UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

Version

1

THURSDAY MARCH 7th, 2019 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 INK 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**

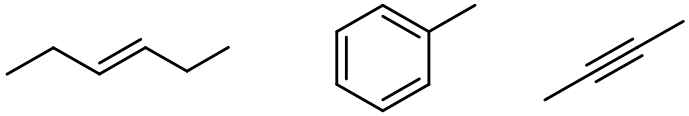
ANSWER ANY EIGHT (8) OF QUESTIONS 1-10.

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.

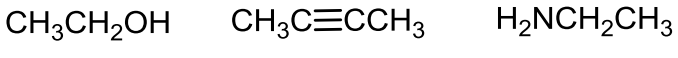
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

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



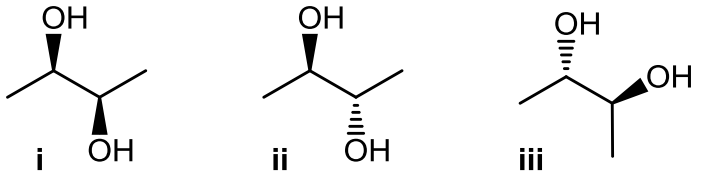
i **ii** **iii**

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



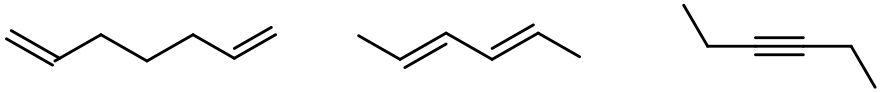
i **ii** **iii**

3. The specific rotations of each of the following molecules given that (2R,3R)-butan-2,3-diol has an $[\alpha]_D$ = -13.2^o :



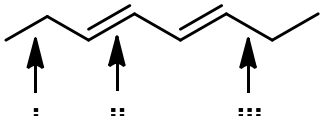
i **ii** **iii**

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



i **ii** **iii**

5. The relative strengths of the indicated **CC** bonds:

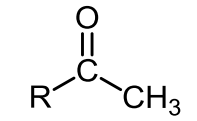


i **ii** **iii**

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**

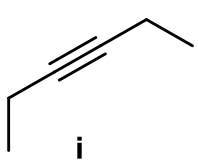
6. The relative yields of a methyl ketone from the reactions of each of the following with (1) BH_3/THF then (2) aq. H_2O_2 / NaOH:

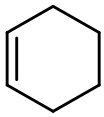


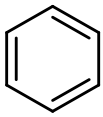
a methyl ketone

$CH_3C{\equiv}CCH_3$ **i** $CH_3C{\equiv}CCH_2CH_3$ **ii** $CH_3C{\equiv}CCH(CH_3)_2$ **iii**

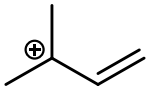
7. The relative rate of reaction of each of the following with hydrogen / palladium:

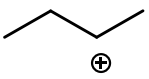
 **i**

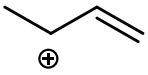
 **ii**

 **iii**

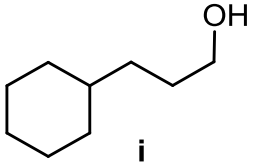
8. The relative stability of the following carbocations:

 **i**

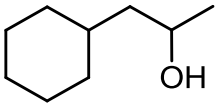
 **ii**

 **iii**

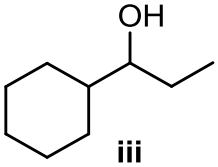
9. The relative yields of each of the following products from the reaction of 1-cyclohexylprop-1-ene with BH_3 followed by the normal work-up with aq. NaOH / H_2O_2:



i



ii



iii

10. The relative yield of hexan-1-ol from the reaction of hex-1-ene with each of the following :

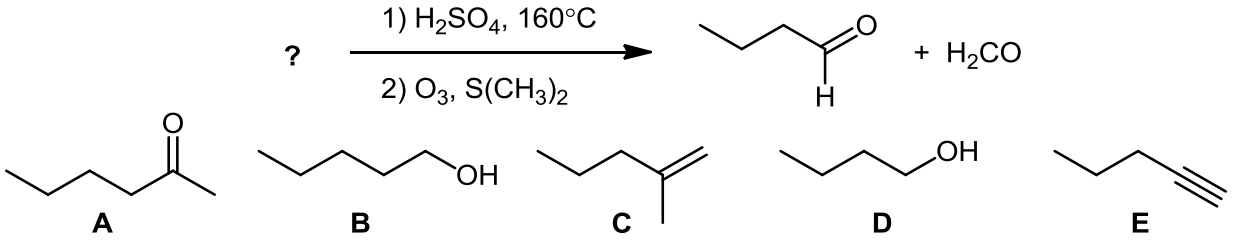
aq. H_2SO_4	1. BH_3 / THF 2. aq. H_2O_2 / NaOH	1. 9-BBN / THF 2. aq. H_2O_2 / NaOH
i	**ii**	**iii**

14% PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS

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

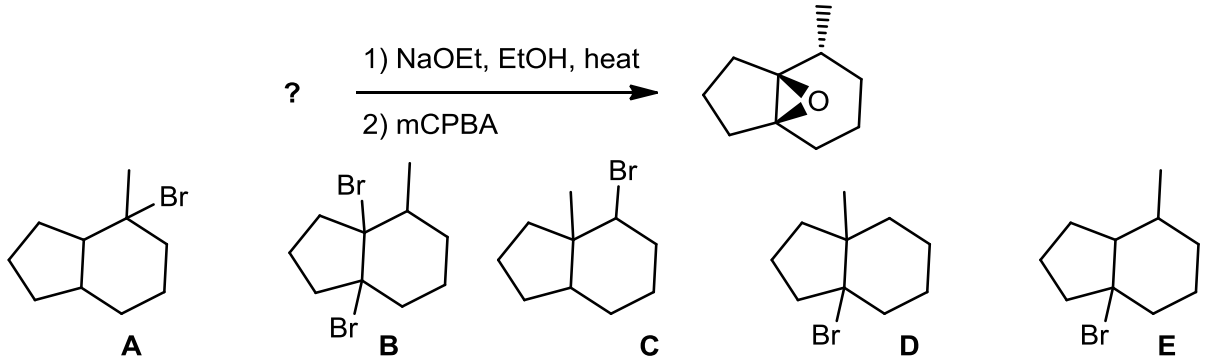
For each of questions 11-18 select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

11.



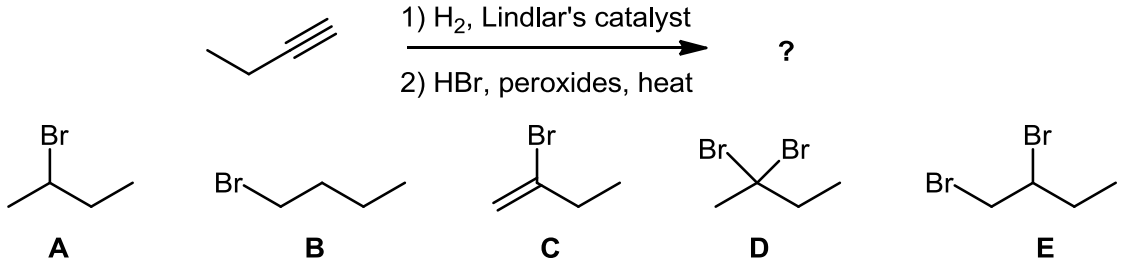
A **B** **C** **D** **E**

12.



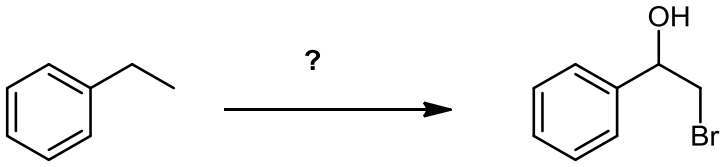
A **B** **C** **D** **E**

13.



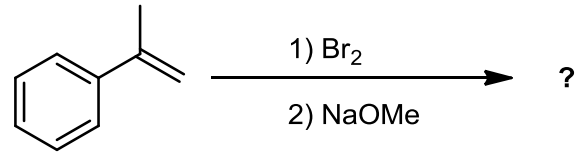
A **B** **C** **D** **E**

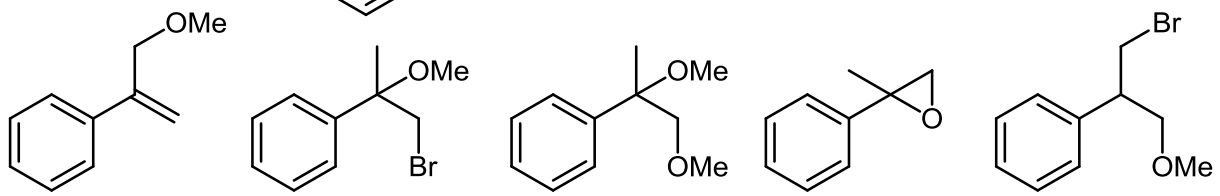
14.



A	**B**	**C**	**D**	**E**
1) Br_2, light	1) HBr	1) Br_2, light	1) KO*t*Bu	1) NBS, heat
2) NaOMe, MeOH	2) NaO*t*Bu, heat	2) NaO*t*Bu, heat	2) mCPBA	2) mCPBA
3) aq. H_2SO_4, heat	3) CH_3CO_3H	3) HOBr	3) HBr	3) HBr

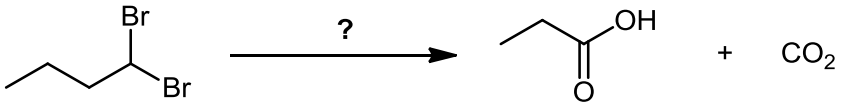
15.





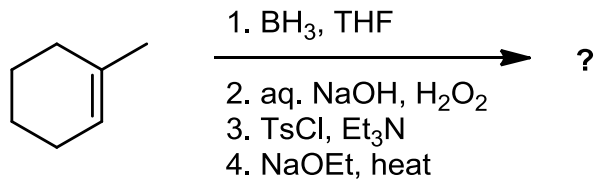
A **B** **C** **D** **E**

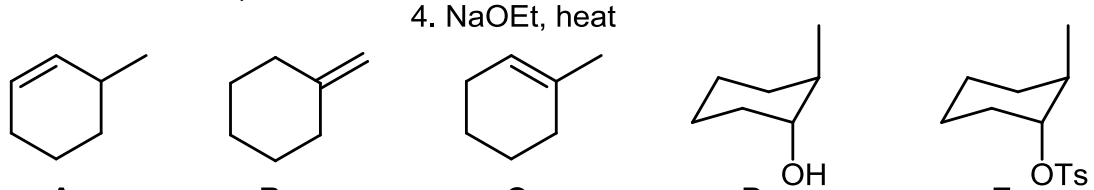
16.



A	**B**	**C**	**D**	**E**
1) excess $NaNH_2$ 2) aq. $KMnO_4$, NaOH cold (0°C)	1) NaOMe 2) $NaNH_2$ 3) O_3 4) Zn, acetic acid	1) O_3, PPh_3 2) $NaNH_2$ 3) Na, NH_3	1) excess $NaNH_2$ 2) O_3 3) H_2O	1) NaOMe 2) $NaNH_2$ 3) $HgSO_4$, H_2O

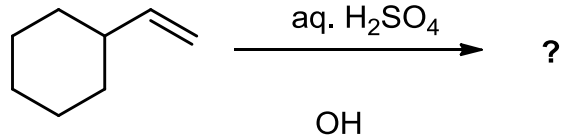
17.

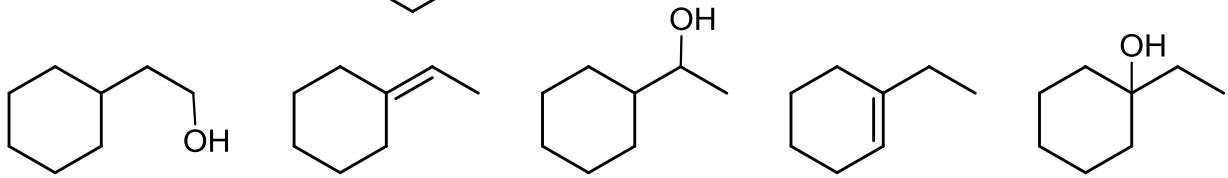




A **B** **C** **D** **E**

18.





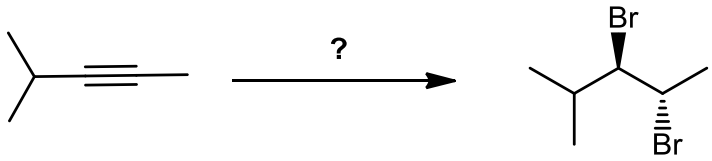
A **B** **C** **D** **E**

18% PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

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

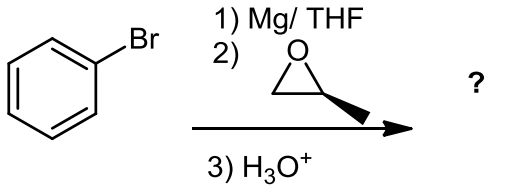
For each of the questions 19-25, select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

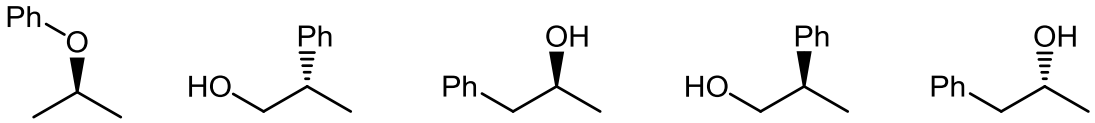
19.



A	B	C	D	E
1) Pd/C, H_2 2) Br_2	Br_2	1) H_2 Lindlar's catalyst 2) Br_2	1) $HgSO_4$, H_3O^+ 2) Br_2	1) Na/NH_3 2) Br_2

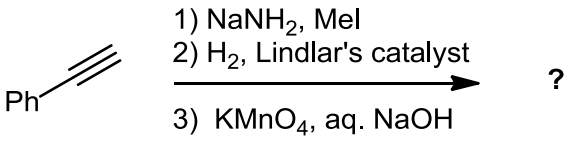
20.

