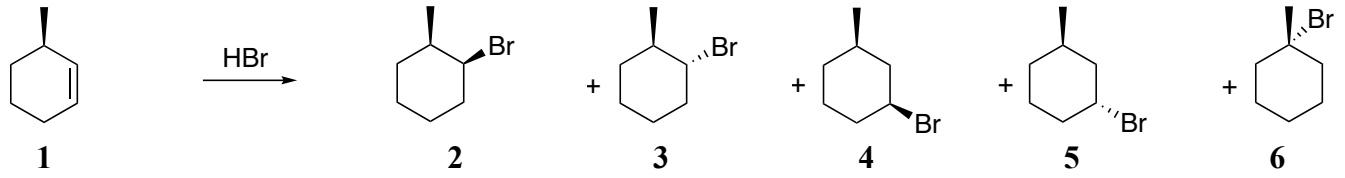
JOHN ABBOTT COLLEGE
ORGANIC CHEMISTRY: 202-DCP-05

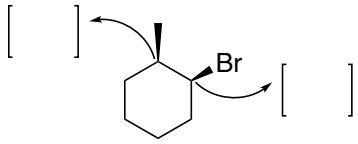
3-hour FINAL EXAMINATION Fall 2020

Question 1 :



1 **2** **3** **4** **5** **6**

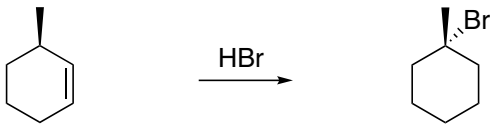
a) Consider compound **2**, assign the stereochemistry of each labeled carbon:



b) Give the full chemical name of compound 1: _____

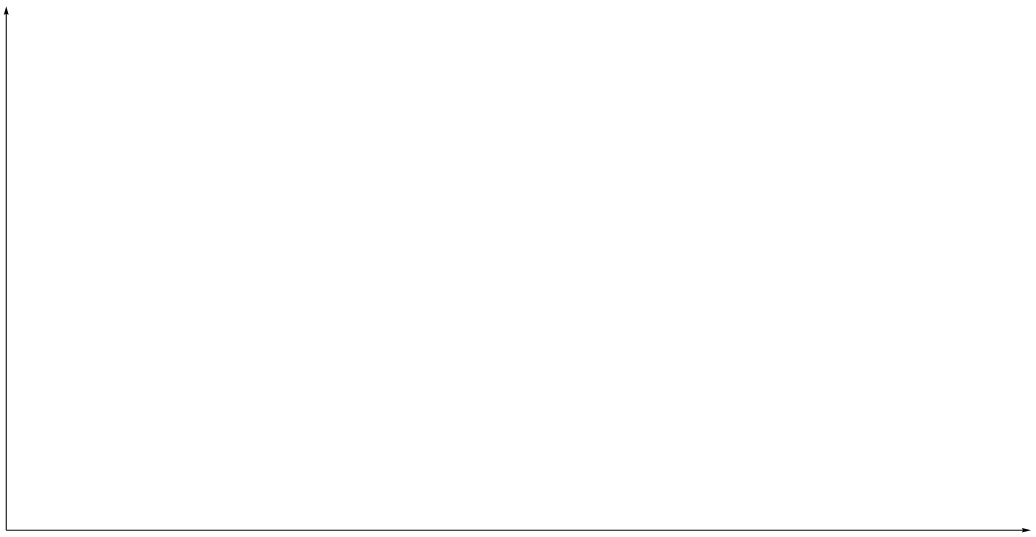
c) Give the full chemical name of compound 2: _____

d) Provide a mechanism for the formation of product **6** when compound **1** reacts with hydrobromic acid. Use the curved arrow formalism.

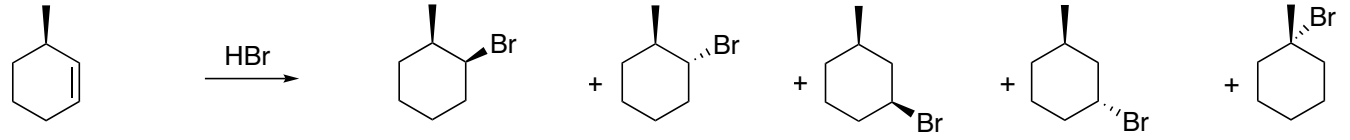


1 **6**

e) Using the axes below, represent the energy changes in the reaction above (**1 d)** reaction of compound **1** with HBr to yield product **6**). Label the axes. Respect the relative activation energy of each step. Assume the overall reaction is exothermic.



