms</u> and show the <u>resonance hybrid structure</u> for the following molecules. **(4 points)**

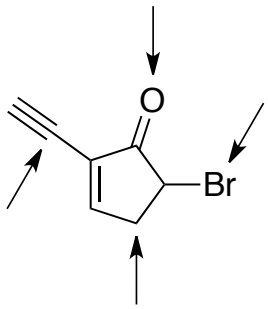
(a)



(b)

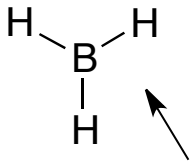


4) Identify the hybrization of each atom indicated by an arrow. **(2 points)**

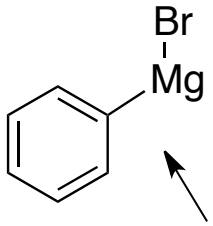


5) Using partial charges (δ^+/δ^-) **<u>and</u>** dipole moment arrows ($\longleftrightarrow$), show the polarization of each bond indicated by an arrow. **(2 points)**

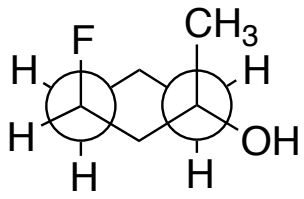
(a)



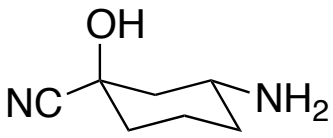
(b)



6) Redraw this Newman projection into a line structure (standard 2-D structure). Use wedges and hashes to indicate stereochemistry. **(3 points)**



7) Assign the configuration of all stereocentres for the molecule below. Draw a constitutional isomer and a diastereomer of this molecule. **(4 points)**

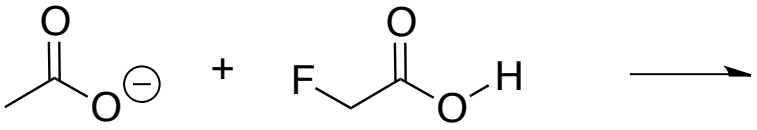


_____ _____

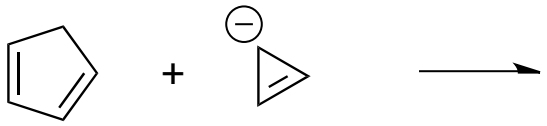
Constitutional Isomer Diastereomer

8) Predict the products for the following acid-base reactions. Include arrows to show the movement of electrons and predict which side of the reaction will be favoured. **(8 points)**

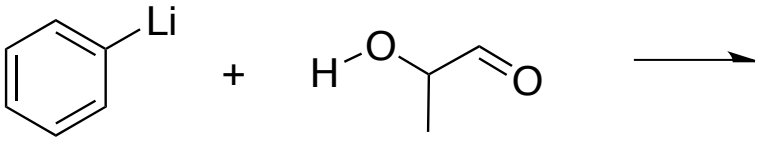
(a)



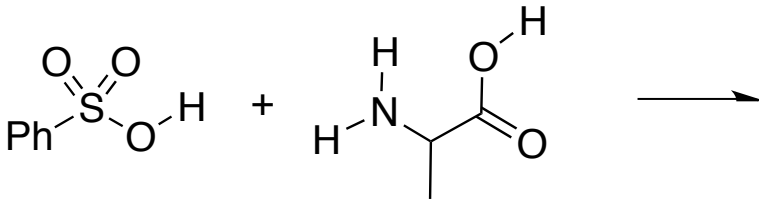
(b)



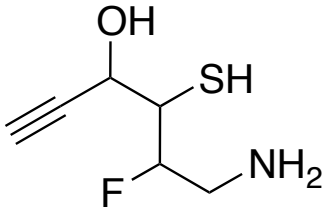
(c)



(d)

