Chemistry 342-75
Spring 2015
Exam 1
Dr. Richter

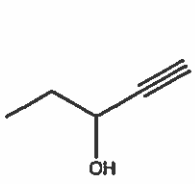
Name KEY

Signature _____

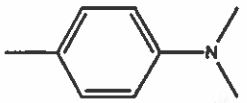
You are required to answer all question sets. Please note that some of the question sets offer you a choice of questions - do only the number of questions asked for. Please write legibly and draw clearly. Points will be deducted for illegible and unclear answers. The point total for this exam is 100 and the value of each question set is shown in parenthesis beside that set. ***READ ALL QUESTIONS CAREFULLY AND APPORTION YOUR TIME ACCORDINGLY***.

PART ONE: SPECTROSCOPY

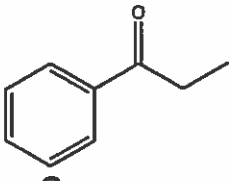
1. Match each structure (A-E) with one IR spectrum (I-V) and one proton NMR spectrum (i-v) (see following pages). *Note: place answers in table on this page.* **(20)**



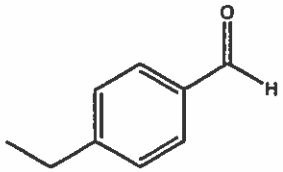
A



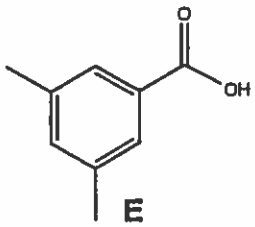
B



C



D

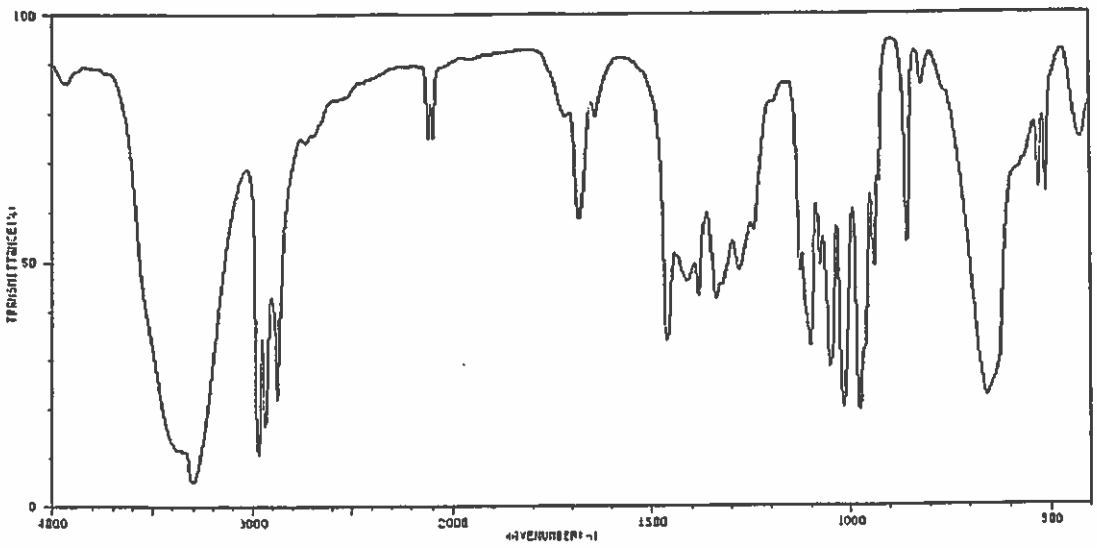


E

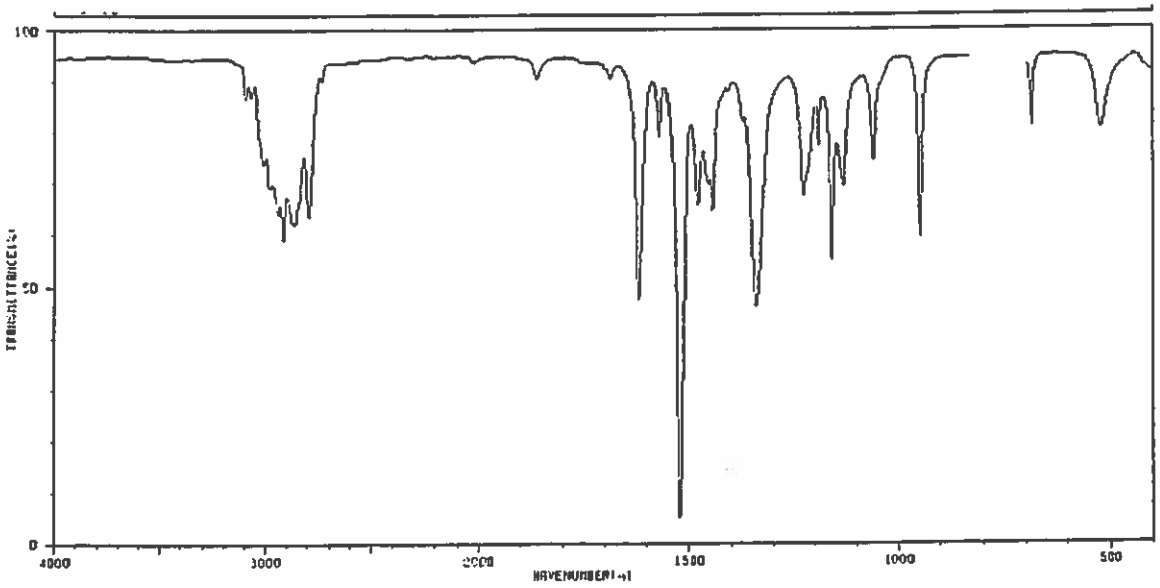
Structure	IR spectrum	NMR spectrum
A	I	iii
B	II	iv
C	V	v
D	III	ii
E	VI	i

IR Spectra:

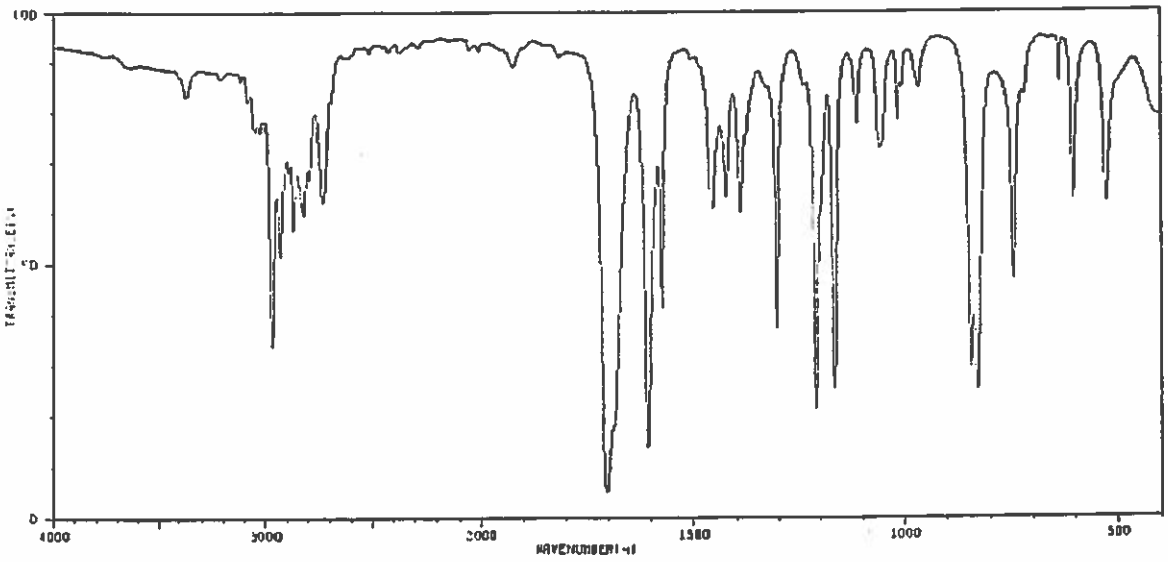
I



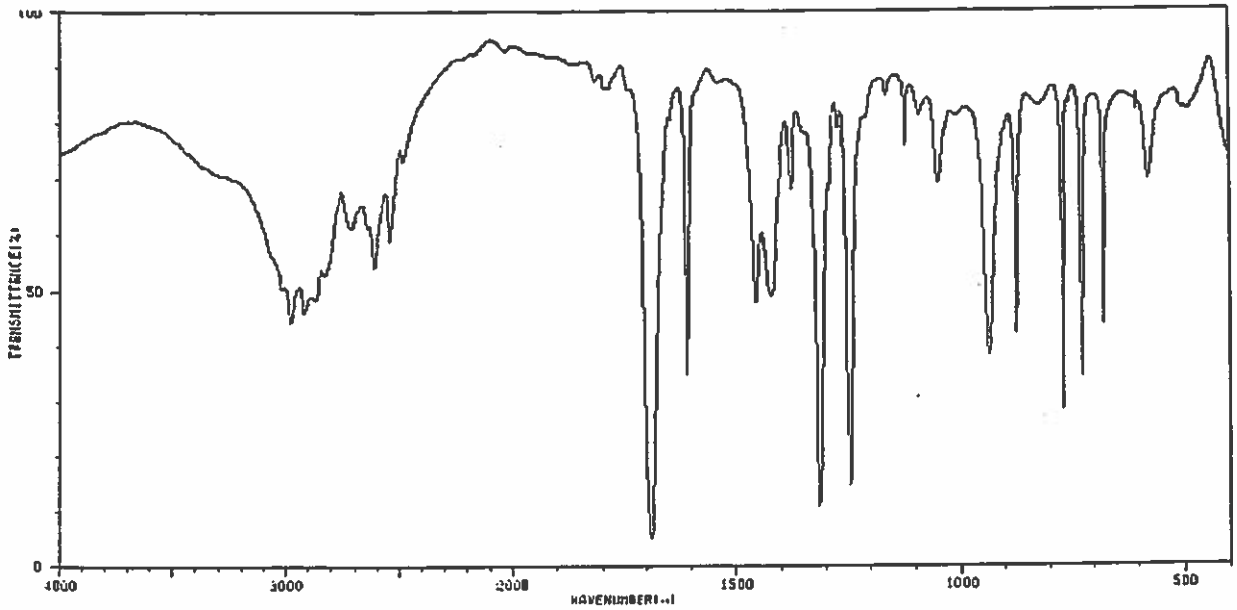
II



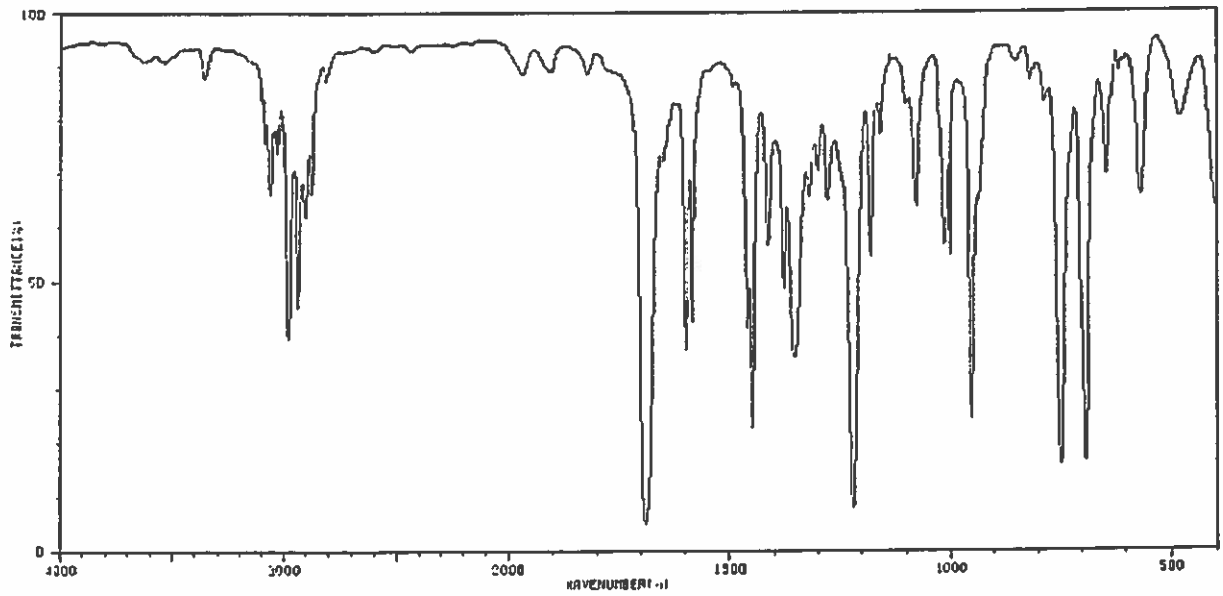
III



IV

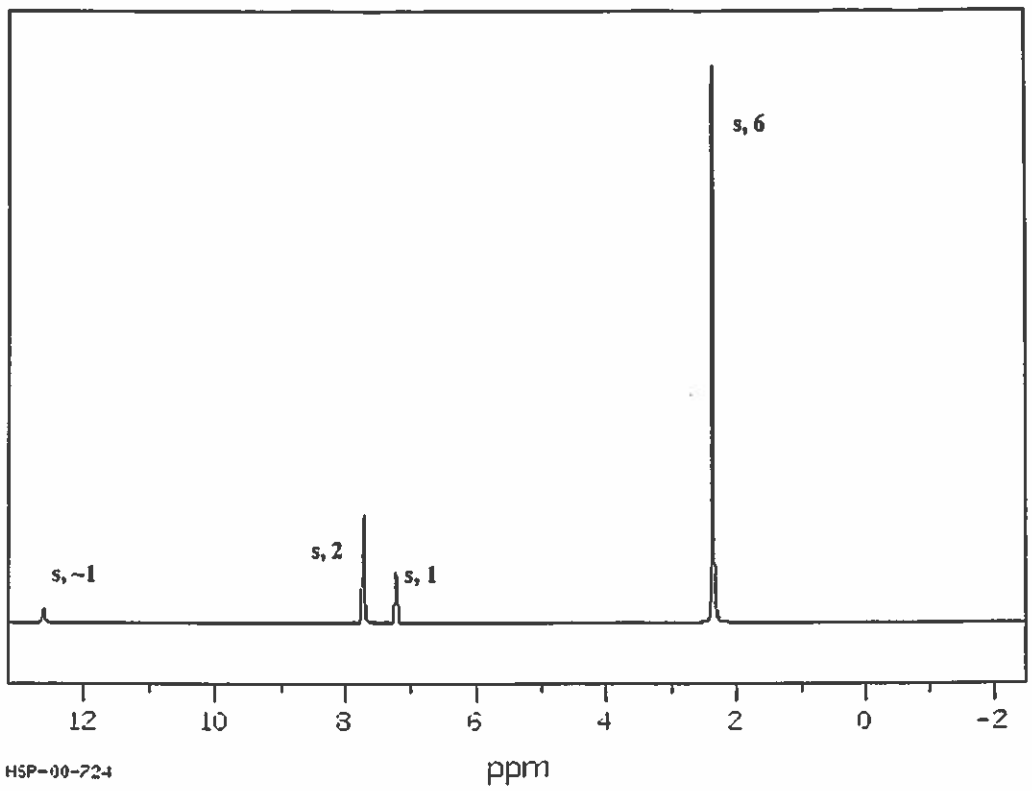

