DAWSON COLLEGE

DEPARTMENT OF CHEMISTRY & CHEMICAL TECHNOLOGY

FINAL EXAMINATION
CHEMISTRY 202-BZF-05
Monday, December 13, 2010
2:00 PM - 5:00 PM

Name:_____***SOLUTION*** _____ **Student Number:**_____

Final Examination Rules

Before you begin your exam:

1. Any student found with an electronic communication device IN THEIR POSSESSION (from the moment they step into the exam room until they pick up their bags after finishing their exam) **whether it is used or not** WILL BE DISQUALIFIED. *(If you do have an electronic communication device, notify an invigilator immediately.)*
2. All pencil cases, calculator covers must be below your chair and only I.D. cards, pens, pencils, erasers, calculators and any other allowed course specific materials can be on your desk.
3. Programmable calculators are not permitted. Calculators may not be shared.
4. You may not open the examination booklets, or read examination questions prior to the commencement of the exam. The examination coordinator or his/her representative will announce the beginning and the end of each examination.
5. Write your name and fill out any other required information on the cover page of your exam.

During the exam:

6. You are not allowed under any circumstances to get up during the exam without permission.
Look for your exam number on the SIGN IN sheet that will be brought around by your teacher and sign your name.
7. You are not allowed to leave the gym area during the first hour of the exam.
8. If you need to use the washroom, raise your hand and an invigilator will come see you.
9. You are expected to abide by the rules outlined by the examination proctor or his/her delegate and be aware of College policy regarding cheating and plagiarism.

Once you finished your exam:

10. Raise your hand and stay seated until your teacher will come see you.
11. During the last 15 minutes of the exam, no students are allowed to leave.
12. Once the examination coordinator announces the end of the exam, everyone must stay seated, quietly, until all exams are collected.

Final Examination Instructions

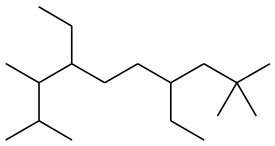
1. This exam set consists of **13** questions. Please ensure that you have a complete set.
2. Answer all questions in the space provided. No books or extra paper are permitted.
3. **Do not detach** any of the sheets in this package.
4. Your attention is drawn to the College ISEP policy on cheating.
5. Calculators are not permitted. Molecular models are permitted but cannot be passed to other students

MARK DISTRIBUTION

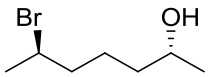
Q1._____	/4	Q6._____	/6	Q11._____	/11
Q2._____	/4	Q7._____	/21	Q12._____	/7
Q3._____	/5	Q8._____	/2	Q13._____	/6
Q4._____	/4	Q9._____	/5	**TOTAL**_____	**/92**
Q5._____	/8	Q10._____	/9		

QUESTION 1 [4 marks]

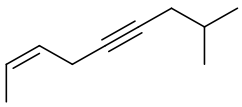
Provide IUPAC names for the following compounds and, where applicable, include R/S or E/Z designation to indicate stereochemistry. (1 mark each)

a) 

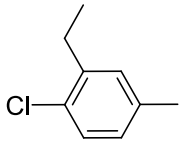
4,7-diethyl-2,2,8,9-tetramethyldecane

b) 

(2*R*,6*R*)-6-bromoheptan-2-ol

d) 

(*Z*)-8-methylnon-2-en-5-yne

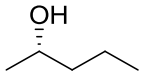
e) 

1-chloro-2-ethyl-4-methylbenzene

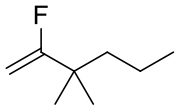
QUESTION 2 [4 marks]

Provide the bond-line structures for each of the following names: (1 mark each)

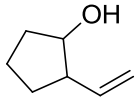
a) *(S)*-pentan-2-ol



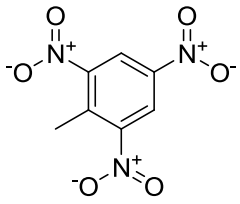
b) 2-fluoro-3,3-dimethylhex-1-ene



c) 2-vinylcyclopentyl alcohol



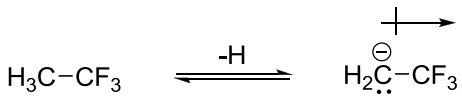
d) 2,4,6-trinitrotoluene



QUESTION 3 [5 marks]

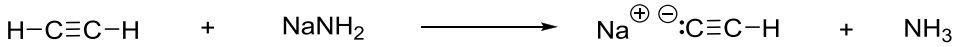
i) The pK_a of 1,1,1-trifluoroethane (CH_3CF_3) is 32; whereas, the pK_a of ethane is 50. Explain the factor that contributes to the lowering of the pK_a of 1,1,1-trifluoroethane. (1 mark)

The negative charge on the carbon of the conjugate base of CH_3CF_3 is inductively stabilized by the electron-withdrawing $-CF_3$ substituent



ii) Considering the following reaction between sodium amide ($NaNH_2$) and acetylene (C_2H_2),

(* pK_a of NH_3 = 38; pK_a of C_2H_2 = 25; pK_a of ethanol = 18; pK_a of water = 15.7)

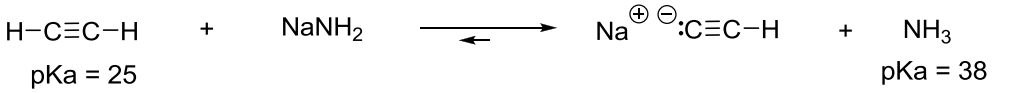


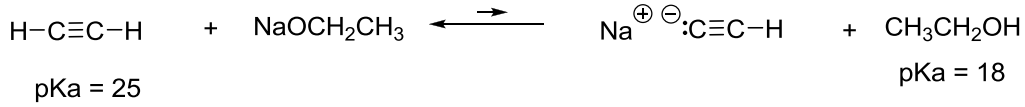
a) The choice of solvent is critical. For instance, the solvent cannot be water. Why? (1 mark)

Because water, a better acid than acetylene, will instead react with $NaNH_2$

b) Would the reaction provide the same product(s) if we use sodium ethoxide in place of sodium amide? Explain your reason using the given pKa values. (2 mark)

