Chemistry 241 – Final Exam

December 4, 2014
Time allowed: 3 hours

Instructor: Dr. Nola Etkin

Name Solutions

Student Number

Signature

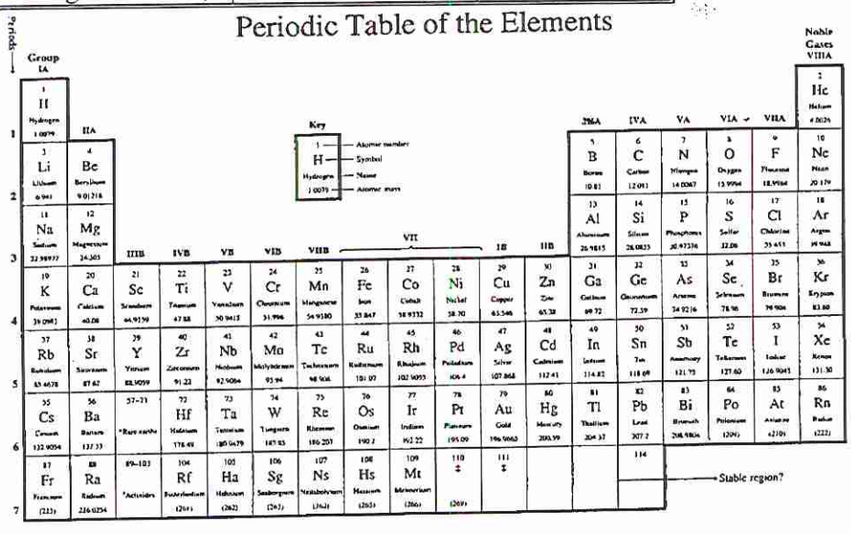
Please read the following instructions carefully:

- This exam has ***8 pages*** including this page. Make sure that it is complete.
- ***Read all questions carefully*** and answer completely in the space provided. If extra space is required, you may use the back of the page, but indicate that you are doing so, or it will not be marked.
- For some questions you have a choice of parts to answer. ***If you answer more than the required number of parts, indicate which ones you want marked. If you do not so indicate, the first parts will be marked.***
- The maximum number of marks for each question is indicated in brackets.
- Molecular models and calculators may be used.

GOOD LUCK AND MERRY CHRISTMAS!!

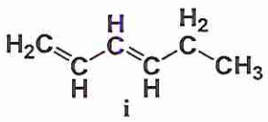
Question #		Maximum Value	Mark
1	C	10	
2	C	3	
3	C	5	
4	C	4	
5	C	6	
6	C	6	
7	N	~~5~~ 6	
8	N	9	
9	N	9	
10	N	5	
11	C	20	
12	N	~~6~~ 5	
13	N	12 (+4 bonus)	
Total (including bonus of 4)		100	

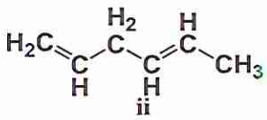
Periodic Table of the Elements



1. Provide short answers for the following. ***Answer any five parts only.*** [10 marks]

a) Arrange the following in order of ***increasing*** stability.


i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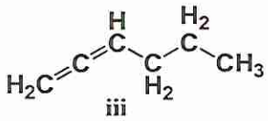
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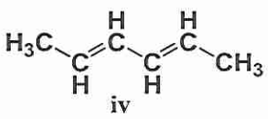
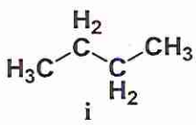
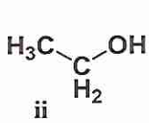

iv

iii < ii < i < iv **most stable**

1 mark

b) Arrange the following in order of ***increasing*** solubility in water.


i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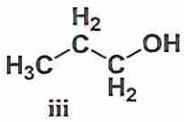
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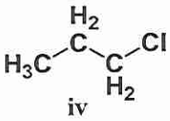
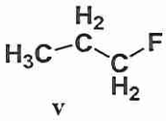

iv


v

i < iv < v < iii < ii **most soluble**

-1½ -½

c) Which of the following molecules are Lewis Acids? Bronsted Acids?