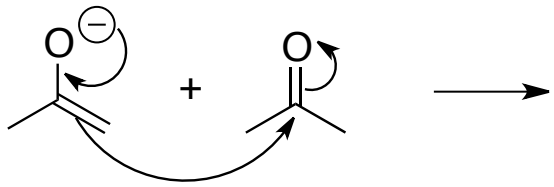


9) Identify the most acidic proton in the molecule below: (**2 points**)



10) Follow the arrow notation and draw the resulting products for the following reactions. These reactions were not covered in class, but you should be able to accurately give the products based on the electron movement. **(4 points)**

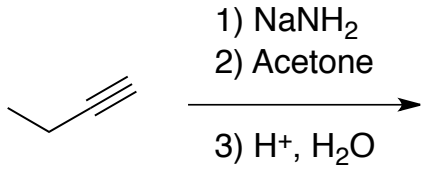
(a)



(b)

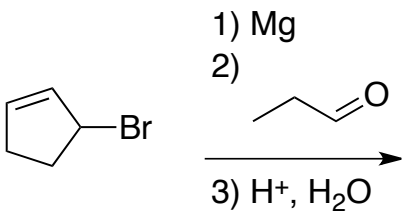
11) Predict the major organic product for the following reactions. Attempt all 6 questions, but only your 5 best answers will be counted. Partial marks will be given; answer all you can. **(10 points)**

(a)



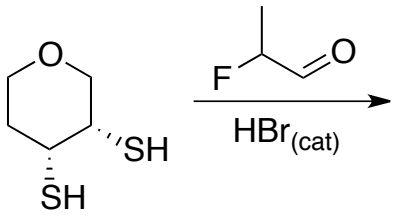
(b)

(c)

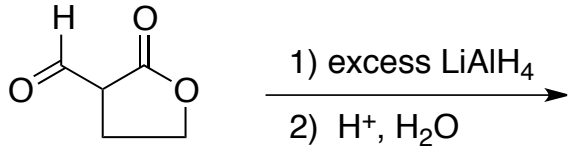


11) (Cont.)

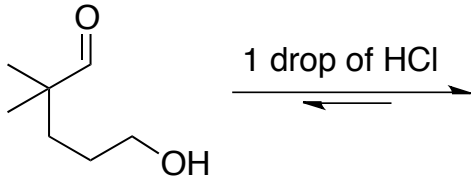
(d)



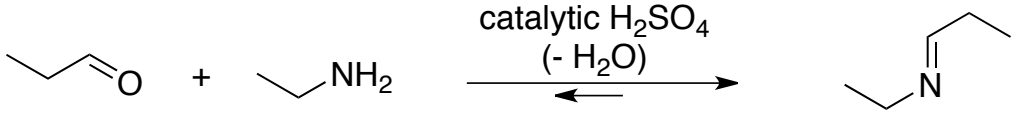
(e)



(f)



12) Show the full mechanism for the following reaction. **(6 points)**



13) A chemistry lab can be a source of unexpected hazards. Circle the best course of action for the following incidents. There may be more than one correct answer; circle all that apply.

(a) You spill a few milliliters of sulphuric acid on your lab coat sleeve, near your hand. You are wearing a t-shirt underneath your lab coat. What should you do? **(2 points)**

I. Make a quick solution of NaOH and titrate yourself.

II. Use a paper towel to clean the sulphuric acid from your lab coat.

III. Activate the emergency shower and fully rinse yourself for at least 15 minutes.

IV. Rinse your arm in the sink under running cold water.

V. Rinse your arm in the sink under running hot water.

VI. Quickly remove your lab coat.

(b) $LiAlH_4$ reductions should be carried out under nitrogen atmosphere in "dry" solvents. A careless researcher did not think of this while adding $LiAlH_4$ to ~100 mL of "wet" tetrahydrofuran (THF) in an open 250mL beaker. *The solvent caught fire!* Which of the following actions are appropriate to undertake? Circle all that apply. **(3 points)**