The equilibrium of acid-base reactions always favours the direction that leads to a WEAKER ACID (or base). For this reason, sodium ethoxide cannot be an alternative choice to sodium amide



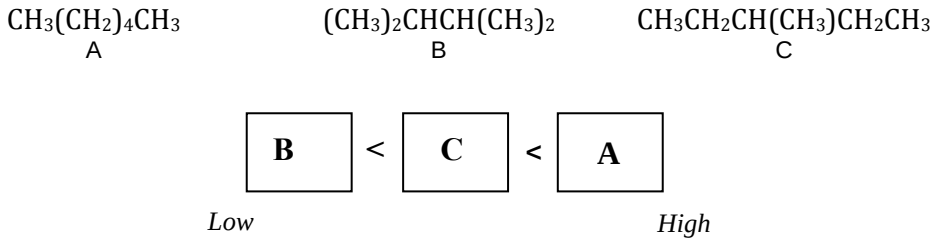


iii) In general, the nucleophilicity of an atom parallels the basicity of the atom; if the atom is highly basic, it is also a good nucleophile. This statement, however, cannot be applied when looking at halides. For instance, iodide (I^-) is a very weak base but is a strong nucleophile. Why? Provide your answer in no more than two sentences (1 mark)

Although iodide is a weak base, it is a strong nucleophile due to its high polarizability

QUESTION 4 [4 marks]

i) List the following alkanes in order of increasing boiling point. (1 mark)



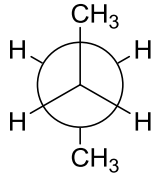
ii) Which compound in each pair has the higher boiling point? Circle the compound of your choice. (1 mark)

a) $(CH_3)_3CBr$ or **$CH_3CH_2CH_2CH_2Br$**

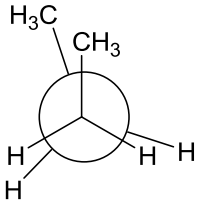
b) $CH_3CH_2CH_2OCH_2CH_3$ or **$CH_3CH_2CH_2OH$**

iii) Provide the most <u>and</u> the least stable Newman projections of butane along its C2-C3 bond. (2 marks)

Most stable



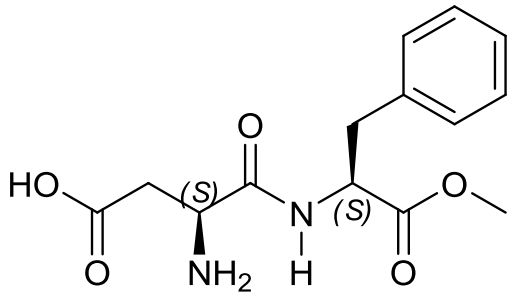
Least stable



QUESTION 5 [8 marks]

i) Aspartame, whose structure is drawn below, is an artificial sweetener. a) Indicate all carbon stereocentres (also known as chiral centres) by putting an asterisk (*) next to each stereocentre. b) For those chiral centres you determined from Part a), assign its (or their) R/S configuration.

[1 mark for a), 2 marks for b)]



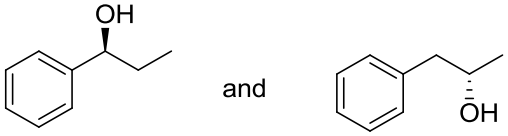
Aspartame

ii) For each of the following pairs of structures, give the stereochemical relationship either as identical, consititutional isomers, enantiomers and/or diastereomers.

(1 mark each)

a) 

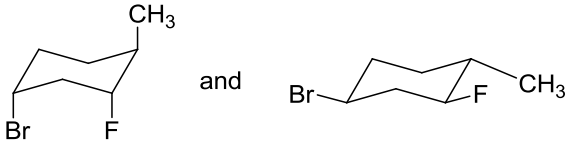
Identical

b) 

Constitutional Isomers

c) 

Identical (meso compound)

d) 

Enantiomers

e) 

Diastereomers

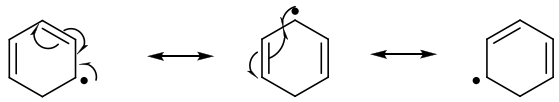
QUESTION 6 [6 marks]

i) For each of the following molecules below, provide all possible resonance structures.

(2 marks each)

a)

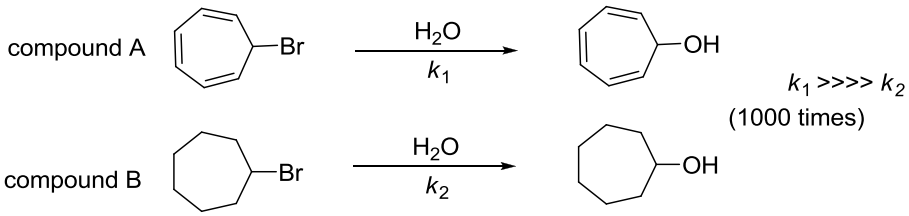
b)

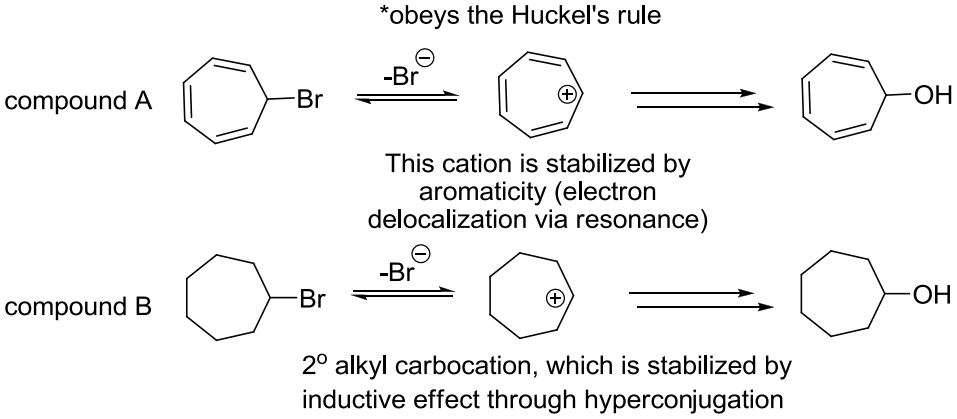


radical

ii) Explain the following observation: cycloheptatrienenyl bromide (compound A) undergoes solvolysis in H_2O nearly 1000 times faster than the analogous 1-bromocycloheptane (compound B).

