



**DEPARTMENT OF CHEMISTRY AND CHEMICAL TECHNOLOGY
202-BZF-05 ORGANIC CHEMISTRY I
FALL 2011**

SOLUTIONS TO FINAL EXAMINATION

Prepared by

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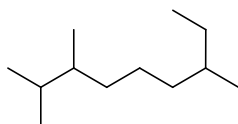
B. Seivewright

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QUESTION 1 [8 marks]

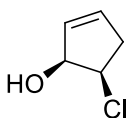
a) Provide IUPAC names for the following compounds and, where applicable, include *R/S* or *E/Z* designation to indicate the stereochemistry. (4 marks)

i)

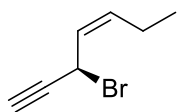


2,3,7-trimethylnonane

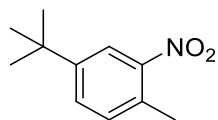
ii)

(1*S*,5*R*)-5-chlorocyclopent-2-en-1-ol

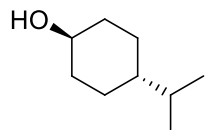
iii)

(R,*Z*)-3-bromohept-4-en-1-yne

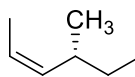
iv)

4-*tert*-butyl-2-nitrotoluene
or
4-*tert*-butyl-1-methyl-2-nitrobenzene

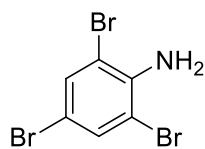
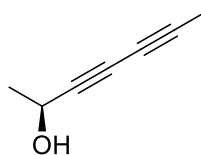
b) Provide the bond-line structures for each of the following names. (4 marks)

i) *trans*-4-isopropylcyclohexanol

or its enantiomer

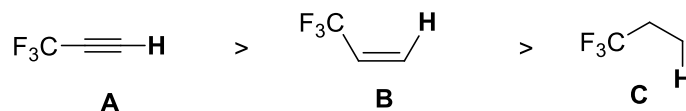
ii) (*Z,R*)-4-methyl-2-hexene

iii) 2,4,6-tribromoaniline

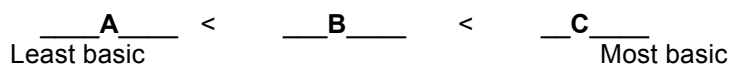
iv) (*S*)-hepta-3,5-diyn-2-ol

QUESTION 2 [8 marks]

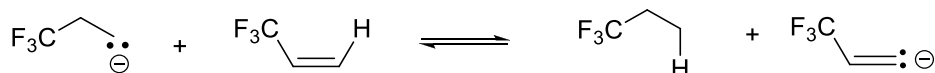
- a) Given the following trend in proton acidity among the following hydrocarbon compounds: (*N.B.* the acidic proton of each compound is indicated in **bold**)



- i) Identify which of A, B and/or C has the largest K_a . (0.5 mark) **A**
- ii) Identify which of the three has the largest pK_a . (0.5 mark) **C**
- iii) Which one of the three has the acidic proton bonded to the most electronegative carbon? (0.5 mark) **A**
- iv) Which one of the three has a C-H bond with the greatest s orbital character? (0.5 mark) **A**
- v) Rank the strength of conjugate bases expected when A, B and C undergo acid-dissociation. (1.5 mark)

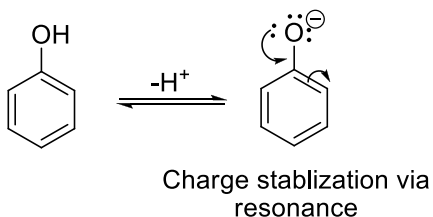


- vi) Identify which of A, B and/or C has at least one sp^2 -hybridized carbon. **B** (0.5 mark)
- vii) Does the following reaction favour the forward or reverse reaction? Explain. (2 mark)



The reaction will favour the forward reaction because alkane is considerably less acidic than alkene (or alkenyl anion is considerably less basic than alkyl anion). The direction of an acid-base reaction favours the side with weaker acid and base.