100
50
0
4000
3000
2000
1500
1000
500

V

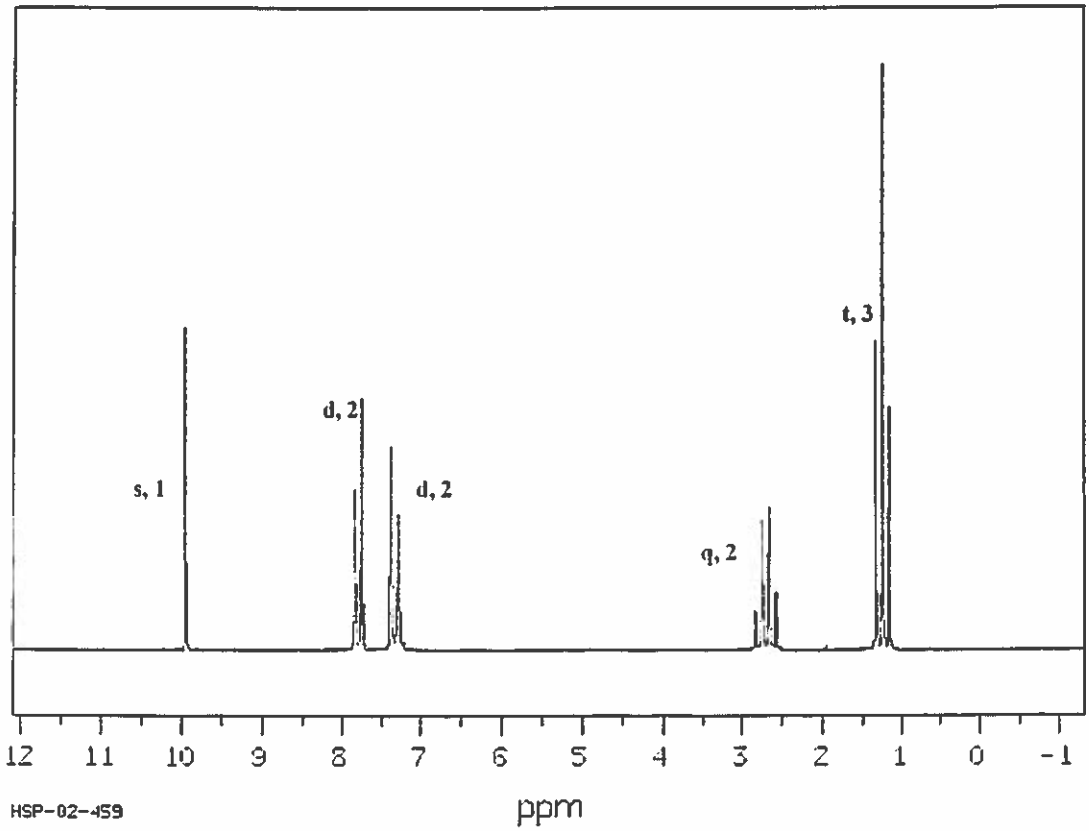

100
50
0
4000
3000
2000
1500
1000
500

NMR Spectra:

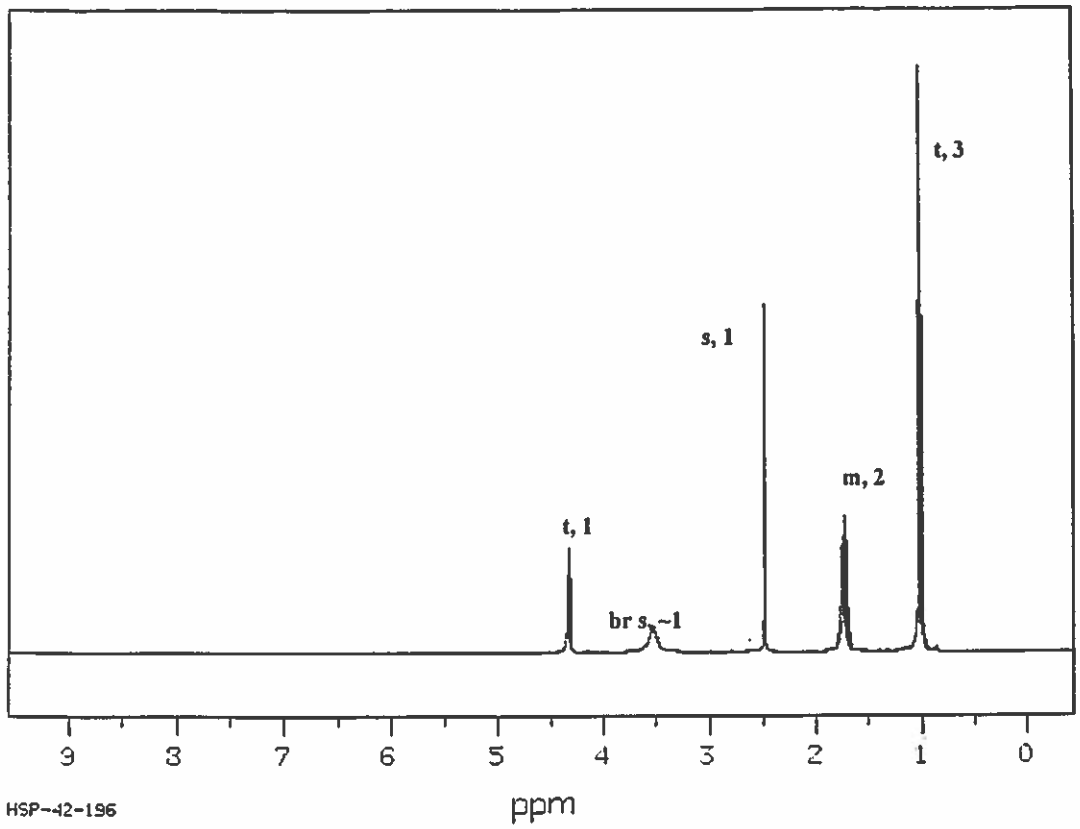
i.