(2 marks)





since the aromaticity (or resonance) can better stabilize the carbocation, the solvolysis of compound A will proceed faster

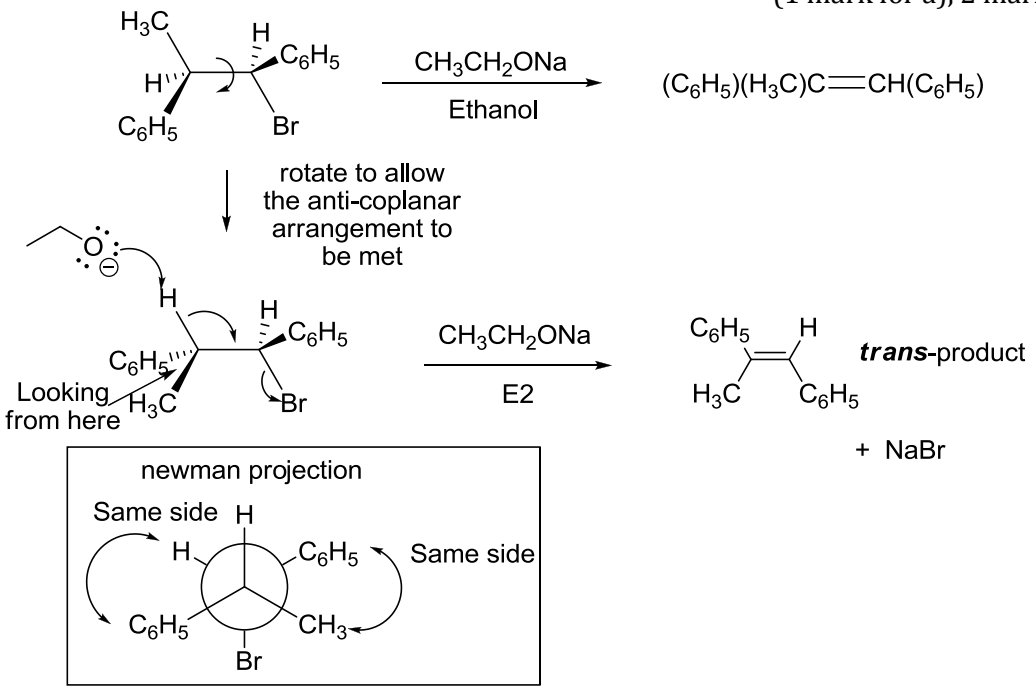
QUESTION 7 [21 marks]

i) Each of the following statements below is written in reference to reactions (S_N1, S_N2, E1 and E2) of alkyl halides. Circle the mechanistic symbol(s) [*no more than two*], that is (or are) most consistent with each statement: (0.5 mark each, 3 marks)

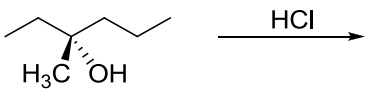
a)	involves carbocation intermediate	**S_N1**	S_N2	**E1**	E2
b)	is first order in alkyl halide and first order in **nucleophile**	S_N1	**S_N2**	E1	E2
c)	involves complete inversion of configuration at the site of the substitution	S_N1	**S_N2**	E1	E2
d)	substitution at the chiral centre gives predominantly a racemic mixture	**S_N1**	S_N2	E1	E2
e)	rearrangements are common	**S_N1**	S_N2	**E1**	E2
f)	order of reactivity for alkyl halide follows $3^o > 2^o > 1^o$	**S_N1**	S_N2	E1	**E2**

ii) Treatment of the following stereoisomer, 1-bromo-2,3-diphenylpropane, with sodium ethoxide in ethanol gives stereoisomer of 1,2-diphenylpropene. a) Predict whether the product is a *Z* or *E* isomer. b) Show the complete mechanism for the product formation.

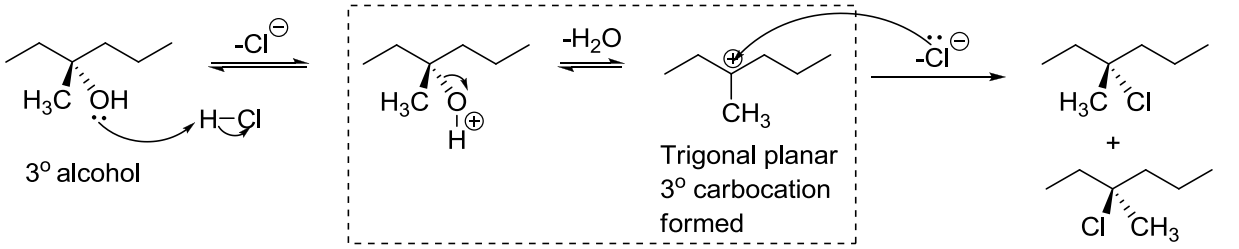
(1 mark for a), 2 marks for b))



iii) Write out the reaction mechanism for the product(s) formed when (*R*)-3-methylhexan-3-ol reacts with HCl. What is the rate determining step? Would doubling the concentration of HCl affect the rate of the reaction? (3 marks)

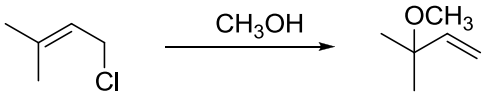


Doubling concentration would NOT affect the rate of reaction since the reaction is unimolecular (the first order to [alkyl halide] only)