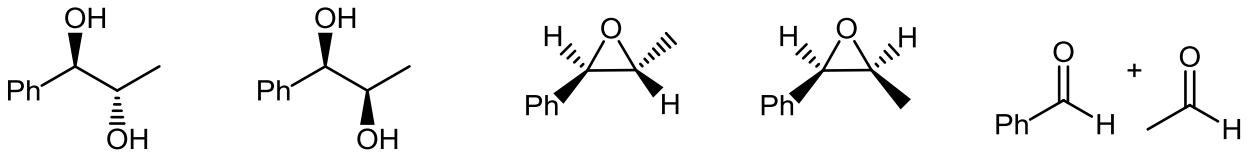




A **B** **C** **D** **E**

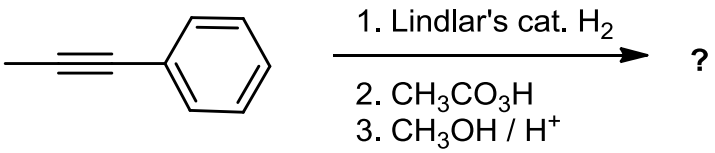
21.

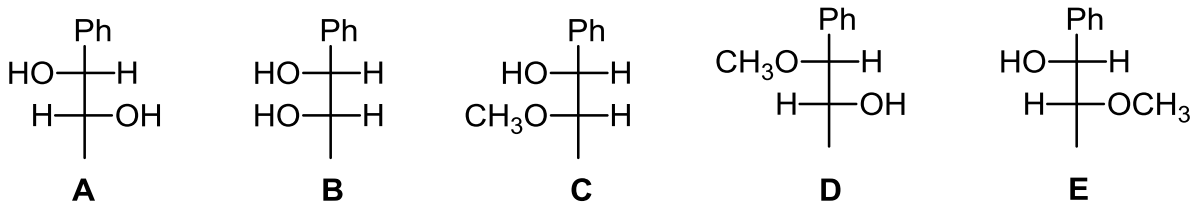




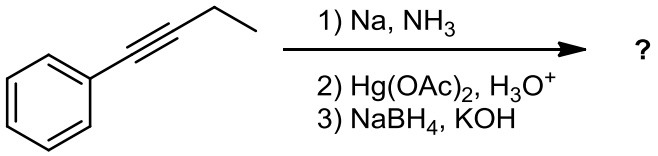
A **B** **C** **D** **E**

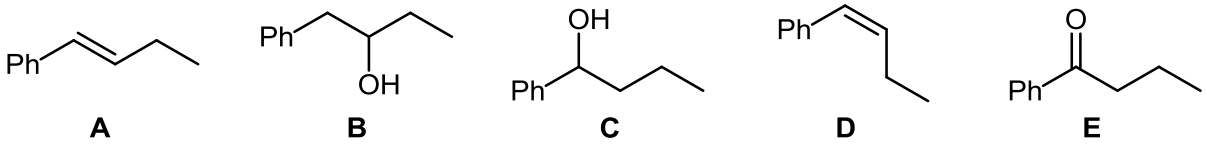
22.



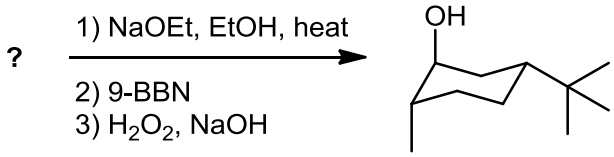


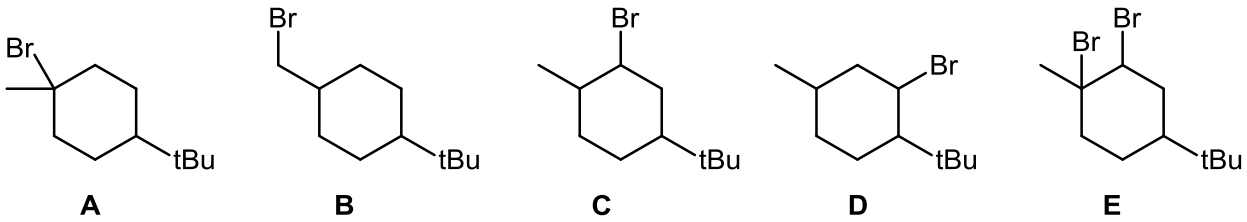
23.





24.