- b) Phenol, $\text{C}_6\text{H}_5\text{OH}$, is an aromatic alcohol. It has a pK_a of 9.9, which is considerably lower than typical pK_a ranges of alcohols ($pK_a = 16 - 20$). Why? (2 mark)



Phenol is considerably more acidic than typical alcohols because the negative charge of the conjugate anion (phenoxide) is stabilized by **resonance** through benzene

QUESTION 4 [6.5 marks]

a) Identify whether each of the following compounds is chiral or achiral. For all molecules that are chiral, indicate the number of chiral centres. (3.5 marks)

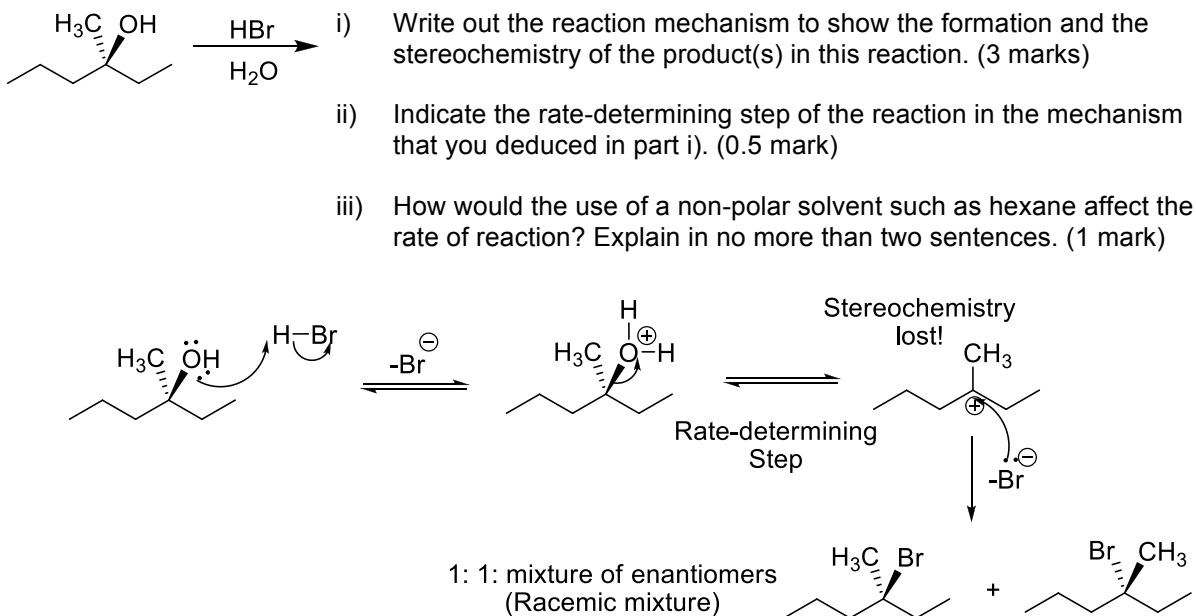
| | | chiral or achiral? | # of chiral centres |
|------|--|--------------------|---------------------|
| i) | | Chiral | 2 |
| ii) | | Achiral | |
| iii) | | Achiral | |
| iv) | | Achiral | |
| v) | | Chiral | 1 |

b) For each of the following pairs, identify their relationships either as identical, constitutional isomers, enantiomers or diastereomers. (3 marks)

| | | | | |
|------|--|-----|--|------------------------|
| i) | | and | | Constitutional Isomers |
| ii) | | and | | Identical |
| iii) | | and | | Enantiomers |

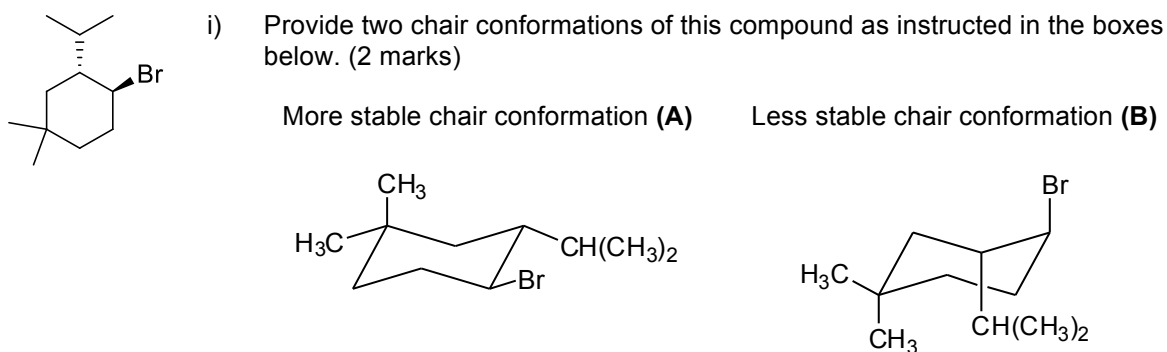
QUESTION 6 [8.5 marks]

a) Answer all questions regarding the reaction shown below:



The use of a non-polar solvent would **lower** the reaction rate of the S_N1 mechanism by minimizing the solvation of the carbocation, hence de-stabilizing the rate determining step.

