UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

Version 1

TUESDAY MARCH 3rd, 2015 Time: 2 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR ANSWER BOOKLET** AND **COMPUTER ANSWER SHEET**.
ENTER **VERSION NUMBER 1** ON THE **COMPUTER 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 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**

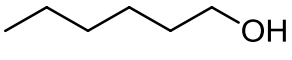
1. The relative reactivity of each of the following towards 2-pentene:

HCl	HF	H_2O
i	**ii**	**iii**

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

$CH_3C{\equiv}C{-}\mathbf{H}$	$H_2N{-}\mathbf{H}$	$HO{-}\mathbf{H}$
i	**ii**	**iii**

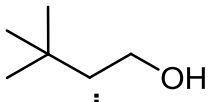
3. The % yield of the alcohol product shown below from the reaction of hex-1-ene with each of the following:



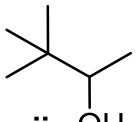
product

H_3O+	1. BH_3 2. aq. NaOH / H_2O_2	1. 9-BBN 2. aq. NaOH / H_2O_2
i	**ii**	**iii**

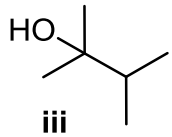
4. The relative yields of the following products from the reaction of 3,3-dimethylbut-1-ene with BH_3 followed by the normal work-up with aq. NaOH / H_2O_2 :



i

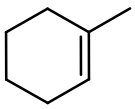


ii

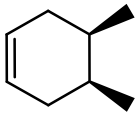


iii

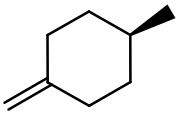
5. The number of stereoisomers produced from the reaction of each of the following cycloalkenes with HCl:



i



ii



iii

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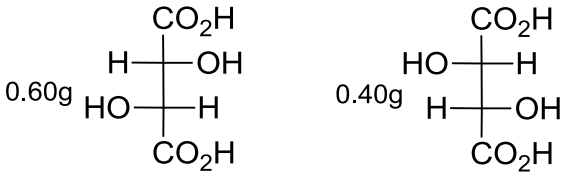
Use the following code to indicate your answers.

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 specific rotation of each of the following samples of tartaric acid dissolved in 10mL of the same solvent given that (R,R)-tartaric acid $[\alpha]_D$ = +12.7 :

i a mixture composed of :



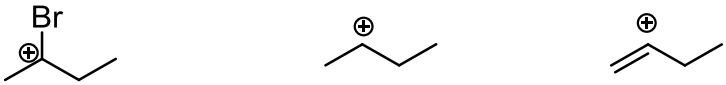
ii a sample whose observed rotation = - 0.635^o when 1.0g of a sample was measured in a standard 10cm polarimeter cell

iii a sample of 1.0 g (2R,3S)-tartaric acid

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

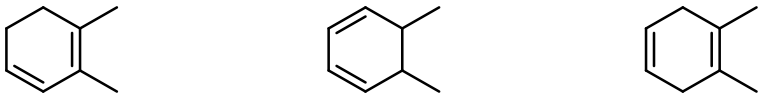
i **ii** **iii**

8. The relative stability of the following carbocations:



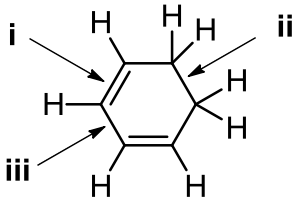
i **ii** **iii**

9. The relative stability of the following isomers:



i **ii** **iii**

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



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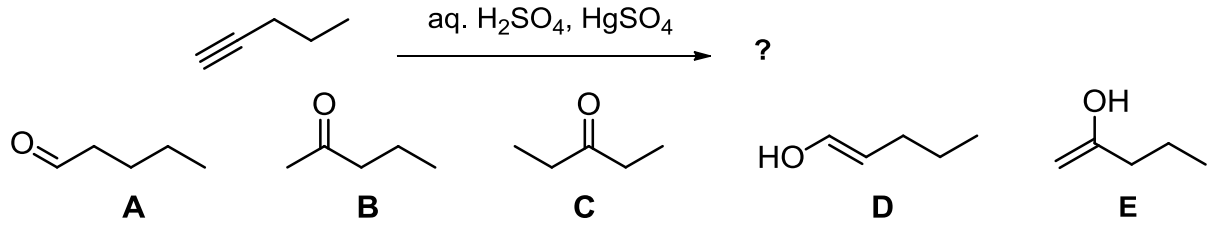
14% **PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS**

