UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

TUESDAY MARCH 5th, 2013 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.**

16% **PART 1: RELATIVE PROPERTIES**

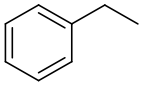
ANSWER ANY EIGHT (8) OF QUESTIONS 1-10.

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

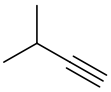
Use the following code to indicate your answers.

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

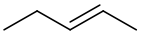
1. The relative reactivity of each of the following towards H_2 / Pd:



i



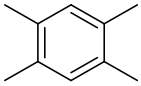
ii



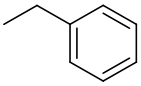
iii

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

i



ii



iii

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

   i. 2.8g ethene with 0.10 mol BH_3 giving 2.3g of ethanol

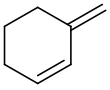
   ii. 2.8g ethene with 0.02 mol BH_3 giving 2.3g of ethanol

   iii. 0.3 mol ethene with 0.3 mol BH_3 giving 0.1 mol of ethanol

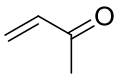
4. The relative reactivity towards but-3-en-2-one (shown below) of each of the following:

i

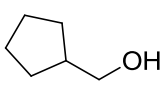
ii



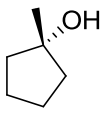
iii



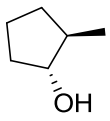
5. The relative yields of each of the following from the reaction of 1-methylcyclopentene with (1) BH_3 then (2) aq. H_2O_2 / NaOH:



i



ii



iii

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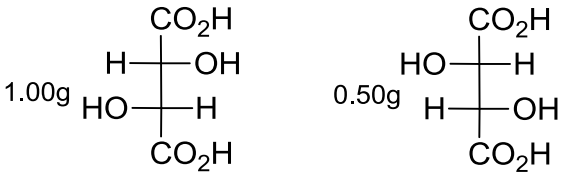
Use the following code to indicate your answers.

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

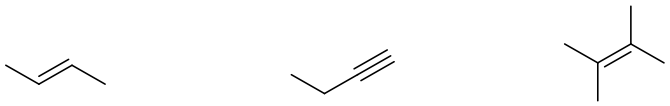
i a mixture composed of :



ii a sample whose observed rotation = + 1.27^o when 1.0g of a sample was dissolved in 10mL and measured in a standard 10cm polarimeter cell

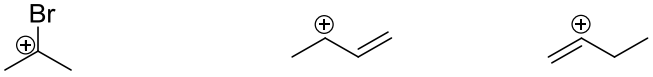
iii a racemic mixture

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



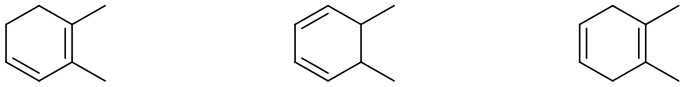
i **ii** **iii**

8. The relative stability of the following carbocations:



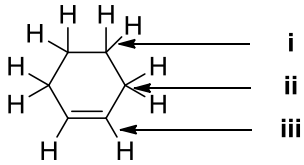
i **ii** **iii**

9. The relative stability of the following isomers:



i **ii** **iii**

10. The relative strength of the indicated C-H bonds:



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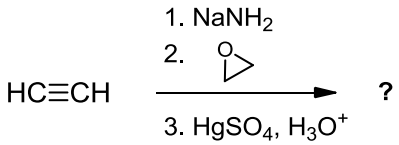
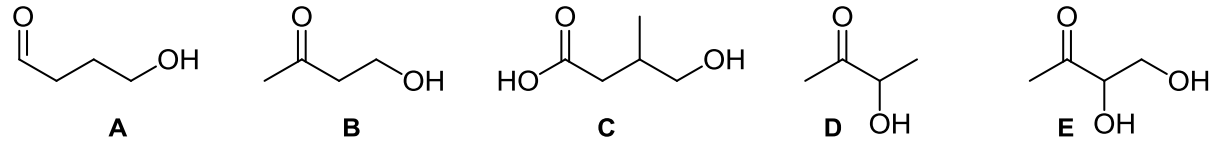
14% PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS

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

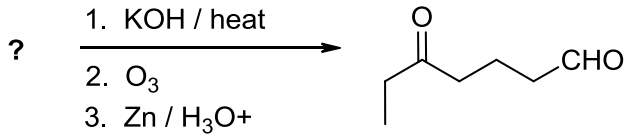
For each of questions 11-18 select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

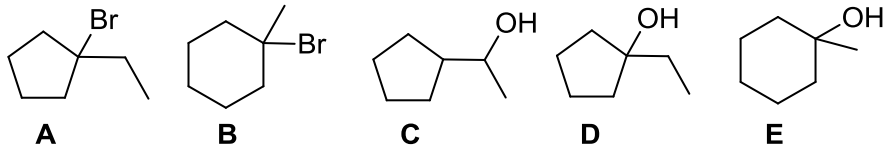
11.





12.





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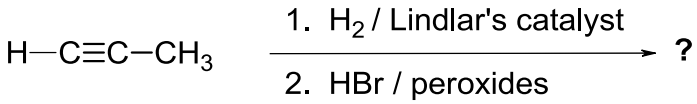

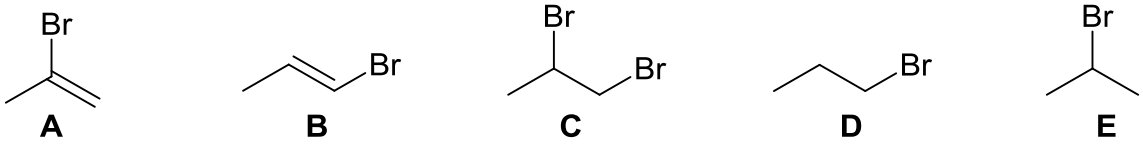

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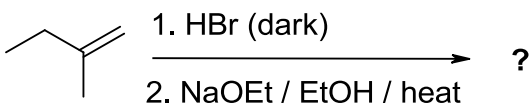

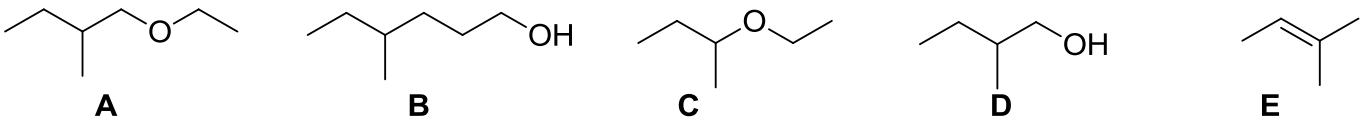

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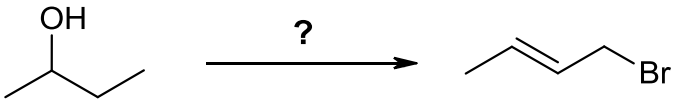
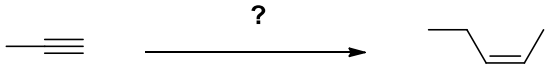
15.



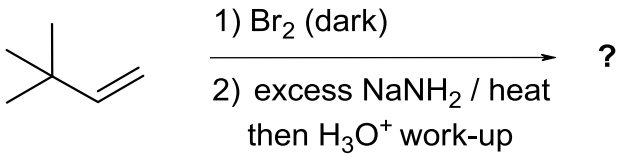
A 1. Thionyl chloride / Et_3N 2. NaOEt / EtOH / heat 3. NBS, heat
B 1. PBr_3 / Et_3N 2. KOH / EtOH / heat 3. HBr
C 1. Br_2, uv light 2. H_2O, heat 3. PBr_3 / Et_3N
D 1. NaOEt / EtOH / heat 2. Br_2, uv light
E 1. HBr 2. KOBu-t / t-BuOH / heat 3. HBr

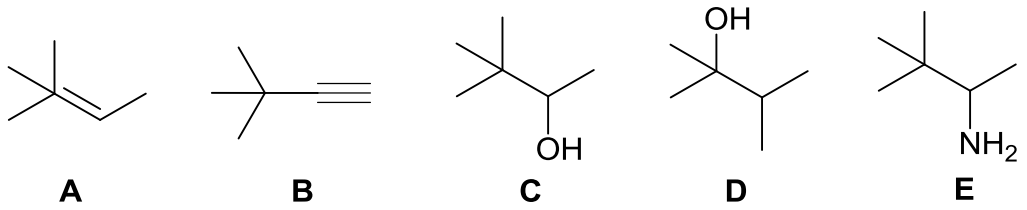
16.



A 1. $NaNH_2$ 2. methyl iodide 3. H_2, Lindlar's cat.
B 1. $NaNH_2$ 2. methyl iodide 3. Na, NH_3
C 1. $NaNH_2$ 2. ethyl iodide 3. Na, NH_3
D 1. $NaNH_2$ 2. ethyl bromide 3. H_2, Lindlar's cat.
E 1. $NaNH_2$ 2. 1-bromopropane 3. H_2, Lindlar's cat.

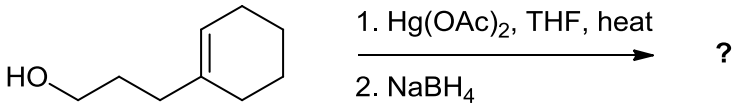
17.

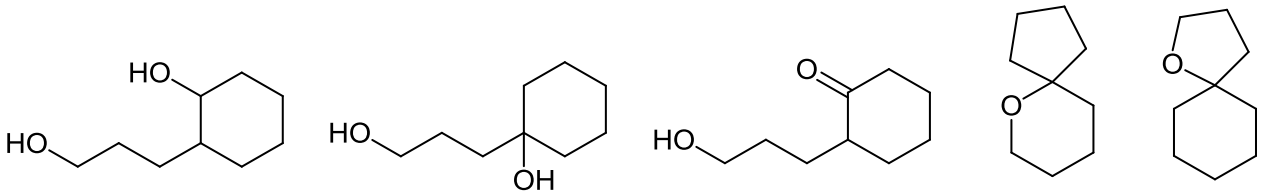




A **B** **C** **D** **E**

18.





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

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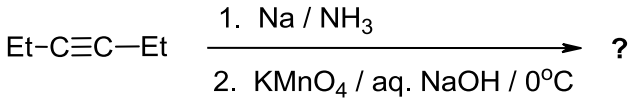
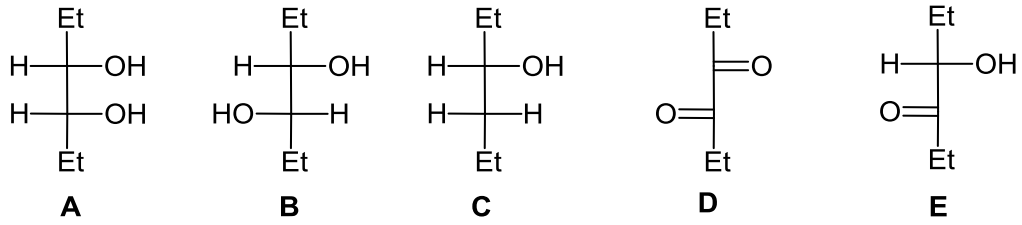
PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

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

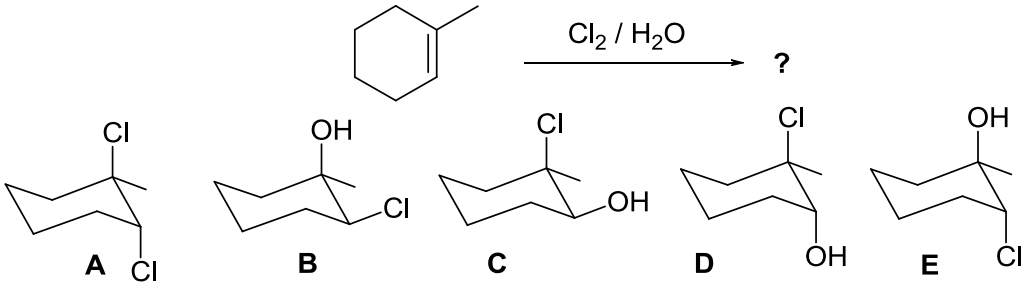
For each of the questions 19-25, select the structure required to BEST complete the reaction shown.

19.

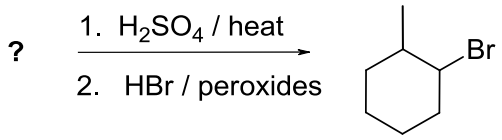


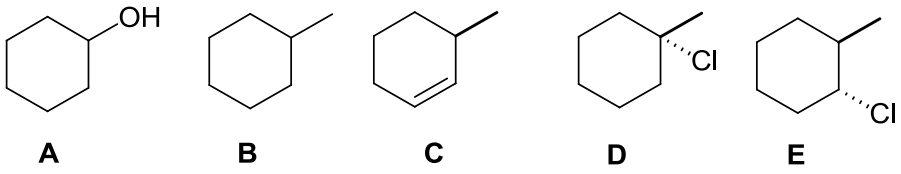


20.



21.





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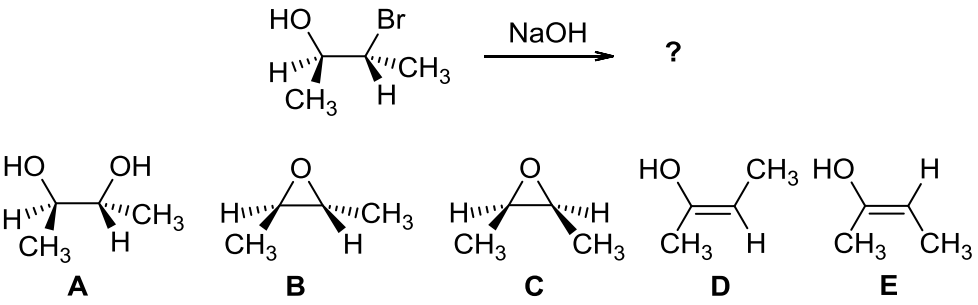
22.



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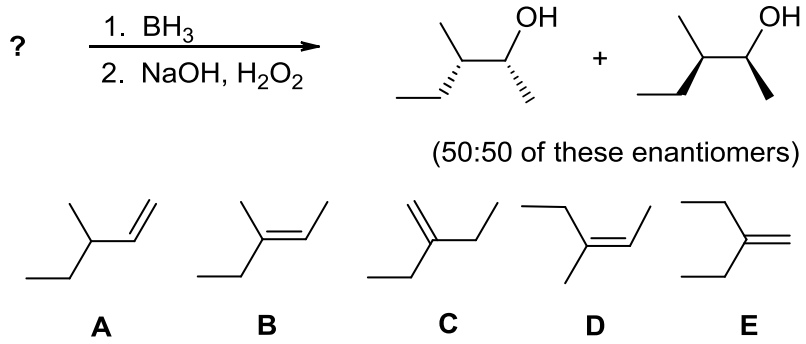
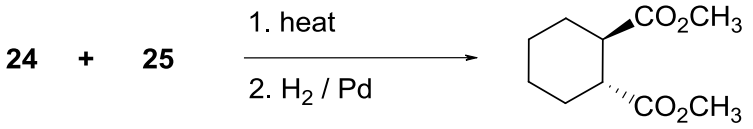
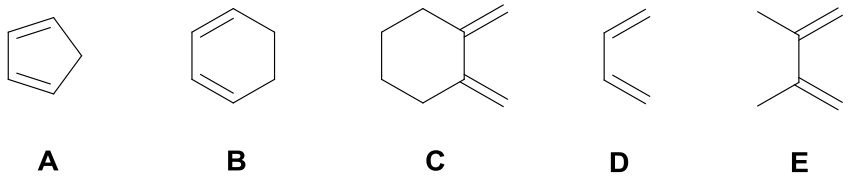