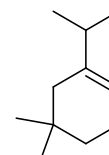
b) Answer all questions regarding the compound given below:



ii) Which of the two chair conformations (between A and B) will undergo a faster E2 reaction using potassium methoxide as base? (1 mark)

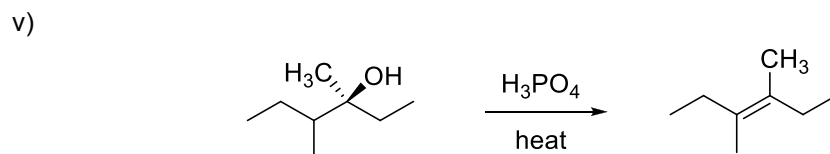
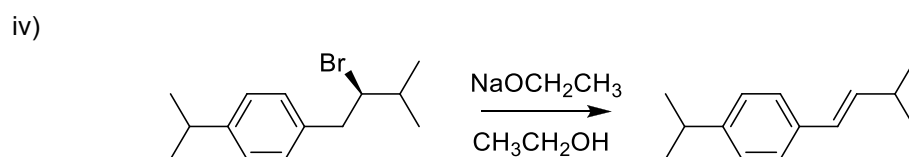
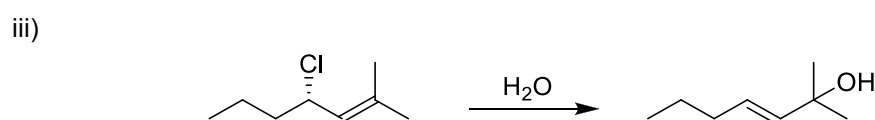
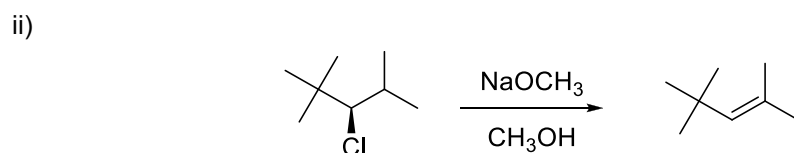
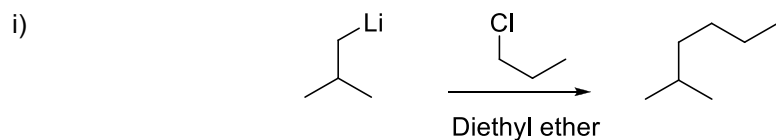
 B

iii) If an E1 mechanism was instead involved in part ii), what would be the structure of the expected final product? (1 mark)

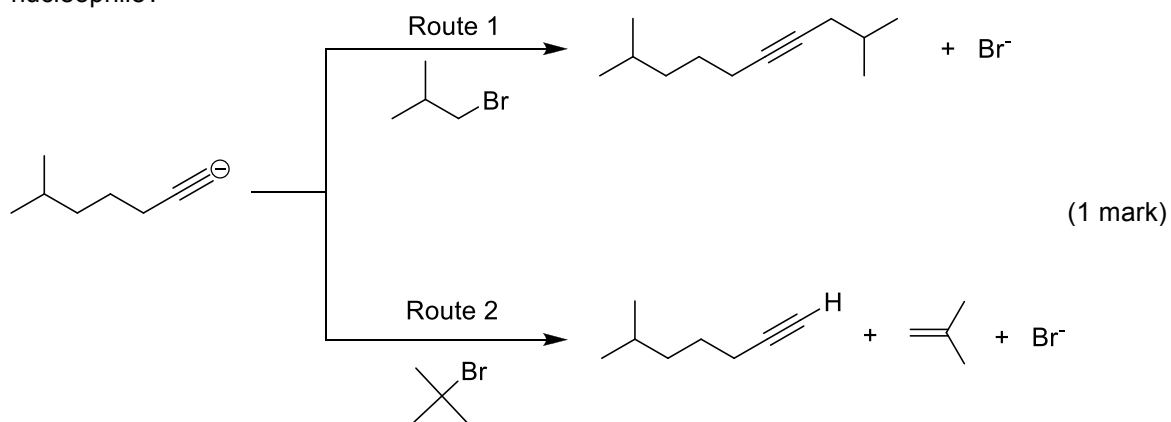


QUESTION 7 [8 marks]

- a) Provide the structure of the major product expected in each of the following reactions. Make sure to indicate the stereochemistry of the product, where applicable. (5 marks, 1 mark each)



- b) i) Provide the structures of the product(s) formed when the following anion reacts with two different alkyl halides, as specified below. ii) Is the role of the anion in route 2 a base or a nucleophile?



