UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

WEDNESDAY MARCH 7th, 2012 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

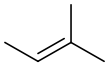
16% **ANSWER ANY EIGHT (8) OF QUESTIONS 1-10**.

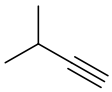
Arrange the items in each of the questions in this section in DECREASING ORDER (i.e. greatest first) with respect to the indicated property.

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 reactivity of each of the following towards HBr:


i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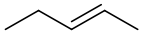
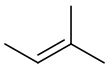
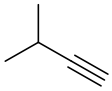

iii

2. The relative number of the vinylic hydrogens in each of the following:


i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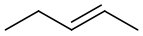
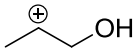

iii

3. The relative stability of the following carbocations:

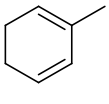
i

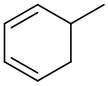

ii

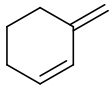


iii

4. The relative reactivity towards methyl acrylate of each of the following:


i


ii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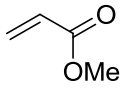
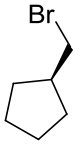
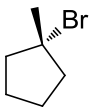


methyl acrylate

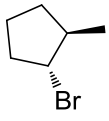
5. The relative yield of 1-methylcyclopentene reacting with HBr / peroxides:



i



ii



iii

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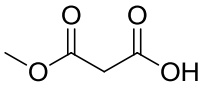
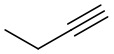
Use the following code to indicate your answers.

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

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



i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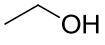
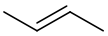
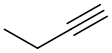


iii

7. The relative reactivity of each of the following towards H_2 / Pt :


i


ii

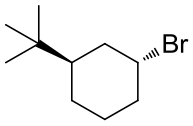

iii

8. The relative yields of (Z)-2-pentene reacting with cold $KMnO_4$ in aqueous KOH:

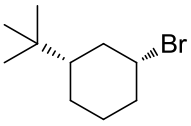
(2*R*,3*S*)-pentane-2,3-diol (*S*)-pentane-1,3-diol (2*S*,3*S*)-pentane-2,3-diol

i ii iii

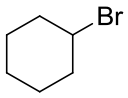
9. The relative reactivity of the following when heated with potassium *tert*-butoxide



i

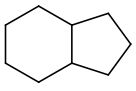


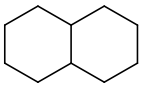
ii



iii

10. The number of possible mono-alkene starting materials that could result in the following products upon hydrogenation:


i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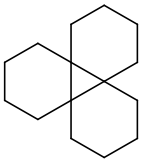
iii

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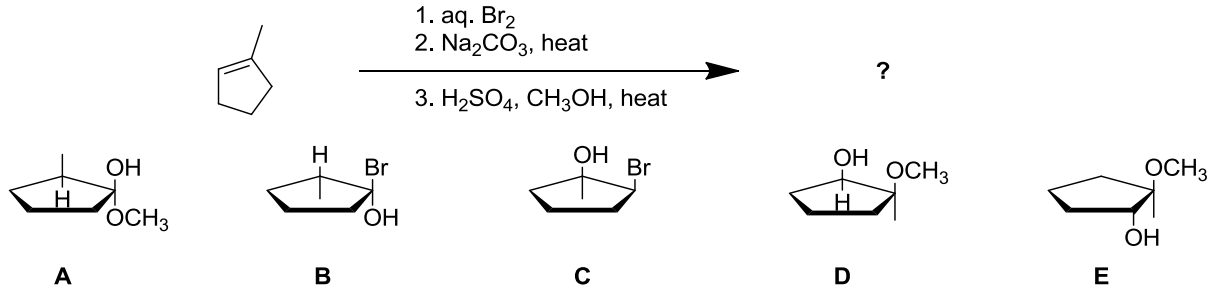
PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS

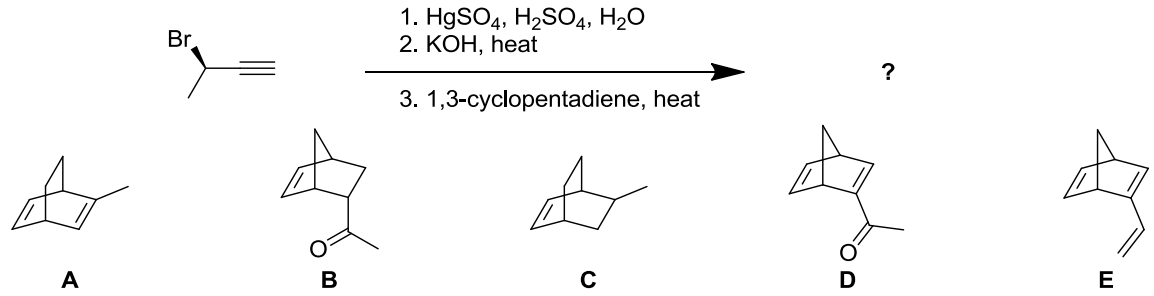
14% **ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.**

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.

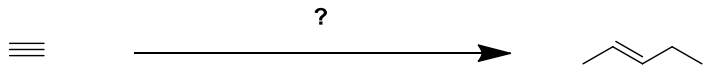
11.



12.

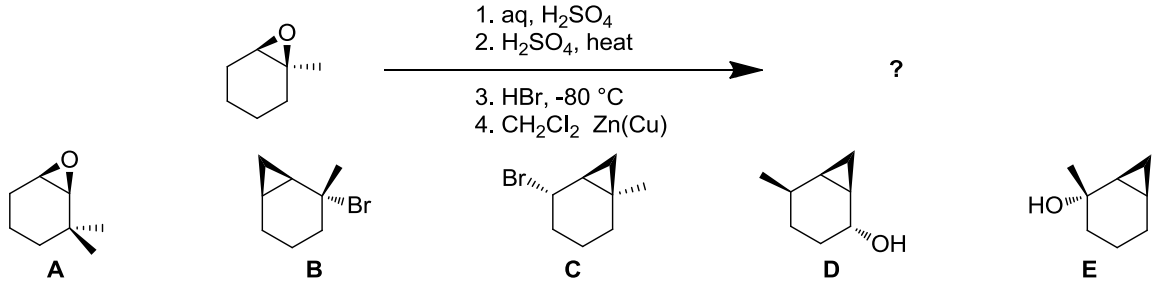


13.



A 1. $NaNH_2$ 2. methylbromide 3. $NaNH_2$ 4. ethyliodide 5. H_2, Lindlar's cat.
B 1. $NaNH_2$ 2. ethylbromide 3. $NaNH_2$ 4. ethyliodide 5. Na, NH_3
C 1. $NaNH_2$ 2. ethylbromide 3. $NaNH_2$ 4. methyliodide 5. Na, NH_3
D 1. $NaNH_2$ 2. ethylbromide 3. Na, NH_3 4. methylbromide 5. H_2, Lindlar's cat.
E 1. $NaNH_2$ 2. methylbromide 3. H_2, Lindlar's cat. 4. $NaNH_2$ 5. ethyliodide

14.



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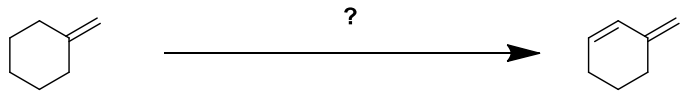
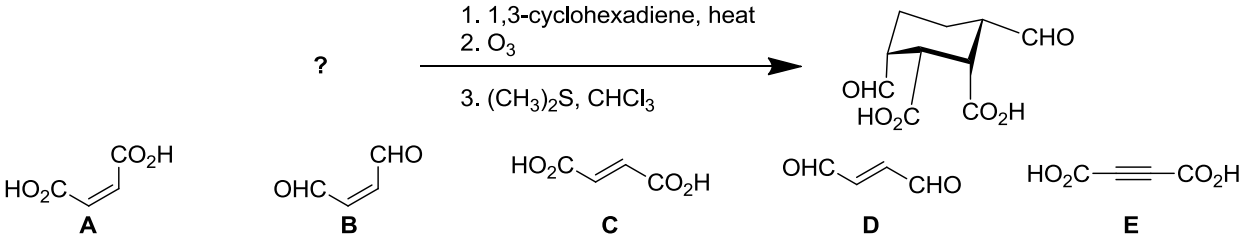
15.