	BH_3	H_2SO_4	Br^-	CH_3^+
Lewis Acid:	X	X		X
Bronsted Acid:		X		

1-2 wrong = 1.5
3-4 wrong = 1
5-6 wrong = 0.5

d) Give ***two*** reasons why cyclopropane has more ring strain (and is therefore less stable) than cyclobutane.

- bond angle is much smaller (60° vs 90° << 109.5) ①
- all H's are eclipsed. (In cyclobutane it can bend to relieve eclipsing) ①

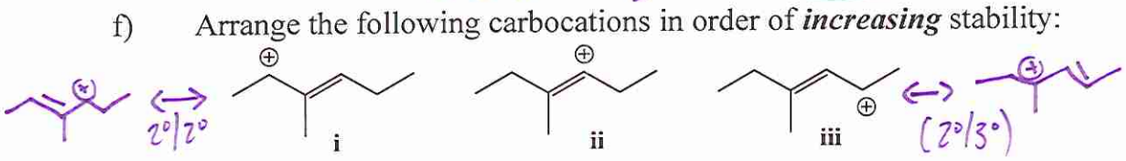
e) The optical rotation of a mixture of enantiomers composed of 75% R and 25% S is -6.5°. What is the specific rotation [α] of the pure *S* enantiomer?

ee = 75% - 25% = 50% = $\frac{-6.5°}{[\alpha]}$ (½)

∴ [α] for R = -13°

[α] for S = ±13° (-½ if ±)

f) Arrange the following carbocations in order of ***increasing*** stability:

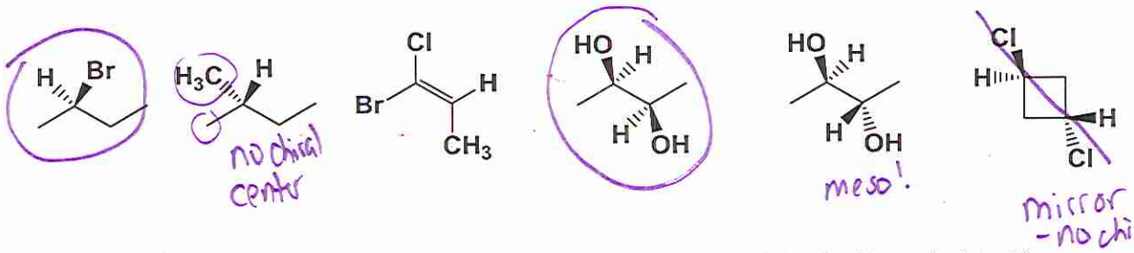


ii < i < iii **most stable**

=1 =1

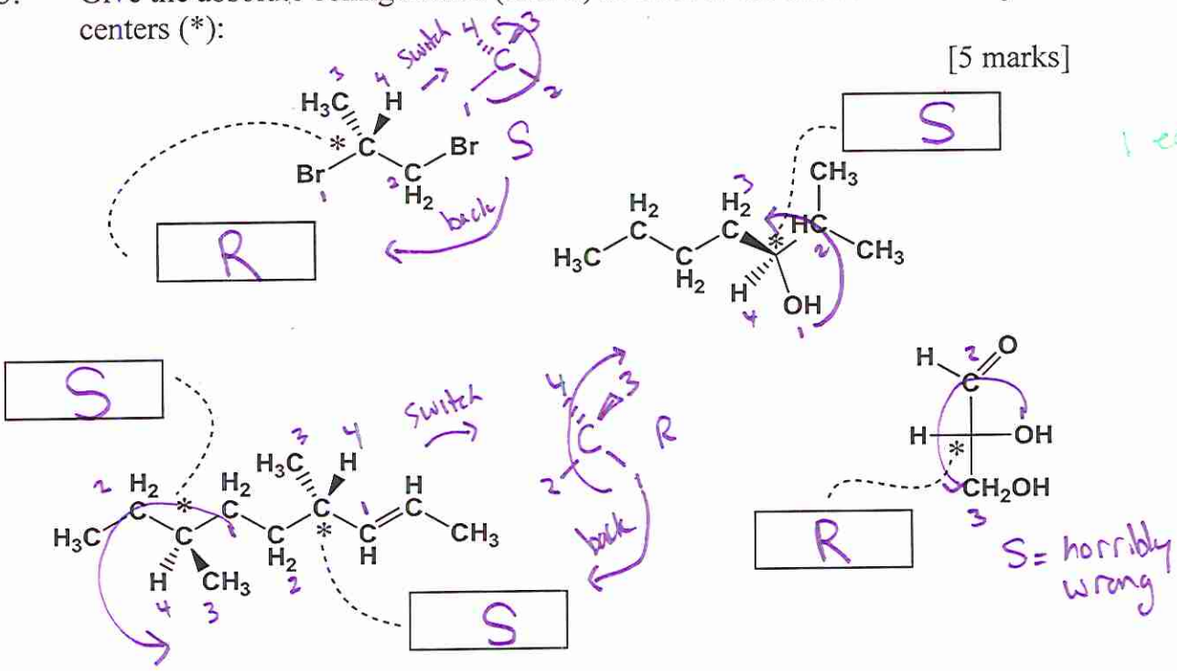
2. Which of the following molecules are chiral? Circle all correct answers.

[3 marks]



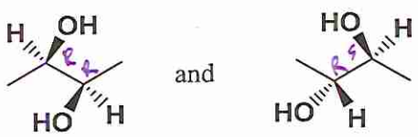
3. Give the absolute configuration (*R* or *S*) of each of the indicated chirality centers (*):

[5 marks]

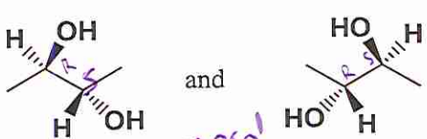


4. For each of the following pairs of structures, write in the box the letter of the word that best describes the structures. Note that each word should only be used once.

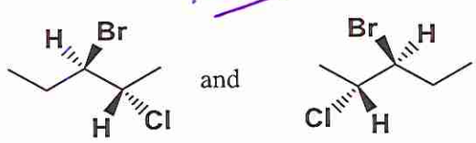
[4 marks]

i 

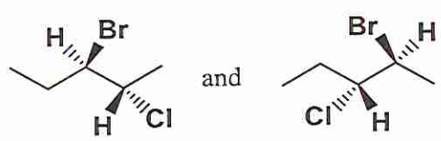
b

ii 

d

iii 

c

iv 

a

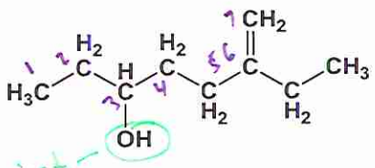
a) constitutional isomers

b) diastereomers

c) enantiomers

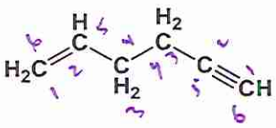
d) identical

5. Provide unambiguous IUPAC names for the following molecules.
[6 marks]



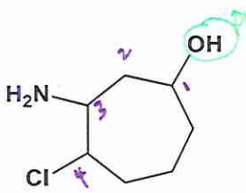
6-ethyl-6-hepten-3-ol
or 6-ethylhept-6-en-3-ol