Circle your choice

The role of the anion in route 2 is

Base

or

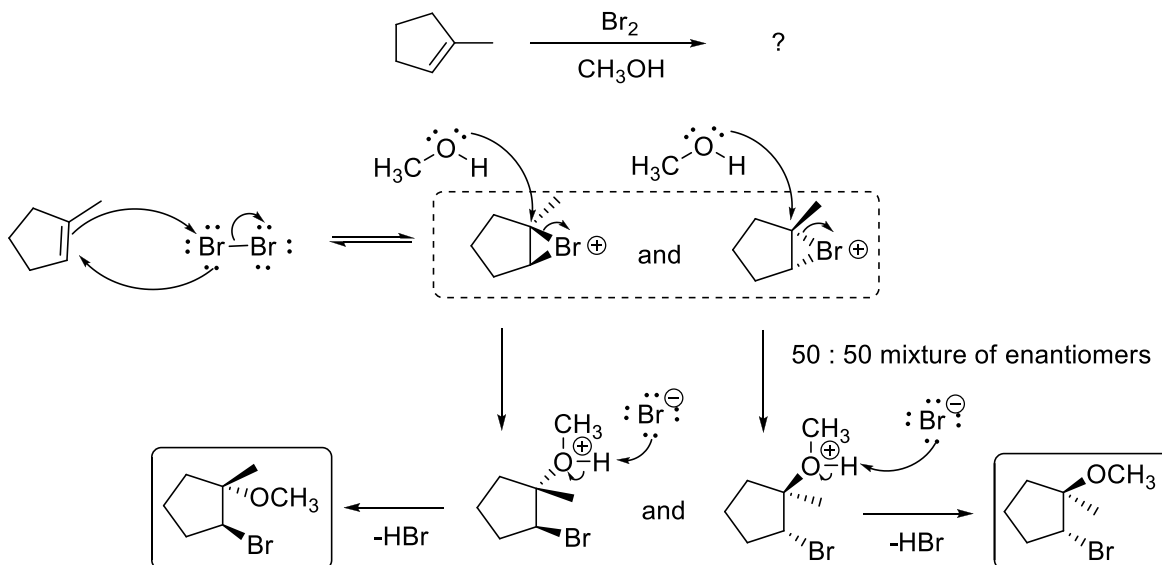
Nucleophile

(1 mark)

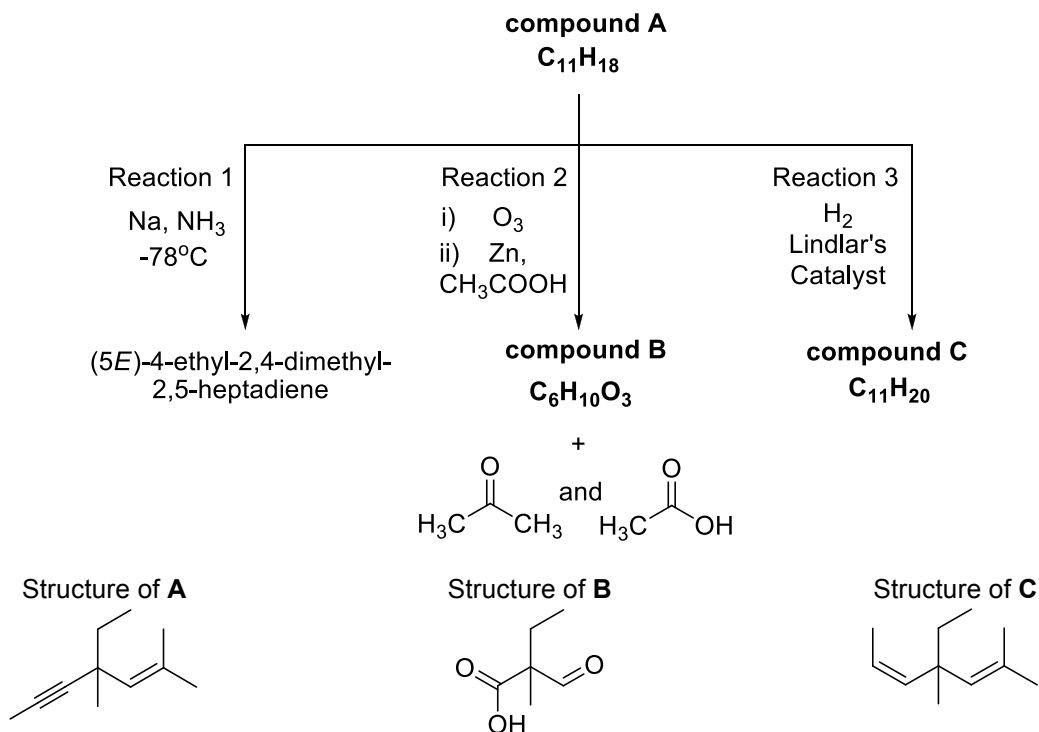
(1 mark)

