UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

WEDNESDAY MARCH 9th, 2011 Time: 2 Hours

PLEASE WRITE YOUR NAME AND FULL STUDENT I.D. NUMBER ON BOTH YOUR COMPUTER ANSWER SHEET and on the **ANSWER BOOKLET** provided.

READ ALL THE INSTRUCTIONS CAREFULLY

The exam consists of Parts 1 - 7, each of which should be attempted. Note that some Parts provide you with a choice of questions, *e.g*. answer any 5 out of 6. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. Parts 1 - 4 will be computer graded, and Parts 5, 6 and 7 are to be answered **IN THE BOOKLET PROVIDED**. A periodic table with atomic numbers and atomic weights and spectroscopic data tables are included with this examination paper.

Parts 1 - 4 consist of a series of multiple choice questions numbered 1 - 34 which are to be answered on the computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a soft pencil only and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***. **Absolutely no other electronic devices are allowed.**

PART 1: RELATIVE PROPERTIES

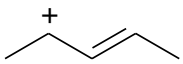
16% **ANSWER ANY EIGHT (8) OF QUESTIONS 1-10**.

Arrange the items in each of the questions in this section in DECREASING ORDER (*i.e.* greatest first) with respect to the indicated property.

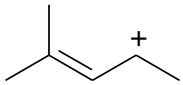
Use the following code to indicate your answers.

A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative stability of each of the following:



i



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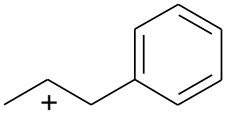
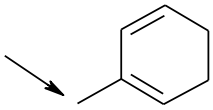
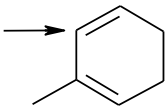


iii

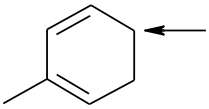
2. The relative strengths of the CH bonds at the positions indicated in each of the following:



i

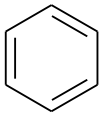


ii

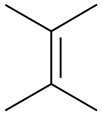


iii

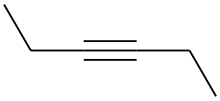
3. The relative reactivity of each of the following towards HCl:



i



ii



iii

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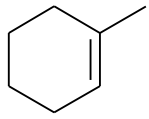
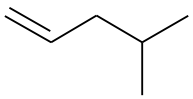
Use the following code to indicate your answers.

A.	**i** > **ii** > **iii**	**D**.	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	**E**.	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	**AB**.	**iii** > **ii** > **i**

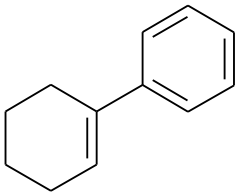
4. The relative rate of reaction of each of the following towards HBr / dark / N_2:



i

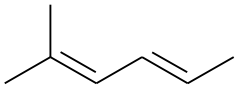


ii

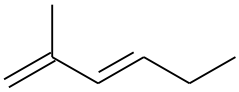


iii

5. The relative stability of the following:



i



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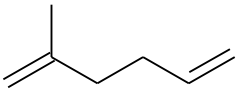
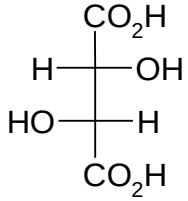


iii

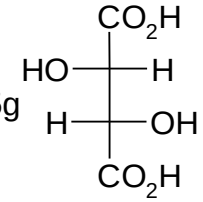
6. The optical purity of the following samples of tartaric acid given that (R,R)-tartaric acid $[\alpha]_D$ = +12.7 :

i a mixture composed of :

0.25g



0.75g



ii a sample whose observed rotation = + 2.54^o when 2.00g of a mixture was dissolved in 10mL and measured in a standard 10cm polarimeter cell

iii a racemic mixture

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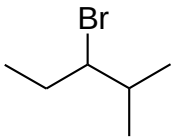
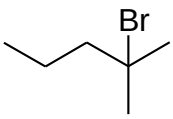
Use the following code to indicate your answers.

A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

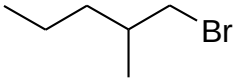
7. The relative yields of the following products from the reaction of 2-methylpent-2-ene with HBr / peroxides :



i



ii



iii

8. The % yield of the product alcohol from each of the following reactions of propene with BH_3 followed by work up with excess alkali H_2O_2:

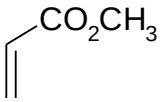
   i. 4.2g propene with 0.10 mol BH_3 giving 3.0g 1-propanol

   ii. 4.2g propene with 0.02 mol BH_3 giving 3.0g 1-propanol

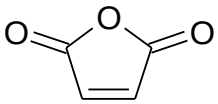
   iii. 0.3 mol propene with 0.1 mol BH_3 giving 6.0g 1-propanol