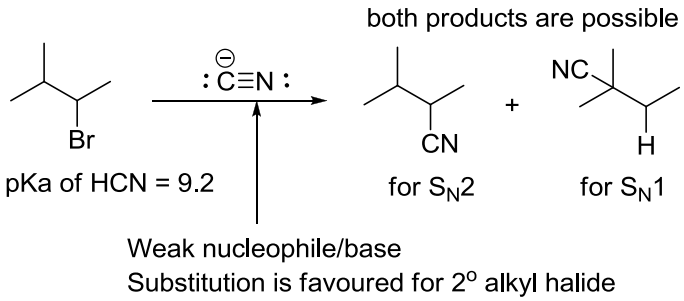
iv) Circle one mechanism that is most consistent with the given conditions and draw the major product for each of the following reactions. (2 marks each, 8 marks total)

a)



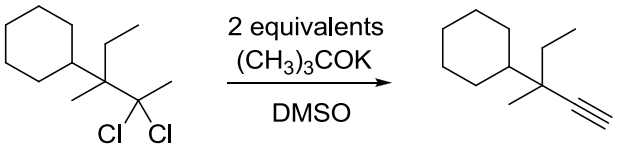
S_N1 S_N2 E1 E2

b)



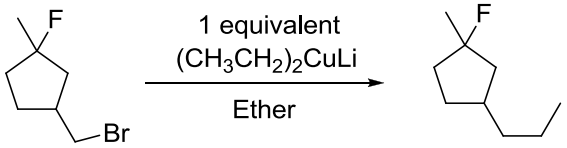
S_N1 **S_N2** E1 E2

c)



S_N1 S_N2 E1 **E2**

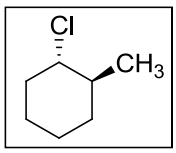
d)

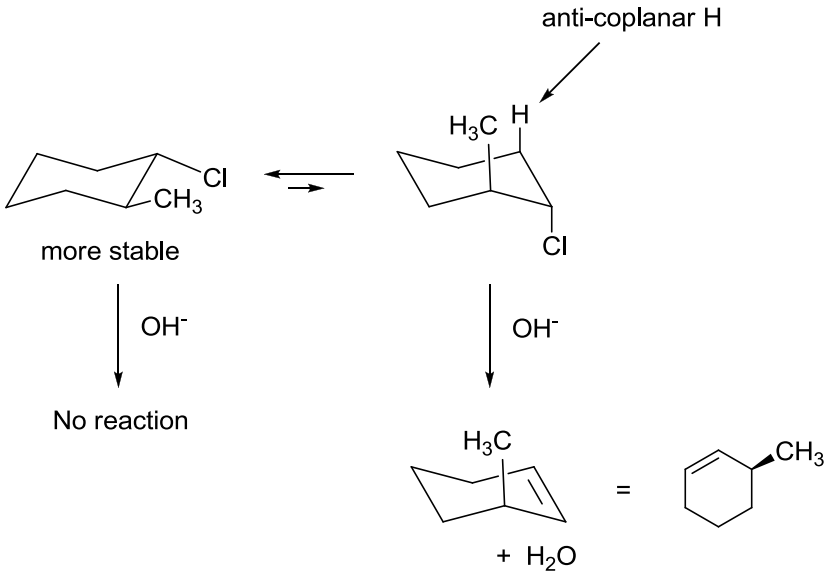


S_N1 **S_N2** E1 E2

v) a) Draw the two chair conformations of the following *trans*-1-chloro-2-methylcyclohexane. b) Indicate which one of the two conformers is more stable? c) Which one of the two conformers will undergo a faster E2 reaction using sodium hydroxide as base?

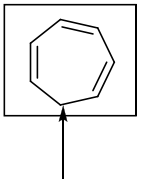
(2 marks for a), 1 mark for b), 1 mark for c))





QUESTION 8 [2 marks]

Determine if cycloheptatriene is aromatic or not. Explain.



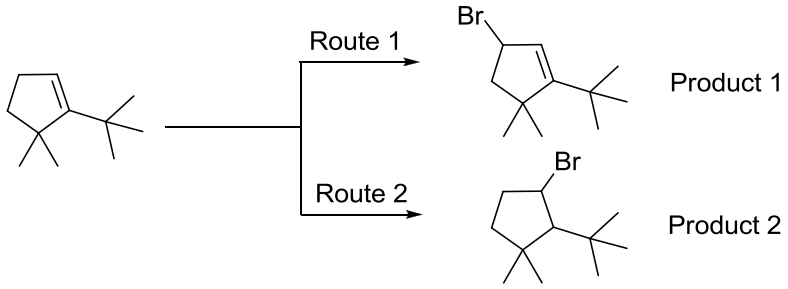
Cycloheptatriene is **NOT** aromatic

Reason – Not all carbons in the ring have available free p-orbitals to delocalize pi-electrons

This carbon is sp^3-hybridized

QUESTION 9 [5 marks]

Using the same starting material, two synthetic routes were explored:



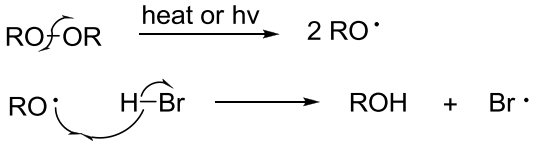
i) Indicate the reagents required in each of route 1 and route 2. (2 marks)

Route 1: **NBS and one of hv or ROOR**

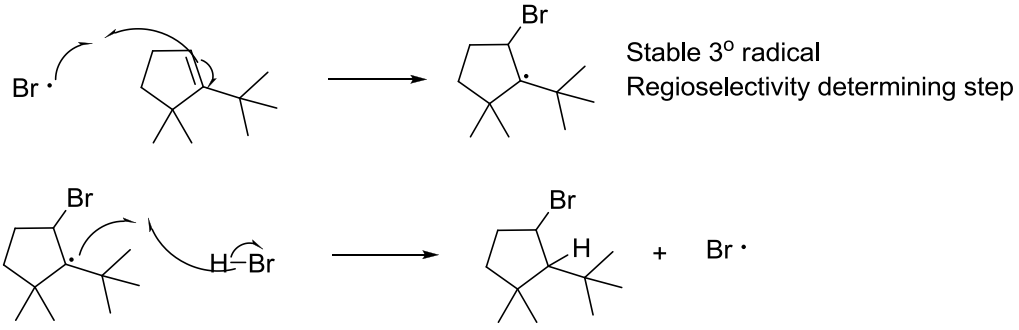
Route 2: **HBr and one of heat, hv or ROOR**

ii) Using curved-arrow, provide the complete mechanism to show the formation of product 2. (3 marks)