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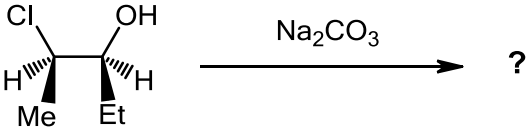
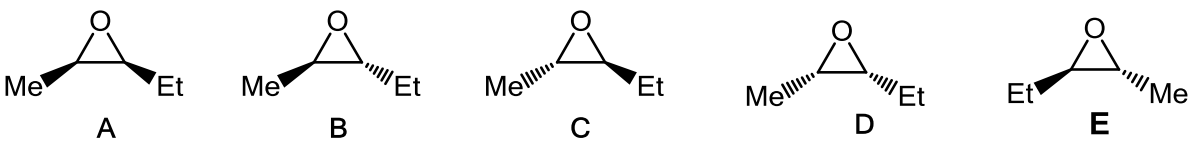


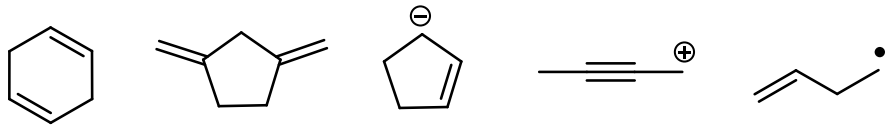


16% PART 4: PI SYSTEMS

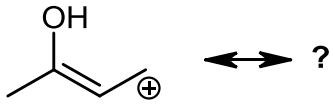
ANSWER ANY EIGHT (8) of the questions 26 - 34.

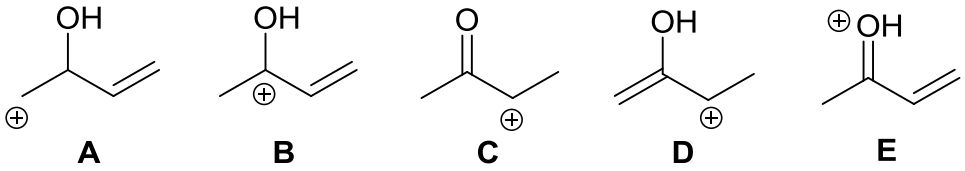
For each of the questions 26-34 select the appropriate answer from the answers provided. In some cases more than one selection may be required for full credit.

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

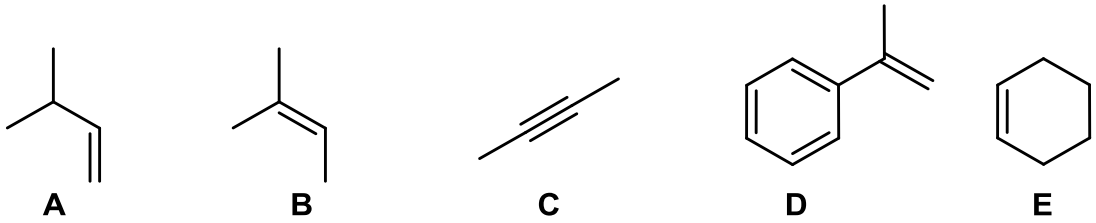


27. Which of the following systems are resonance contributors of the cation shown to the right ? **(select all that apply)**

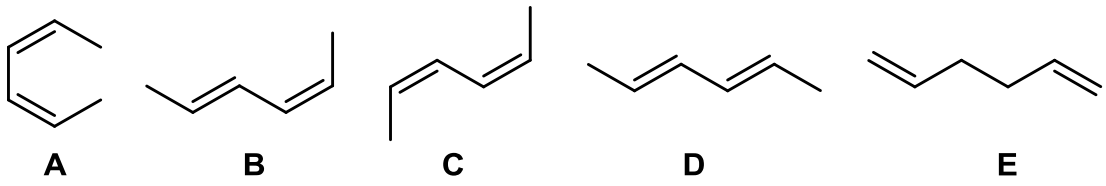




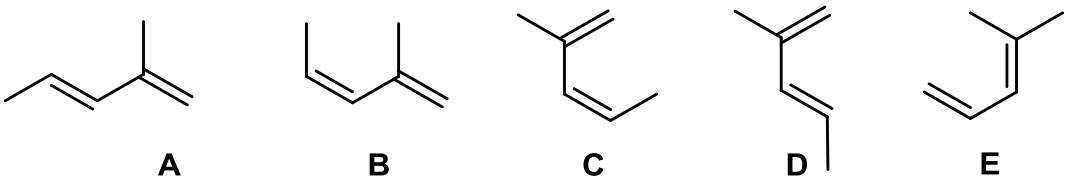
28. Which of the following systems would be the most reactive towards HCl ?



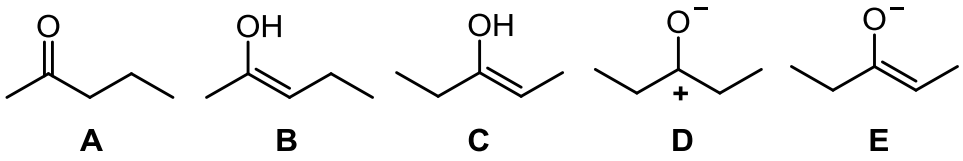
29. Which of the following isomers is the **most** stable as drawn ?