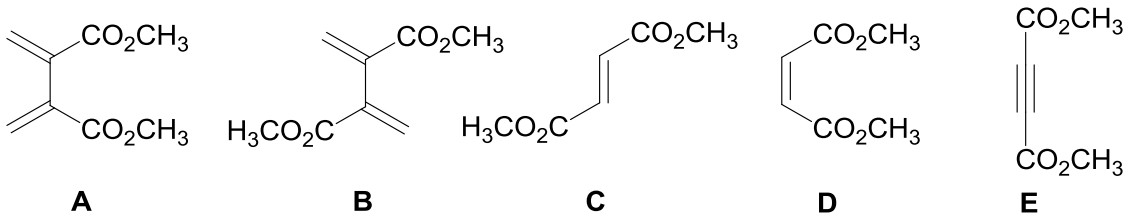
Questions 24 and 25 both apply to the following reaction scheme:



24.



25.



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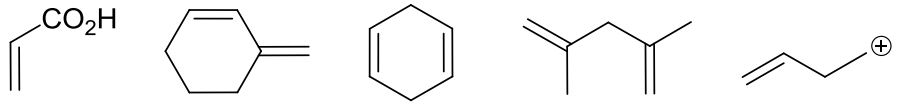
16% PART 4: PI SYSTEMS

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

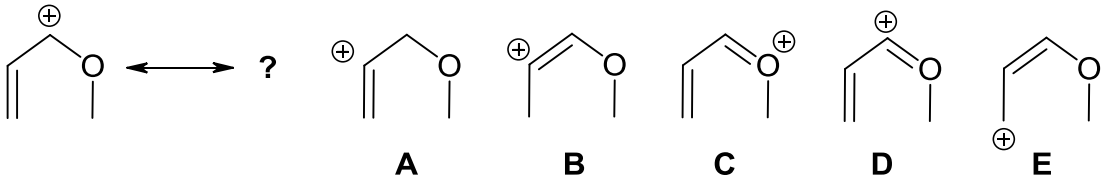
For each of the questions 26-34 select the appropriate answer from the answers provided. In some cases more than one selection may be required for full credit.

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



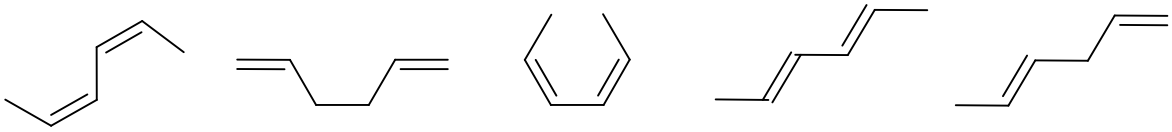
A **B** **C** **D** **E**

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



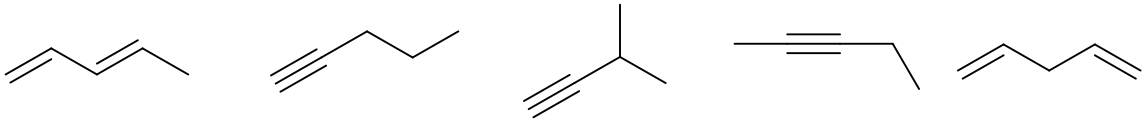
A **B** **C** **D** **E**

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



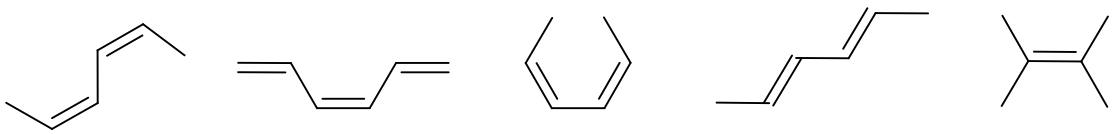
A **B** **C** **D** **E**

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



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

30. Which of the following systems has the most resonance energy ?



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

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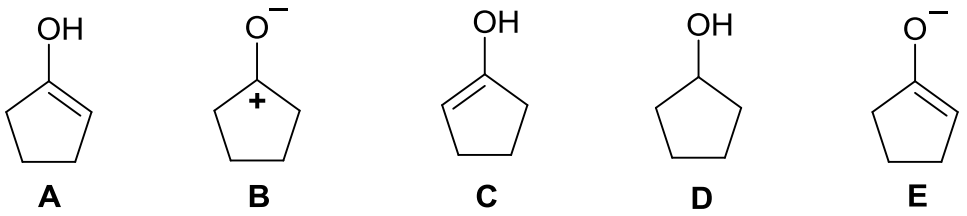
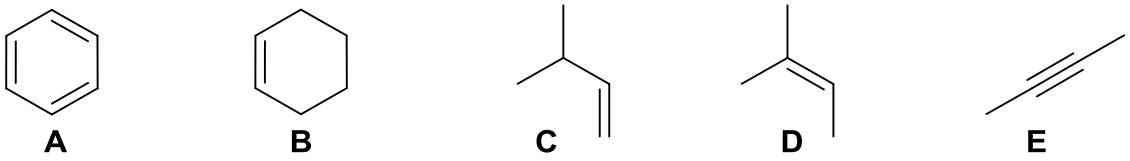
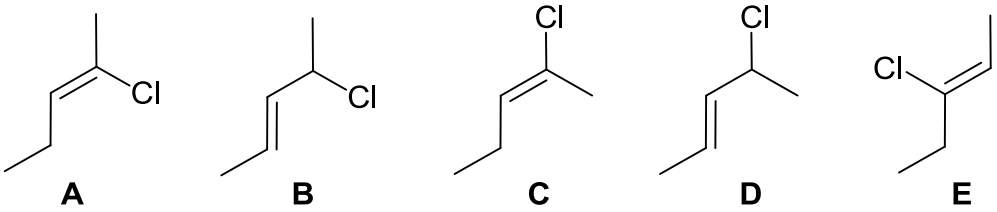
31. Which of the following systems are tautomers of cyclopentanone? **(select all that apply)**



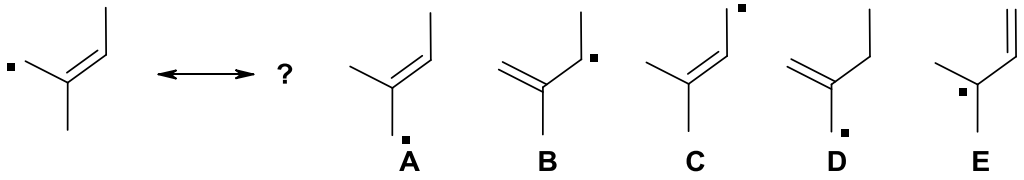
32. Which of the following systems would be the most reactive towards H_2 / Pd ?



33. Which of the following molecules is (E)-2-chloropent-2-ene?



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



CONTINUED -->

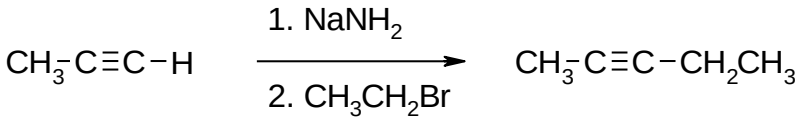
10% **PART 5: MECHANISMS**

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

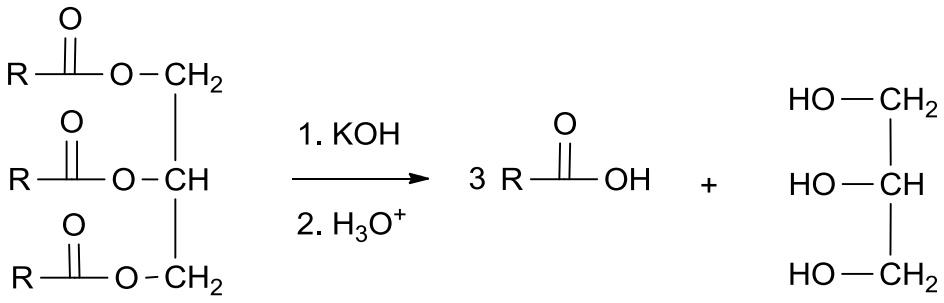
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

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:

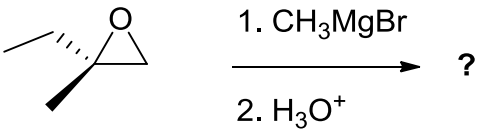


OR

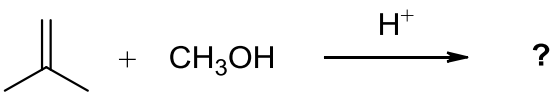


AND

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



OR



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15% PART 6: SYNTHESIS

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)

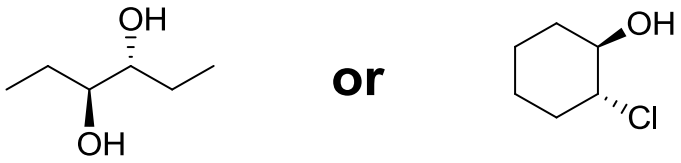
Allowed starting materials and reagents:

- **Cyclopentene**
- **Any hydrocarbons with 4 or less C atoms**
- **You may use any solvents or reagents that do not contribute carbon atoms to the final structure.**

A

B

C



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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_7H_{14}), was reacted with H_2 over Pd catalyst to give **B** (C_7H_{16}). When **B** was reacted with Br_2/uv light, **C** was obtained as the major product. **C** was also obtained as the major product when **A** was reacted with HBr (dark / N_2).

Subsequent reaction of **C** with $KOC(CH_3)_3$ / heat gave **D** as the major product. **D** was found to be a constitutional isomer of **A**. Reaction of **D** with H_2 over Pd catalyst to give also gave **B**.

Reaction of **A** with O_3 followed by work up with zinc in acid gave two products, **E** (IR 1715 cm^{-1}) and **F** (IR 1731 cm^{-1}) whose H-NMR included a peak at about 9.5ppm.

In contrast, reaction of **D** with O_3 followed by work up with H_2O_2 gave **G** (IR 1715 cm^{-1}) and carbon dioxide was also evolved.

G could also be made by the reaction of 1-hexyne with aq. H_2SO_4 / $HgSO_4$.

Draw the structures of A to G.

Give the complete IUPAC name for A.

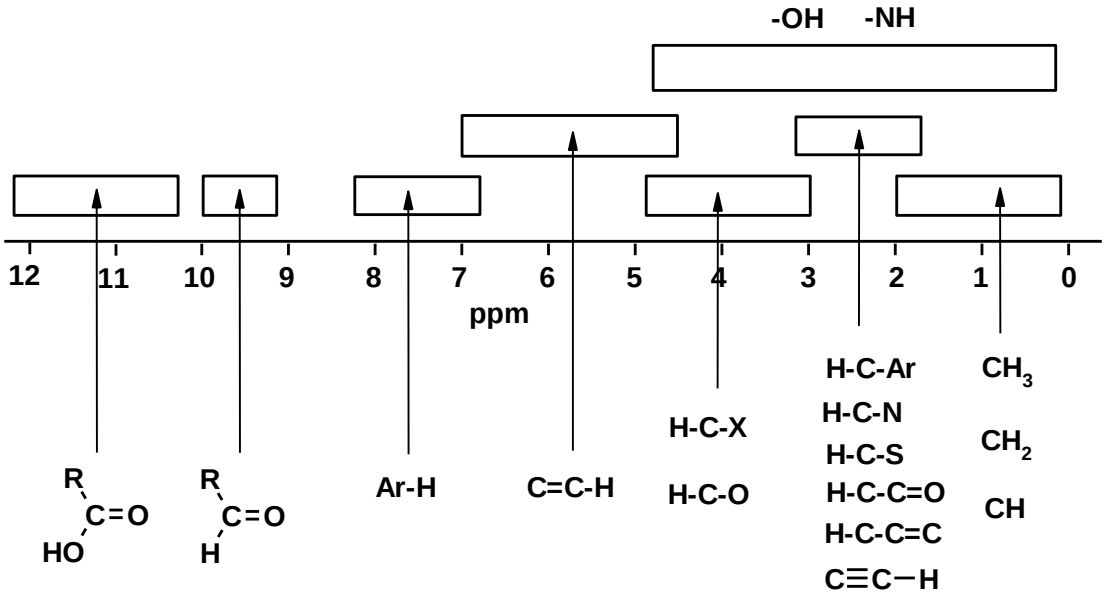
*** THE END ***

ASC / IRH / W13

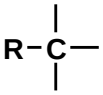
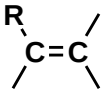
CONTINUED -->

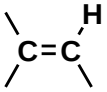
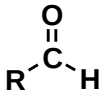
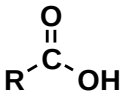
SPECTROSCOPIC TABLES

^{1}H NMR



^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	methyl CH_3-	methylene -CH_2-	methyne CH
	0.9	1.4	1.5
	1.6	2.3	2.6
	2.1	2.4	2.5
	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
	5.5
Ar-H	7.3
	10
	9-12

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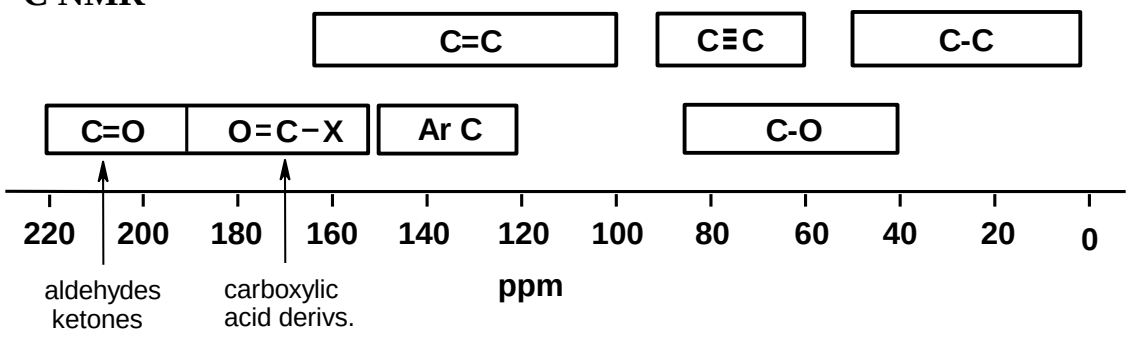
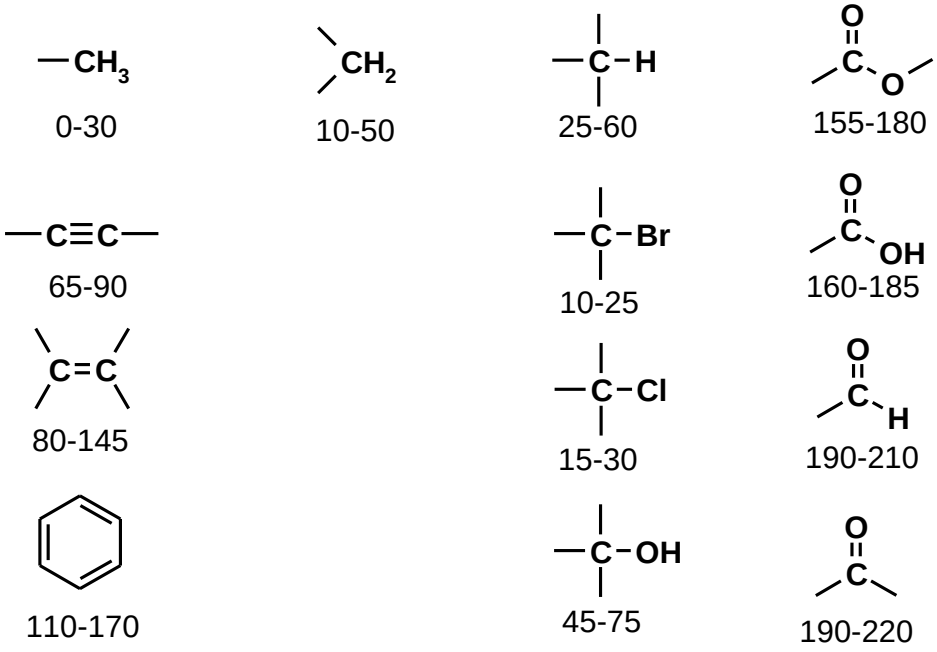
^{13}C NMR



^{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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