Question 1 continued:



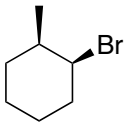
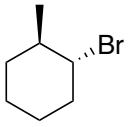
1 **2** **3** **4** **5** **6**

f) Isomeric relationship between compound **2** and compound **3:** _____

g) Isomeric relationship between compound **3** and compound **4:** _____

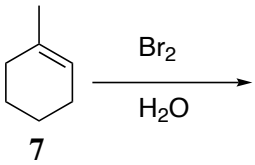
h) Consider compounds **2** and **3** below**:**

i) Draw the two chair conformations for each alkyl bromide, and circle the most stable chair conformer;
ii) Give all possible elimination product(s) obtained from each alkyl bromide under second order reaction conditions (E2); and
iii) Give all possible elimination product(s) obtained from each alkyl bromide under first order reaction conditions (E1).

	Chair Conformations	Possible E2 product(s)	Possible E1 product(s)
 2			
 3			

i) Consider the reaction of compound **7** below with bromine:

i) Draw a 3-D structure of the intermediate for the rate limiting step;
ii) Provide the structure of the major product.
iii) Pay attention to stereochemistry.



7

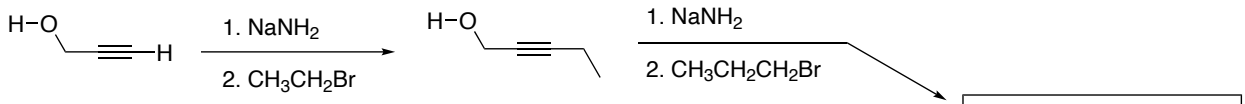
Intermediate	Major product

iii) Explain the source of regioselectivity of your major final product using suitable chemical structures.

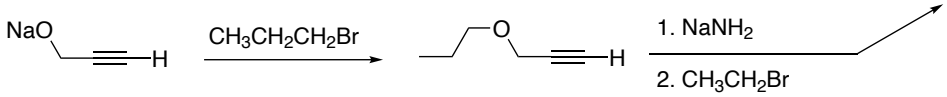
Question 2: Consider the two synthetic pathways (**Synthesis I** and **Synthesis II**), which would lead to a common final product:

Note that each reagent is used in stoichiometric amounts (no excess).

Synthesis I



Synthesis II



a) Which path would be better, Synthesis **I** or Synthesis **II**? Circle one. Explain why the other synthesis would not be suitable. You may include a mechanism to justify your answer.
b) Draw a stepwise mechanism of the best synthesis (**I** or **II**) to show the formation of the final product. Use curved arrow formalism and draw every intermediate.
c) Draw the transition state of the first step of **Synthesis II**.

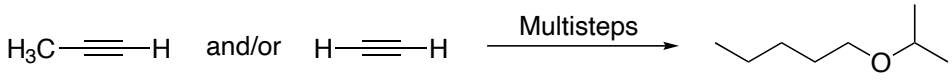
Question 3: Propose one synthetic route for the following two syntheses.

If two syntheses are provided, only the first one will be graded for marks.

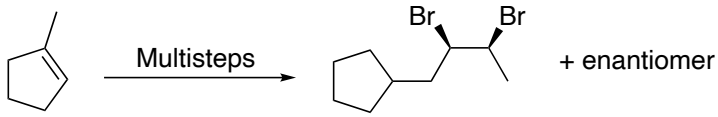
i. Provide a retrosynthetic analysis for **synthesis A** or **synthesis B.**

ii. Provide the reagents (and conditions, if necessary) required to complete **synthesis A** or **synthesis B**:
Take the following requirements into consideration:
- Carbon-containing molecules to be incorporated into the structures must be synthesized from propyne (CH_3CCH) or acetylene (HCCH).
- Show the product of each transformation.
- Pay attention to stereochemistry when applicable.

Synthesis A:



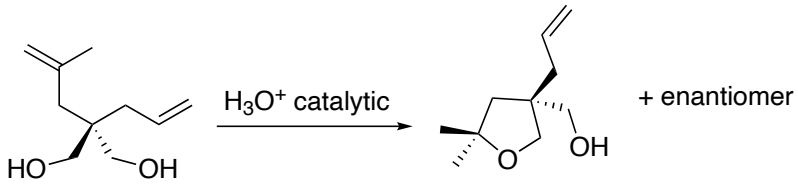
Synthesis B:



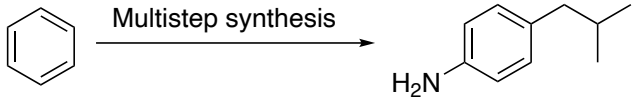
Retrosynthesis:

Synthesis:

Question 4: Provide a mechanism for the following transformation, from the diol to one of the two enantiomers. Use the curved arrow formalism. Draw the structure of each intermediate.