-½ numbering



hex-1-en-5-yne
or 1-hexen-5-yne

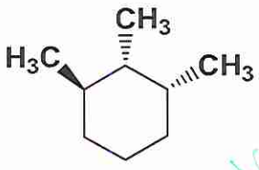
-½ numb

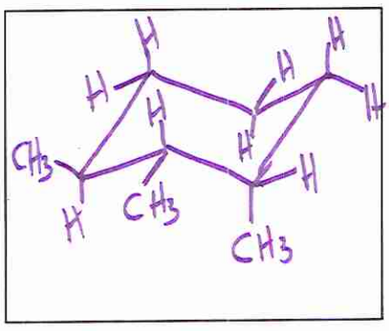


3-amino-4-chlorocyclo-heptanol

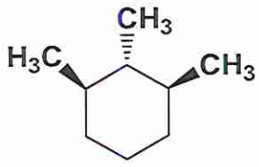
-½ numb

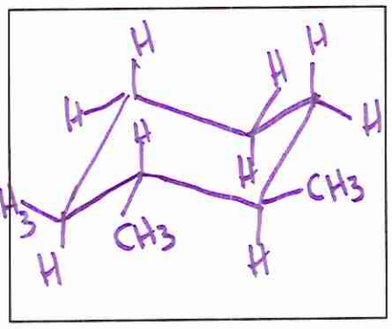
6. Draw the most stable chair conformation of each of the following two molecules, and then ***indicate which of the molecules is more stable, and explain briefly why***.
[6 marks]





more stable (✔) ☐

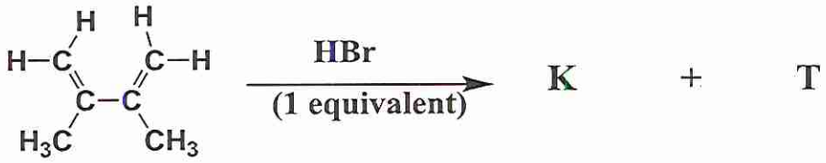




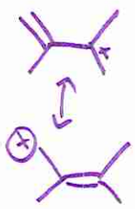
✔

why?
The second structure has no axial groups ∴ more stable.

7. Consider the following reaction: [6 marks]



a) Identify the kinetic (**K**) and thermodynamic (**T**) products of the reaction.



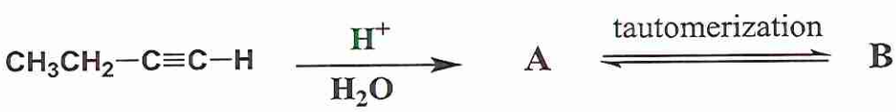
= K (1,2)

= T (mos sub)

b) Which product (K or T) would be major if the reaction was performed at 60°C? Explain *briefly*.

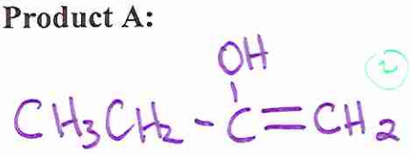
At higher temperature the thermodynamic product (T) is major, because there is enough energy to get to equilibrium. and T is more stable.

8. Consider the following reaction. Addition of H^+/H_2O gives an initial product **A** which is in equilibrium with a second product **B**. [9 marks]

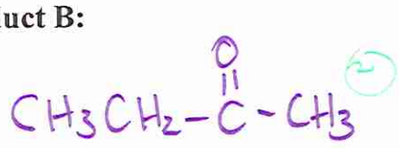


a) Give the structure of products **A** and **B**.

Product A:



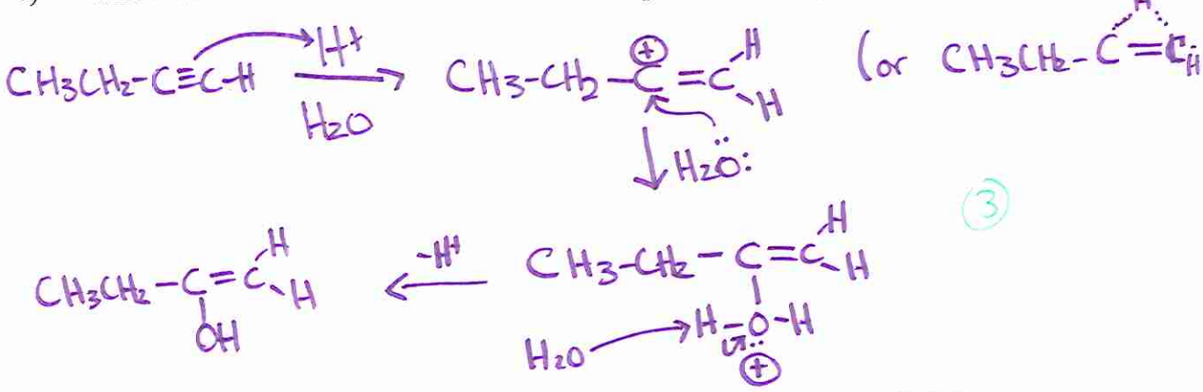
Product B:



b) Which of the products (**A** or **B**) is major at equilibrium?

(B) - the ketone (C=O) is more stable than the enol!

c) Show the mechanism for the formation of product **A** only.

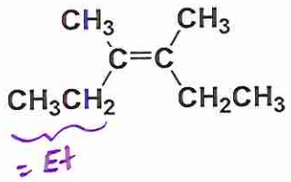


d) If you wanted to add the new functional group to the other end of the triple bond, what reagents would you use?

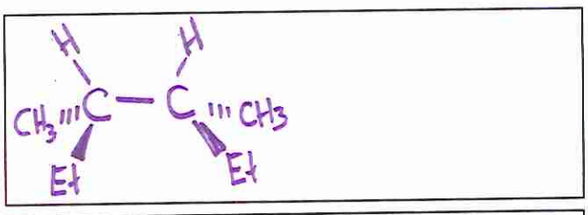
Anti-Markovnikov!

1) BH_3
2) H_2O_2/ H_2O/OH^-

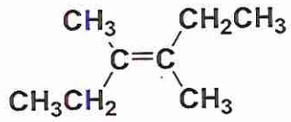
9. Consider the following Hydrogenation reactions: [9 marks]

i) 

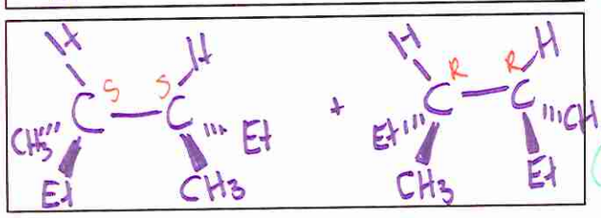
H_2 / Pd / C →



(6)

ii) 

H_2 / Pd / C →



(5) (3)

a) Give the products of the two reactions above. In each case show all stereoisomers formed.

b) Is the reaction stereoselective? Stereospecific? Why?

(2) Both! Stereoselective because prefers 1 (or 2) isomers.
Stereospecific because E → RR + SS
Z → RS (meso)
} each isomer of reactant gives different products.

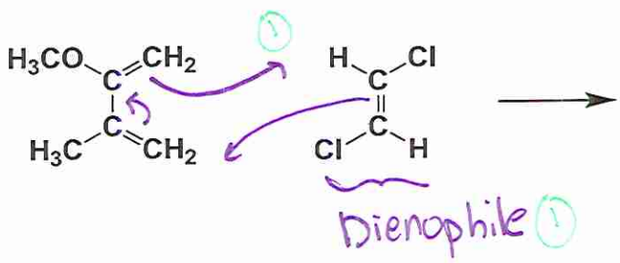
c) One of the above products is chiral while the other is not. Explain…

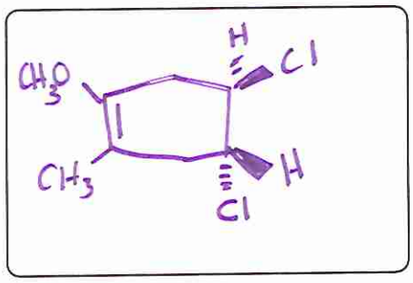
(1) The product in part i is meso - it has a mirror plane ∴ is not chiral

d) Which of the two starting alkenes (in i or ii) would you expect to be more stable? Why?…

(1) ii) is more stable because big groups are farther away (E > Z)

10. Consider the following Diels-Alder reaction: [5 marks]





(3) stereo = 1

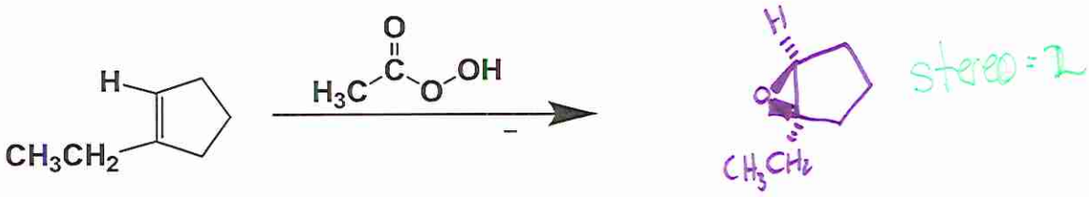
a) Draw arrows on the reactants (above) to show the mechanism.

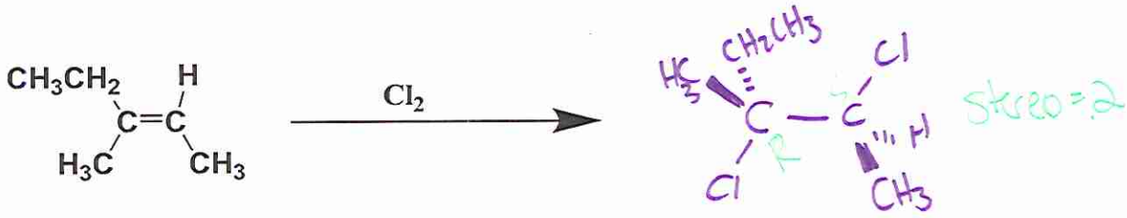
b) Give the product of the reaction, being sure to show the stereochemistry of the major product.

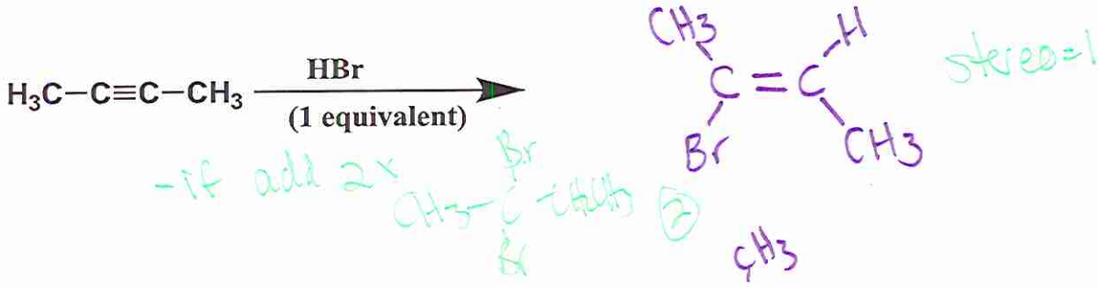
c) Identify the ***dienophile*** in the reaction (circle or label it).

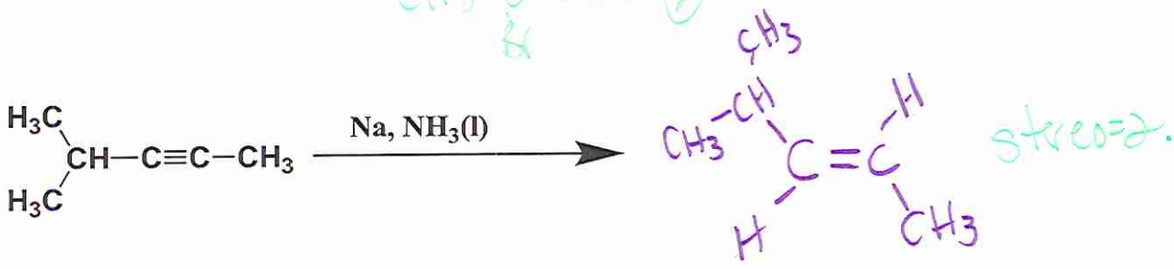
11. Predict *the major* organic product(s) of the following reactions. ***Answer any five parts only***. ***Show the stereochemistry*** of the major product or, for those reactions that are not stereoselective, so indicate.

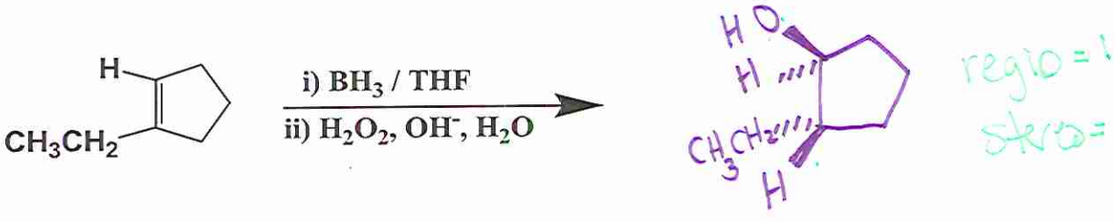
[20 marks] 4 each

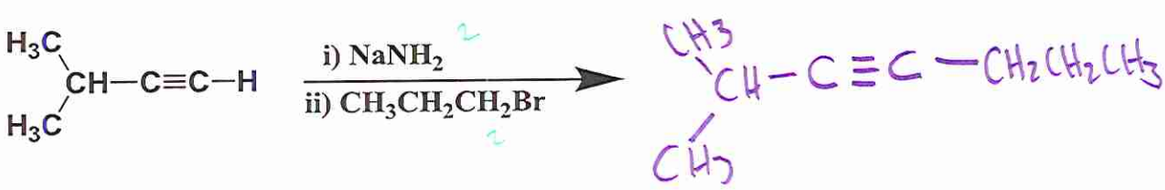
a) 

b) 

c) 

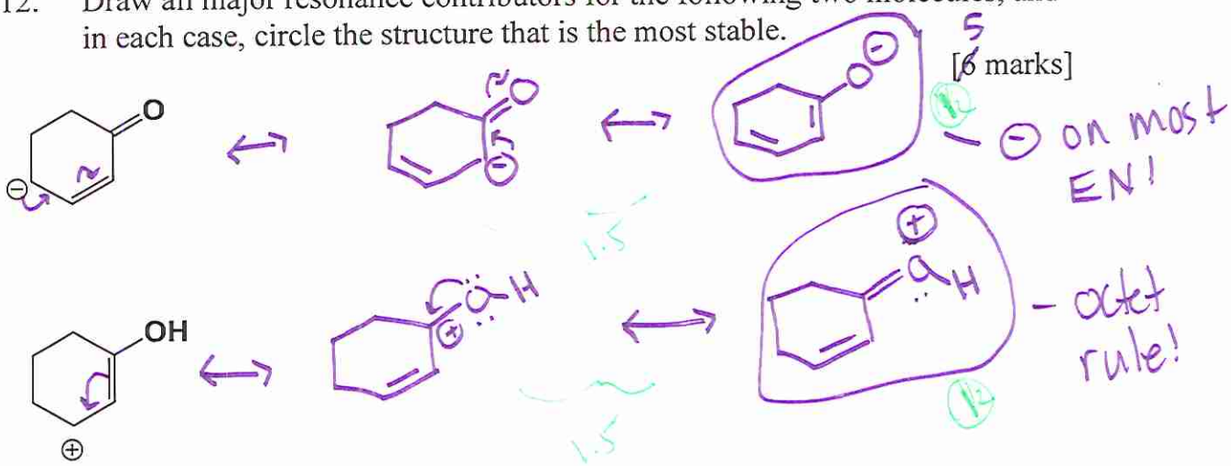
d) 

e) 

f) 

12. Draw all major resonance contributors for the following two molecules, and in each case, circle the structure that is the most stable.

[6 marks]



13. *Electrophiles Inc.*, a successful start-up company in West Royalty, has had some recent success in making organic molecules which it sells to a multinational pharmaceutical company. They just bought 3 tonnes (each) of 1-butyne and 2-butyne on sale at Canadian Tire, and want to turn it into some more useful compounds to sell at a big profit so that they can hire some UPEI Chemistry students next summer. Can you suggest ways to make ***three of the following four*** compounds? In each case choose the starting alkyne and suggest reagents. Make sure you add them in the right order to give the required product!

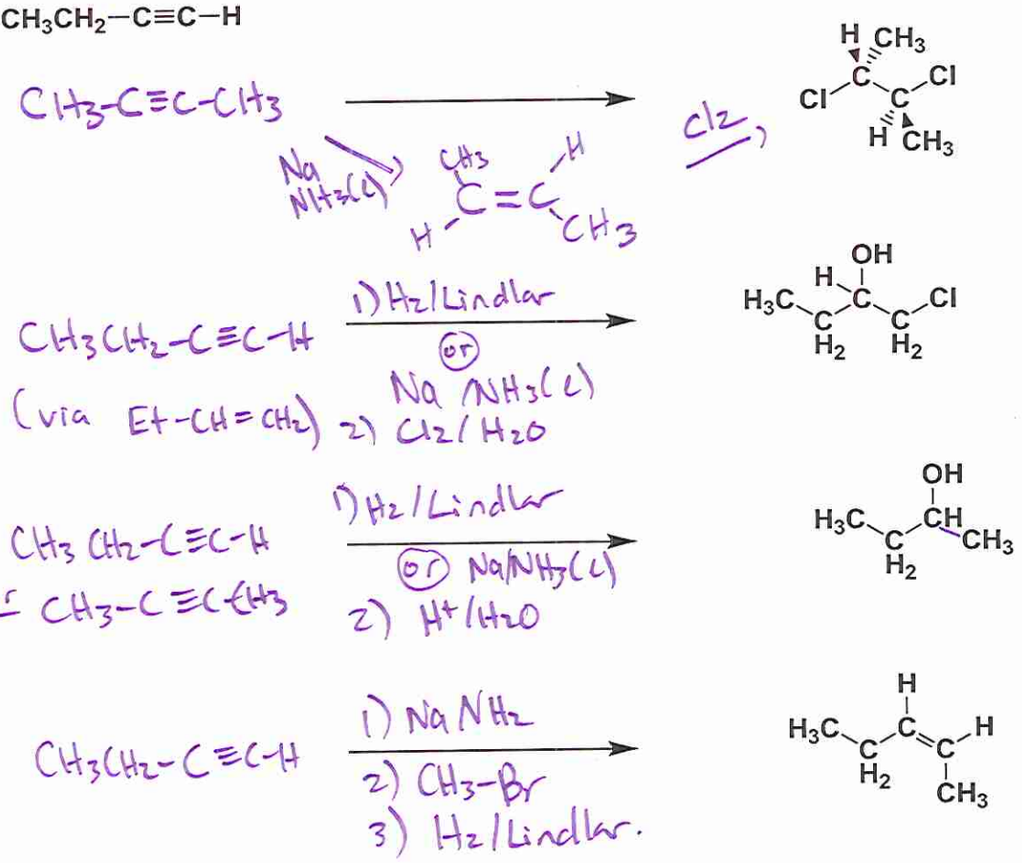
[12 marks]

4 each

$H_3C-C\equiv C-CH_3$

or

$CH_3CH_2-C\equiv C-H$



For ***4 bonus marks*, make them all!