

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

WEDNESDAY MARCH 7th, 2007

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 THE INSTRUCTIONS CAREFULLY

The exam consists of Parts 1 - 8, each of which should be attempted. Note that some Parts provide you with a choice of questions, e.g. 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 - 5 will be computer graded, and Parts 6, 7 and 8 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 - 5 consist of a series of multiple choice questions numbered 1 - 45 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.

Absolutely no electronic devices are allowed.

PART 1: RELATIVE PROPERTIES

12% ANSWER ANY SIX (6) OF QUESTIONS 1-8.

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 |

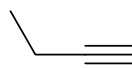
1. The pK_a 's of the most acidic hydrogen in each of the following:



i

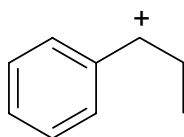


ii

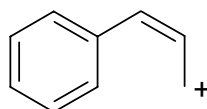


iii

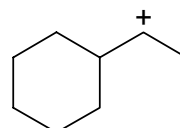
2. The relative stability of each of the following:



i

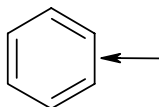


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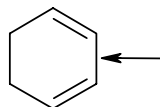


iii

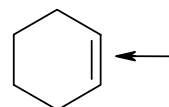
3. The relative CC bond length indicated in each of the following:



i

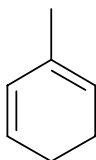


ii

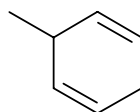


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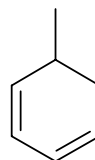
4. The relative heat of combustion (least negative to most negative) of each of the following:



i



ii



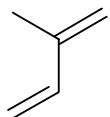
iii

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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 |

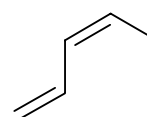
5. The relative reactivity towards *cis*-dimethyl butendioate (also known as dimethyl maleate) of each of the following:



i



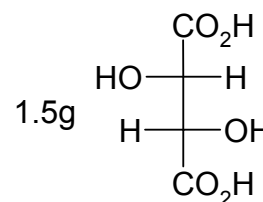
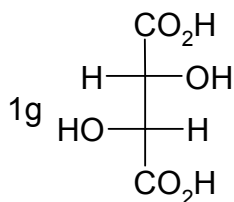
ii



iii

6. The enantiomeric excesses for the following mixtures given that (R,R)-tartaric acid $[\alpha]_D = +12.7$:

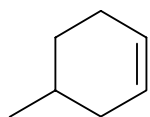
i a sample composed of :



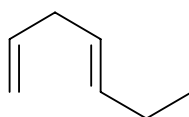
ii a sample whose observed rotation = -0.806° when 1.27g of the sample was dissolved in 10mL and measured in a standard 10cm polarimeter cell

iii a racemic mixture

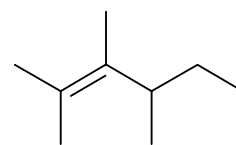
7. The number of different organic products obtained by the reaction of each of the following with ozone followed by Zn in water:



i



ii



iii

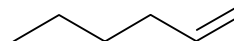
8. The relative reactivity of each of the following towards aq. H_2SO_4 :



i



ii



iii

CONTINUED -->

PART 2: LABORATORY

14% ANSWER ANY FOURTEEN (14) OF THE SIXTEEN (16) TRUE / FALSE QUESTIONS 9-24.

Questions 9-24 are based on the laboratory component of Chem 353. In each case decide whether the statements are true or false. If the statement is true select "A", if it is "false" then select "B"

Questions 9-12 are from the experiment about the hydrolysis of sucrose.

9. Addition of one equivalent of an alcohol to an aldehyde results in a hemi-acetal.
10. The anomeric carbon is attached to two oxygen atoms.
11. Glucose is a monosaccharide and exists primarily as a six-membered ring in aqueous solution.
12. The rate of a pseudo first order reaction is affected by temperature.

Questions 13-16 are from the experiment about the chemistry of alcohols.

13. Oxidation of a tertiary alcohol results in a ketone.
14. A solution of bromine in chloroform catalyses the dehydration of alcohols.
15. A carboxylic acid and a ketone can be distinguished by the reaction with 2,4-dinitrophenol.
16. Concentrated sulfuric acid is put into the organic waste for disposal.

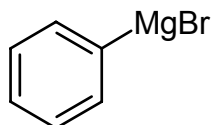
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Questions 17-20 are from the experiment about polymers and plastics.

17. Addition polymers are formed by reaction of bi- or poly-functional molecules, with the elimination of some small molecule (such as water, ammonia, or hydrogen chloride) as a by-product.
18. Nylon is an example of a polyester.
19. Depolymerisation of PET (polyethyleneterephthalate) results in an di-alcohol and a di-carboxylic acid.
20. The reflux apparatus allows solvents to be heated above their normal boiling point.

Questions 21-24 are from the experiment about the synthesis of benzoic acid.

21. Grignard reagents can react with aldehydes, ketones, esters, and epoxides.
22. Exposure to a cryogen results in tearful eyes.
23. In a separatory funnel that contains two solutions, diethyl ether and saturated sodium bisulfite solution, the benzoic acid product would be in the ether layer.
24. Benzylmagnesium bromide is the structure shown below:



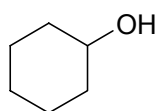
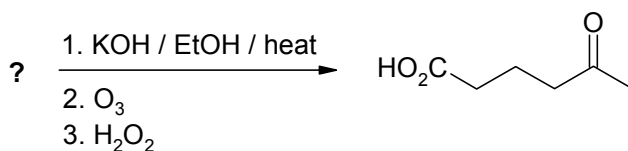
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PART 3: STARTING MATERIALS, REAGENTS AND PRODUCTS

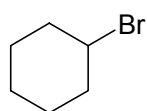
12% ANSWER ANY SIX (6) OF QUESTIONS 25-31.

For each of questions 25-31 select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

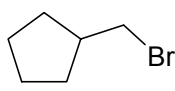
25.



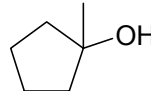
A



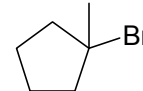
B



C

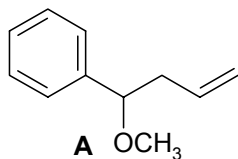
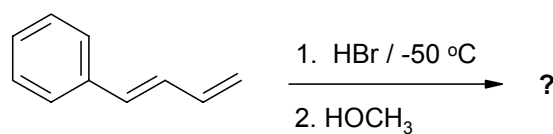


D

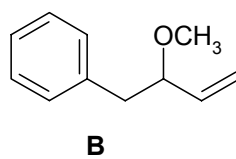


E

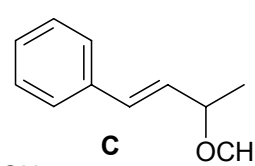
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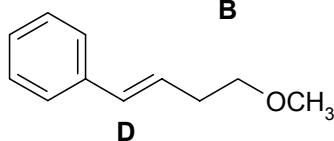
A



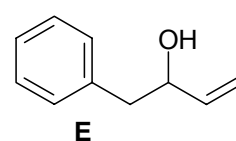
B



C

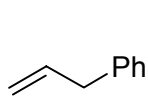
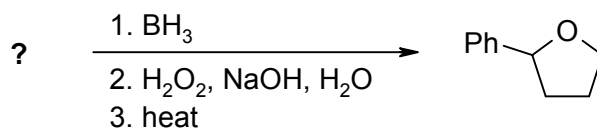


D

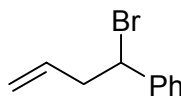


E

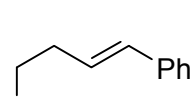
27.



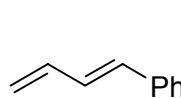
A



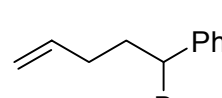
B



C



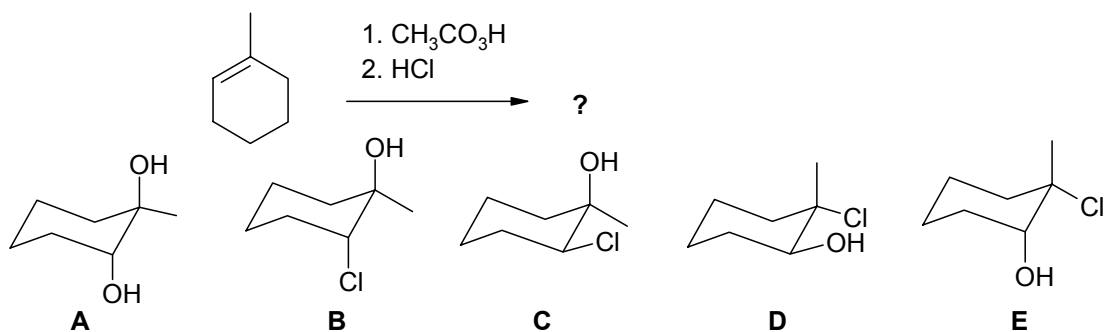
D



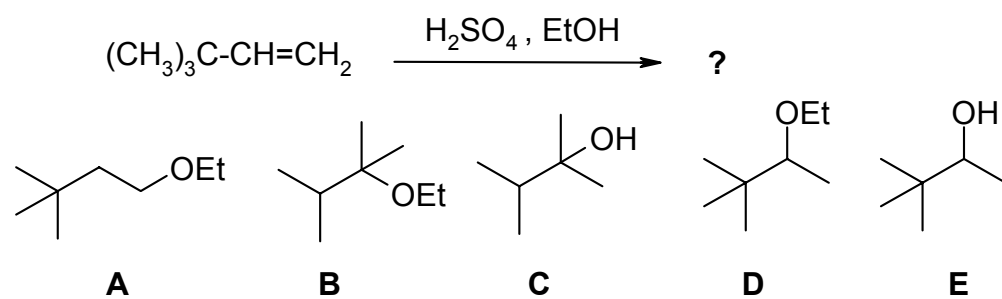
E

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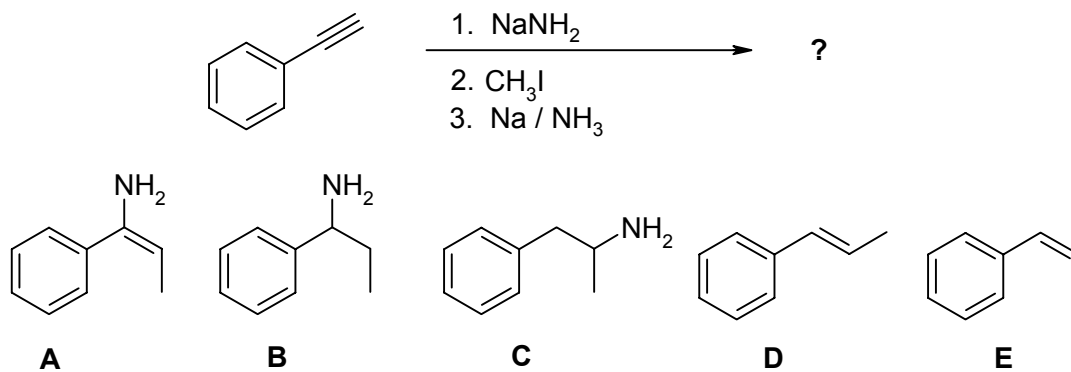
28.



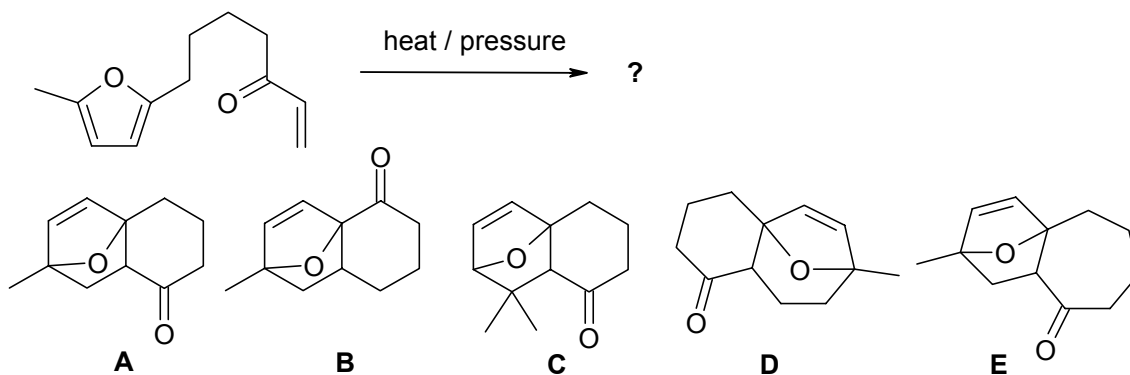
29.



30.



31.



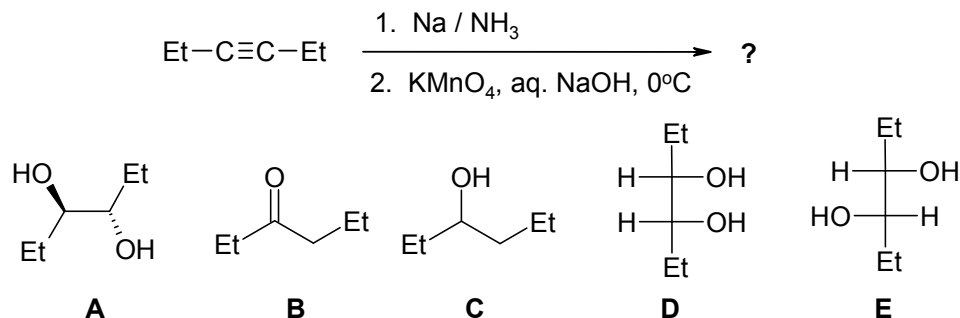
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PART 4: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

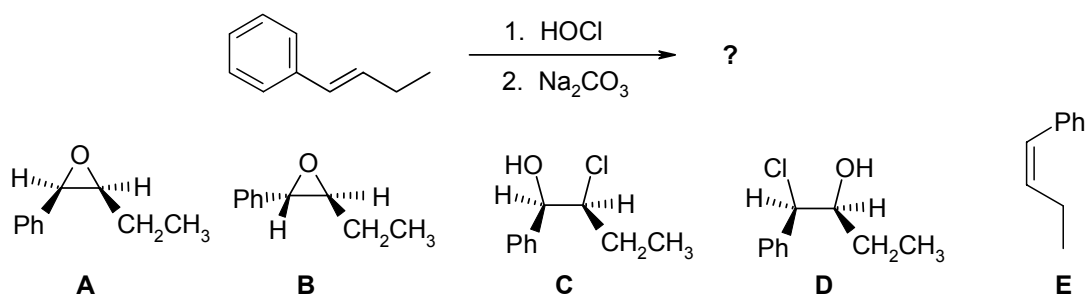
15% ANSWER ANY FIVE (5) OF QUESTIONS 32-37.

For each of the questions 32-37, select the structure required to complete the reaction shown. If two products are equally abundant, then you must indicate both for full marks. If two starting materials will give the same product, then you must indicate both for full marks. In order to indicate more than one structure, blacken the spaces corresponding to each one.

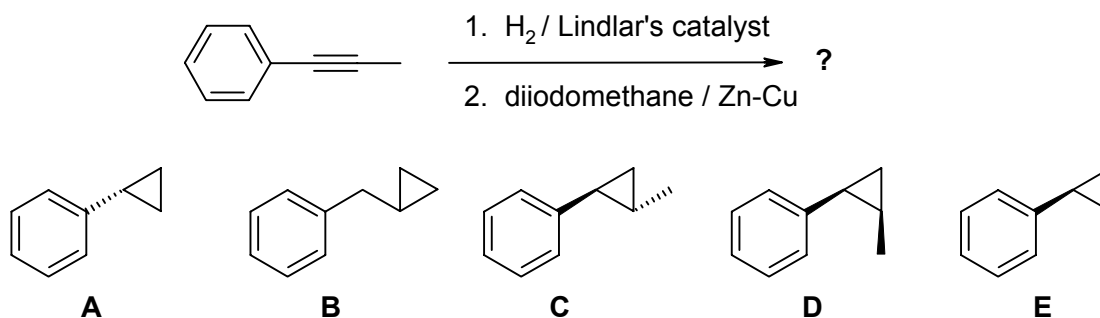
32.



33.

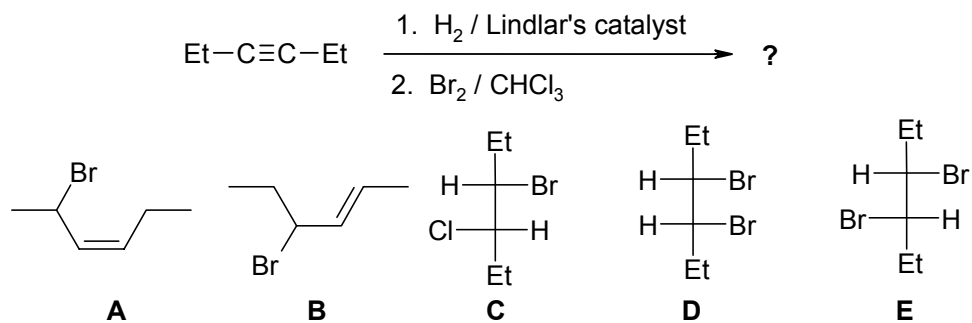


34.

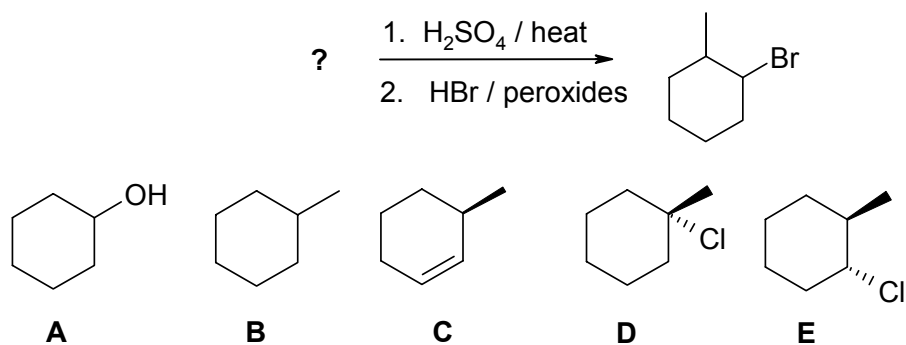


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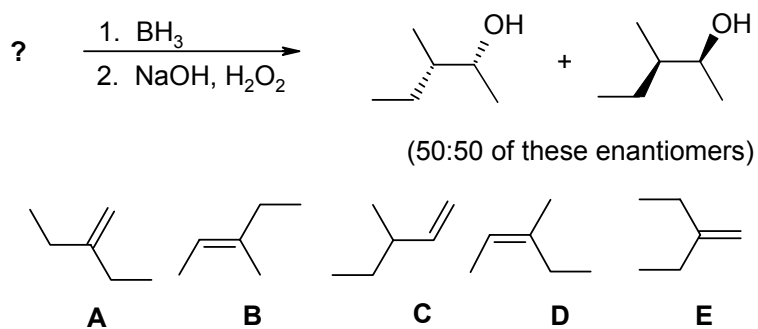
35.



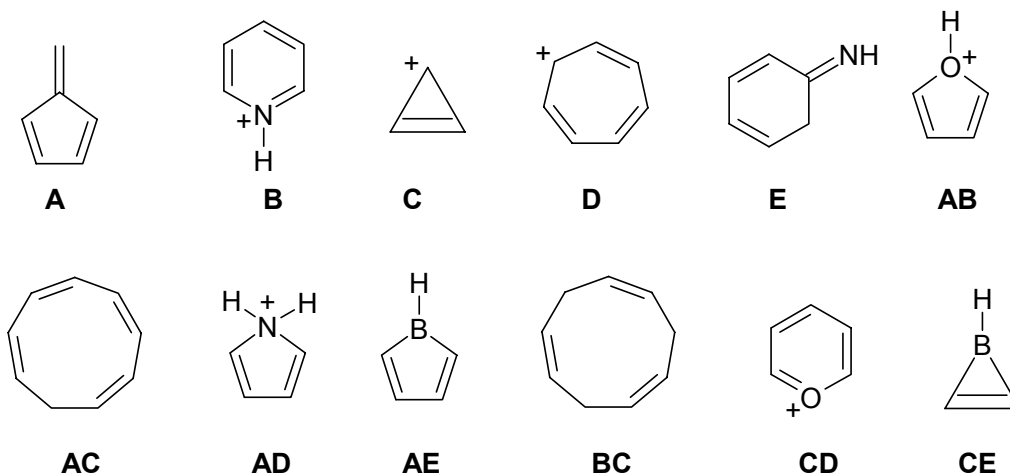
36.



37.



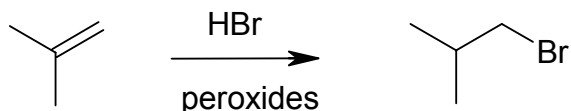
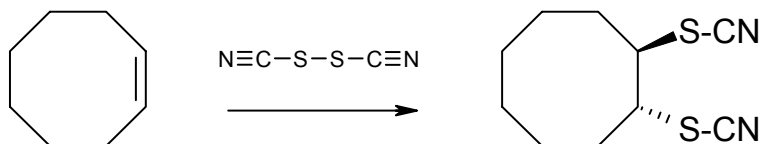
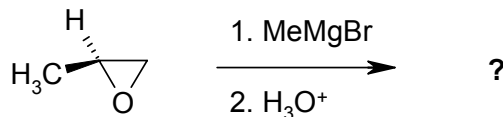
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PART 5: AROMATICITY AND RESONANCE**14% ANSWER ANY SEVEN (7) of the questions 38 - 45.**

For each of the questions 38-45 select a single compound from the list above that best matches each of the following descriptions:

38. An ionic molecule that is non-aromatic as drawn.
39. An uncharged molecule that is aromatic as drawn.
40. A hydrocarbon molecule that is non-aromatic as drawn, but gives an aromatic carbanion upon deprotonation.
41. Not aromatic as drawn, but has an aromatic tautomer.
42. An aromatic hydrocarbon where $n=1$ in the Hückel rule.
43. A hydrocarbon that is not fully conjugated.
44. A non-aromatic conjugated triene.
45. An anti-aromatic heterocyclic molecule.

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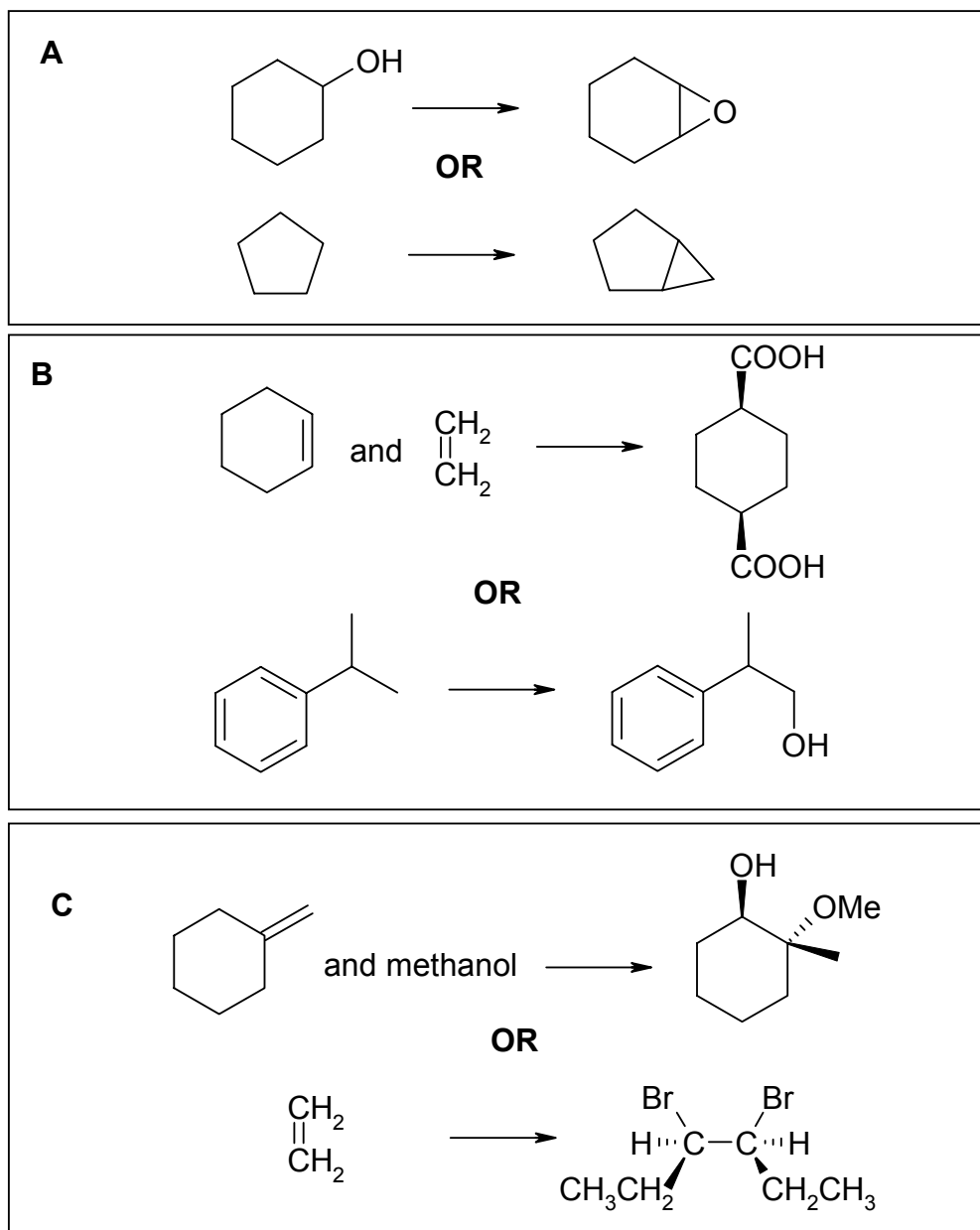
PART 6: MECHANISMS8% **ANSWER ANY TWO (2) OF QUESTIONS A - C****WRITE YOUR ANSWER IN THE BOOKLET PROVIDED****Draw curly arrow mechanisms to explain any two (2) of the following reactions / observations. No other reagents are required.****A.** Show the mechanism for the following reaction sequence. Explain the observed regioselectivity:**B** The reaction of thiocyanogen ($\text{N}\equiv\text{C}-\text{S}-\text{S}-\text{C}\equiv\text{N}$) with cyclooctene proceeds by anti addition. A bridged sulfonium ion is presumed to be an intermediate:**C** Draw the structure (including stereochemistry), and name the major product(s) of the following reaction, and outline the mechanism for both steps of this reaction:**CONTINUED -->**

PART 7: SYNTHESIS

12% WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

Using the starting materials shown, design efficient syntheses of ONE from each of the parts A, B and C (4% for each section):

DO NOT SHOW MECHANISMS (i.e. curly arrows are NOT required)
SHOW YOUR ANSWER AS A REACTION SCHEME SHOWING EACH STEP



You may use any solvents you wish (but they can not become part of the structure, *i.e.* they can be used as solvents not as starting materials or reagents)

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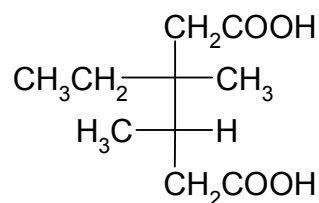
PART 8: STRUCTURE DETERMINATION**13% WRITE YOUR ANSWER IN THE BOOKLET PROVIDED**

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

A, **B** and **C** are isomers with no chiral centres and the molecular formula C_6H_{12} . When comparing the relative heats of hydrogenation, **B** was found to be the most exothermic, followed by **A**, with **C** being the least exothermic. **A**, **B** and **C** all react with HBr (dark) to give the same achiral molecule **D** ($C_6H_{13}Br$) as the major product. When **B** is reacted with BH_3 , followed by aqueous H_2O_2 / OH^- it yields an achiral molecule **E** as the only product. **E** can be converted to its tosylate via treatment with tosyl chloride (TsCl) in the presence of an organic base; this tosylate can react with the sodium salt of propyne to give **F** (C_9H_{16}). When **F** is treated with ozone followed by water, 3-ethylpentanoic acid and acetic (ethanoic) acid are the two isolated products.

When **B** is treated with *n*-bromosuccinimide, both enantiomers of the chiral molecule **G** ($C_6H_{11}Br$) are produced as the major products. Solvolysis of **G** using ethanol, produced **H** ($C_8H_{16}O$) as the kinetic product, and **I** ($C_8H_{16}O$) as the thermodynamic product.

J ($C_{10}H_{18}$) is the product when **A** is heated together with 1,3-butadiene in a sealed tube. When **J** is treated with ozone followed by hydrogen peroxide the following product is isolated:



- What are the structures of **A** to **J**? (12 marks)

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

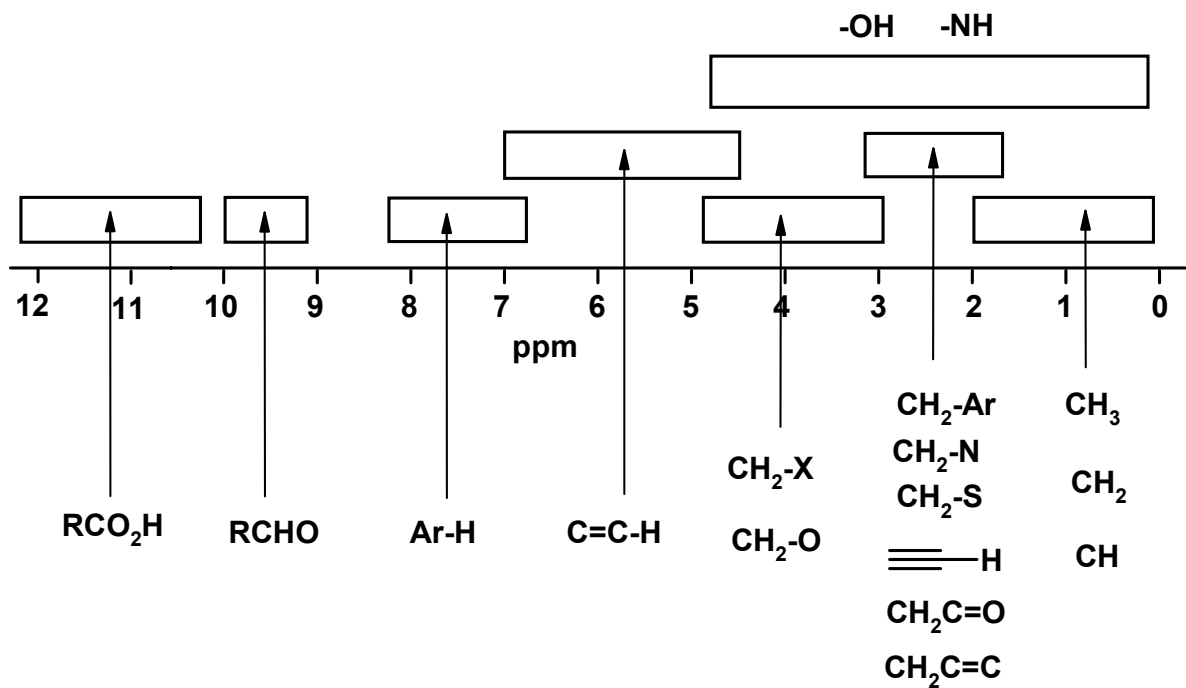
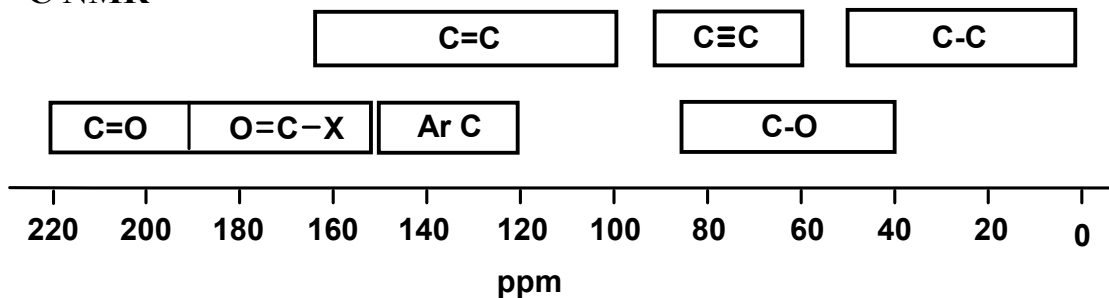
PERIODIC TABLE

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
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)

Actinides **

Schematic diagrams of NMR chemical shift data for H and ¹³C NMR¹H NMR¹³C NMR

A Correlation Table of Infra-Red Group Absorption Frequencies

	TYPE OF VIBRATION	FREQUENCY (cm ⁻¹)	WAVELENGTH (μ)	INTENSITY
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
C-C	Alkane	not interpretatively 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
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*	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

(* note that the -OH absorption of carboxylic acids which are solids and run as a nujol mull can be difficult to see as they maybe very broad)