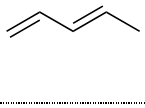


Question 5: Propose a synthetic route for the synthesis below. Provide the reagents (and conditions, if necessary) required to complete the synthesis and show the product of each transformation.



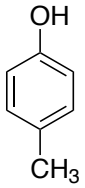
Question 6:

a) Consider the following molecules and label them as aromatic, anti-aromatic, or non-aromatic.

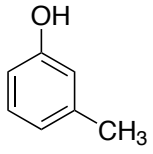
	 **A**	 **B**	 **C**	 **D**	 **E**	 **F**
Aromatic						
Anti-Aromatic						
Non-Aromatic						

b) Which of compounds **A**, **B**, **C**, or **D** will be the strongest acid? Justify your choice with the relevant chemical structure(s).

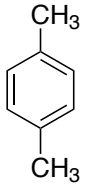
Question 7: Consider the following molecules:



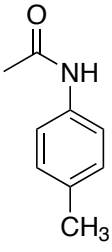
A



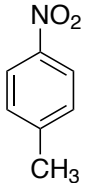
B



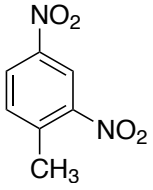
C



D



E



F

a) Which molecule is **<u>most</u>** reactive toward electrophilic aromatic substitution?

Letter: ____. Briefly explain:

b) Which molecule is **<u>least</u>** reactive toward electrophilic aromatic substitution?

Letter: ____. Briefly explain:

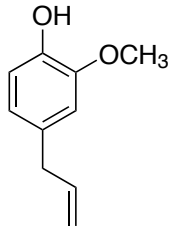
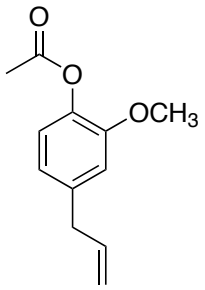
c) Provide the full name of compound **F** above: _____

d) For the transformation below:

i. Provide the appropriate reaction conditions.

ii. Provide a mechanism for the transformation, using the curved arrow formalism. Draw the structure of each intermediate, including the formation of the electrophile and all relevant resonance structures.

Question 8: Your goal is to isolate two essential oils, Eugenol and Acetyleugenol, from cloves by steam distillation.

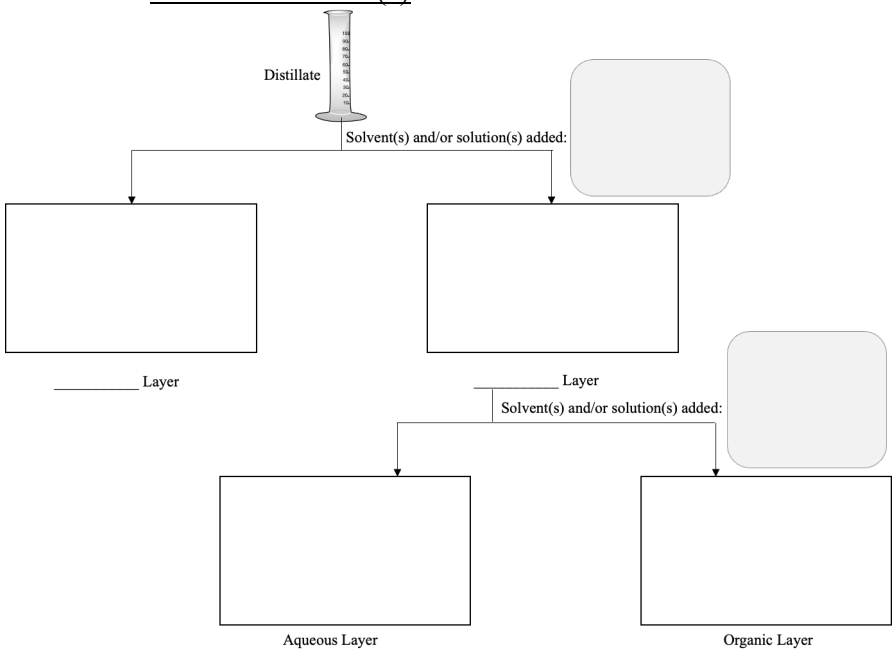
		**a)** Which substance/s do you expect to collect in the distillate?
Eugenol (E)	Acetyleugenol (AE)	
bp = 254 °C	bp = 281-286 °C	