QUESTION 8 [6.5 marks]

- a) The following compound shown below was subject to the reaction with Br_2 using CH_3OH as solvent. Show the formation of the final product(s) with the correct stereochemical outcome by providing a plausible reaction mechanism. (3.5 marks)

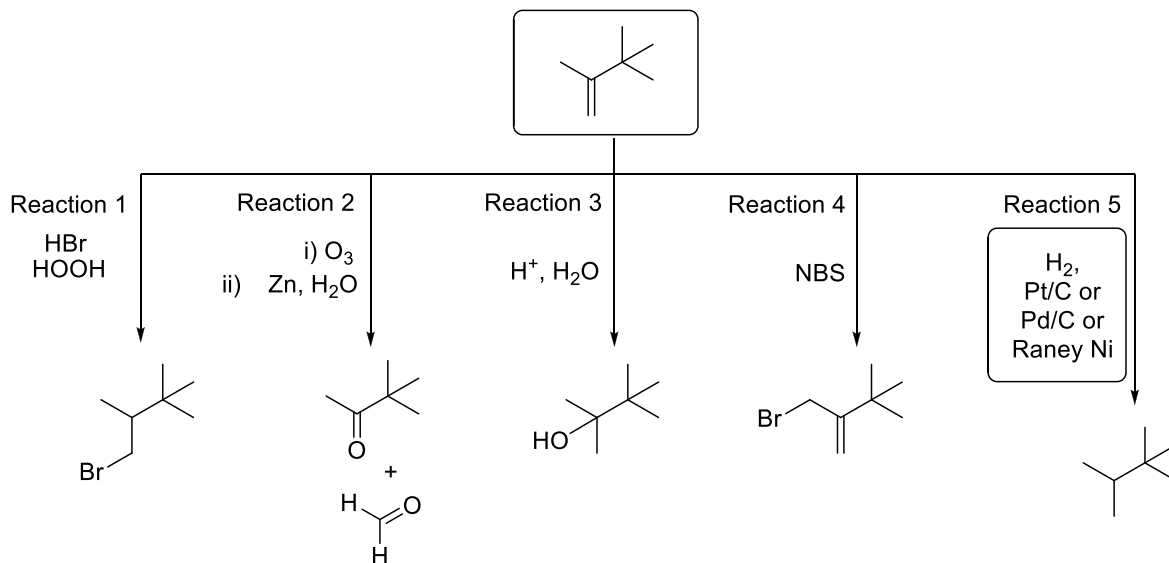


- b) Unsaturated hydrocarbon compound A whose molecular formula is $\text{C}_{11}\text{H}_{18}$ was subject to several reactions as shown below. Provide the bond-line structures of compounds A, B and C. (3 marks)

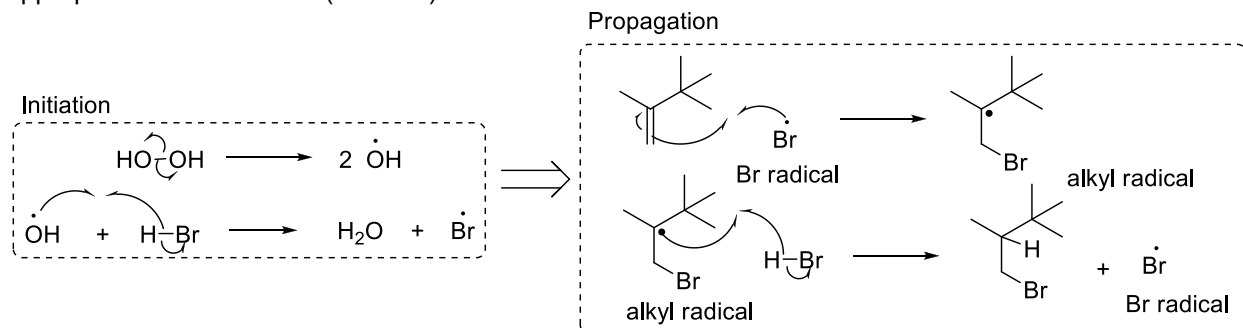


QUESTION 9 [11 marks]