Initiation

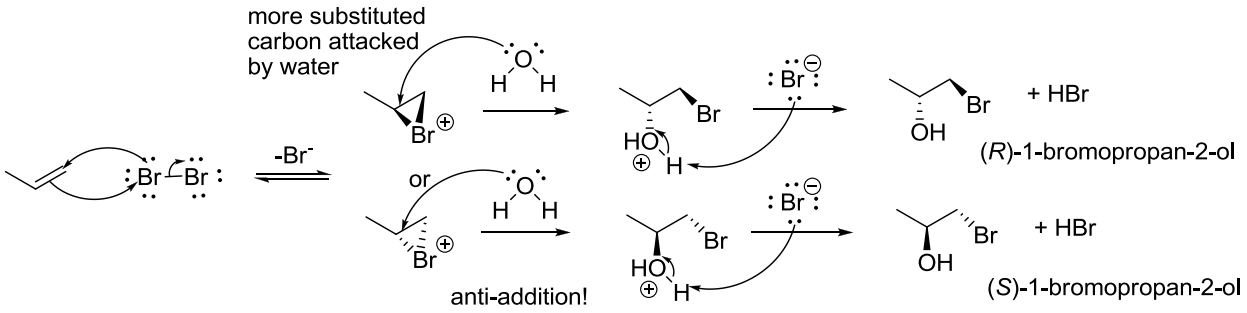


Propagation

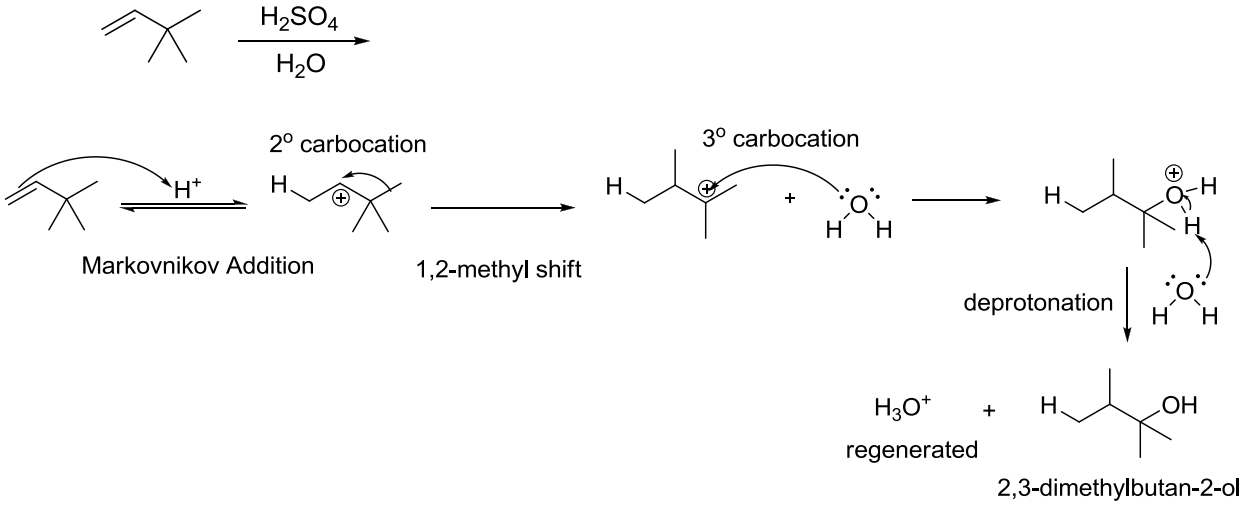


QUESTION 10 [9 marks]

i) Show the mechanism for the formation of the racemic products when propene gas is passed through an aqueous solution containing Br_2. (2 marks)

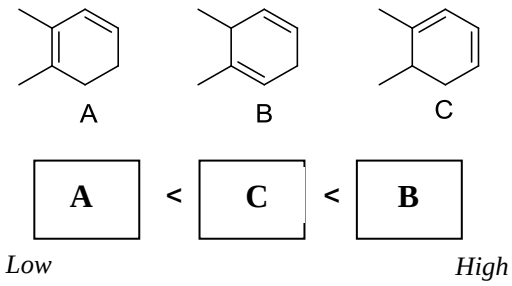


ii) When 3,3-dimethyl-but-1-ene is treated with water in the presence of a catalytic amount of H_2SO_4, the reaction results in the production of 2,3-dimethyl-butan-2-ol. Draw the mechanism to account for this observation. (3 marks)

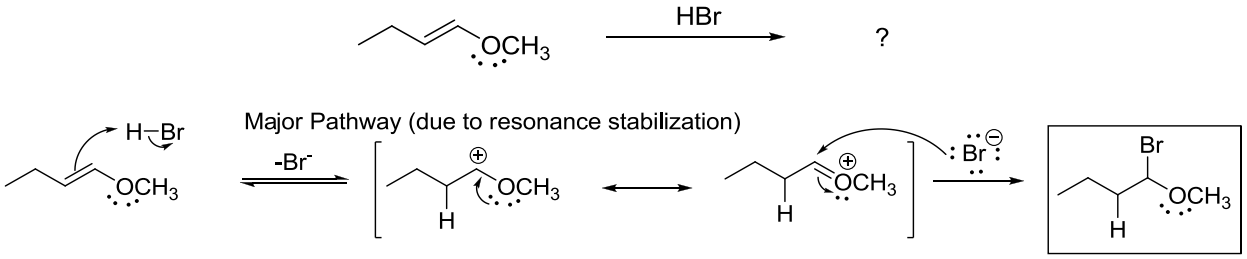


iii) Rank the following dienes in order of increasing heat of hydrogenation.