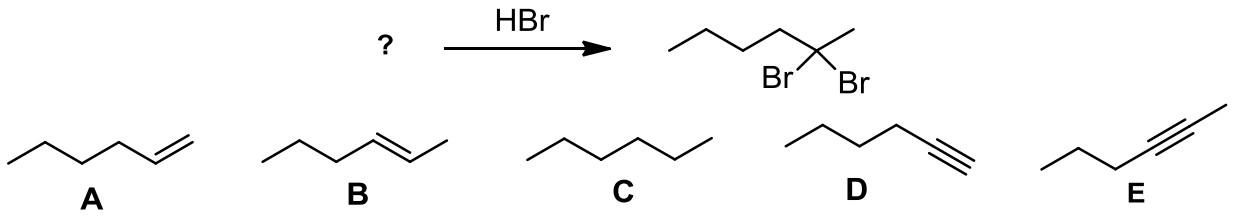
ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.

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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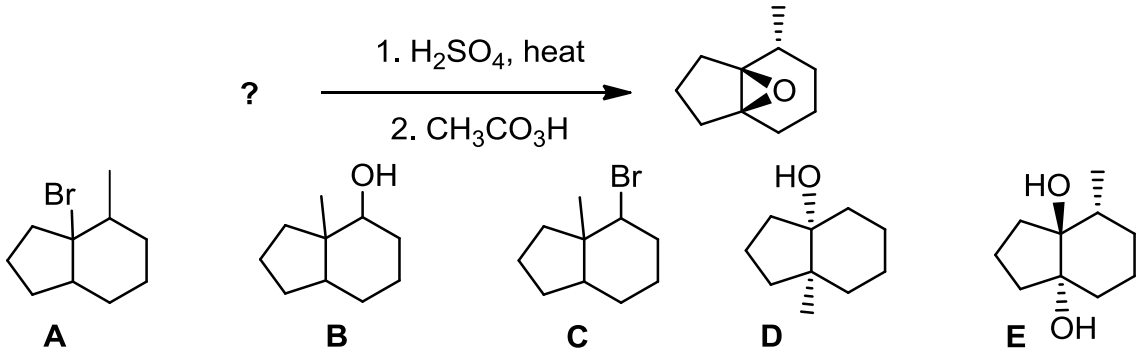

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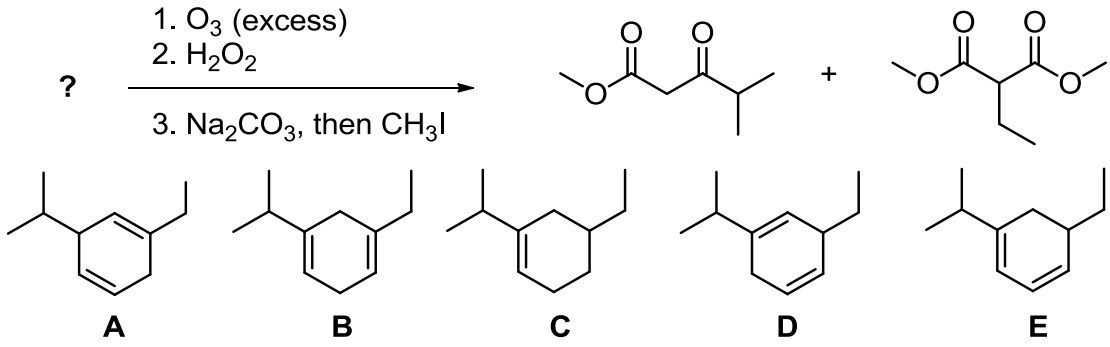