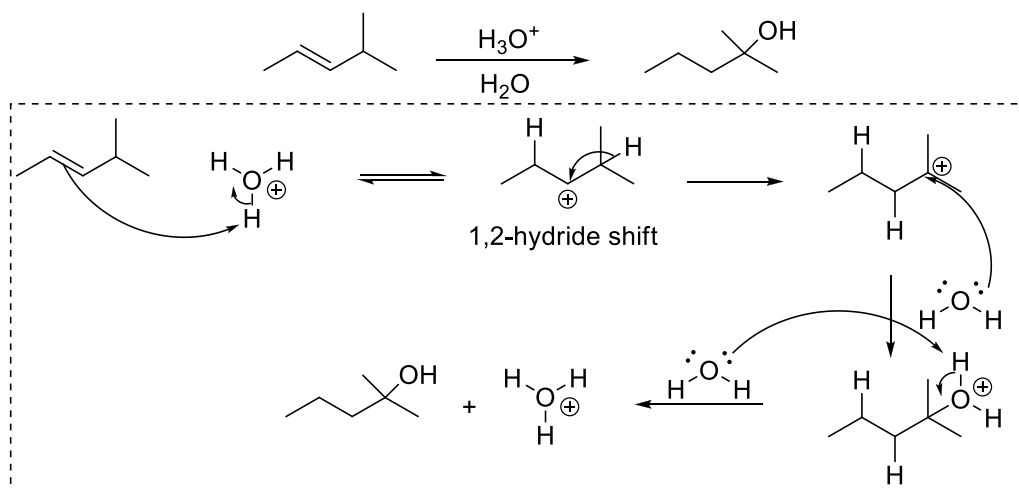
a) Fill in the boxes with the structures of expected product(s) or reagents necessary (for reaction 5) when the following molecule, drawn below, was subject to different reaction conditions. (5 marks)



b) Referring to reaction 1 part a), provide a mechanism to show the formation of the product(s) using appropriate curved-arrows (3 marks)

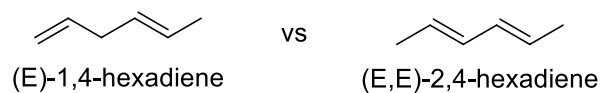


c) Show a plausible mechanism to account for the following transformation. (3 marks)



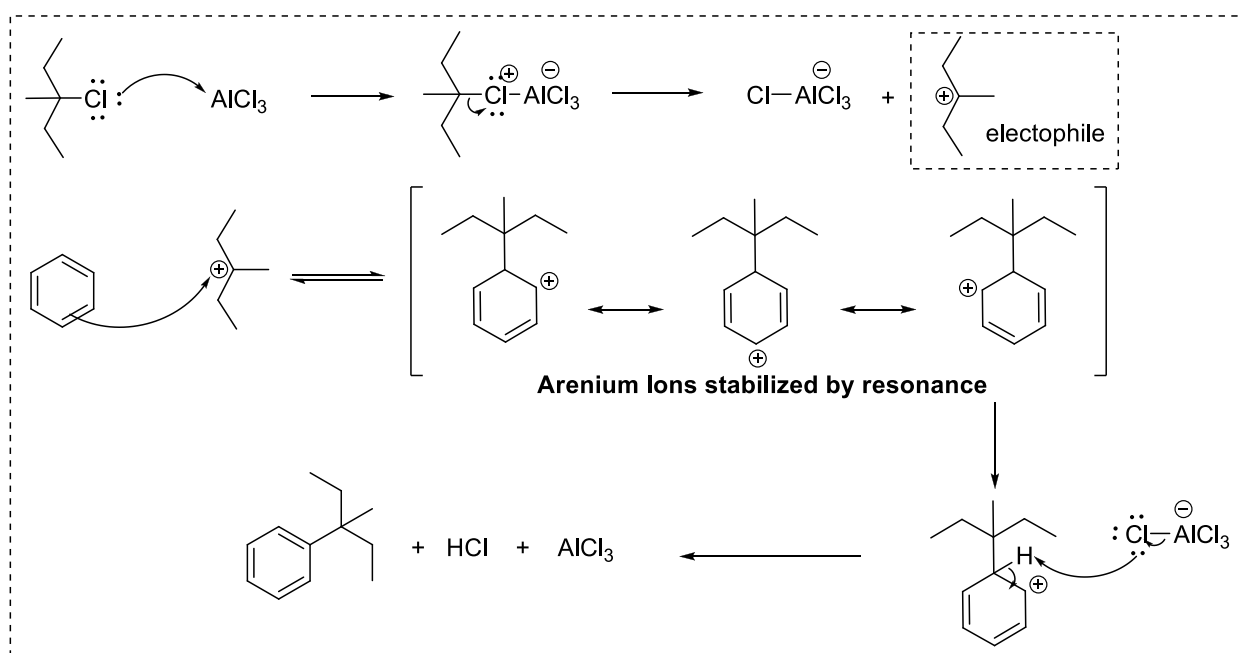
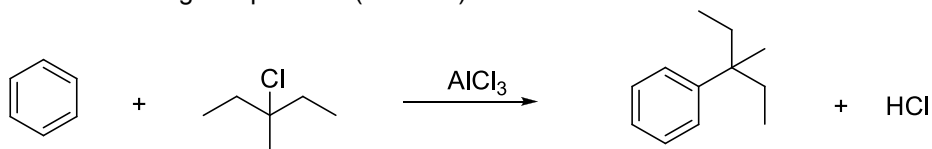
QUESTION 11 [6 marks]