b) What do you expect the temperature reading to be while the distillate is being collected?_____

c) Once the steam distillation is completed, show how you would extract from the distillate the two essential oils, and separate acetyleugenol from eugenol using acid/base extraction methodology. The following solvents/solutions are available to you:

tert-Butyl methyl ether	10% CH_3CO_2H aqueous solution	3 mol/L NaOH
Ethanol	Deionized water	NH_4Cl saturated aqueous solution
3 mol/L HCl	NaCl saturated aqueous solution	10% $NaHCO_3$ aqueous solution

Complete the flow sheet below, including the nature of each phase; the solvent(s)/solution(s) required; relevant chemical structures and relevant chemical reaction(s).



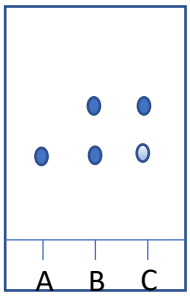
Question 8 continued:

d) After separation and complete recovery of the two essential oils a TLC was taken to assess whether the separation was successful. See results below.

i) Assign each lane with the appropriate letters: **EE** (Eugenol Extract), **AEE** (Acetyleugenol Extract), and **Co** (co-spot):

Lane A: _____ Lane B: _____ Lane C: _____

(1 mark)

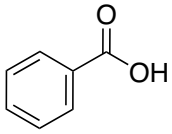


ii) Based on this TLC picture, was the separation using acid/base extraction methodology successful? Briefly explain.

(2 marks)

e) A student suggested to take melting point in order to identify and assess the purities of the oils. Is this a good idea? Circle yes or no and explain in ONE sentence.

Question 9: You have to re-crystalize benzoic acid and are provided with the two following solvents: water and ethanol. Please note that benzoic acid is soluble in both solvents at elevated temperatures.



a) Circle the solvent that will be best choice for the recrystallization of benzoic acid. Water or Ethanol?

b) Explain your decision. Make sure to support your decision with intermolecular forces arguments. (No more than 30 words)

c) Complete the recrystallization procedure below of benzoic acid. Fill the blanks or circle **one** appropriate answer.

1. Accurately mass 1 gram of benzoic acid and place in _____ (piece of glassware).

   Recrystallize the compound in the solvent chosen above:

2. Initially use (**1 mL / 5mL / 10mL**) of (**cold / warm / hot / boiling**) solvent to dissolve benzoic acid.

3. While keeping the mixture at (**cold / warm / hot / boiling**) temperature, add (**approximately/precisely**)

   (**1 mL / 5mL / 10mL**) of (**cold / warm / hot / boiling**) solvent, until _____

   _____.

4. Then let the solution _____

   _____.

5. When ready, filter the benzoic acid crystals by suction filtration.

6. Wash the crystals with (**1 mL / 5mL / 10mL**) of the (**cold / warm/ hot /boiling)** solvent that you used for the recrystallization, repeat a second time.

7. Let your crystals dry before taking a melting point to assess purity.

Organic Chemistry Exam Information Sheet

THE PERIODIC TABLE of ELEMENTS

1 A												3 A	4 A	5 A	6 A	7 A	8 A
1 H 1.008	2 A						8 B			1 B	2 B						2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.990	12 Mg 24.305	3 B	4 B	5 B	6 B	7 B	8	9	10	1 B	2 B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.30
55 Cs 132.9	56 Ba 137.3	57 La * 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac ** (227)	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

*	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
**	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

Selected Compound List

Acetic acid	Heat (Δ)	NBS
Acetone	$Hg(OAc)_2$	NH_2NH_2
Acetonitrile	HNO_3	NH_3
$AlCl_3$	HX	Pd/C
BH_3/THF	$KMnO_4$	Pt
CCl_4	Li	RCO_3H
CH_2Cl_2	Light (hν)	R-COX
DMF	Lindlar's catalyst	$R\text{-}O^-$
DMS	MeOH	R-OH
DMSO	Na	ROOR
EtOH	$Na_2Cr_2O_7$	R-O-R
FeX_3	$NaBH_4$	R-X
H_2	NaH	Water
H_2O_2	$NaNH_2$	X^-
H_2SO_4	$NaNO_2$	X_2
HCl	NaOH	Zn(Hg)

X = appropriate halogen

Work sheet: