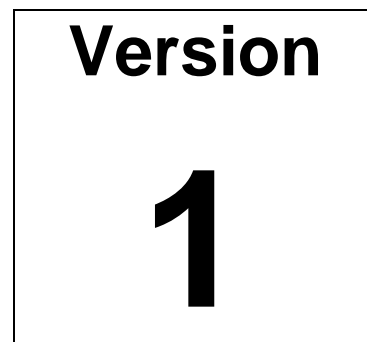


UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 353



WEDNESDAY MARCH 7th, 2018

Time: 2 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME, STUDENT I.D. NUMBER** ON **BOTH YOUR BLUE BOOKLET AND OPTICAL SCORE ANSWER SHEET.**

ENTER **VERSION NUMBER 1** ON THE **OPTICAL SCORE ANSWER SHEET**

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 BLUE 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 optical score answer sheet. Indicate your answer by blackening out the appropriate space(s), A, B, C, D or E on the answer sheet. Use a soft / dark 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.**

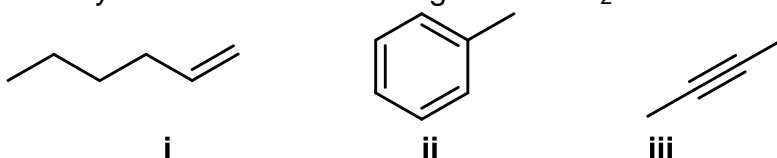
16% **PART 1: RELATIVE PROPERTIES****ANSWER ANY EIGHT (8) OF QUESTIONS 1-10.**

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

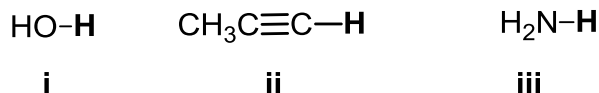
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

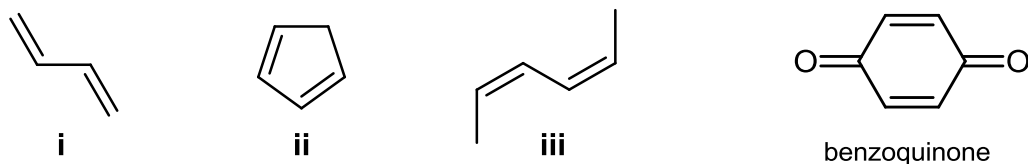
1. The relative reactivity of each of the following towards H_2 / Pd :



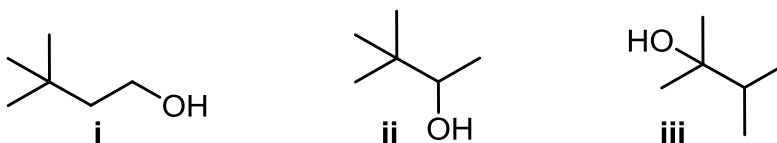
2. The relative acidity of the **H** atom in each of the following:



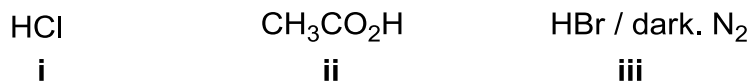
3. The relative reactivity towards benzoquinone (shown below) of each of the following:



4. The relative yields of the following products from the reaction of 3,3-dimethylbut-1-ene with BH_3 followed by the normal work-up with aq. $NaOH / H_2O_2$:



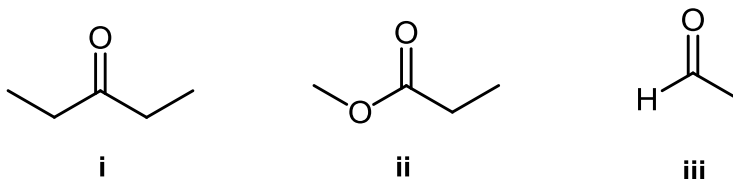
5. The relative reactivity of each of the following towards 1-methylcyclohexene:



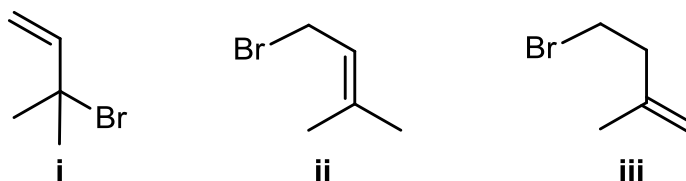
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

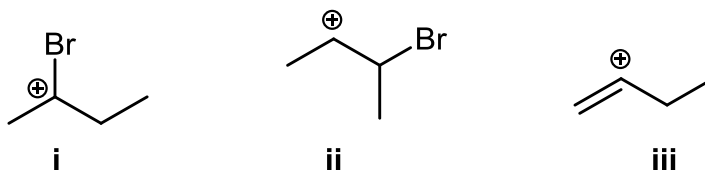
6. The relative reactivity towards sodium borohydride of each of the following:



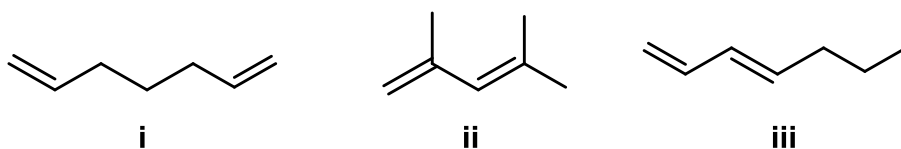
7. The relative yields of each of the following from the reaction of HBr / dark / N₂ with 2-methylbuta-1,3-diene at 60 °C:



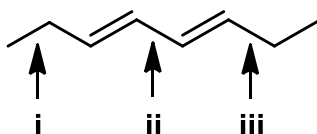
8. The relative stability of the following carbocations as drawn:



9. The relative stability of each of the following isomers:



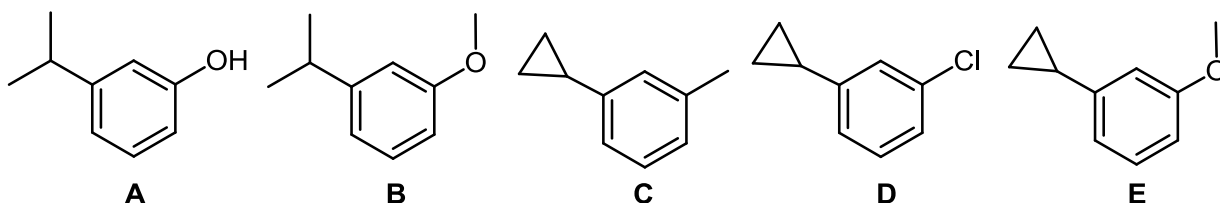
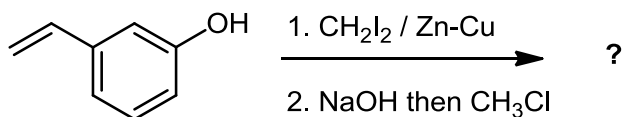
10. The relative lengths of the indicated **CC** bonds:



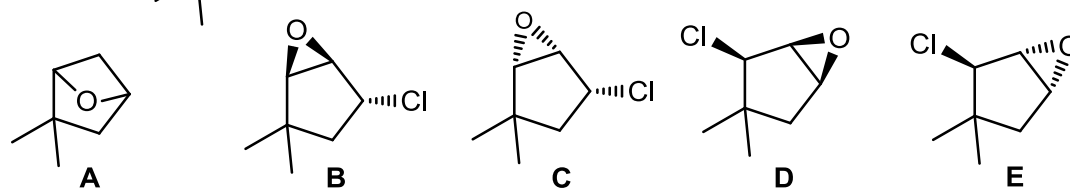
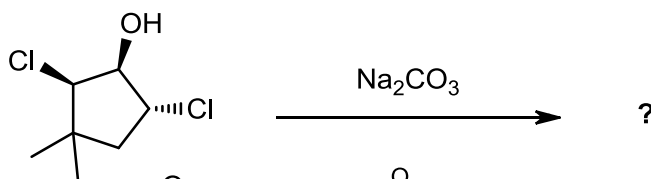
14% PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS**ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.**

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.

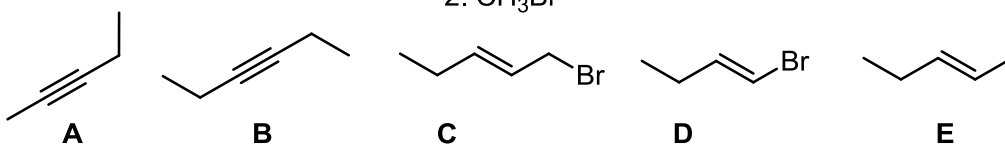
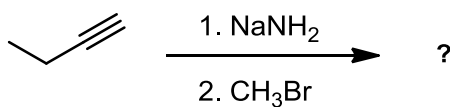
11.



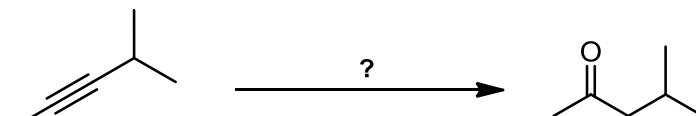
12.



13.

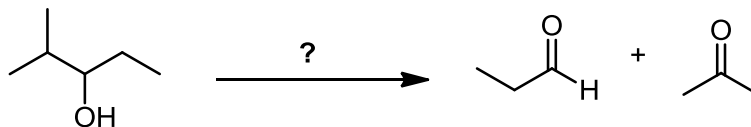


14.



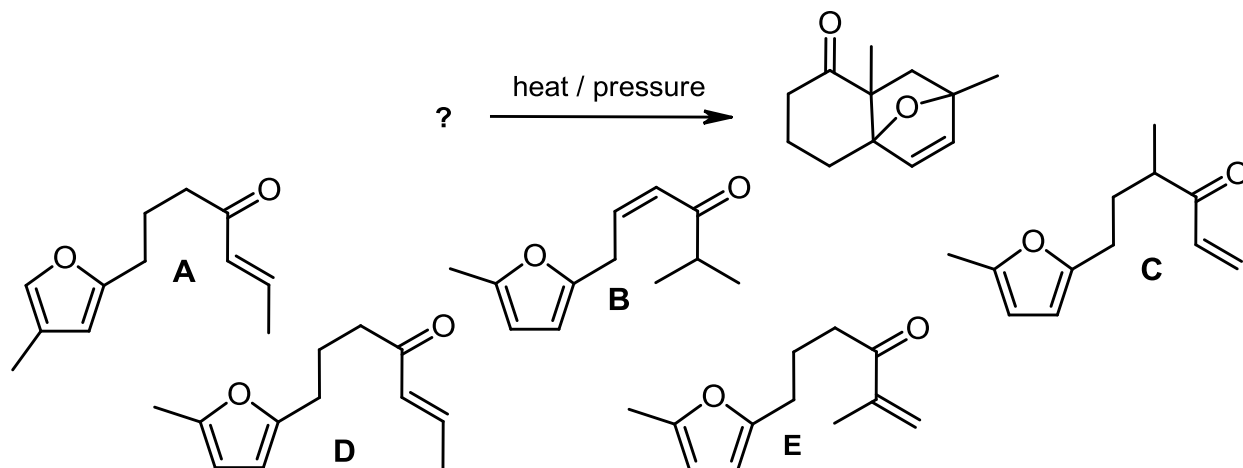
- A** aq. H_2SO_4 , HgSO_4
B 1. aq. H_2SO_4 , HgSO_4 2. NaBH_4
C 1. BH_3 2. aq. NaOH , H_2O_2
D 1. 9-BBN 2. aq. NaOH , H_2O_2
E 1. O_3 2. Zn , H_3O^+

15.

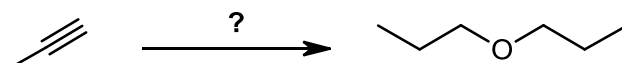


- A 1. KOH, heat 2. O₃ 3. H₂O₂
 B 1. aq. H₂SO₄ 2. O₃ 3. Zn, H₃O⁺
 C 1. KOH, heat 2. O₃ 2. H₂O₂
 D 1. H₂SO₄, heat 2. O₃ 3. Zn, H₃O⁺
 E 1. H₂SO₄, heat 2. O₃ 3. H₂O₂

16.

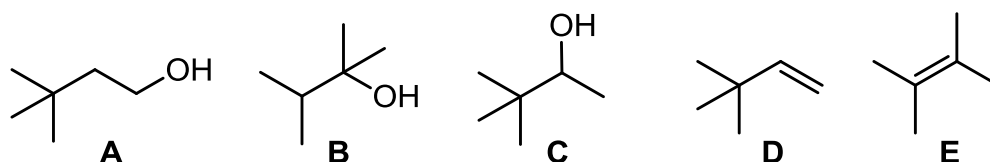
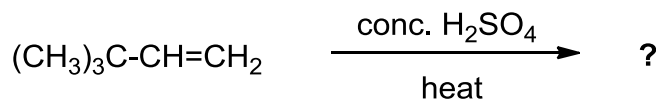


17.



- A. 1. H₂ / Lindlar's cat. 2. 9-BBN then H₂O₂ / aq. NaOH 3. Na then 1-bromopropane
 B. 1. NaNH₂ 2. 1-bromopropane 3. CH₃COOH 4. NaOH
 C. 1. NaNH₂ 2. 1-propanol 3. H₂ (excess) / Pd cat.
 D. 1. NaNH₂ 2. 1-bromopropane 3. CH₃COOH 4. H₂SO₄ / H₂O
 E. 1. H₂ / Lindlar's cat. 2. CH₃COOH 3. H₂SO₄ / 1-propanol

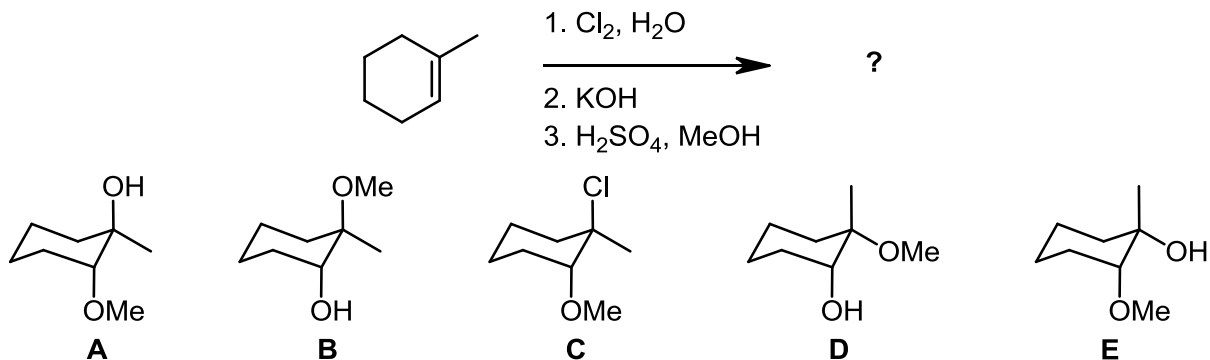
18.



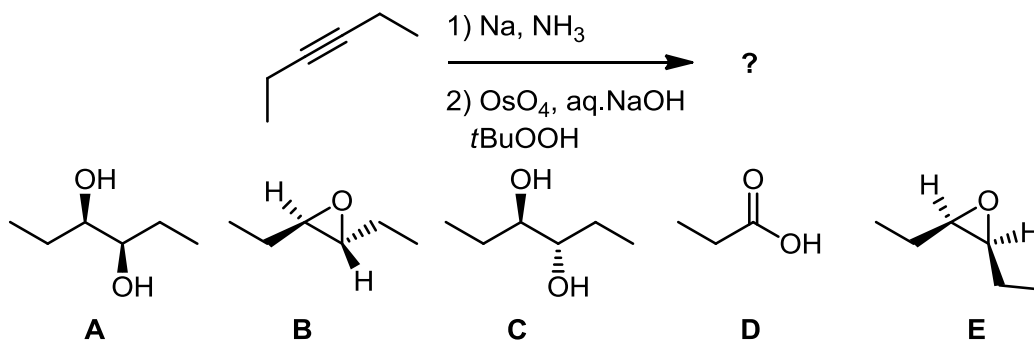
18% PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS**ANSWER ANY SIX (6) OF QUESTIONS 19-25.**

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

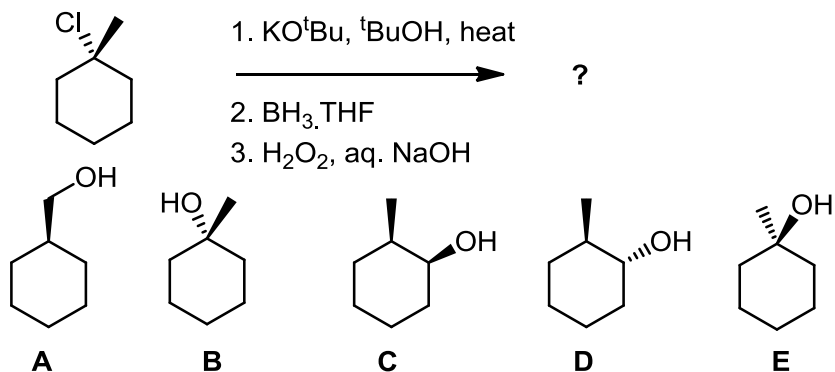
19.



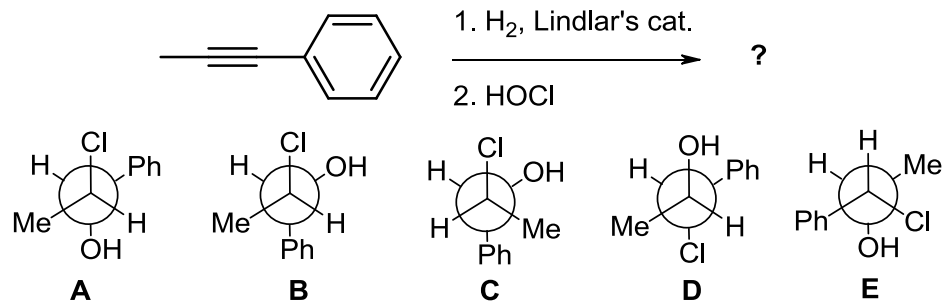
20.



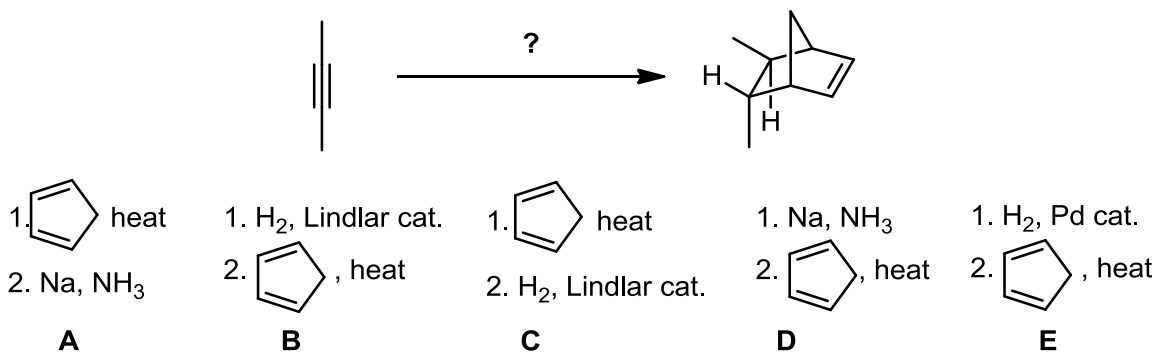
21.



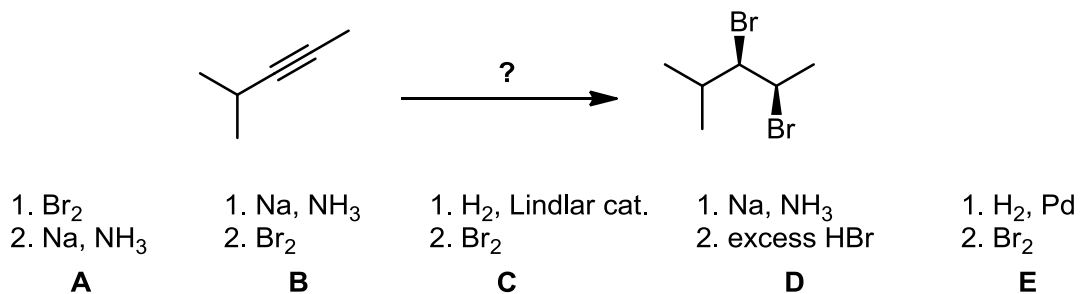
22.



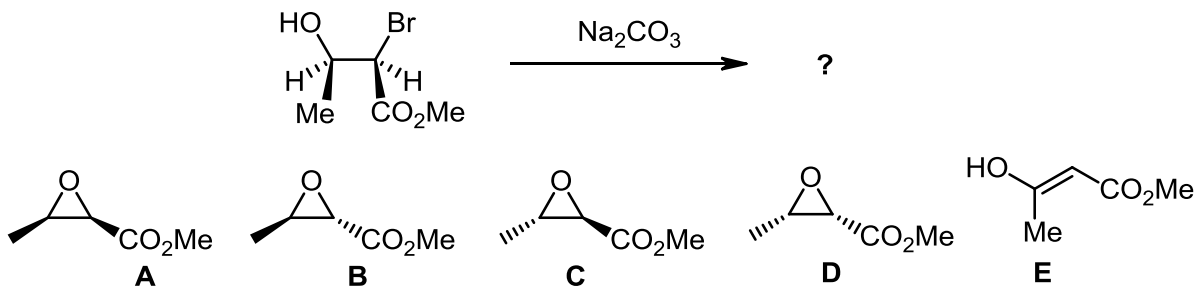
23.



24.



25.

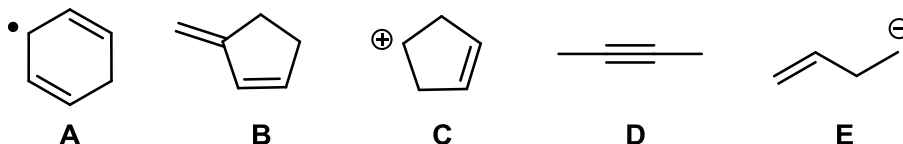


16% **PART 4: PI SYSTEMS**

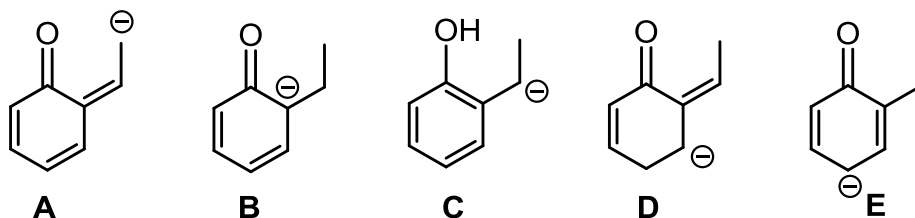
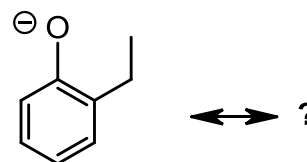
ANSWER ANY EIGHT (8) of the questions 26 - 34.

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.

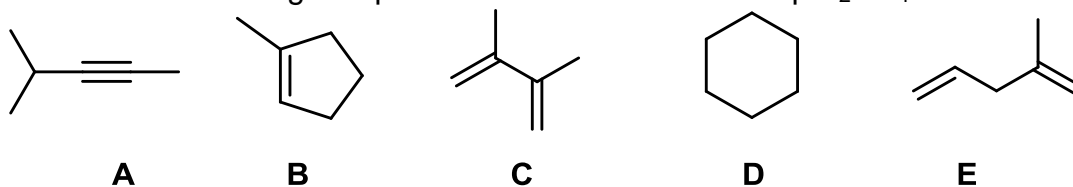
26. Which of the following contain conjugated systems? (**select all that apply**)



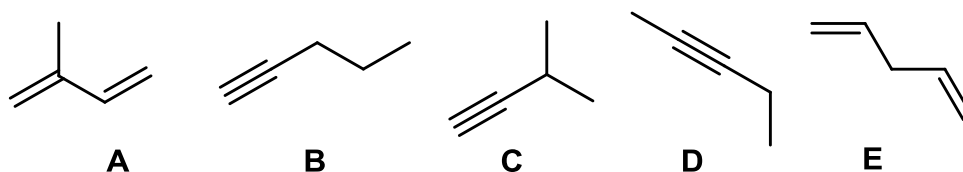
27. Which of the following systems are resonance contributors of the anion shown to the right?
(**select all that apply**)



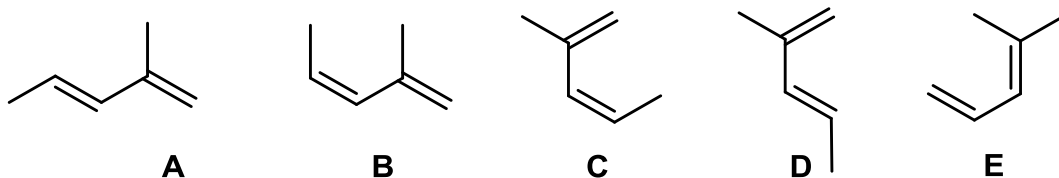
28. Which of the following compounds reacts **fastest** with aq. H_2SO_4 ?



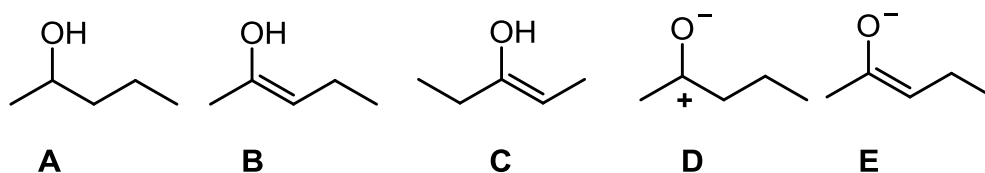
29. Which of the following isomers is the **least** stable ?



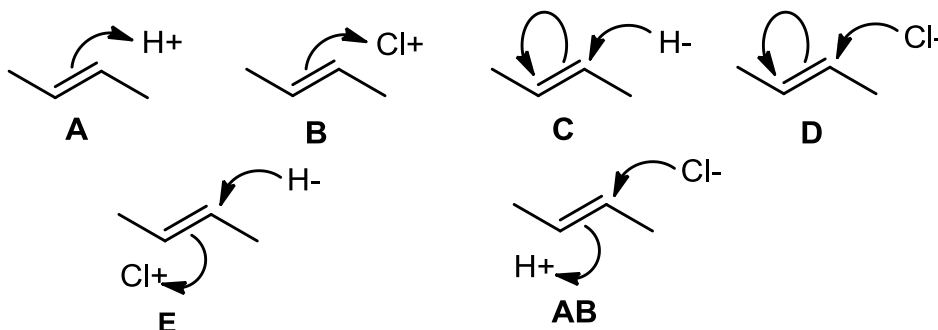
30. Which of the following molecules show the *s-cis* form of (3*Z*)-2-methylpenta-1,3-diene ? (**select all that apply**)



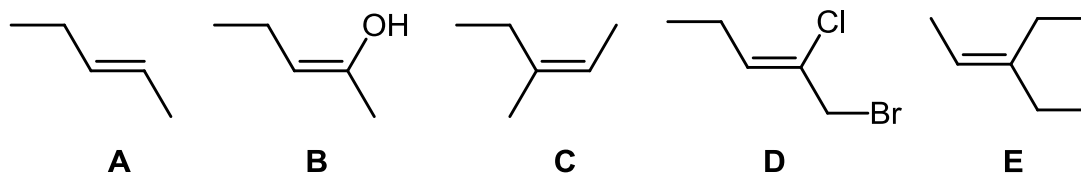
31. Which of the following systems are tautomers of pentan-2-one ? (**select all that apply**)



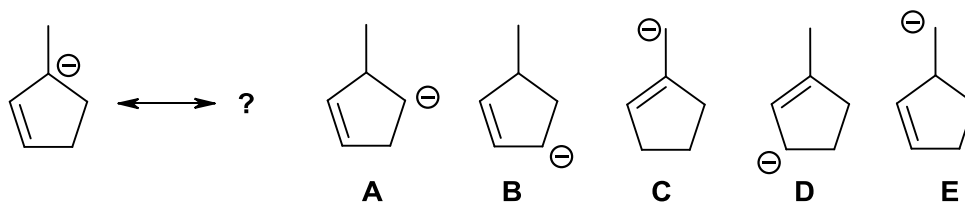
32. Which of the following **best** represents the first step of the mechanism of the reaction of an alkene with HCl ?

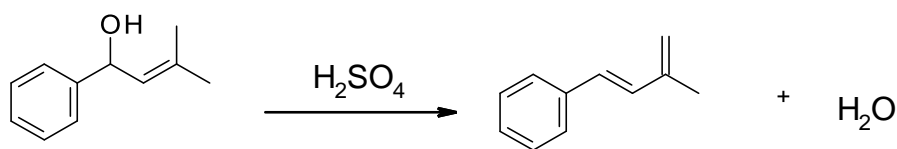
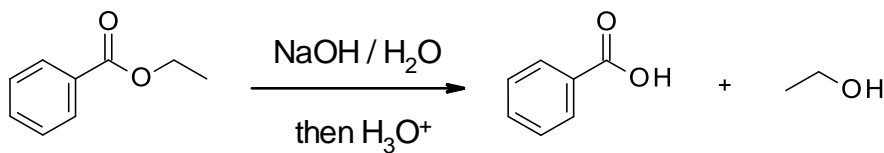
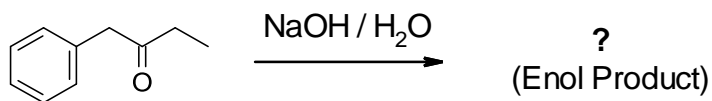
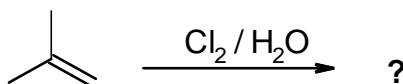


33. Which of the following molecules would be named as *Z* ? (**select all that apply**)



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



10% PART 5: MECHANISMS**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.****No other reagents are required.****A.** Show the mechanism for **one** of the following reactions:**OR****AND****B.** Show the mechanism for **one** of the following reactions and draw the major product. Briefly justify your choice:**OR**

15% PART 6: SYNTHESIS

ANSWER THREE (3) QUESTIONS, ONE FROM A, ONE FROM B AND ONE FROM C.

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

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

SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE REAGENT REQUIRED AND PRODUCT OF EACH STEP.

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

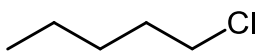
Allowed starting materials and reagents:



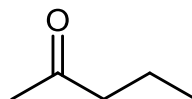
Any hydrocarbons with 3 or less C atoms

Any solvents or reagents that do not contribute carbon atoms to the final structure.

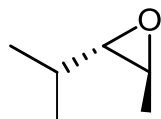
A



or



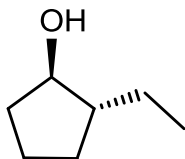
B



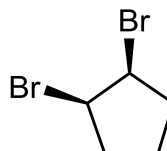
or

meso-butane-2,3-diol

C



or



11% PART 7: STRUCTURE DETERMINATION**WRITE YOUR ANSWER IN THE BOOKLET PROVIDED****Use the information in the following paragraph to answer the questions below.**

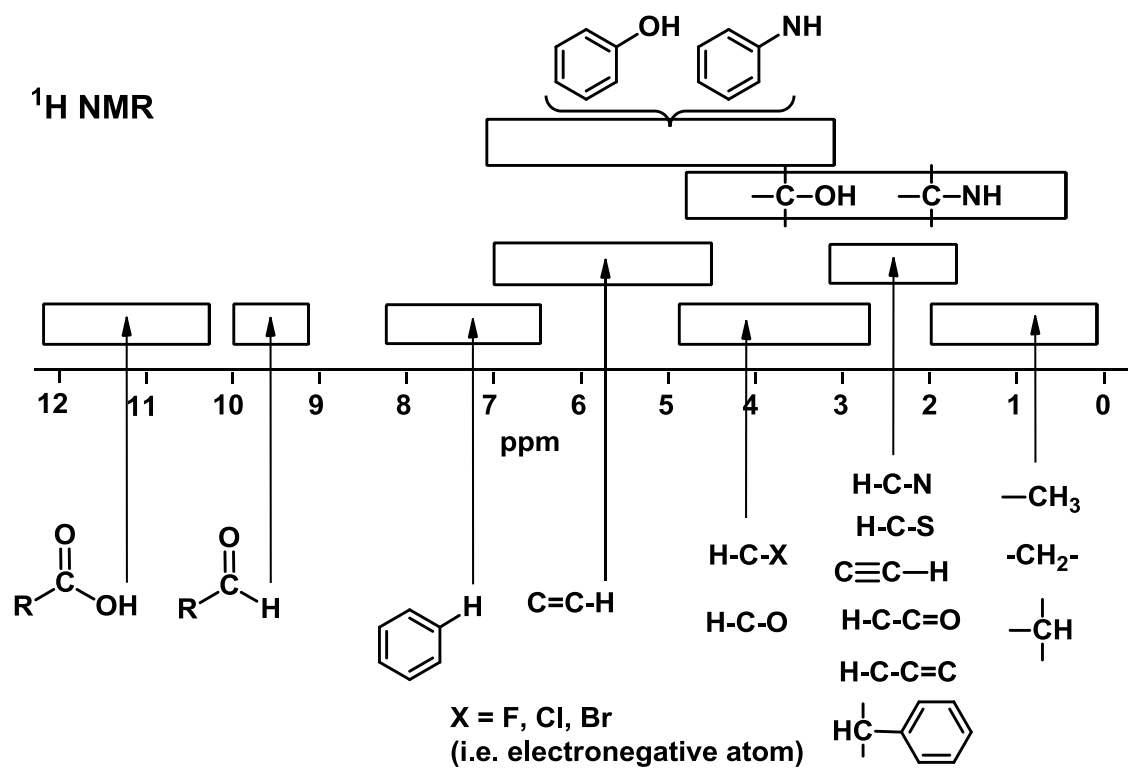
Compound **A**, C_6H_{10} , showed 3 sets of peaks in the H-NMR and 3 peaks in the ^{13}C -NMR spectrum. When **A** was heated with **B**, C_4H_8 (which had 2 set of peaks in the H-NMR and 2 peaks in the ^{13}C -NMR), product **C**, $C_{10}H_{18}$ was produced. **C** was then reacted with cold alkaline $KMnO_4$ to give **D**, $C_{10}H_{20}O_2$.

When **D** was heated with sulfuric acid, the major product isolated was **E**, $C_{10}H_{16}$. **E**.

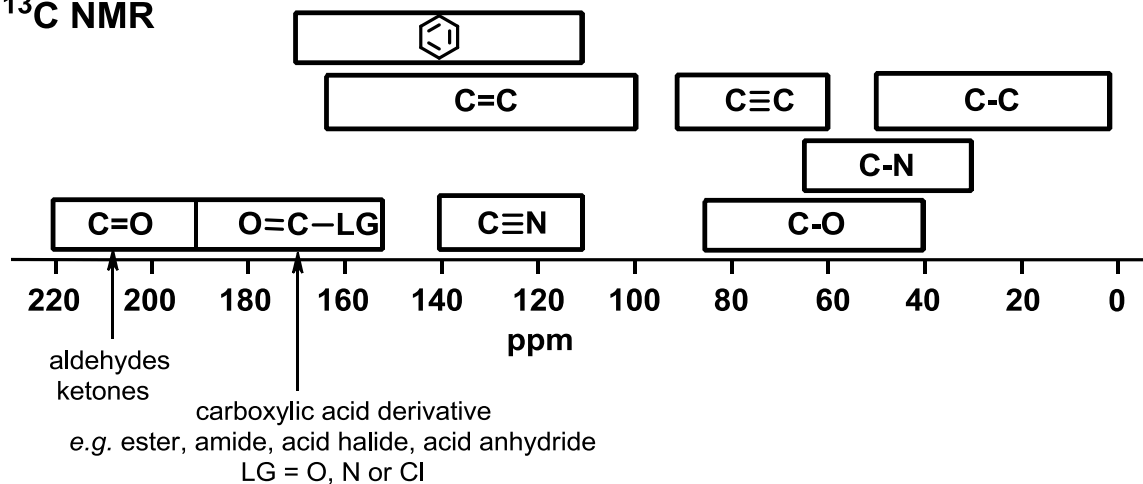
E was then reacted with Br_2 at $50\text{ }^\circ C$, **F**, $C_{10}H_{16}Br_2$, was obtained as a mixture of diastereomers. **F** was then heated with ethanolic KOH to give a single product, **G**, $C_{10}H_{14}$ (H-NMR/ppm: 6.71 (1H,s) and 2.27 (6H, s), ^{13}C -NMR/ppm: 134, 131 and 20).


Identify **A - G**.

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

SPECTROSCOPIC TABLES**¹H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

	R = methyl	methylene	methyne	other
<chem>R-C</chem>	<chem>-CH3</chem> 0.9	<chem>-CH2-</chem> 1.4	<chem>-CH</chem> 1.5	<chem>sp3C-OH</chem> 1-5 <chem>sp3C-NH</chem> 1-3
<chem>R-C=C</chem>	1.6	2.3	2.6	<chem>C#CH</chem> 2.5
<chem>R-C(=O)</chem>	2.1	2.4	2.5	<chem>C=C-H</chem> 4.5-6.5
<chem>R-N</chem>	2.2	2.5	2.9	<chem>H-C6H5</chem> 6.5-8
<chem>R-C6H5</chem>	2.3	2.7	3.0	<chem>R-C(=O)H</chem> 9-10
<chem>R-Br</chem>	2.7	3.3	4.1	<chem>R-C(=O)OH</chem> 9-12
<chem>R-Cl</chem>	3.1	3.4	4.1	
<chem>R-O</chem>	3.3	3.4	3.7	

^{13}C NMR **^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

—CH_3 0-30	>CH_2 10-50	—C—H 25-60	—C(=O)—O— 155-180
$\text{—C}\equiv\text{C—}$ 65-90	>C=C< 80-145	—C—Br 10-25	—C(=O)OH 160-185
 110-170		—C—Cl 15-30	—C(=O)H 190-210
		—C—OH 45-75	—C(=O)— 190-220
		—C—N 30-65	$\text{—C}\equiv\text{N}$ 110-140

INFRA-RED GROUP ABSORPTION FREQUENCIES

		<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm⁻¹)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>	
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	
			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

											13 3A						14 4A	15 5A	16 6A	17 7A	18 8A
1 1A																				2 He 4.003	
1 H 1.008	2 2A											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18				
3 Li 6.941	4 Be 9.012											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95				
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12										
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)