I. Keep working. The fire will just accelerate the reaction.

II. Announce the fire by loudly saying "Fire! My THF beaker is on fire!"

III. Remain calm.

IV. Remove any flammable solvents and turn off gas lines in the vicinity.

V. If the fire is contained in the beaker, choke it by covering the beaker.

VI. Immediately over-fill the beaker with water.

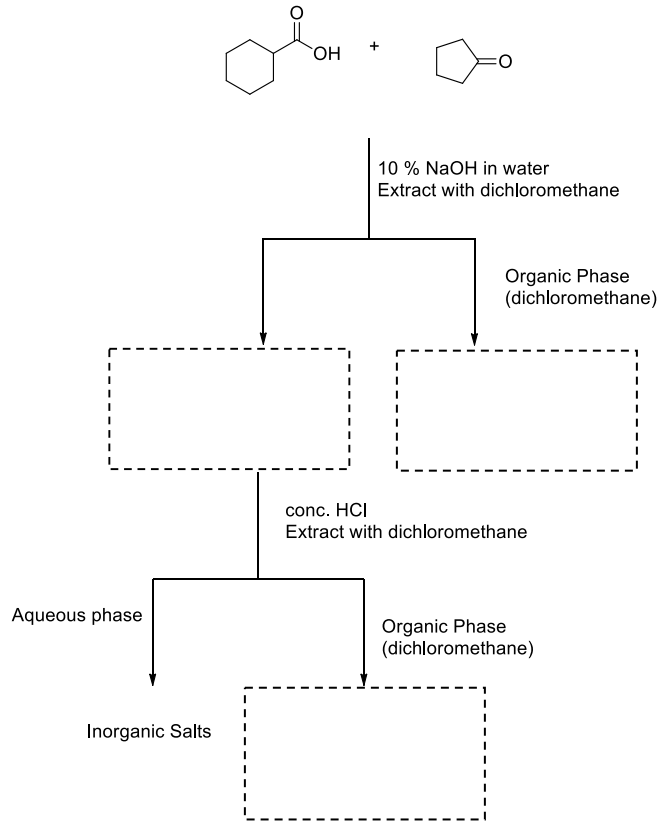
VII. If the fire spreads, pull the fire alarm and lead bystanders to safety.

14) Write a balanced equation for the overall reaction described in the following lab procedure. Do not assume steps such as a standard work-up, etc. **(3 points)**

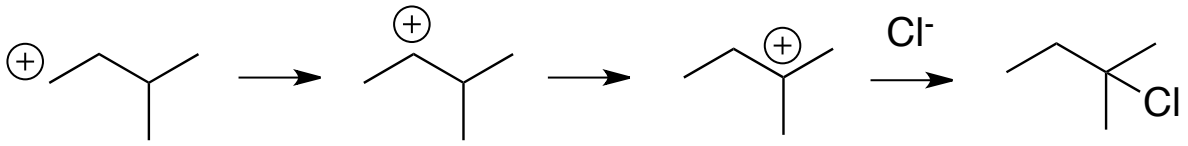
> "Place 0.8 g of magnesium turnings and one or two small crystals of iodine in a 50 mL round bottom flask. Prepare a solution of 3.0 mL of bromobenzene in about 20 mL of anhydrous diethyl ether. […] When the addition of the bromobenzene solution is complete, allow the mixture to boil on its own to ensure that the reaction is indeed taking place. […] Decant the solution carefully with stirring (use a Teflon rod), over a period of 15-30 seconds, into some freshly obtained dry ice powder in a dry 100 mL beaker."

_____ ⟶ _____

15) Complete the following extraction flow chart with the major organic (non-solvent) molecules found at each step of the extraction. **(3 points)**



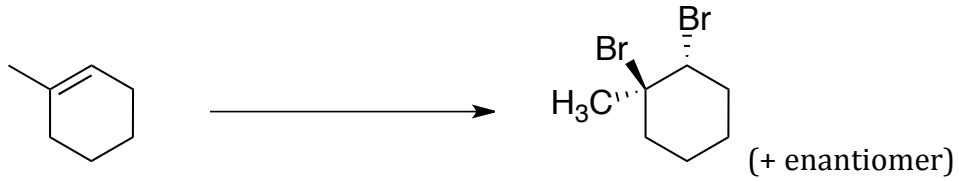
16) Draw a potential energy diagram (also called free energy surface) for the following steps. **(2 points + 1 bonus point for extra accuracy)**