(2 marks)

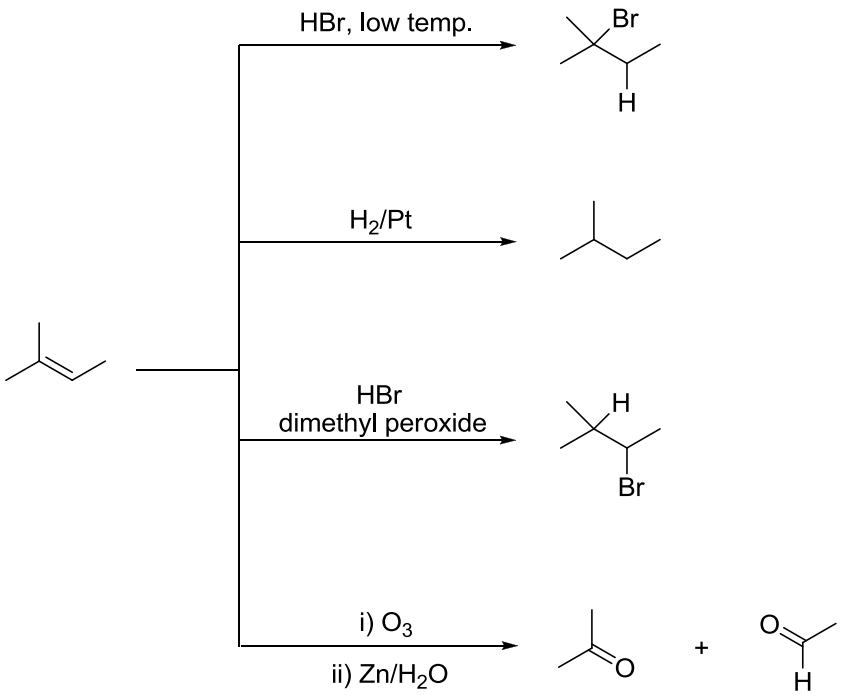


iv) The following alkene undergoes a regioselective addition with HBr. Provide the structure of the only product formed and explain your answer. (2 marks)

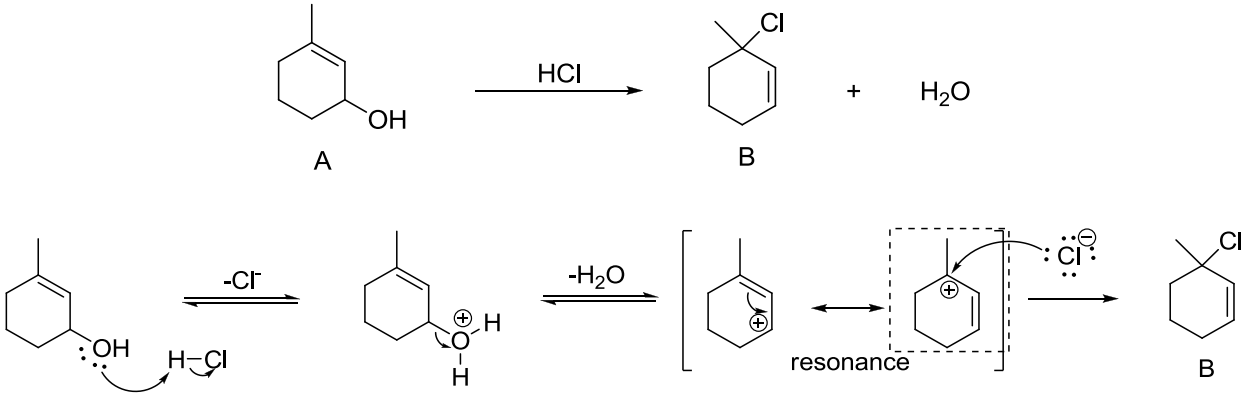


QUESTION 11 [11 marks]

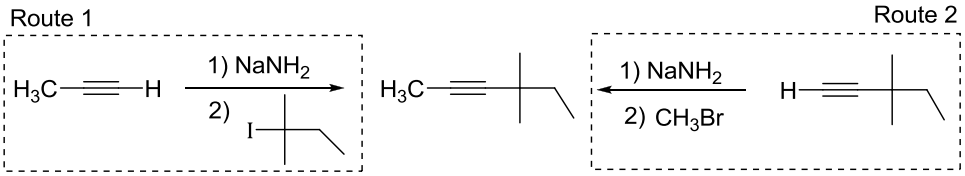
i) Provide the structure of product(s) for the reaction of 2-methyl-2-butene with each given reagent. (1 mark each, 4 marks total)



ii) When allylic alcohol A was treated with HCl, the reaction resulted in an allylic chloride, B. Draw a plausible mechanism that illustrates the formation of product B. (2 marks)

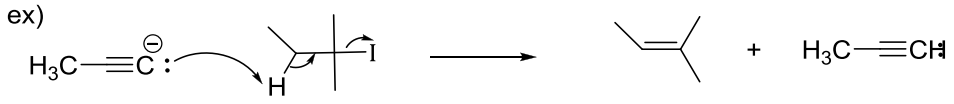


iii) Which of the two routes would provide the desired alkyne product? Explain your answer. (2 marks)

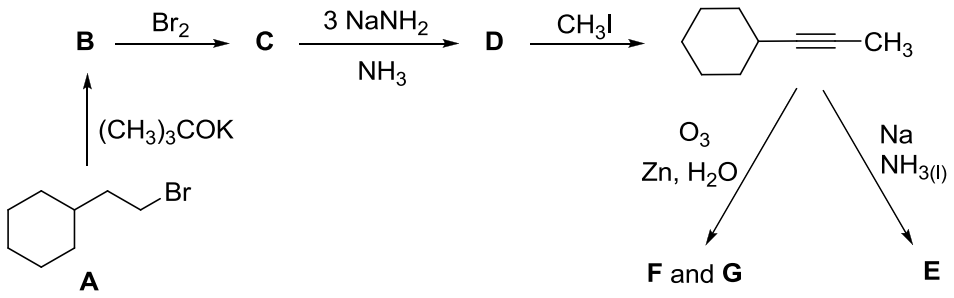


Answer : **Route 2**

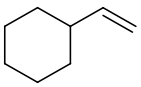
Route 1 results in the E2 elimination of 3° alkyl iodide because of acetylide ion being a strong base