- a) Which of the following compounds has the higher heat of hydrogenation? Explain. (2 marks)



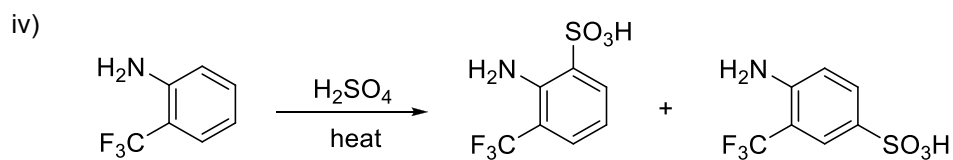
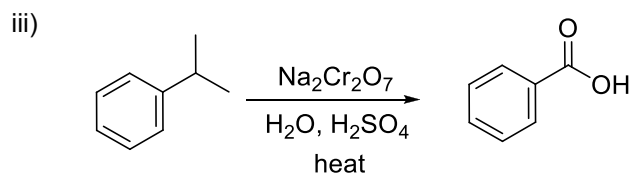
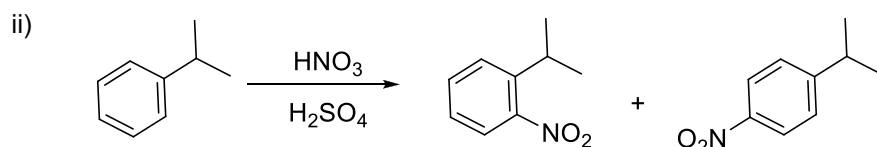
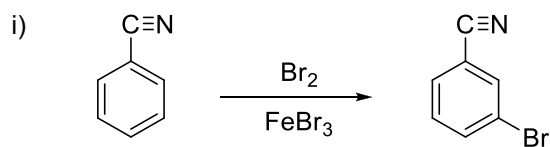
(E)-1,4-hexadiene will release a greater amount of heat of hydrogenation since it is an isolated diene which lacks the resonance character observed in a conjugated diene, *(E,E)*-2,4-hexadiene

- b) Provide a mechanism, showing the activation of the alkyl halide by the catalyst and all of resonance stabilized arenium ion (also known as σ -complex/cyclohexadienyl) intermediates, for the formation of the given product. (4 marks)



QUESTION 12 [4 marks]

Draw the major product(s) expected from each of the following reactions.

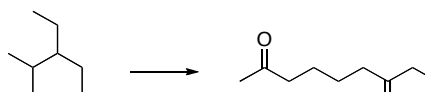


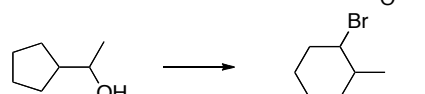
QUESTION 13 [7 marks]

Four synthesis questions are given below. Select **TWO** questions of your choice by putting \checkmark 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.