17) Give the missing reagents **OR** the major organic product(s) for the following reactions. **(10 points)**

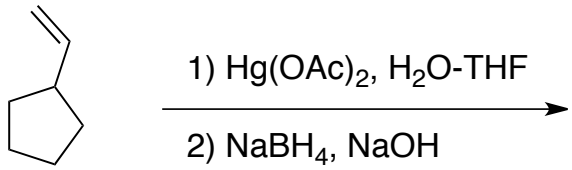
Note: Indicate relative stereochemistry when it is dictated by the reaction. Mechanisms are not required, but part marks may be given for an incorrect answer with a plausible mechanism.

(a)

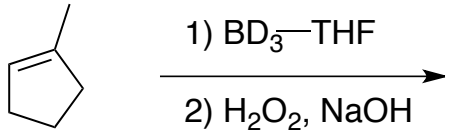


(+ enantiomer)

(b)

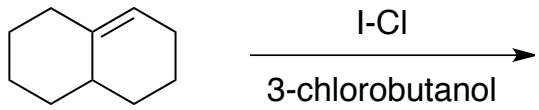


(c) **Note:** D in BD_3 stands for deuterium, which is an isotope of hydrogen.



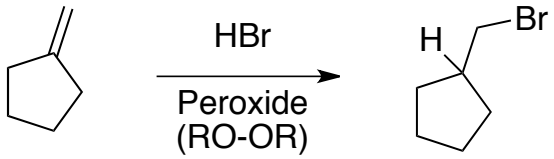
(d)

(e)

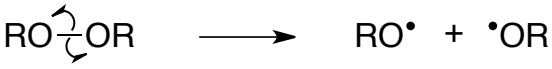


18) Complete the two propagation steps for the following reaction mechanism. **(4 points)**

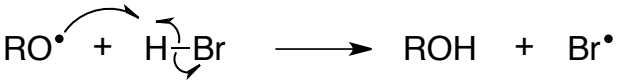
Overall Reaction:



Initiation:

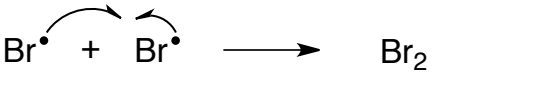


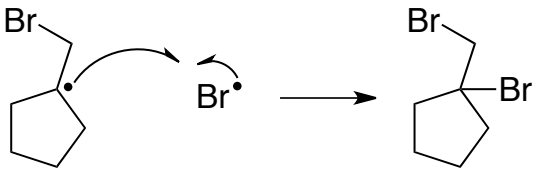
Chain transfer:



Propagation: (2 steps)

Termination: (Recombination of any two radicals from the mechanism)

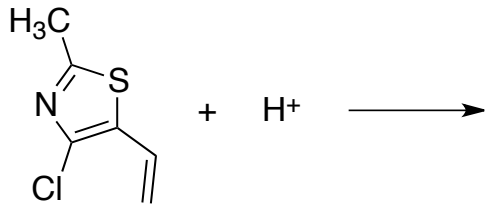




+ others…

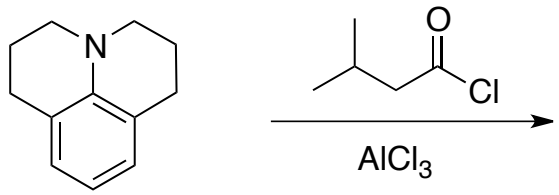
19) Circle <u>all</u> the aromatic molecules below. **(3 points)**

20) At which position would the molecule below preferably protonate? **(2 points)**