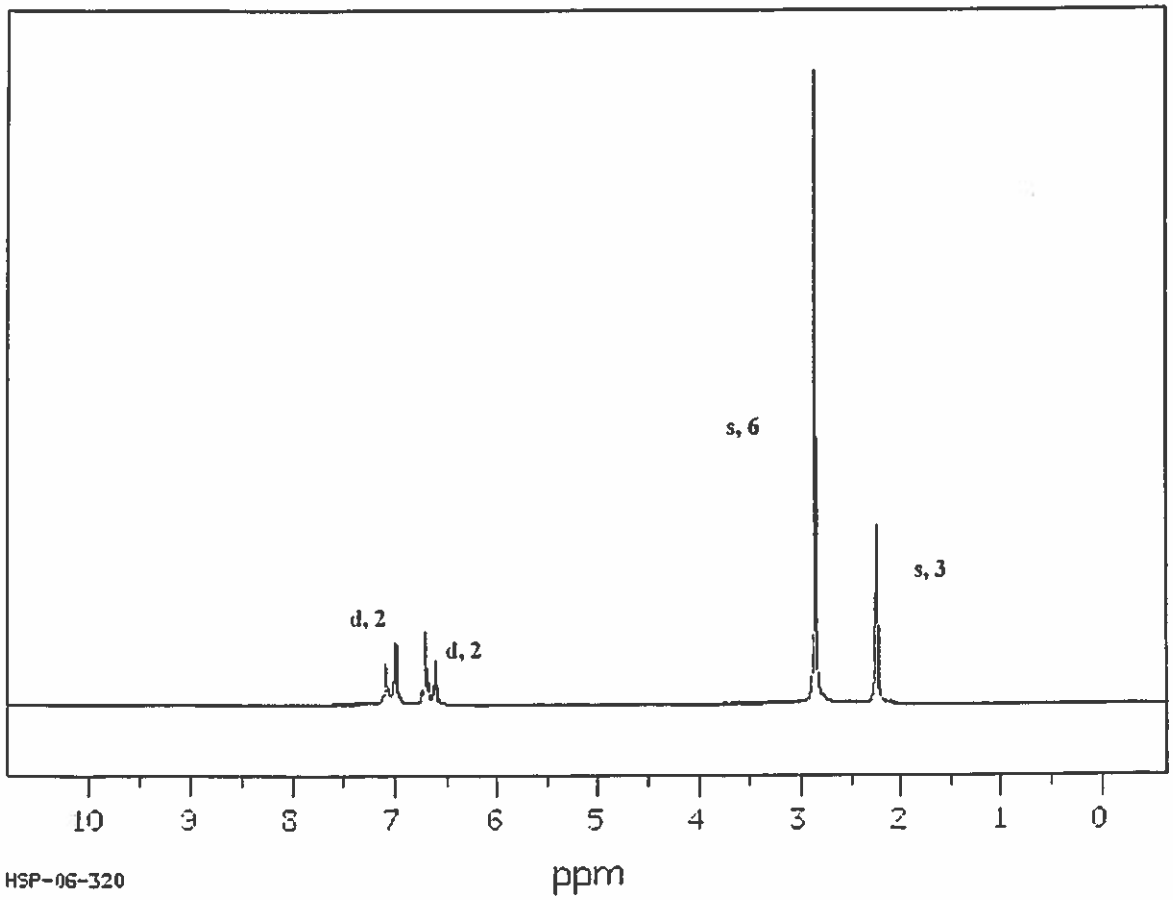
ii.



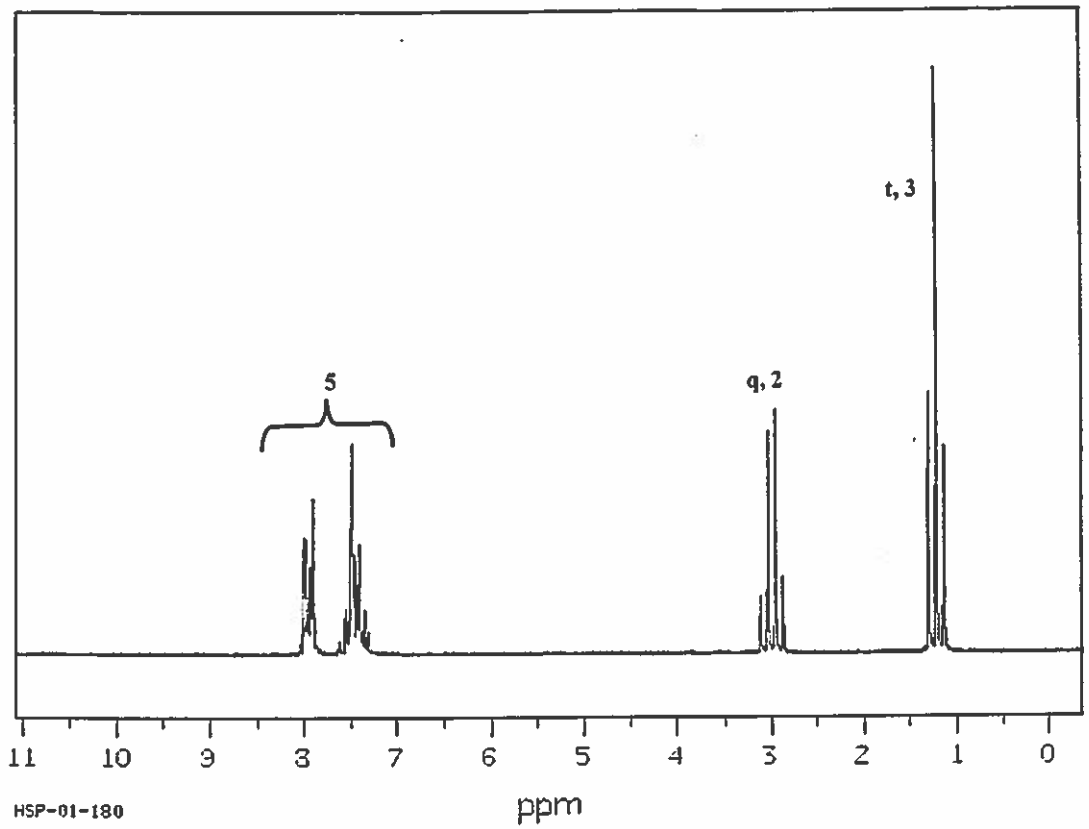
iii.


t, 3
s, 1
m, 2
t, 1
br s, ~1
9
8
7
6
5
4
3
2
1
0
HSP-42-196
ppm

iv.


s, 6
s, 3
d, 2
d, 2
10
9
8
7
6
5
4
3
2
1
0
HSP-06-320
ppm

V.