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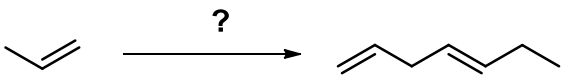
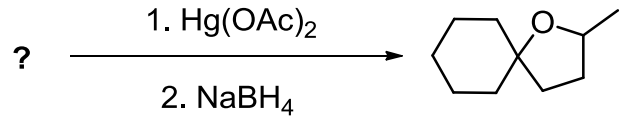
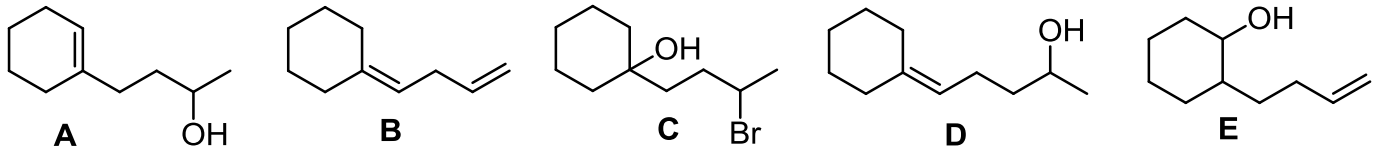
15.



A 1. NBS, heat; 2. 1-butyne, $NaNH_2$; 3. H_2, Lindlar Pd
B 1. HBr, peroxide; 2. 2-butyne, $NaNH_2$; 3. Na, NH_3
C 1. NBS, heat; 2. 1-butyne, $NaNH_2$; 3. Na, NH_3
D 1. HBr, dark; 2. 1-butyne, $NaNH_2$; 3. Na, NH_3
E 1. NBS, heat; 2. 1-butene, $NaNH_2$

16.





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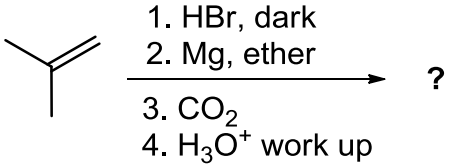
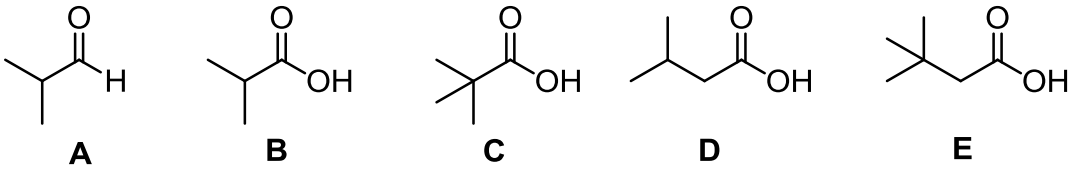
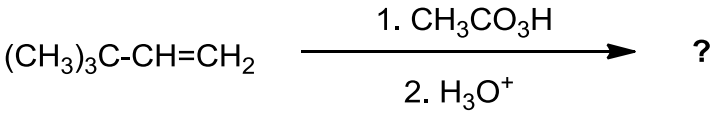
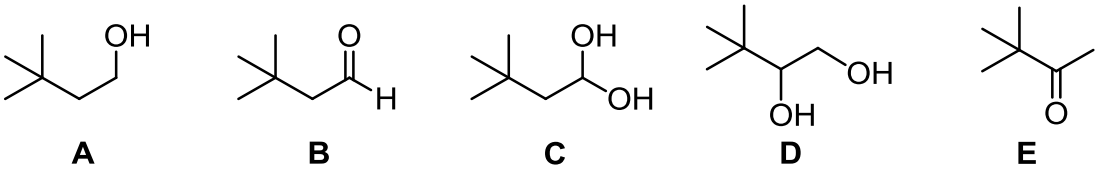




18.





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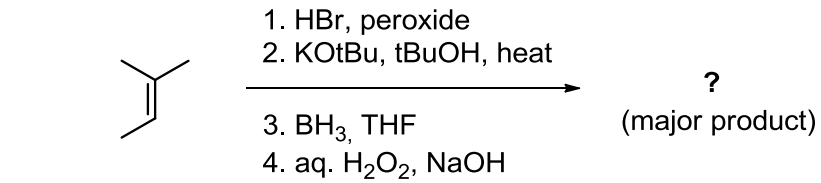
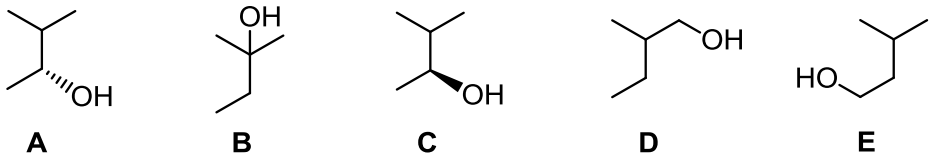
PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

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

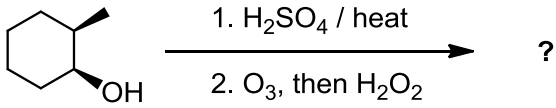
For each of the questions 19-25, select the structure required to BEST complete the reaction shown.

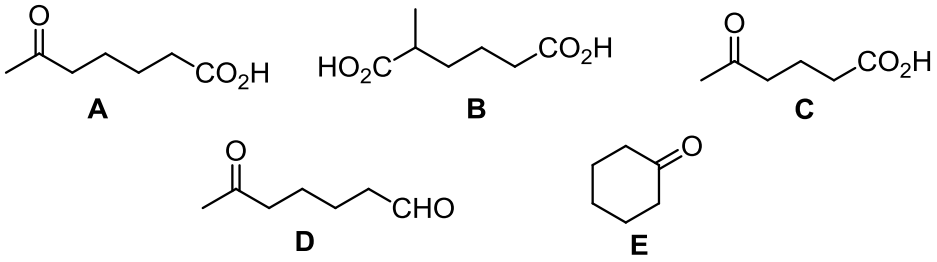
19.



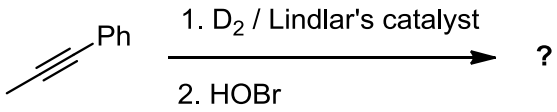


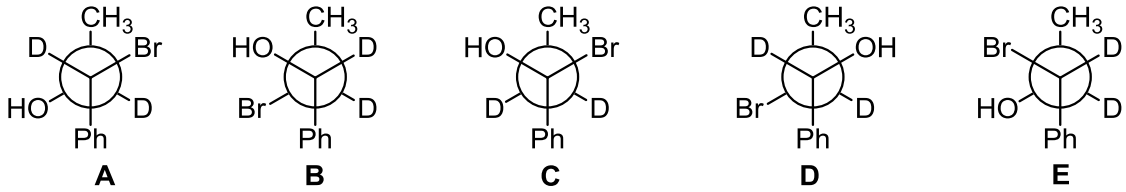
20.





21.