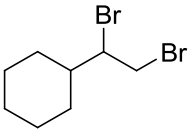
iv) Provide the structures of compounds **B – G** in the following reaction scheme.
(0.5 mark each, 3 marks total)



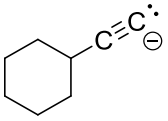
Structure B:



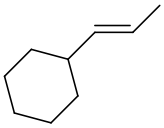
Structure C:



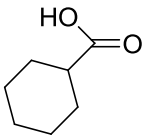
Structure D:



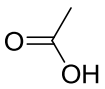
Structure E:



Structure F:

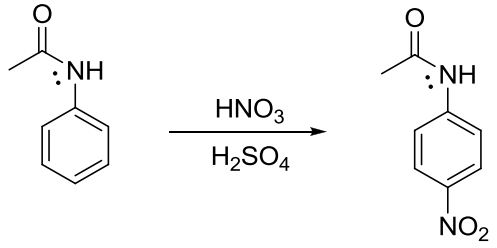


Structure G:

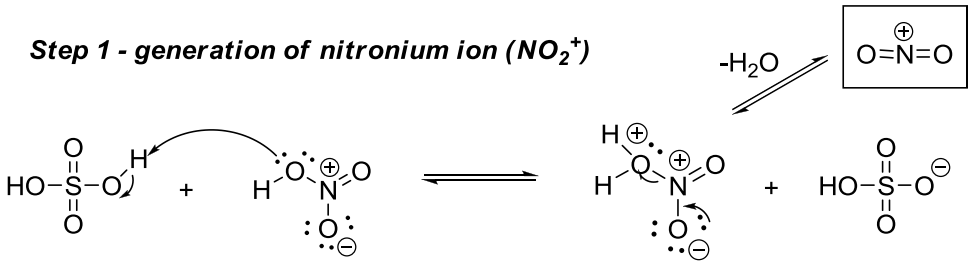


QUESTION 12 [7 marks]

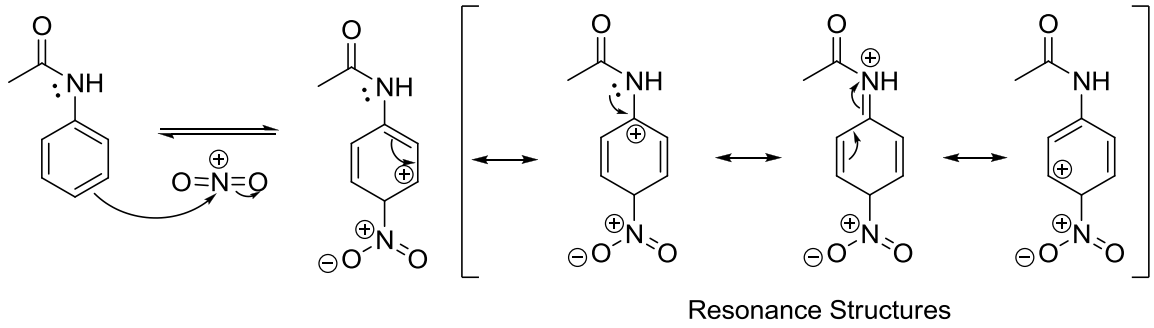
i) Provide a mechanism, showing all of resonance stabilized arenenium ion (also known as σ-complex/cyclohexadienyl) intermediates, for the formation of the following *para*-isomer product. (3 marks)



Step 1 - generation of nitronium ion (NO_2^+)

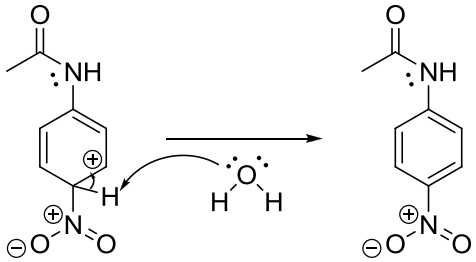


Step 2 - Attack by pi-electrons of benzene

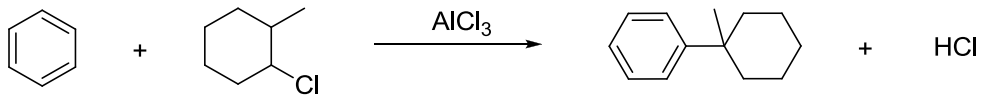


Resonance Structures

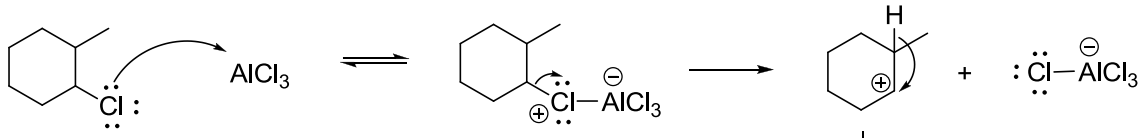
Step 3 - Elimination to restore aromaticity



ii) Show a mechanism for the following reaction. (2 marks)