2. Which of the statements **A-E** regarding IR spectroscopy is FALSE? *Circle all that apply.* **(6)**

   (A.) When matter is exposed to electromagnetic radiation, it always causes vibrational excitations to take place.
   B. A bond between two lighter atoms will vibrate at a higher frequency than a bond between two heavier atoms.
   (C.) Wavenumber is inversely proportional to energy.
   (D.) Amide carbonyls absorb at slightly higher frequencies than aldehyde or ketone carbonyls.
   E. Bonds between sp^3-hybridized atoms tend to vibrate at slightly lower frequencies than do bonds between sp^2- or sp-hybridized atoms.

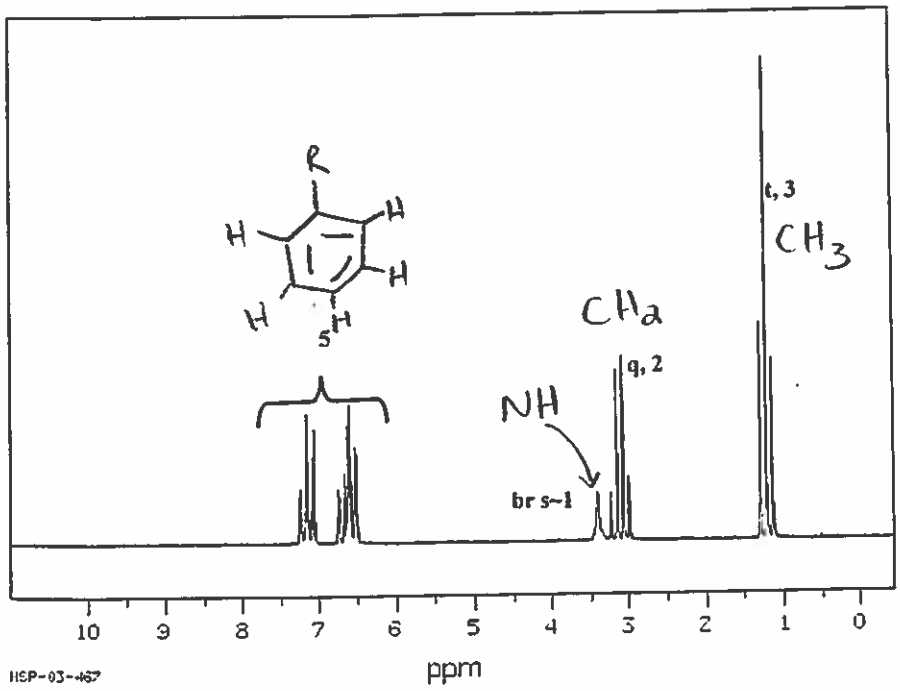
3. Which of the statements **A-E** regarding NMR spectroscopy is TRUE? *Circle all that apply.* **(6)**

   (A.) For a nuclear spin excitation to occur, the nucleus must be subjected to a specific frequency of EM radiation in the radiofrequency region.
   (B.) The more electron density around a given nucleus, the less of the applied magnetic field is "felt" by the nucleus.
   C. All NMR-active nuclei will absorb the same frequency of radiation.
   (D.) The amount of energy required to cause nuclear spin excitation is directly proportional to the strength of the magnetic field to which the nucleus is exposed.
   E. In an NMR spectrum, signals that are to the left are said to be "upfield" from signals to the right.

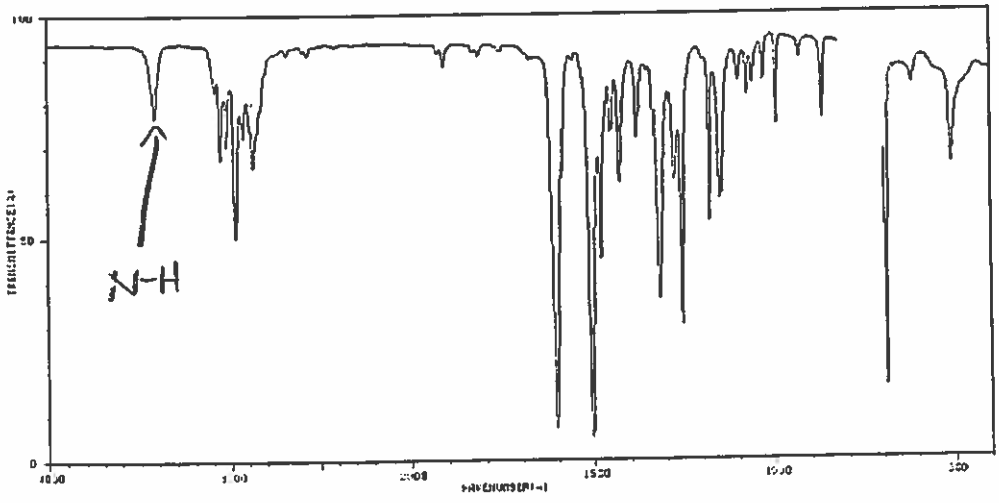
4. Solve the structures. The IR and proton NMR spectroscopy data for three isomers (A-C) of $C_8H_{11}N$ is given below. Propose a structure for each isomer that is consistent with the data. *Remember to show your work for partial credit.* **(15)**

IHD (or "units of unsaturation") calculation: $\frac{[(8\times2)+2]-10}{2} = \frac{8}{2} = 4$