D = deuterium, an isotope of H that reacts just like H

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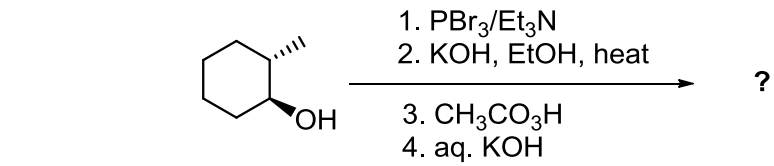
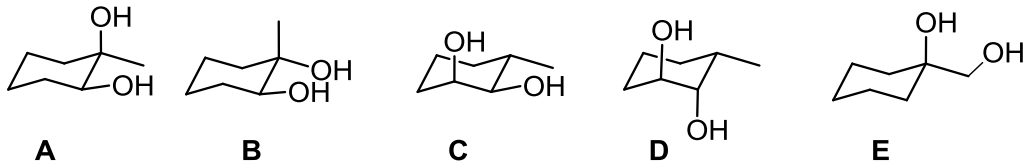
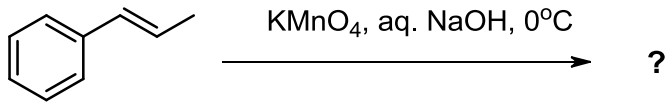
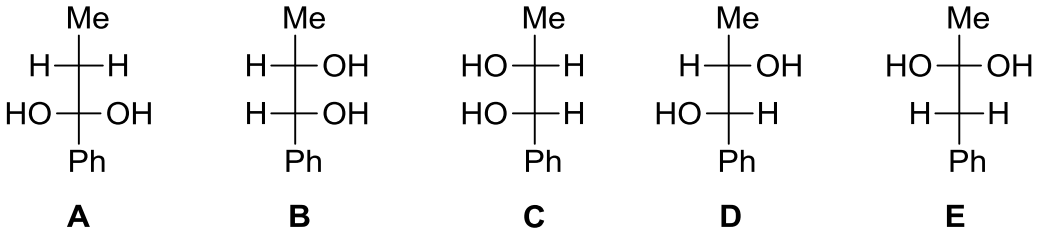
22.





23.





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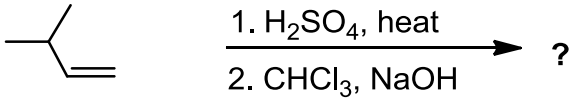

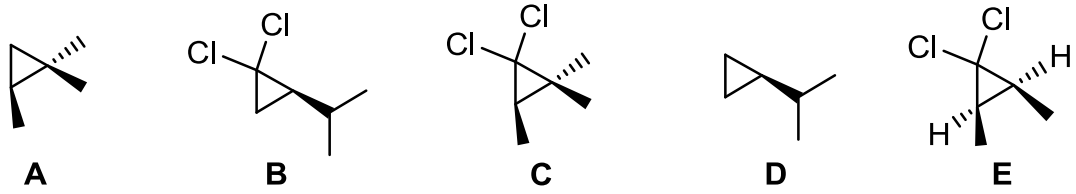

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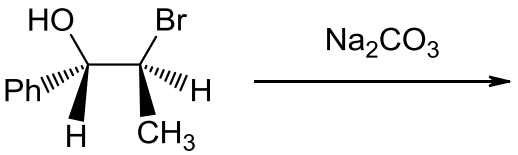

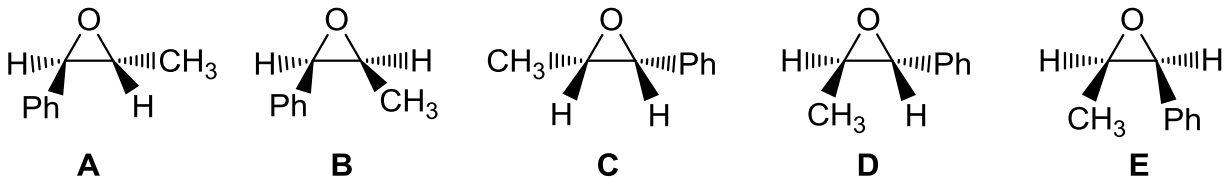

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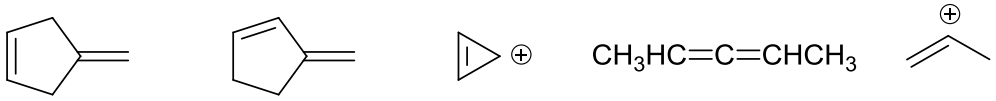
16% PART 4: PI SYSTEMS

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

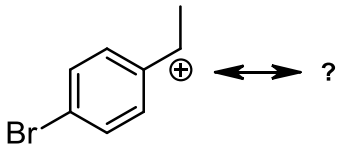
For each of the questions 26-34 select the appropriate answer from the answers provided. In some cases more than one selection may be required for full credit.