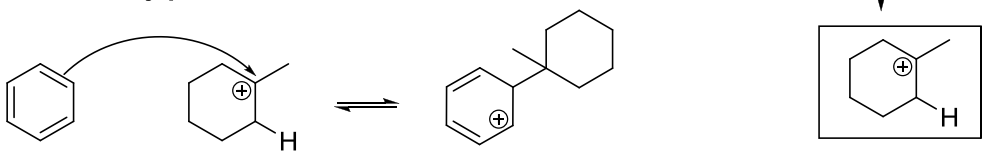


Step 1 - alkyl halide activation

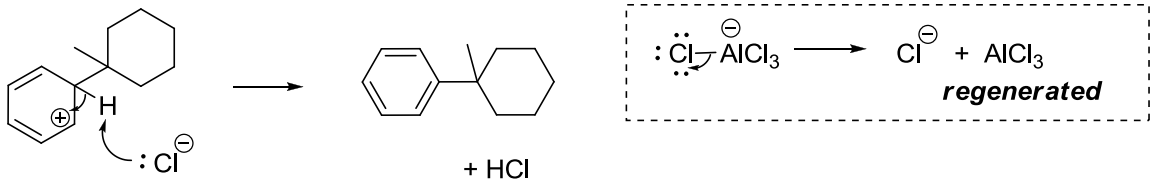


1,2-hydride shift

Step 2 - Attack by pi-electrons of benzene

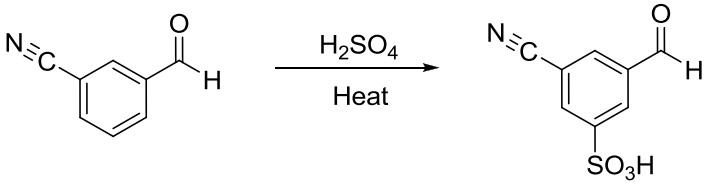


Step 2 - Elimination to restore aromaticity

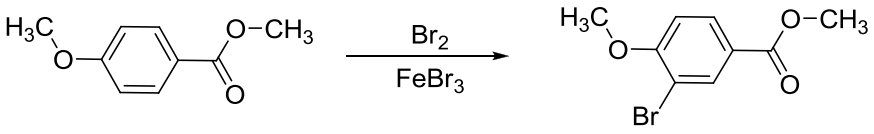


iii) Draw the <u>major</u> product(s) expected from each of the following reactions. (2 marks total)

a)



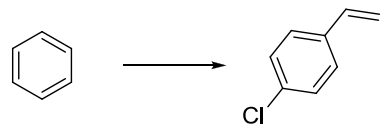
a)



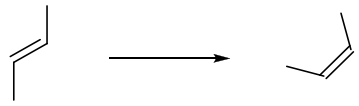
QUESTION 13 [6 marks]

Instruction – Four synthesis questions are given below. Select **TWO** questions of your choice by putting √ inside the box next to the reaction equation. For each question chosen, devise a synthesis of the final product from the given starting material by using any necessary reagent. Mechanisms are not required.

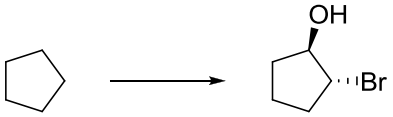
Synthesis 1)



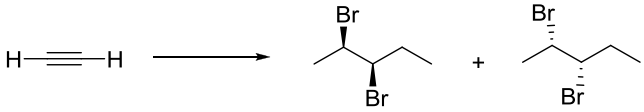
Synthesis 2)



Synthesis 3)

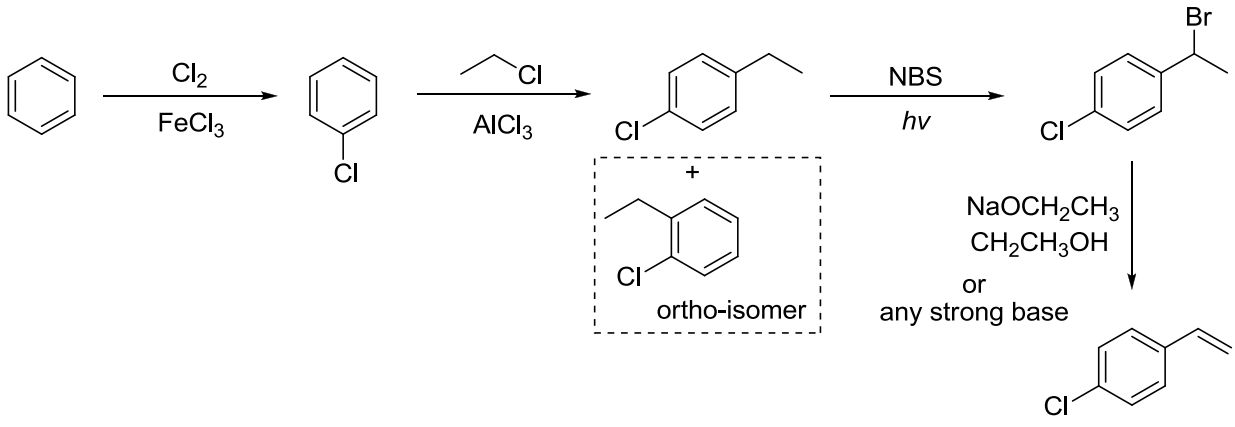


Synthesis 4)

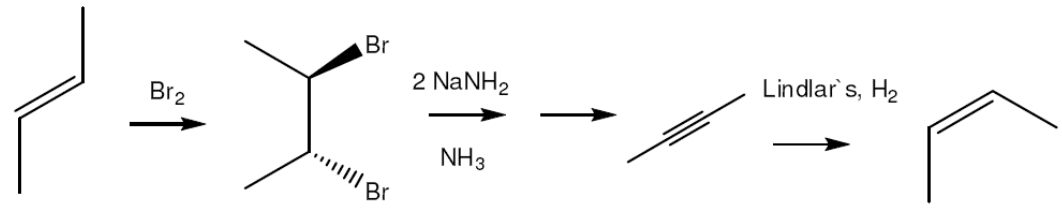


Continues onto the next page.

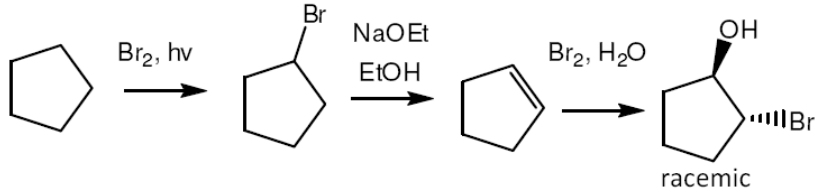
Synthesis 1



Synthesis 2



Synthesis 3



Synthesis 4