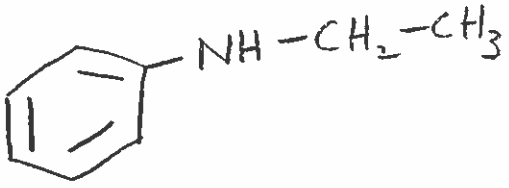
Isomer A



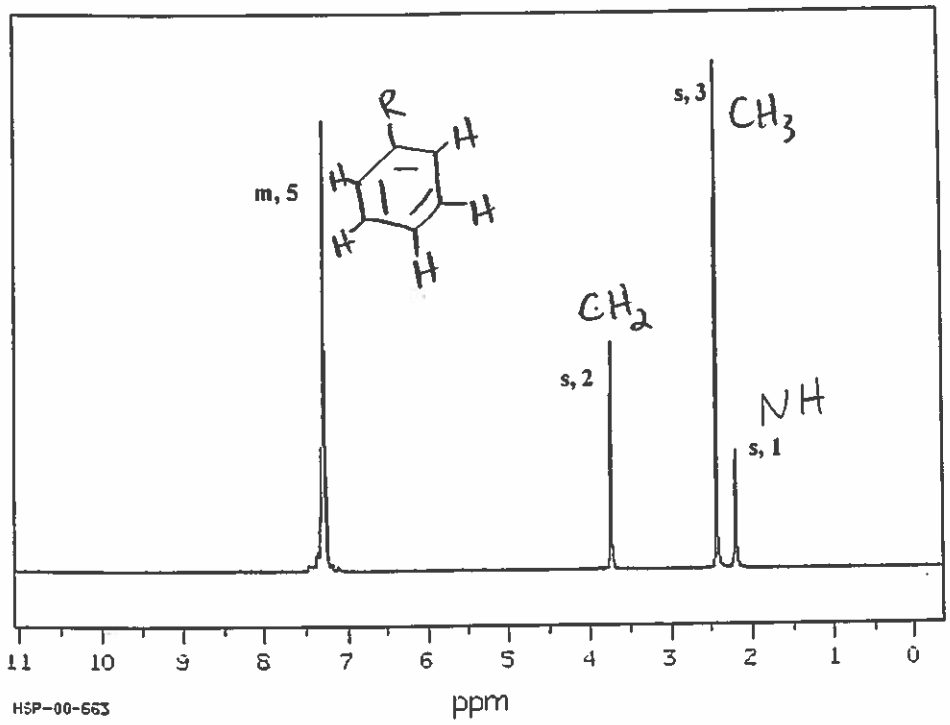
q t
$-CH_2-CH_3$



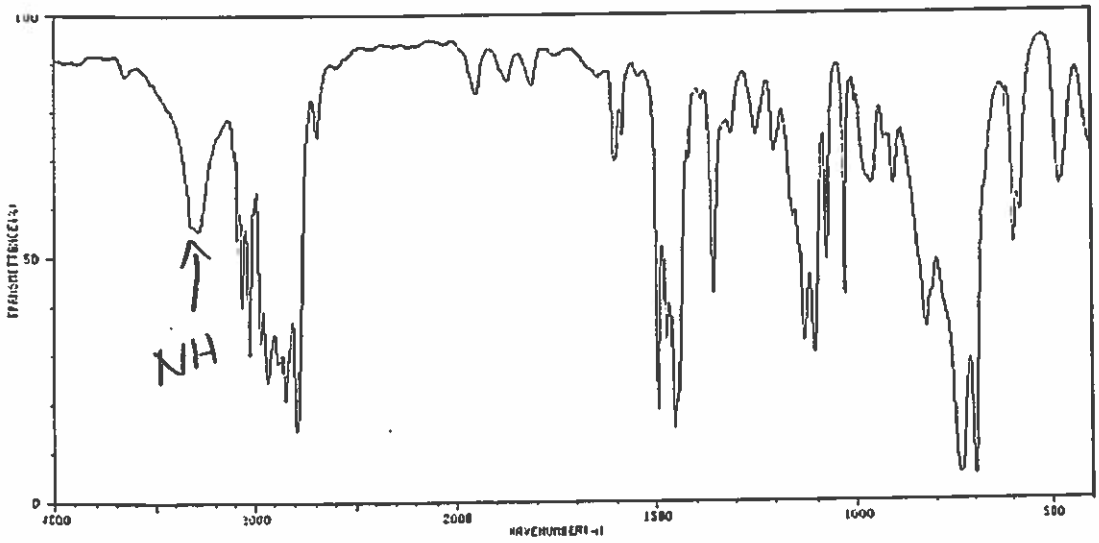
Structure of Isomer A:



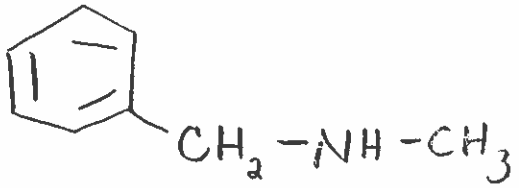
Isomer B



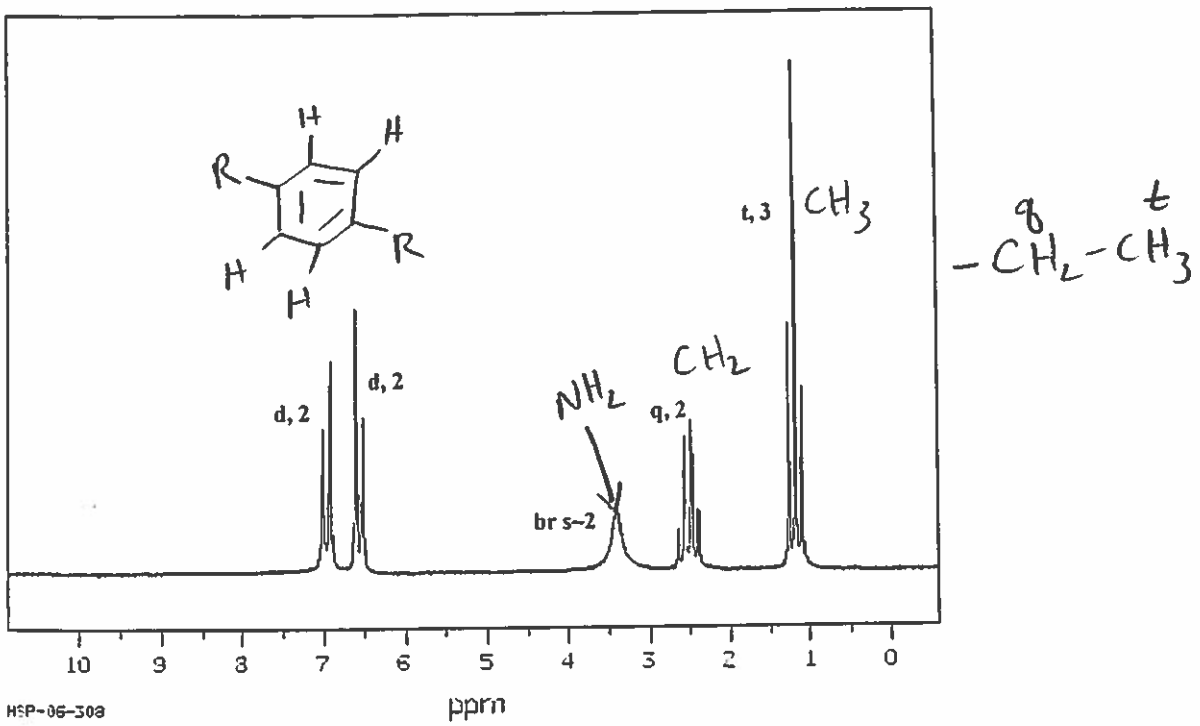
- NH does not always participate in splitting (discussed in class)
- Shift & integration can vary

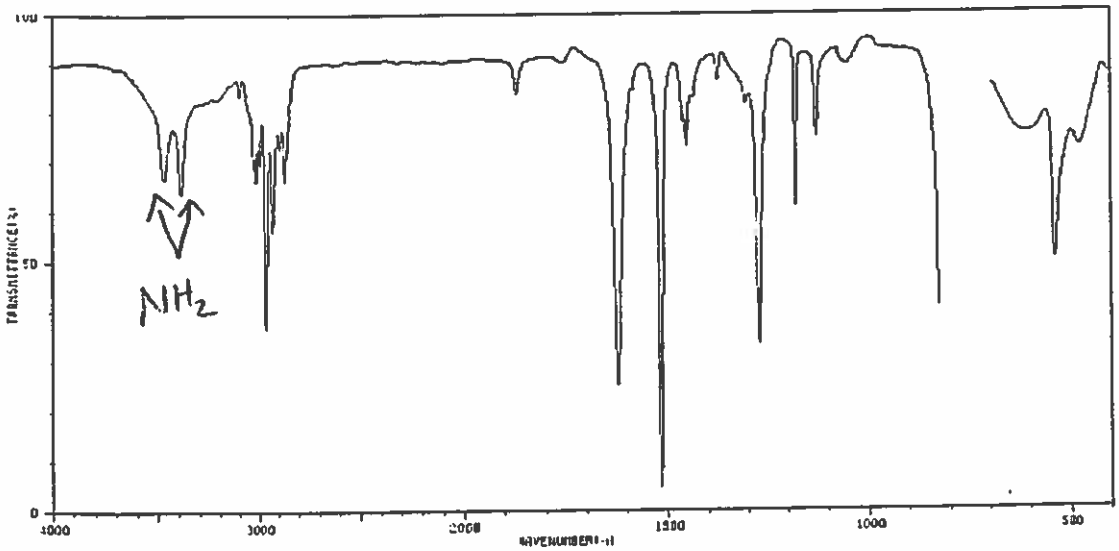


Structure of Isomer B:

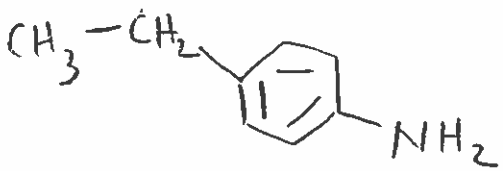


Isomer C





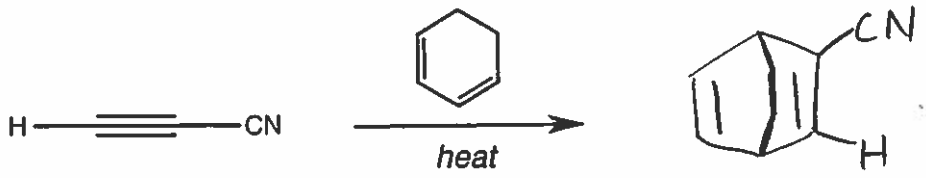
Structure of Isomer C:



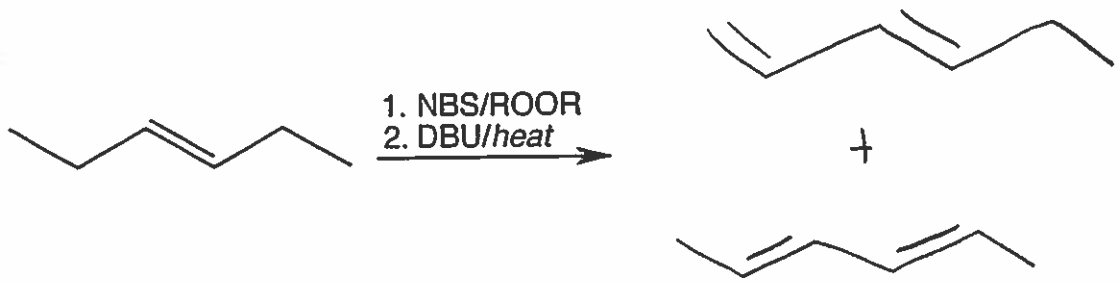
PART TWO: PREDICT THE PRODUCT

For each the following questions **5-10** predict the **major** organic product(s) showing stereochemistry where appropriate. **(18)**

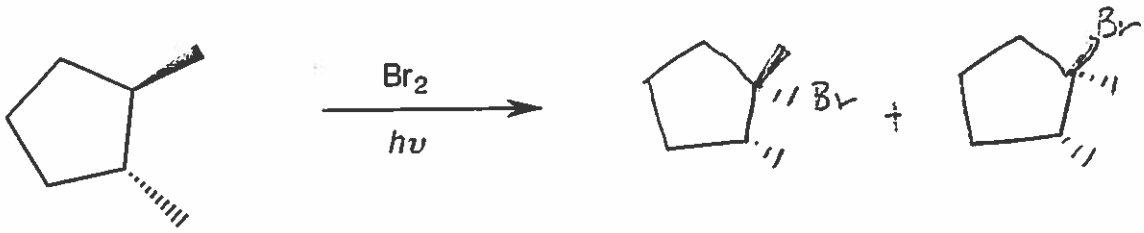
5.



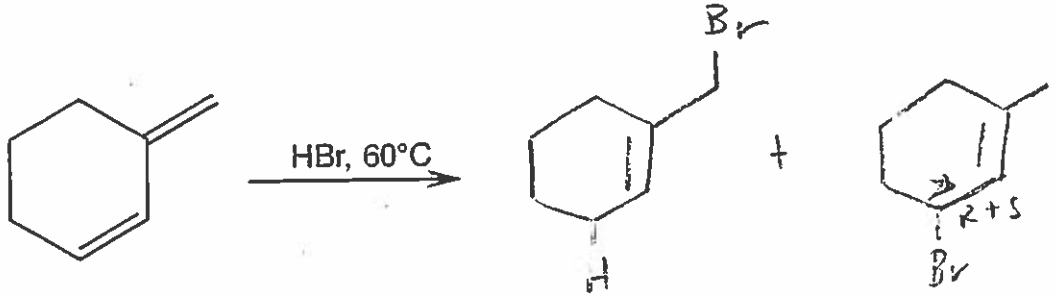
6.



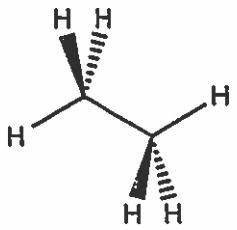
7.



8.



9.

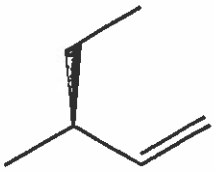


1. Cl_2, *hv*

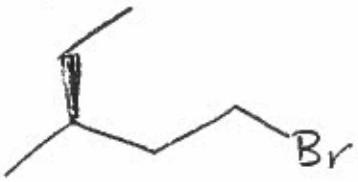
2. ^{t}BuOK, *heat*

$CH_2 = CH_2$

10.

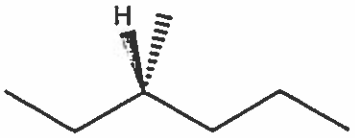


HBr, *hv*



PART THREE: MECHANISM/STRUCTURE/REACTIVITY

Consider the free-radical halogenation of 3-methylhexane (shown below). **(10)**



X_2

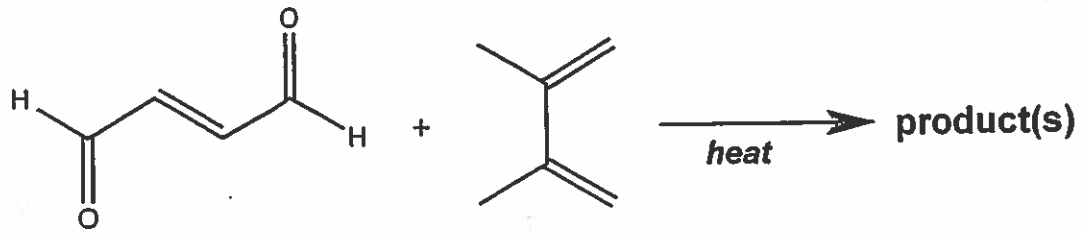
initiator

organic product(s) + inorganic by-product(s)

Indicate if each statement (**11-15**) is true (**T**) or false (**F**) regarding the reaction above.

11. The reaction rate would be faster if X = Br than if X = Cl. F
12. The initiation and propagation steps of the reaction both produce radical products. T
13. A possible organic product of this reaction would have the formula $C_{14}H_{30}$. T
14. The product of the reaction will be achiral overall. T
15. The pH of the reaction medium should become acidic as the reaction proceeds. T

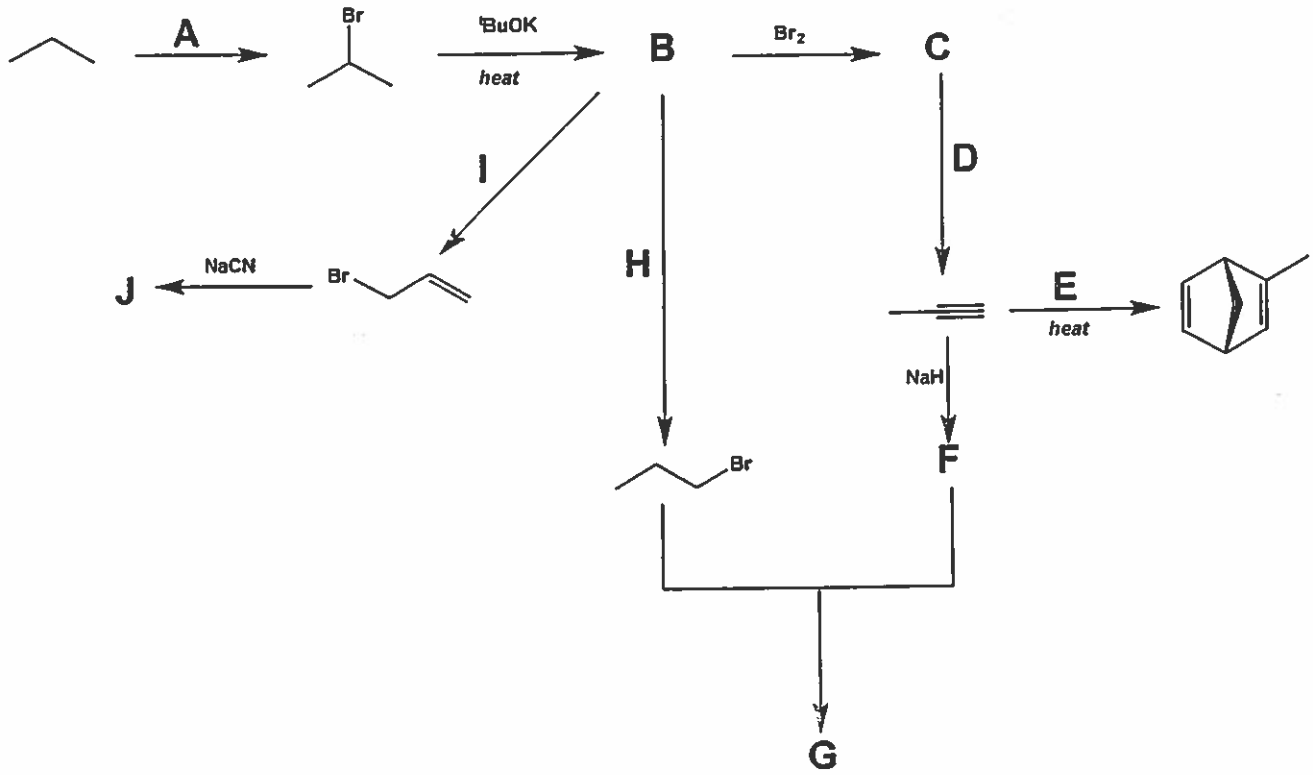
16. Circle the FALSE statement (A-E) regarding the following Diels-Alder reaction. (5)

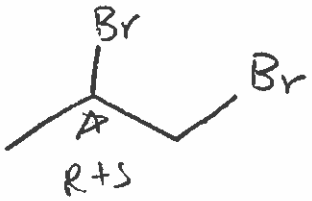


A. The reaction will form a six-membered ring.
B. The reaction will generate a *meso* product. (racemic)
C. The reaction product(s) will have *trans* geometry.
D. The reaction proceeds through a concerted mechanism.
E. During the reaction two new C-C σ-bonds are formed.

PART THREE: SYNTHESIS

17. Fill in the missing reagents and/or products in the synthetic scheme outlined below. **Place your answers in the table provided on the next page.** (20)



Letter	Missing Reagent/Product	Letter	Missing Reagent/Product
A	Br_2 → (hv or Δ or ROOR)	F	$-C\equiv C:^{\ominus}$
B		G	$-C\equiv C-$ 
C		H	HBr → (hv or Δ or ROOR)
D	$2\ NaNH_2$ or $2\ K\ ^tBuO$ (2 NaH also accepted)	I	NBS → (hv or Δ or ROOR)
E		J