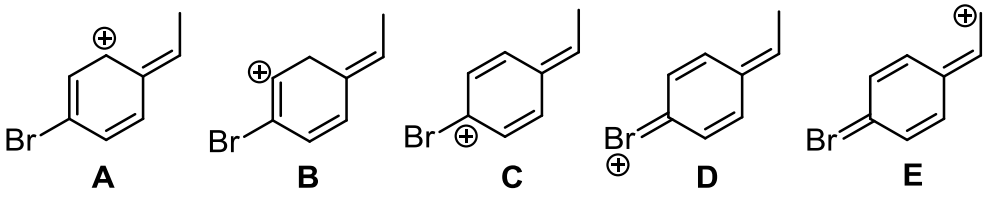
26. Which of the following contain conjugated systems? **(select all that apply)**



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

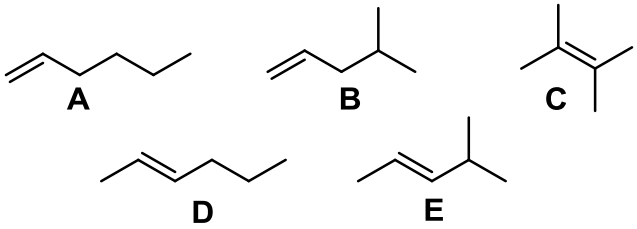
27. Which of the following systems are resonance contributors of the cation shown to the right ? **(select all that apply)**





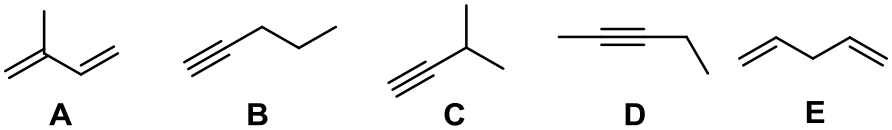
A **B** **C** **D** **E**

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



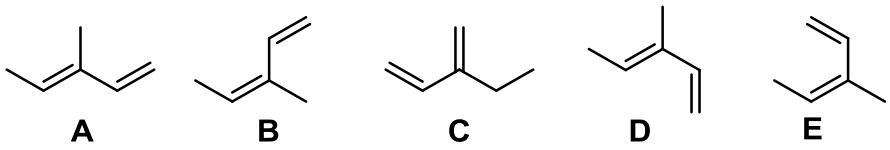
A **B** **C** **D** **E**

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

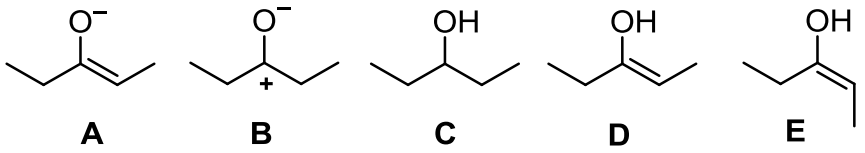


A **B** **C** **D** **E**

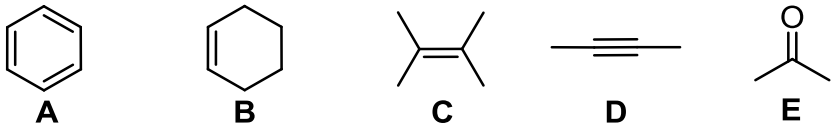
30. Which of the following molecules is the *s-trans* form of (3Z)-3-methylpenta-1,3-diene?



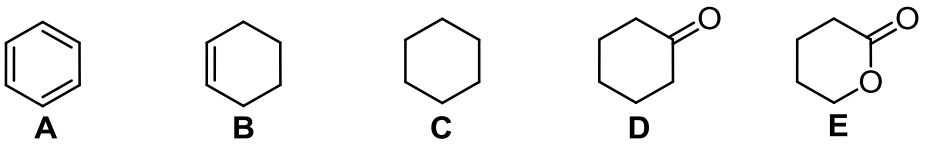
31. Which of the following systems are tautomers of pentan-3-one? **(select all that apply)**



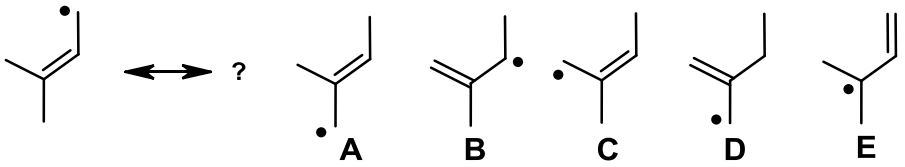
32. Which of the following systems would be the most reactive towards H_2 / Pd ?