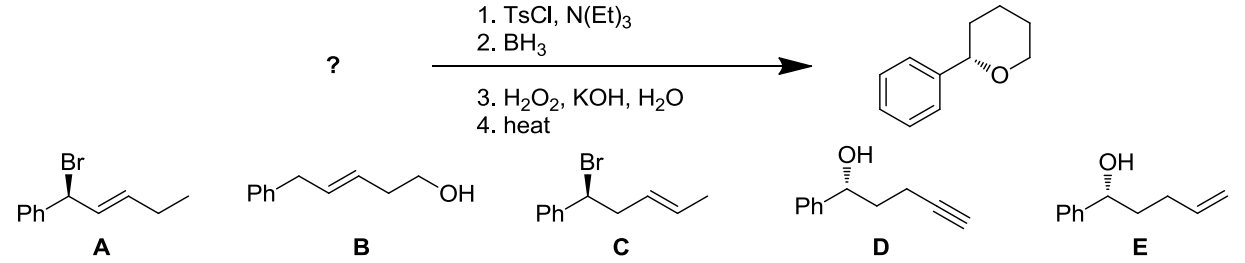


A 1. Br_2 2. Potassium tert-butoxide, heat
B 1. HBr, dark, N_2 2. N-bromosuccinimide, $CHCl_3$ 3. NaOEt, EtOH, heat
C 1. N-bromosuccinimide, $CHCl_3$ 2. Br_2 3. Potassium tert-butoxide, heat
D 1. HBr, peroxides 2. NaOEt, EtOH, heat 3. Br_2 4. NaOEt, EtOH, heat
E 1. N-bromosuccinimide, $CHCl_3$ 2. HBr, peroxides 3. NaOEt, EtOH, heat

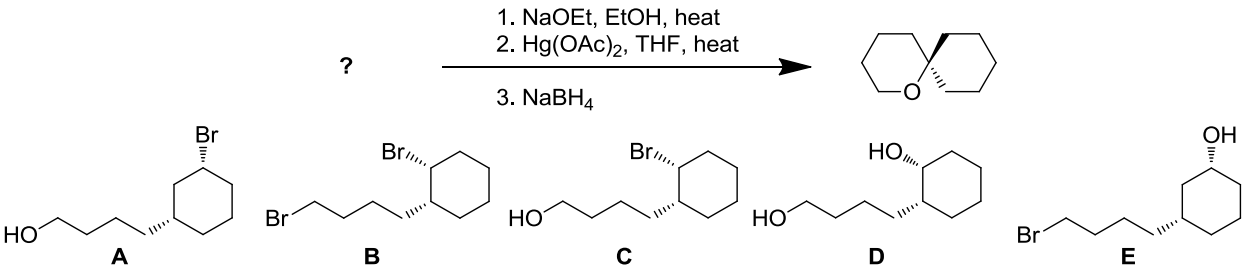
16.



17.



18.



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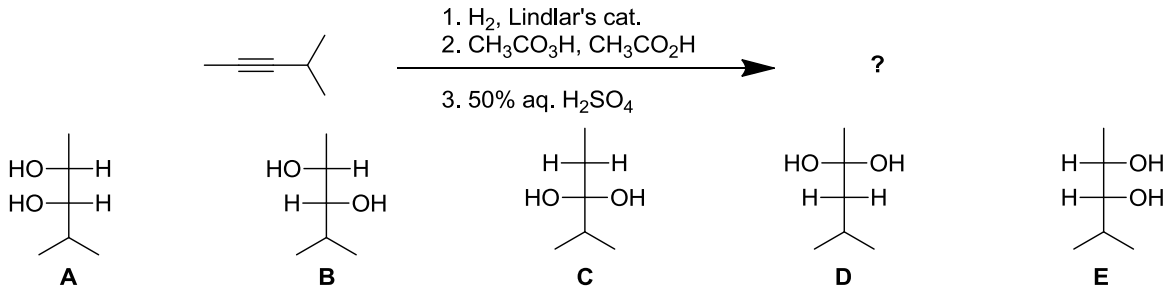
PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