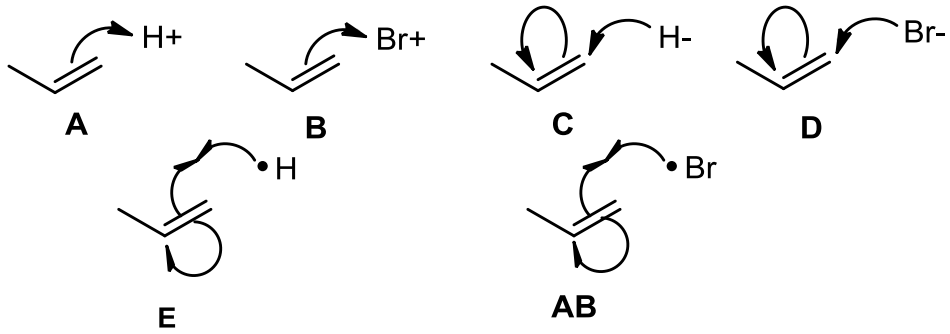
30. Which of the following molecules show the *s-cis* form of (3E)-2-methylpenta-1,3-diene ? **(select all that apply)**



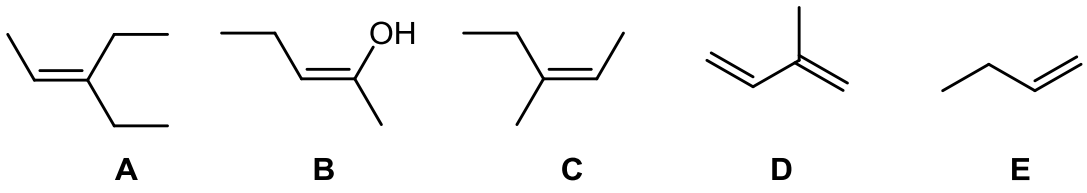
31. Which of the following systems are tautomers of pentan-3-one ? **(select all that apply)**



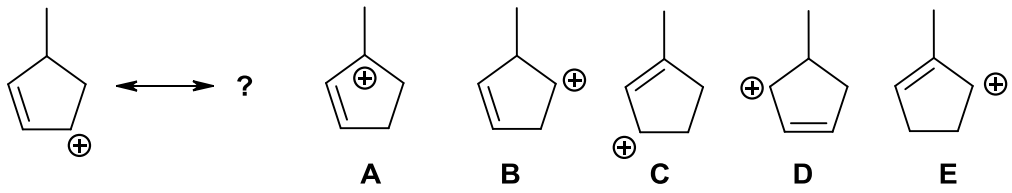
32. Which of the following **best** represents a step in the mechanism of the reaction of propene with HBr / uv light ?



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



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



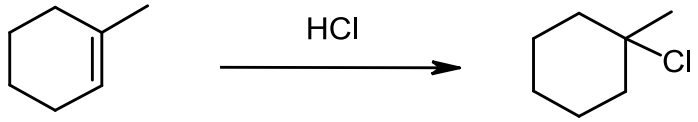
10% PART 5: MECHANISMS

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

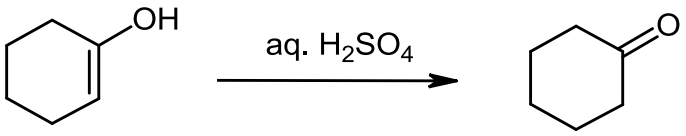
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

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

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

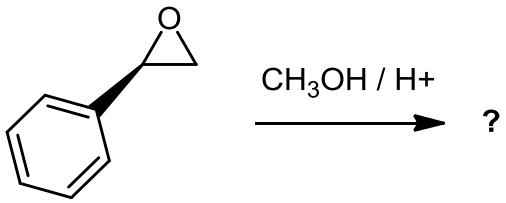


OR

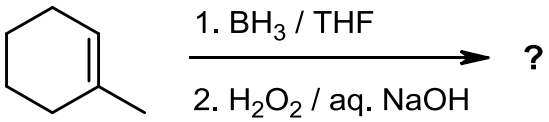


AND

B. Show the mechanism for **one** of the following reactions to give the major product and briefly justify the product formation :



OR



15% PART 6: SYNTHESIS

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

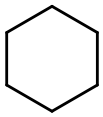
WRITE YOUR ANSWERS IN THE BLUE BOOKLET PROVIDED.

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)

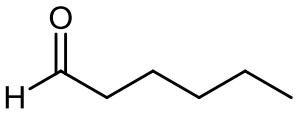
Allowed starting materials and reagents :



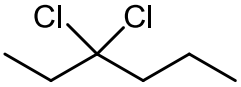
Any hydrocarbons with 4 or less C atoms

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

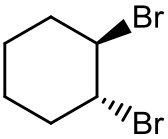
A



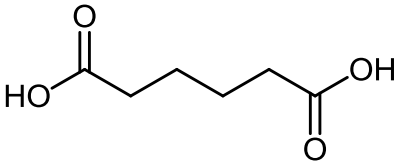
or



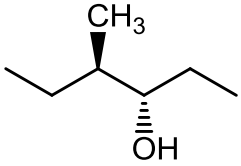
B



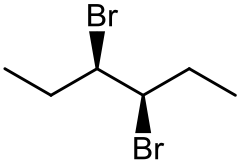
or



C



or



11% PART 7: STRUCTURE DETERMINATION

WRITE YOUR ANSWER IN THE BLUE BOOKLET PROVIDED

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

A sample of hydrocarbon **A**, C_5H_8, IR: 2120 cm^{-1}, was reacted with sodium amide then treated with isopropyl bromide to give **B**, C_8H_{14}. **B** was then reacted with hydrogen / Lindlar's catalyst to give **C**, C_8H_{16} that gave a colourless solution when tested with Br_2 in chloroform. Reaction of **C** with cold aq. alkaline $KMnO_4$, gave **D**, $C_8H_{18}O_2$ as a single meso compound, IR: 3500 cm^{-1} (very broad), 13C-NMR δ/ppm: 75, 30, and 17.

In contrast, when **B** was reacted with sodium in liquid ammonia, it gave **E**, a stereoisomer of **C**. Reaction of **E** with cold aq. alkaline $KMnO_4$, it gave **F**, $C_8H_{18}O_2$ as a racemic mixture of a pair of enantiomers that were subsequently found to be diastereomers of **D**.

When **B** was reacted with aq. H_2SO_4 and $HgSO_4$ it gave a single compound **G**, $C_8H_{16}O$, IR: 1711 cm^{-1}, 13C-NMR δ/ppm: 215, 50, 41, 24, 23 and 18.

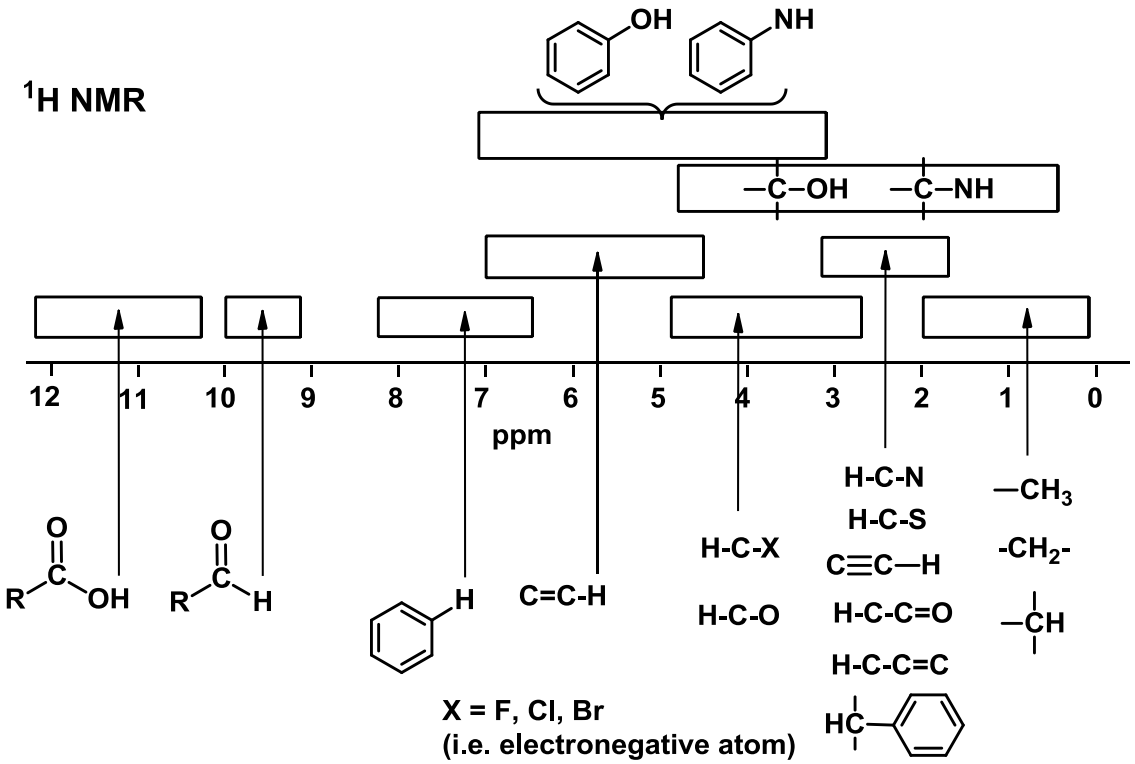
Reaction of **C** or **E** with ozone followed by a work-up using hydrogen peroxide gave 2-methylpropanoic acid as the only product.

- **What are the structures of A to G ?**
- **Provide a systematic IUPAC name for C.**

*** THE END ***

IRH / DD / W19

SPECTROSCOPIC TABLES

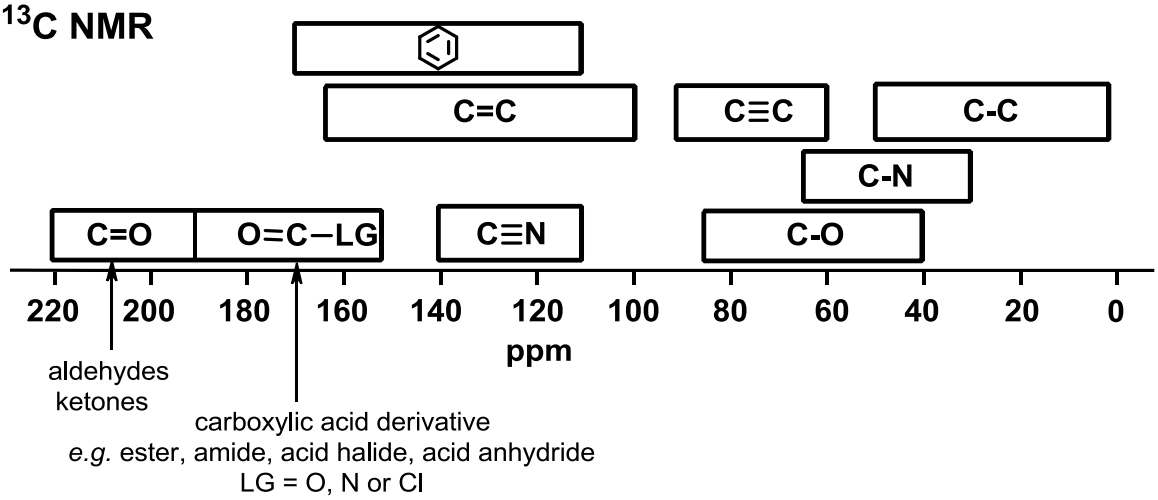


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

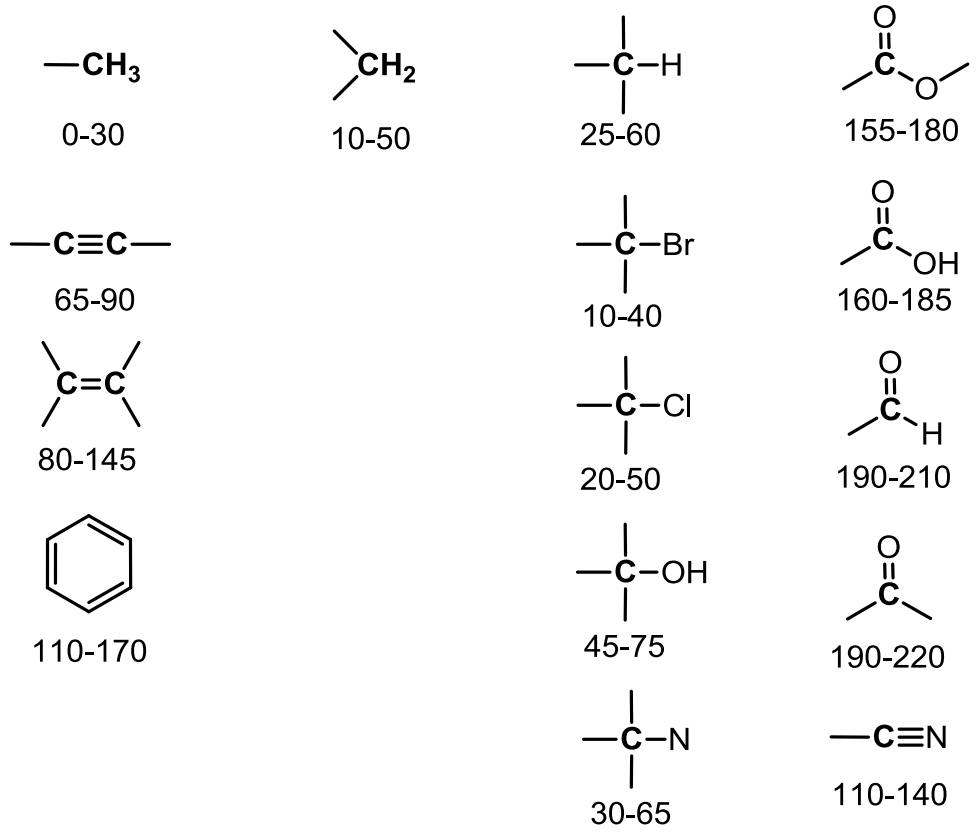
R =	methyl $-CH_3$	methylene $-CH_2-$	methyne $-CH$
R–C—	0.9	1.4	1.5
R, C=C	1.6	2.3	2.6
R–C(=O)—	2.1	2.4	2.5
R–N	2.2	2.5	2.9
R–Ar	2.3	2.7	3.0
R–Br	2.7	3.3	4.1
R–Cl	3.1	3.4	4.1
R–O—	3.3	3.4	3.7

other	
sp^3C-OH	1-5
sp^3C-NH	1-3
C≡CH	2.5
C=C(H)—	4.5-6.5
H–Ar	6.5-8
R–C(=O)–H	9-10
R–C(=O)–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)