9. The relative reactivity of each of the following towards cyclopentadiene:

i

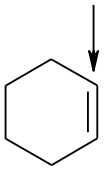


ii

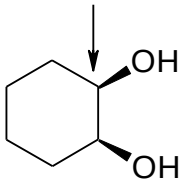


iii

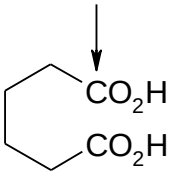
10. The relative oxidation states of the C atoms indicated in each of the following:



i



ii



iii

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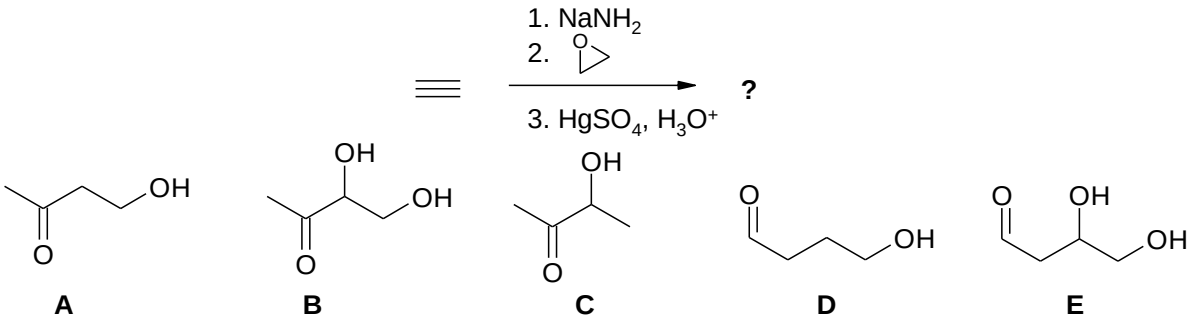
PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS

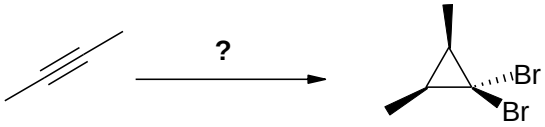
14% **ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.**

For each of questions 11-18 select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

11.

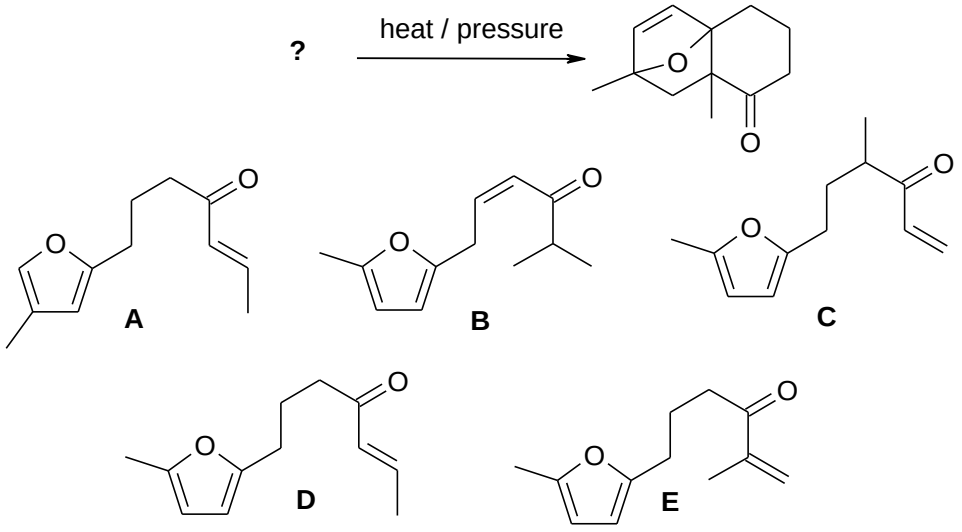


12.



A	1. H_2 / Pd	2. CH_2Br_2 / Zn Cu
B	1. Na / NH_3	2. CH_2Br_2 / Zn Cu
C	1. H_2 / Lindlar's catalyst	2. CH_2Br_2 / Zn Cu
D	1. Na / NH_3	2. $CHBr_3$ / $KOC(CH_3)_3$
E	1. H_2 / Lindlar's catalyst	2. $CHBr_3$ / $KOC(CH_3)_3$

13.