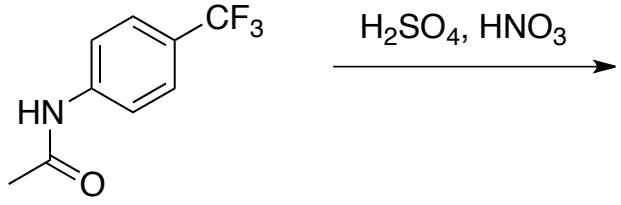


21) Use the table attached at the end this exam and your knowledge of mechanisms to predict which product(s) will be formed during the following reactions. **(4 points)**

(a)

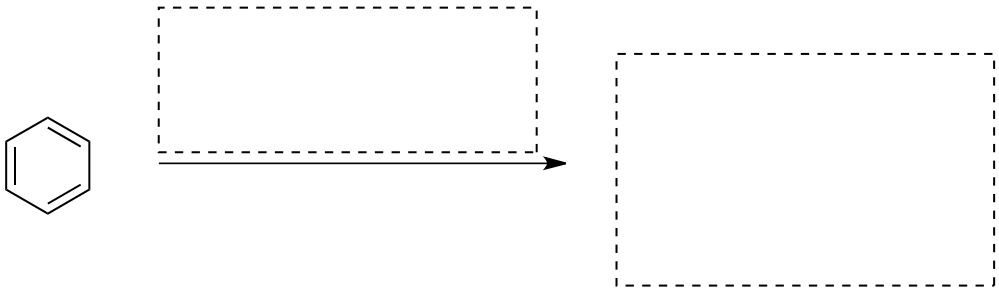


(b)



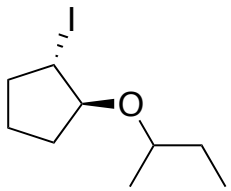
22) Give the complete mechanism for one electrophilic aromatic substitution reaction of your choice on benzene using reagents we have seen in class. **(4 points)**

Overall Reaction:



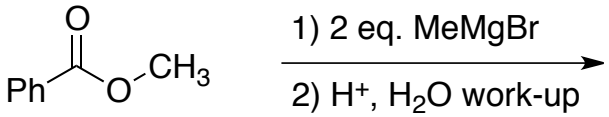
Mechanism:

23) Give a plausible synthesis of the compound below <u>using only alkenes with fewer than 6 carbons</u> and any other reagents not containing carbon as starting materials. More than one step is necessary. **(5 points)**

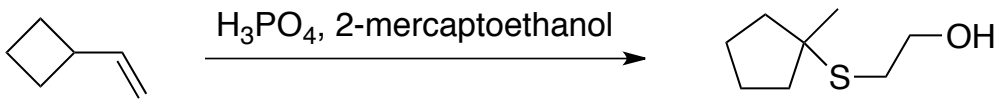


BONUS!!

Give the final product (+ 1 point)



Give a mechanism to account for this transformation. Write your answer at the back of the page. (+ 2 points)



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Summary of Substituent Effects on Electrophilic Aromatic Substitution

Ortho/para directing and activating	*Ortho/para* directing and deactivating	*Meta* directing and very deactivating
$-\ddot{N}R_2$	$-\ddot{F}:$	$-NO_2$
$-\ddot{O}-H$	$-\ddot{Cl}:$	$-\overset{+}{N}R_3$
$-\ddot{O}-R$	$-\ddot{Br}:$	$-CF_3$, $-CCl_3$
$-\ddot{N}HC(=O)R$	$-\ddot{I}:$	$-COOR$
$-R$		$-C(=O)R$
$-Ar$		$-C\equiv N$
		$-SO_3H$

The reactivity order of substituted benzenes in electrophilic aromatic substitution reactions is:

$-\ddot{N}R_2 > -\ddot{O}-H > -\ddot{N}HC(=O)R > -\ddot{O}-R > -R, -Ar > -\ddot{X}: >$ All *meta* directors

Among the *meta* directors, the reactivity order is:

$-C\equiv N, -C(=O)R, -COOH, -SO_3H > -NO_2, -\overset{+}{N}R_3, -CF_3$