32. Which of the following systems would be the most reactive towards $NaBH_4$?



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



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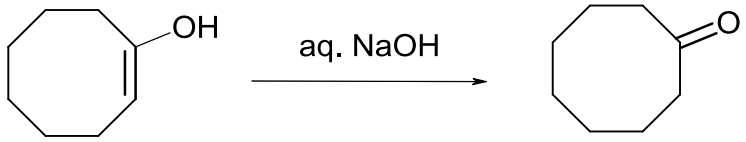
10% **PART 5: MECHANISMS**

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

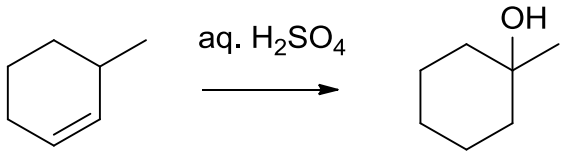
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

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:

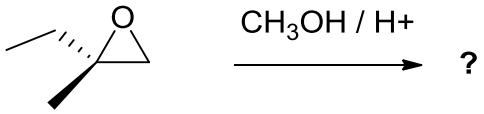


OR

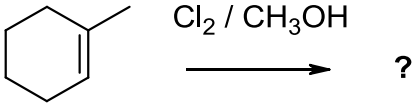


AND

B. Predict the product and show the mechanism for **one** of the following reactions:



OR



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15% PART 6: SYNTHESIS

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

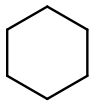
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

Design an efficient synthesis for 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

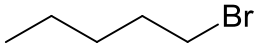
DO NOT SHOW MECHANISMS (*i.e.* curly arrows are NOT required)

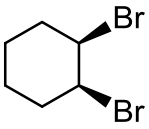
Allowed starting materials and reagents:

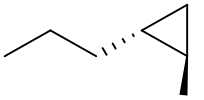


Any hydrocarbons with 3 or less C atoms

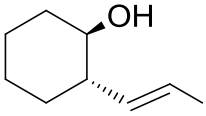
Any solvents or reagents that do not contribute carbon atoms to the final structure.

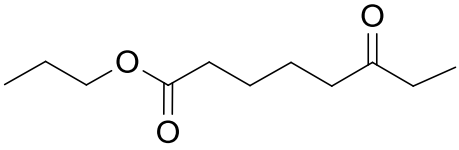
A 

or 

B 

or *meso*-2,3-dibromobutane

C 

or 

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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_6H_{10}), was reacted with H_2 over Pd / $CaCO_3$ / quinoline to give **B** (C_6H_{12}). When **B** was reacted with HCl, **C** was obtained as the major product. When **C** was reacted KOH / EtOH / heat, **D** was the major product and **D** was found to be a constitutional isomer of **B**.

Subsequent reaction of **D** with *either* aq. H_2SO_4 *or* (1) BH_3 (2) aq. H_2O_2 / NaOH gave **E** ($C_6H_{14}O$) as the only product.

When **C** was reacted $KOC(CH_3)_3$ / heat, **F** was the major product which was also a constitutional isomer of **B** and **D**.

Reaction of either **D** or **F** with H_2 over Pd catalyst gave 2,3-dimethylbutane.

Reaction of **B** with O_3 followed by work up with zinc in acid gave two products, **G** (IR 1712 cm^{-1}, H-NMR/ppm 1.1 (9H, s) and 9.5 (1H, s)) and **H** (IR 1750 cm^{-1}, H-NMR/ppm 9.6 (s)).