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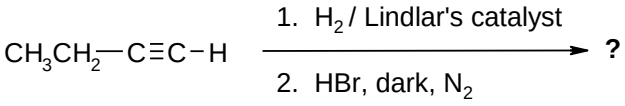
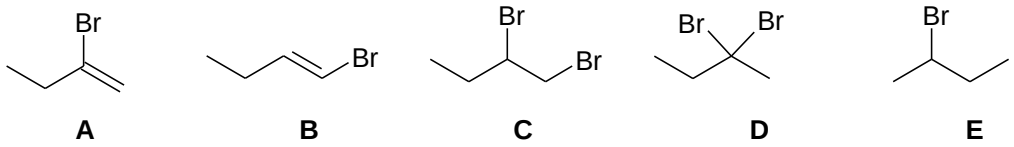
14.





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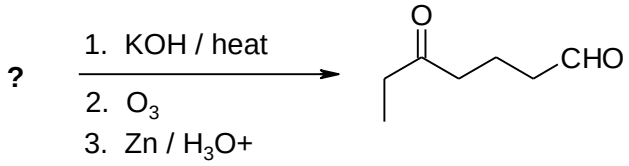

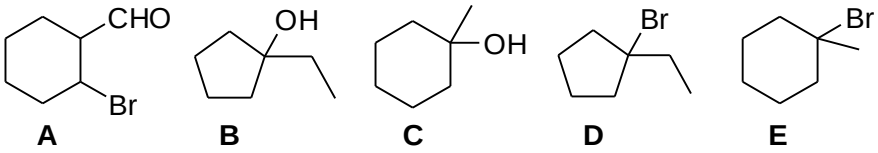

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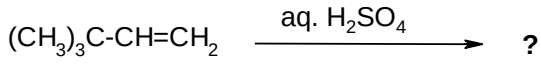

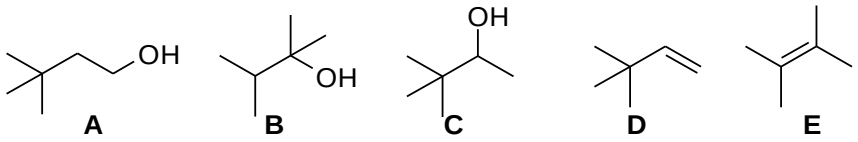

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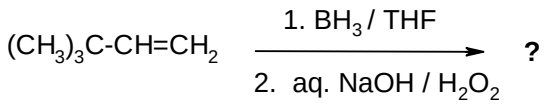

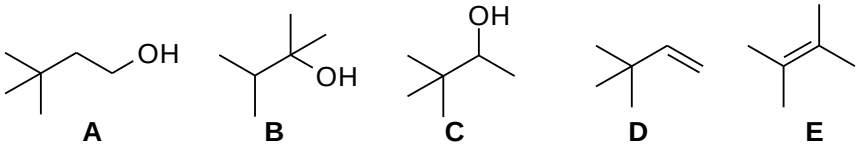

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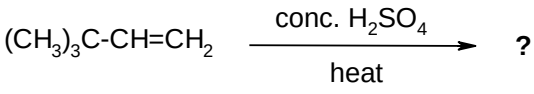

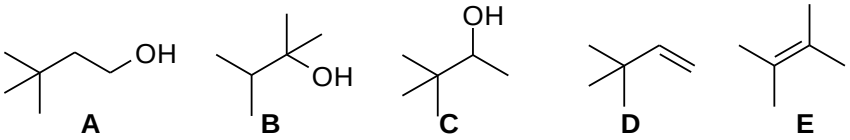

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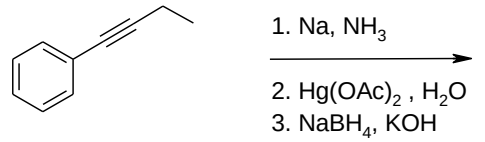
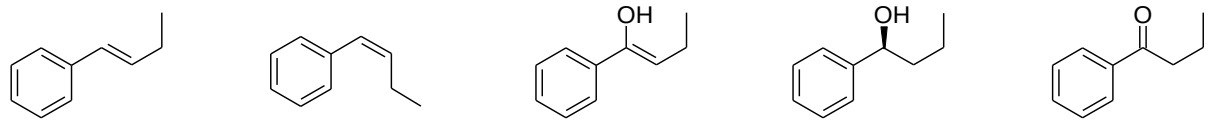
PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

18% **ANSWER ANY SIX (6) OF QUESTIONS 19-25**.

For each of the questions 19-25, select the structure required to BEST complete the reaction shown.

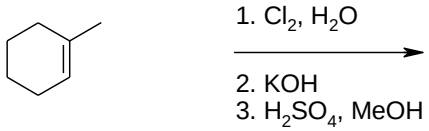
19.

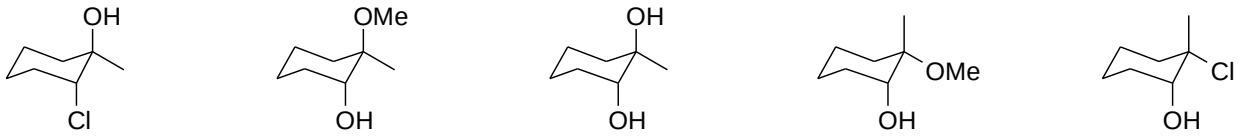




A **B** **C** **D** **E**

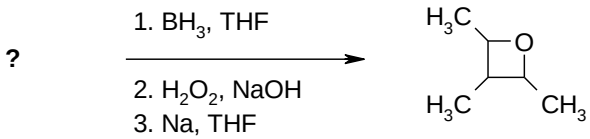
20.

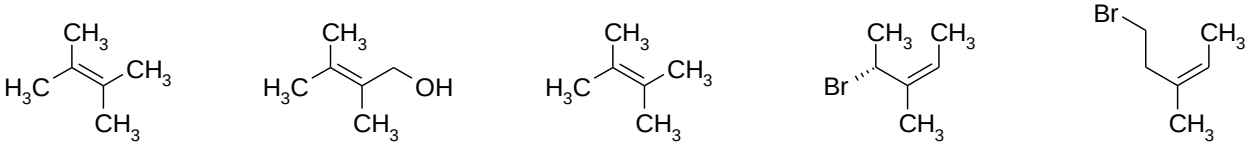




A **B** **C** **D** **E**

21.





A **B** **C** **D** **E**

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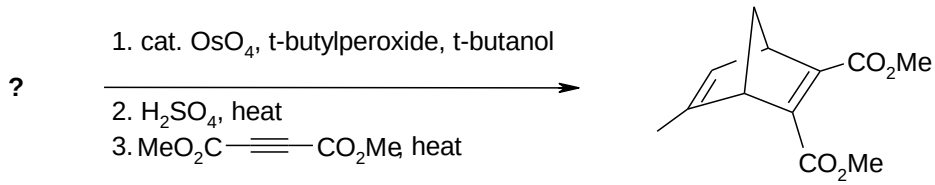
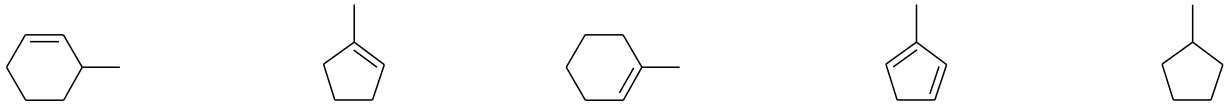
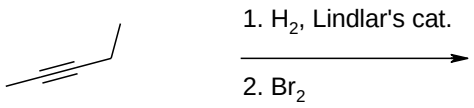
22.

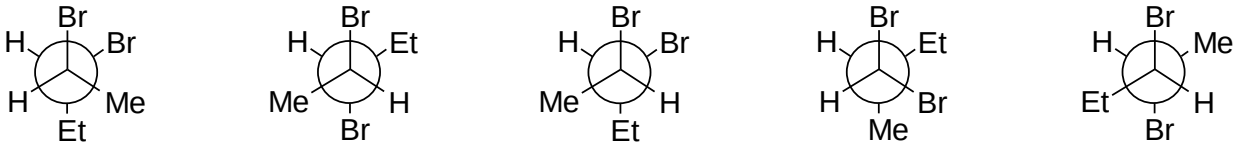




A **B** **C** **D** **E**

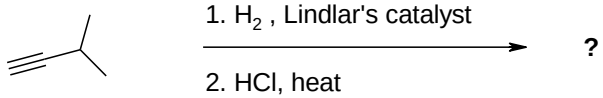
23.

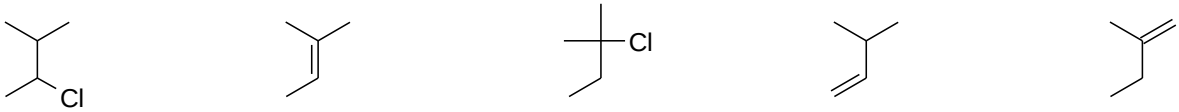




A **B** **C** **D** **E**

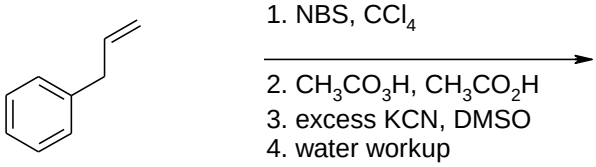
24.

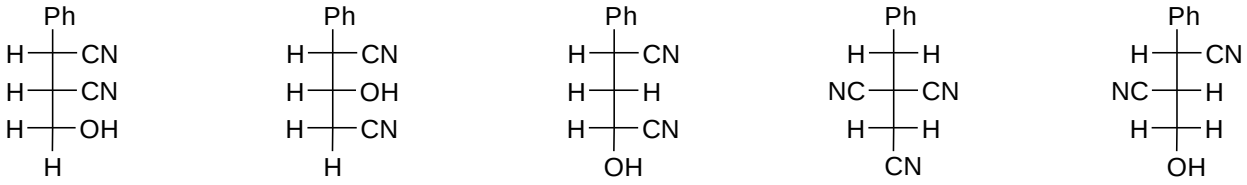




A **B** **C** **D** **E**

25.





A **B** **C** **D** **E**

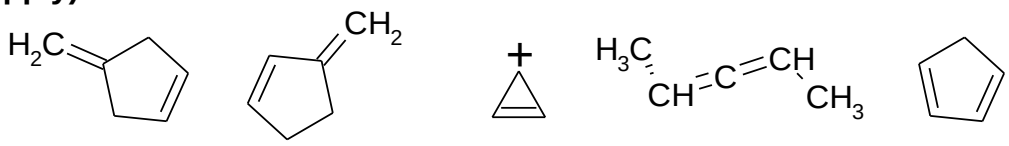
CONTINUED -->

PART 4: PI SYSTEMS

16% **ANSWER ANY EIGHT (8) of the questions 26 - 34.**

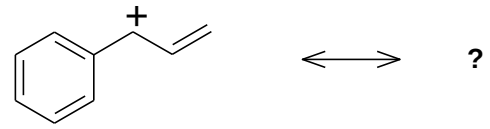
For each of the questions 26-34 select the appropriate answer from the answers provided. In some cases more than one selection may be required for full credit.

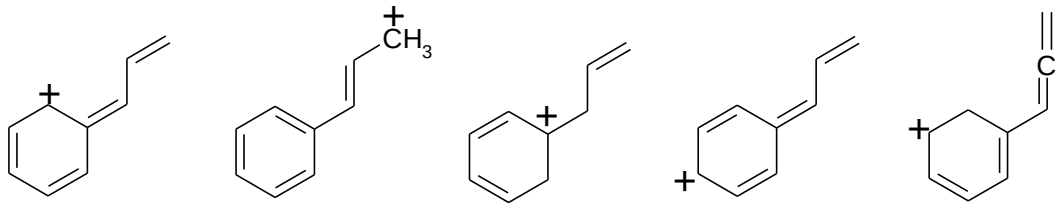
26. Which of the following molecules are **NOT** conjugated systems? **(select all that apply)**



A **B** **C** **D** **E**

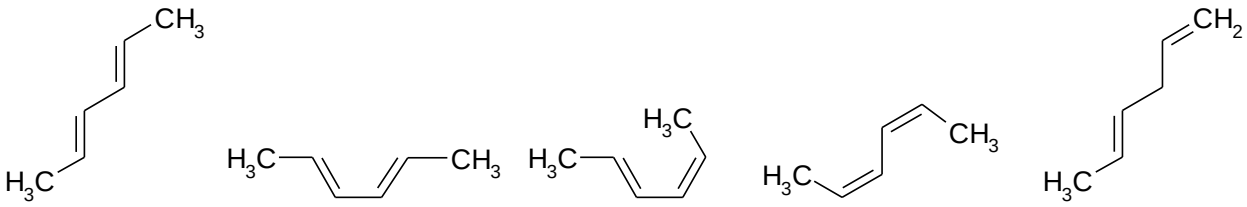
27. Which of the following systems are resonance contributors of the carbocation shown below ? **(select all that apply)**





A **B** **C** **D** **E**

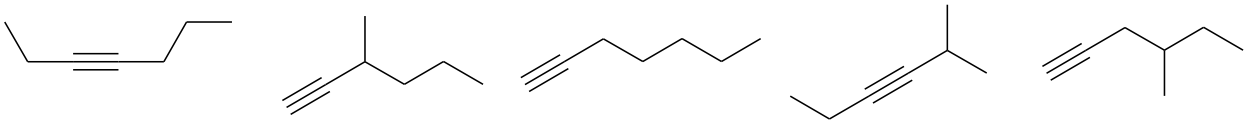
28. Which of the following isomers is the **most** stable as drawn ?



A **B** **C** **D** **E**

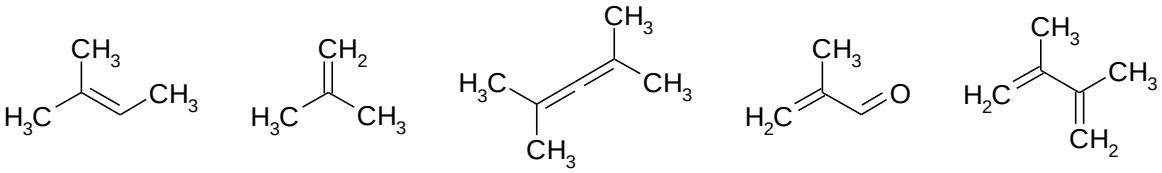
CONTINUED -->

29. Which of the following isomers is the **most** stable ?



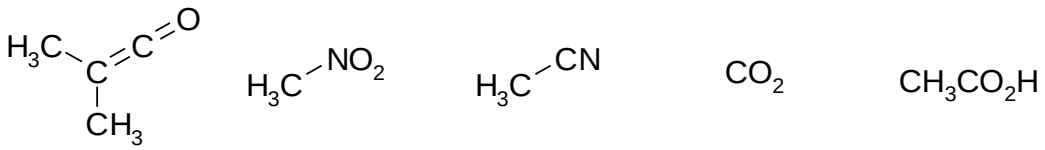
A **B** **C** **D** **E**

30. Which of the following systems has the **most** vinylic carbons ?



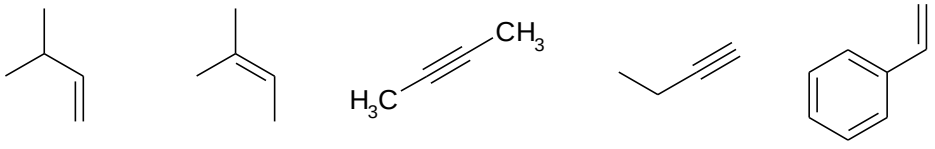
A **B** **C** **D** **E**

31. Which of the following molecules contain sp-hybridised atoms ? **(select all that apply)**?



A **B** **C** **D** **E**

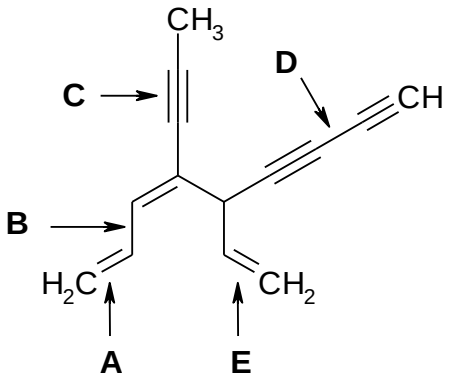
32. Which of the following systems would be the **most** reactive towards aq. H_2SO_4 ?



A **B** **C** **D** **E**

CONTINUED -->

33. Which of the bonds indicated below is the shortest ?



34. Which of the following compounds used in the Chem 353 laboratory experiments will show ^{13}C-NMR resonances between 190-220 ppm ? **(select all that apply)**

A. glycerol (also known as 1,2,3-propane-triol)

B. biodiesel

C. terephthalic acid (the monomer recovered from PETE depolymerisation)

D. benzophenone

E. benzaldehyde

CONTINUED -->

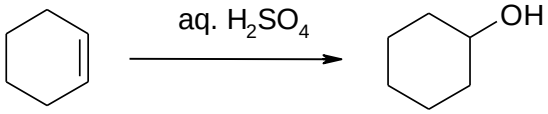
PART 5: MECHANISMS

10% **ANSWER TWO (2) QUESTIONS, ONE FROM PART A and ONE FROM PART B**

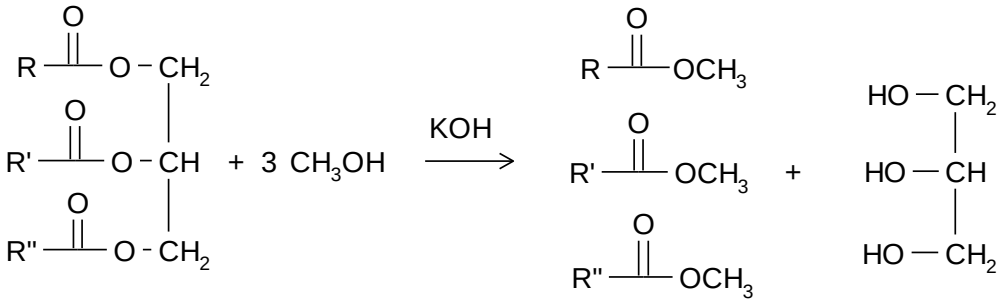
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

Draw curly arrow mechanisms to explain the following reactions / observations. No other reagents are required.

A. Show the mechanism for **one** of the following reactions:

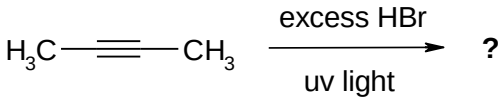


OR



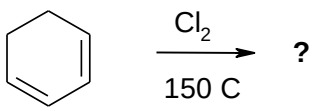
(you only need to show the reaction of one of the chains)

B. Use your knowledge of the reaction of alkenes with HBr and peroxides (or uv light) and of alkynes with HBr (dark / N_2 atmosphere) to predict based on a mechasism the outcome of the following reaction:



OR

Use your knowledge of the reactions of alkenes and dienes with halogens at high temperature to predict the outcome of the following reaction:



CONTINUED -->

PART 6: SYNTHESIS

15% **ANSWER ANY THREE (3) OF QUESTIONS**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

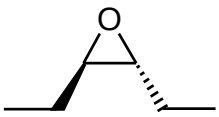
Design an efficient synthesis for any THREE (3) of the following target molecules

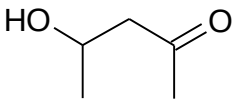
SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE PRODUCT OF EACH STEP

DO NOT SHOW MECHANISMS (i.e. curly arrows are NOT required)

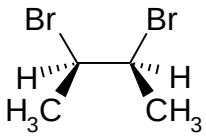
Allowed starting materials and reagents: any compounds with 3 or less C atoms

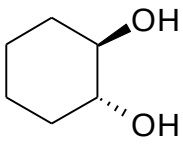
In addition, you may use any solvents or reagents that do not contribute carbon atoms to the final structure.





1,2-dimethylbenzene





CONTINUED -->

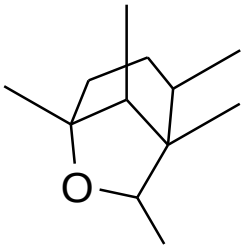
PART 7: STRUCTURE DETERMINATION

11% **WRITE YOUR ANSWER IN THE BOOKLET PROVIDED**

Use the information in the following paragraph to answer the questions below.

Compound **A** ($C_6H_{12}O$), an alkene, was reacted with PBr_3 / Et_3N in THF to give **B** ($C_6H_{11}Br$). **A** was also reacted with H_2SO_4 and heat to give **C** (C_6H_{10}). Hydrocarbon **C** quickly reacted with Br_2 at high temperatures to give **D** ($C_6H_{10}Br_2$) as a racemic mixture. The enantiomers of **D** were separated and one enantiomer of **D** was treated with potassium permanganate, in the presence of KOH at 0°C to give (2S,3S,4R)-1,4-dibromo-3-methylpentane-2,3-diol and (2R,3R,4R)-1,4-dibromo-3-methylpentane-2,3-diol in equal amounts.

Molecules **B** and **C** were heated in a sealed tube to give **E** ($C_{12}H_{21}Br$), which was further reacted with aqueous acid to give **F** ($C_{12}H_{23}BrO$). **F** was dissolved in THF and sodium metal was added, which resulted in the formation of the molecule shown below.



Draw the structures of A to F.

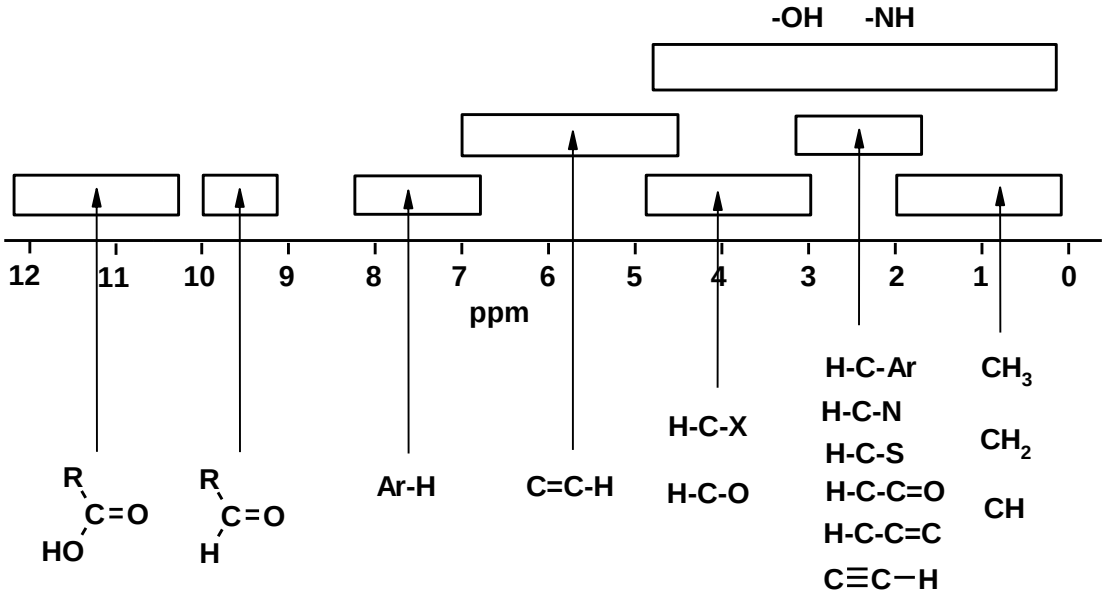
Which isomer of D was used in the reaction?

How many configurational isomers of D are theoretically possible?

***** THE END *****

SPECTROSCOPIC TABLES

^{1}H NMR

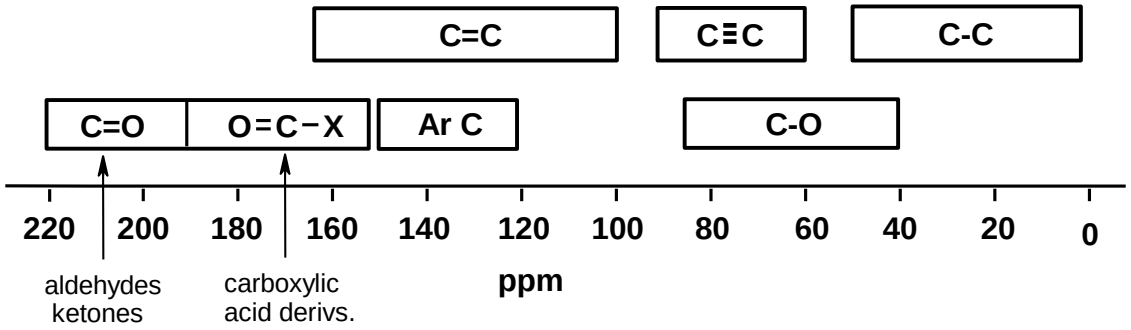


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

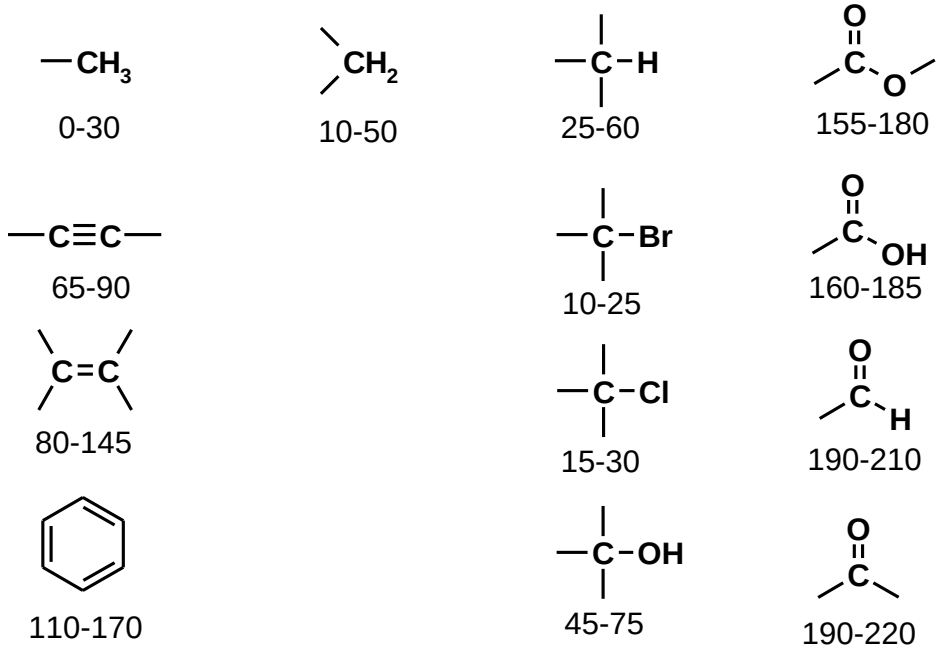
	methyl CH_3-	methylene -CH_2-	methyne CH
R−C(−)(−)—	0.9	1.4	1.5
R, C=C	1.6	2.3	2.6
O, C, R	2.1	2.4	2.5
R−N(−)(−)	2.2	2.5	2.9
R-Ar	2.3	2.7	3.0
R−Br	2.7	3.3	4.1
R−Cl	3.1	3.4	4.1
R−O—	3.3	3.4	3.7

other	
-OH	1-5
-NH	1-3
C≡CH	2.5
C=C, H	5.5
Ar-H	7.3
O, C, R, H	10
O, C, R, OH	9-12

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
	$-CH_3$	(bend)	1450 and 1375	6.90 and 7.27	m
	$-CH_2-$	(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R-NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad.

PERIODIC TABLE

1 1A																	**18** 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	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** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	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** 65.38	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** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	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** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	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
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)