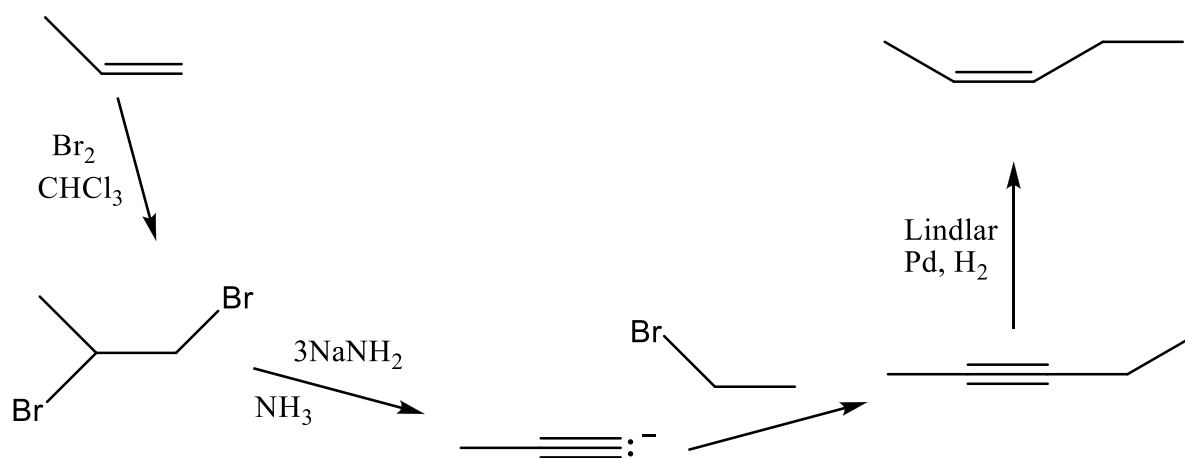
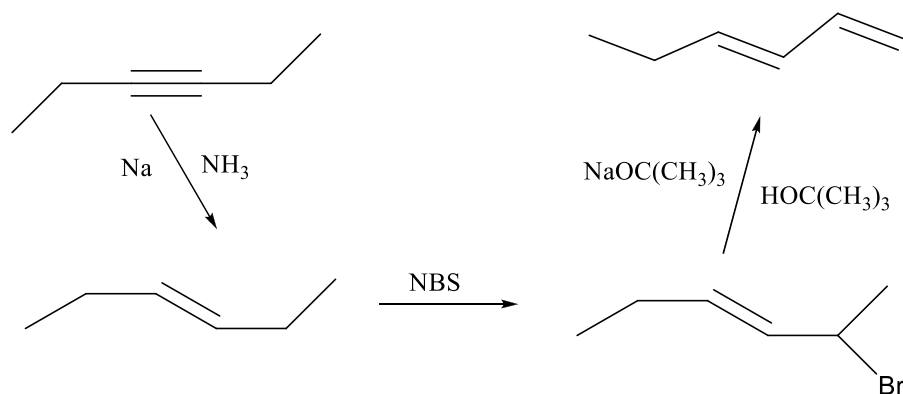
i. (Z)-pent-2-ene from propene

ii. (E)-hexa-1,3-diene from hex-3-yne

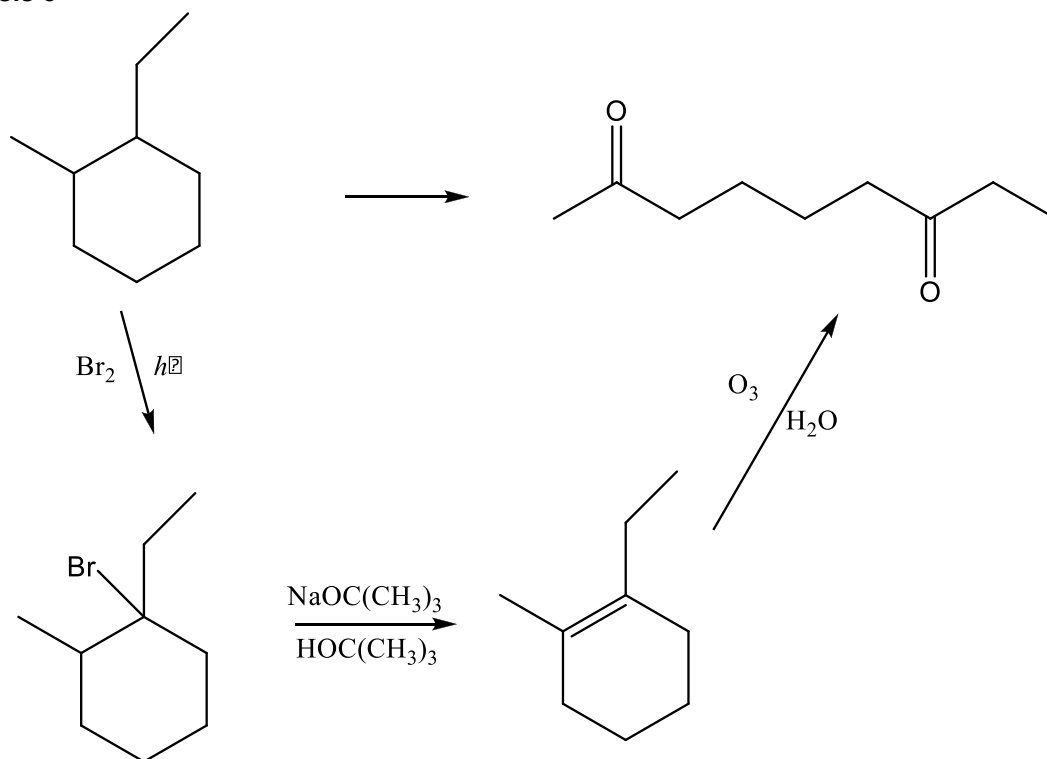
iii. 

iv. 

Hint : this problem involves a rearrangement of some sort

Synthesis 1**Synthesis 2**

Synthesis 3



Synthesis 4