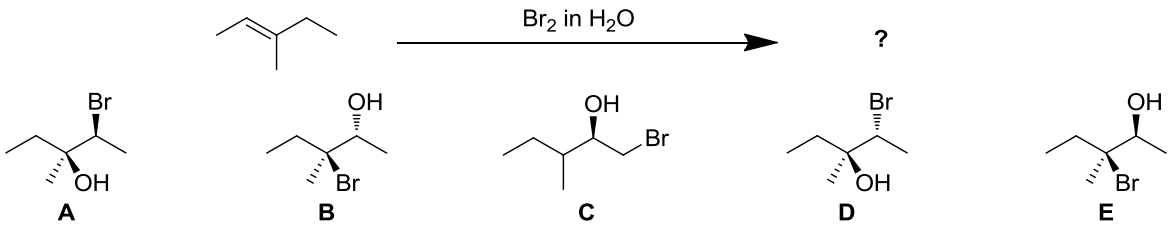
18% **ANSWER ANY SIX (6) OF QUESTIONS 19-25**.

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

19.



20.



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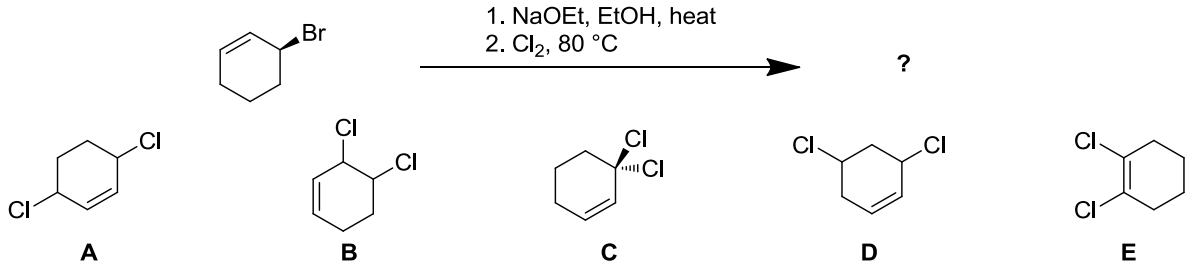
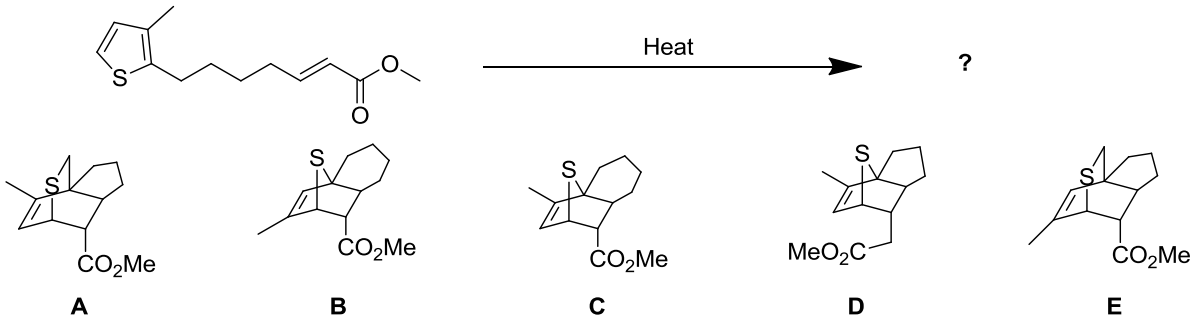


22.



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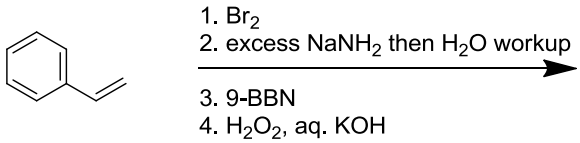
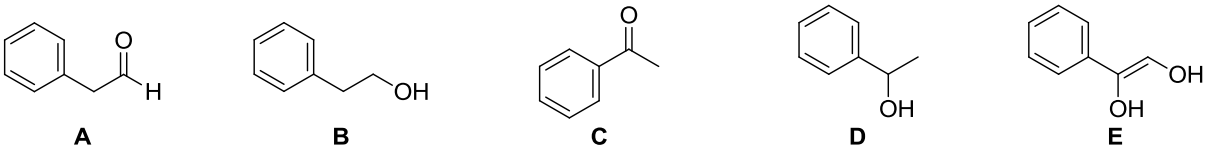
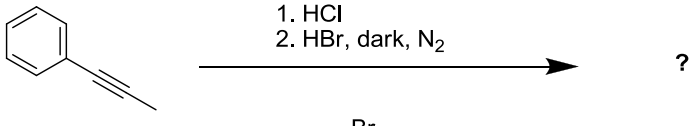
23.

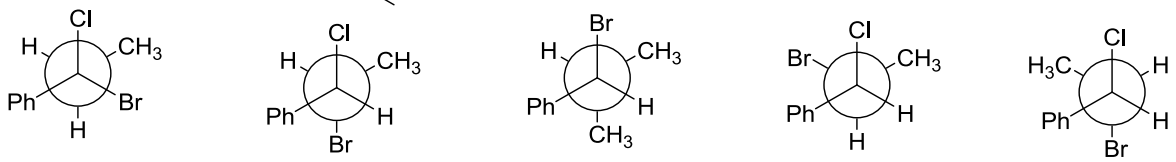




A **B** **C** **D** **E**

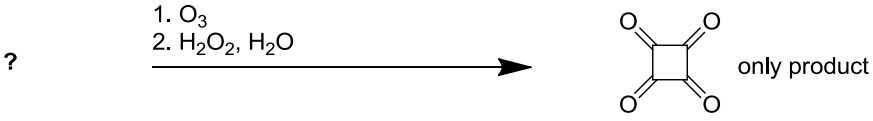
24.

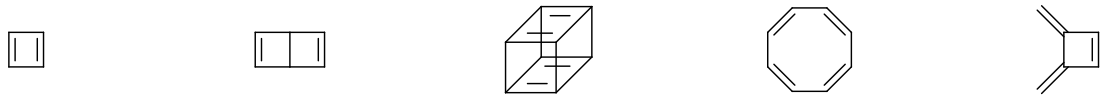




A **B** **C** **D** **E**

25.





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

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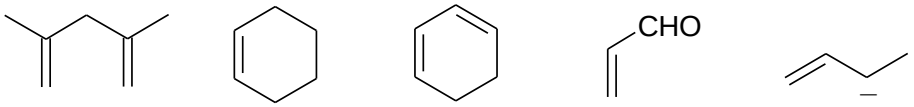
PART 4: PI SYSTEMS

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

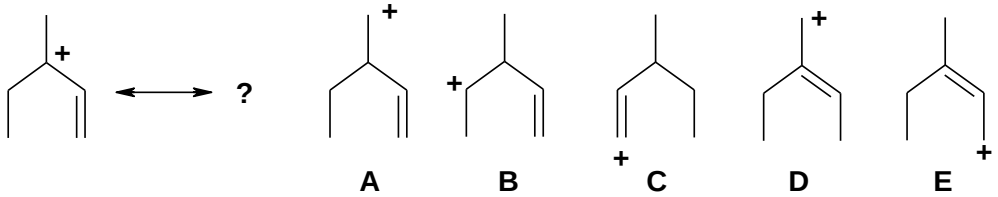
For each of the questions 26-34 select the appropriate answer from the answers provided. In some cases more than one selection may be required for full credit.

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



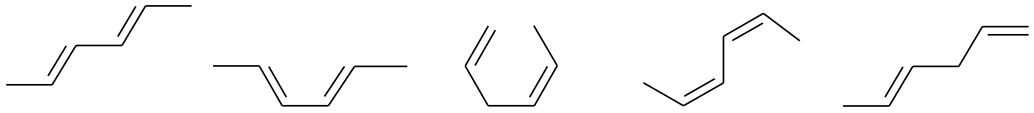
A **B** **C** **D** **E**

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



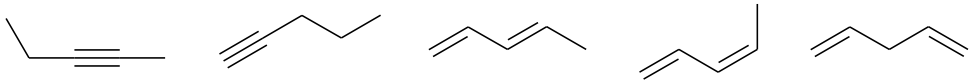
A **B** **C** **D** **E**

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



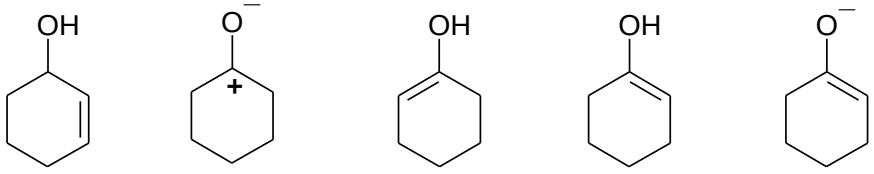
A **B** **C** **D** **E**

29. Which of the following isomers has the least exothermic heat of hydrogenation ?



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

30. Which of the following systems are resonance contributors of cyclohexanone?
(select all that apply)



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

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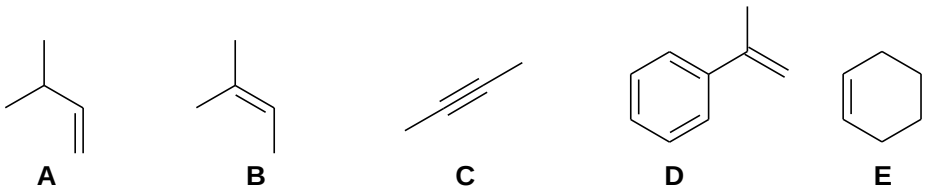
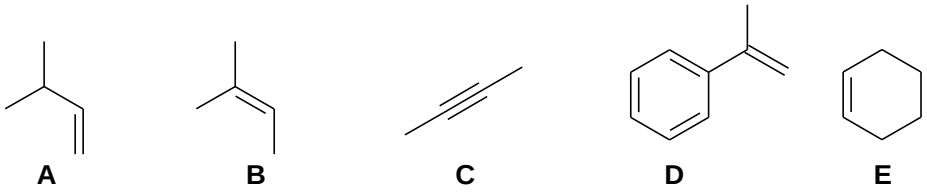
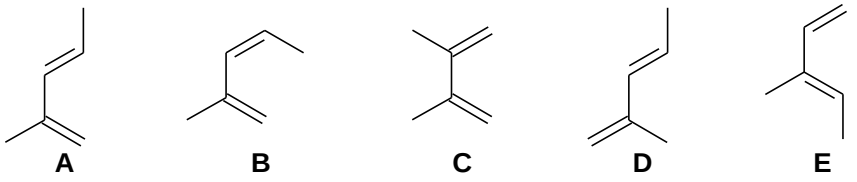
31. Which of the following systems would be the most reactive towards Na / NH_3 ?



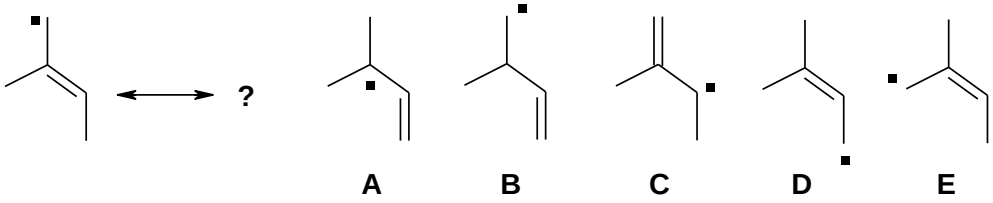
32. Which of the following systems would be the most reactive towards HCl ?



33. Which of the following molecules is the s-cis form of (3E)-2-methylpenta-1,3-diene?



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



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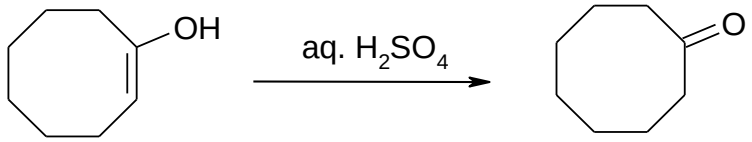
PART 5: MECHANISMS

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

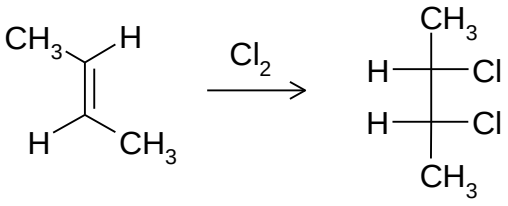
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

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:

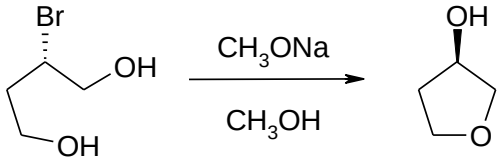


OR

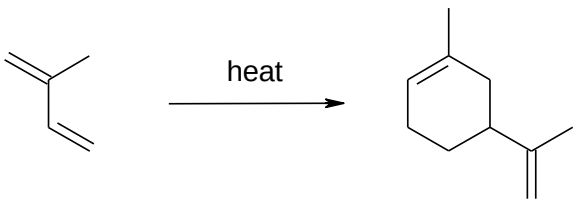


AND

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



OR



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PART 6: SYNTHESIS

15% **ANSWER A TOTAL OF 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 any 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**
- **You may use any solvents or reagents that do not contribute carbon atoms to the final structure.**

A

B

C

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_8H_{14}), was reacted with H_2 over Lindlar's catalyst to give **B** (C_8H_{16}). When **B** was reacted with aq. H_2SO_4, **C** was obtained (IR = 3500 cm^{-1}, brd) as the major product. Subsequent reaction of **C** with H_2SO_4 / heat gave a mixture of two products, **D** (major) and **E** (minor). Reaction of either **D** or **E** with O_3 followed by work up with zinc in acid gave a single product, butan-2-one. Reaction of **A**, **B**, **D** or **E** with H_2 over Pd gave the same alkane, C_8H_{18}. When **D** was reacted with Br_2 in chloroform, an optically inactive compound was obtained while **E** gave a pair of enantiomers.

When **A** was reacted with aq. $HgSO_4$ / H_2SO_4, a single compound **F** (IR = 1715 cm^{-1}) was obtained, while when **A** was reacted with 9-borabicyclononane (*i.e.* 9-BBN) followed by aq. NaOH / H_2O_2 it gave an isomer of **F** that had a H-NMR peak at about 9.5ppm.

Draw the structures of A to F.
Give the complete IUPAC name for D.
Why is the product of the reaction of D with Br_2 optically inactive ?

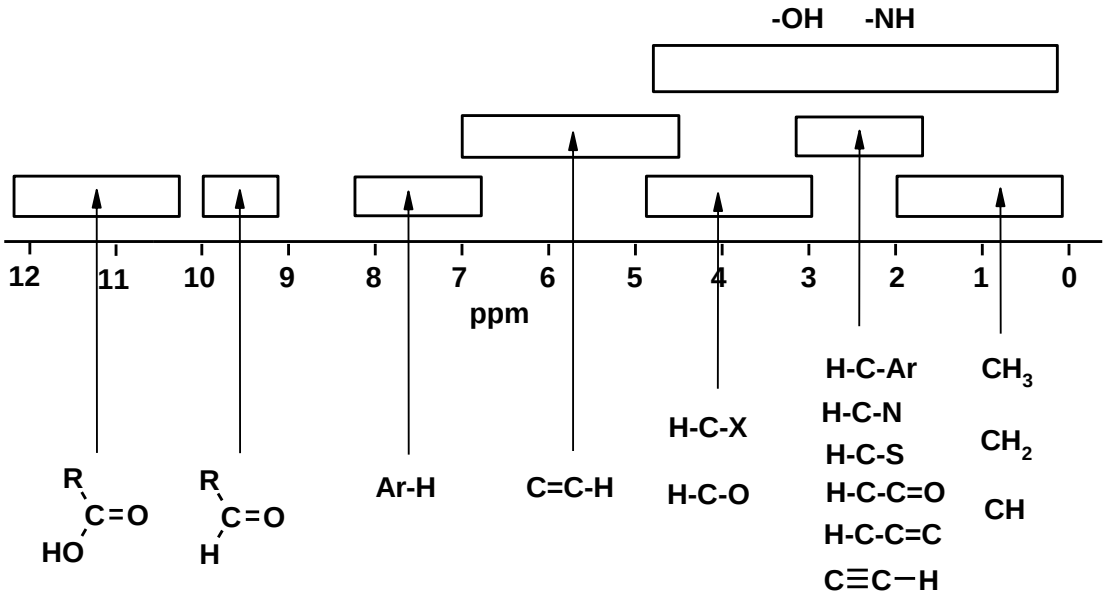
*** THE END ***

CCL / IRH / W12

CONTINUED -->

SPECTROSCOPIC TABLES

^{1}H NMR



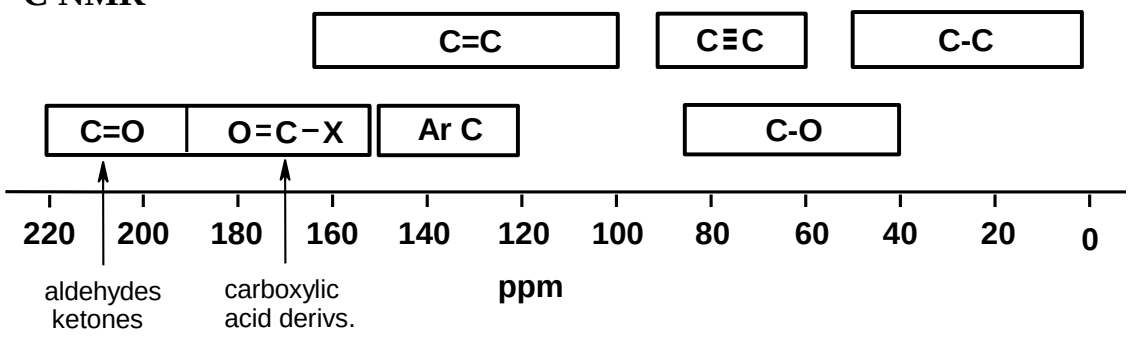
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	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

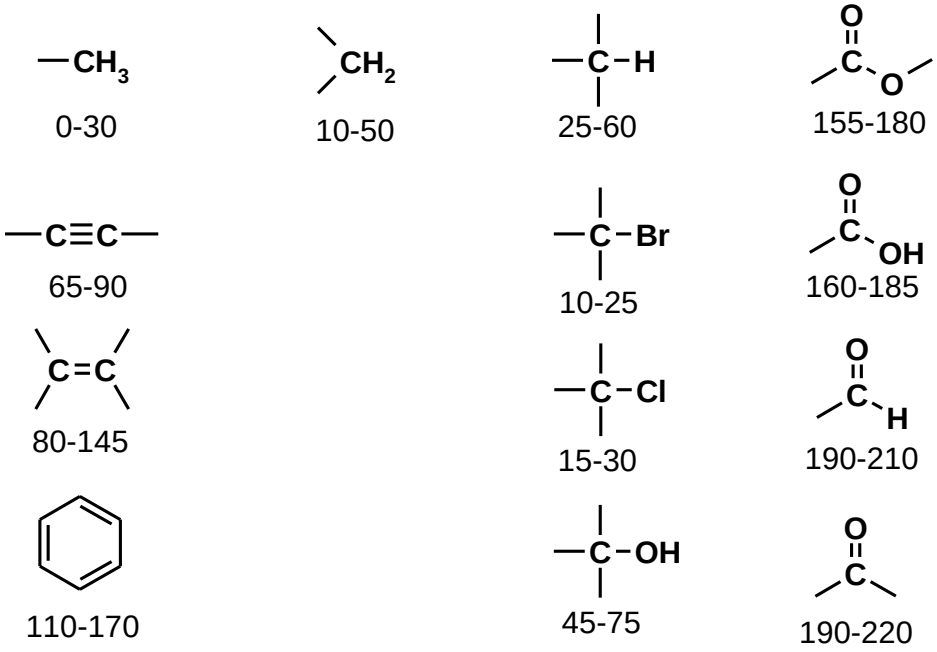
other	
-OH	1-5
-NH	1-3
C≡CH	2.5
C=C, H	5.5
Ar-H	7.3
O, C, R, H	10
O, C, R, OH	9-12

CONTINUED -->

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



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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.

CONTINUED -->

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)

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