Reaction of **D** with O_3 followed by work up with H_2O_2 gave one product **I** (IR 1715 cm^{-1}, H-NMR/ppm 2.1 (s).

Draw the structures of A to I.

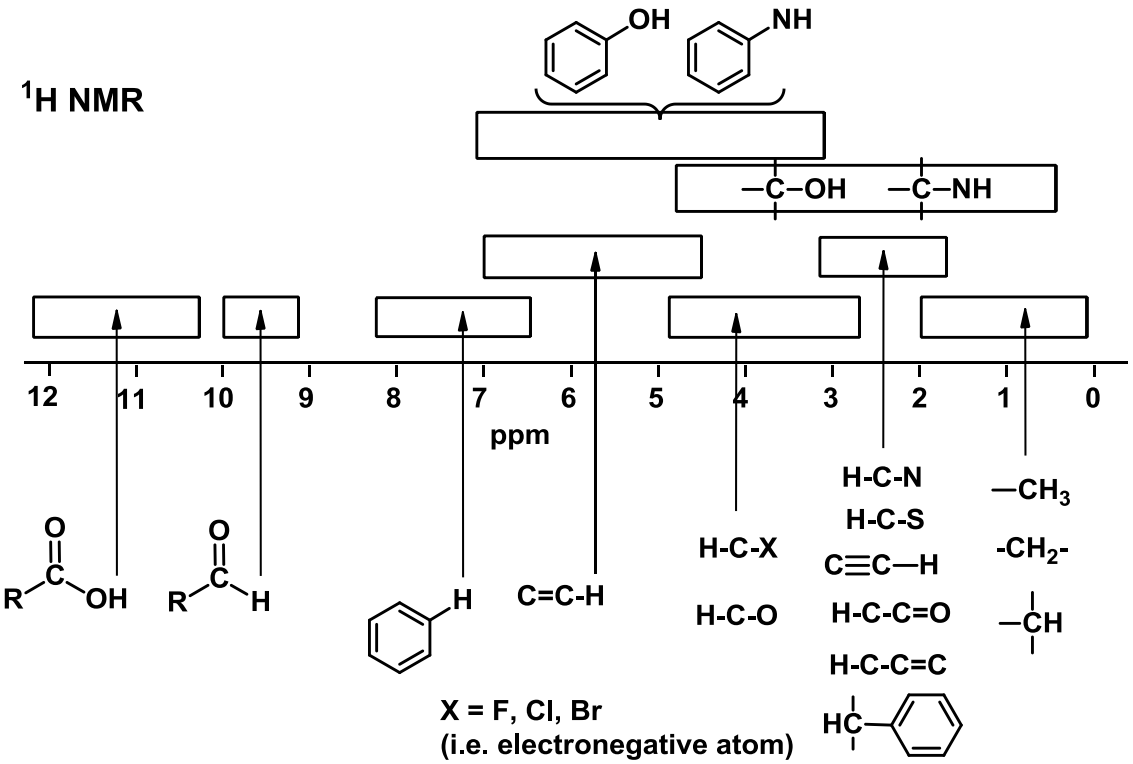
Draw the curly arrow mechanism for the reaction of B to C.

*** THE END ***

IRH / CCL / W15

CONTINUED -->

SPECTROSCOPIC TABLES



^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

R =	methyl —CH_3	methylene -CH_2-	methyne —CH	other	
R–C—	0.9	1.4	1.5	sp^3C-**OH**	1-5
R, C=C	1.6	2.3	2.6	sp^3C-**NH**	1-3
				C≡CH	2.5
R–C(=O)—	2.1	2.4	2.5	C=C, H	4.5-6.5
R–N	2.2	2.5	2.9	H–Ar	6.5-8
R–Ar	2.3	2.7	3.0	R–C(=O)–H	9-10
R–Br	2.7	3.3	4.1	R–C(=O)–OH	9-12
R–Cl	3.1	3.4	4.1		
R–O—	3.3	3.4	3.7		

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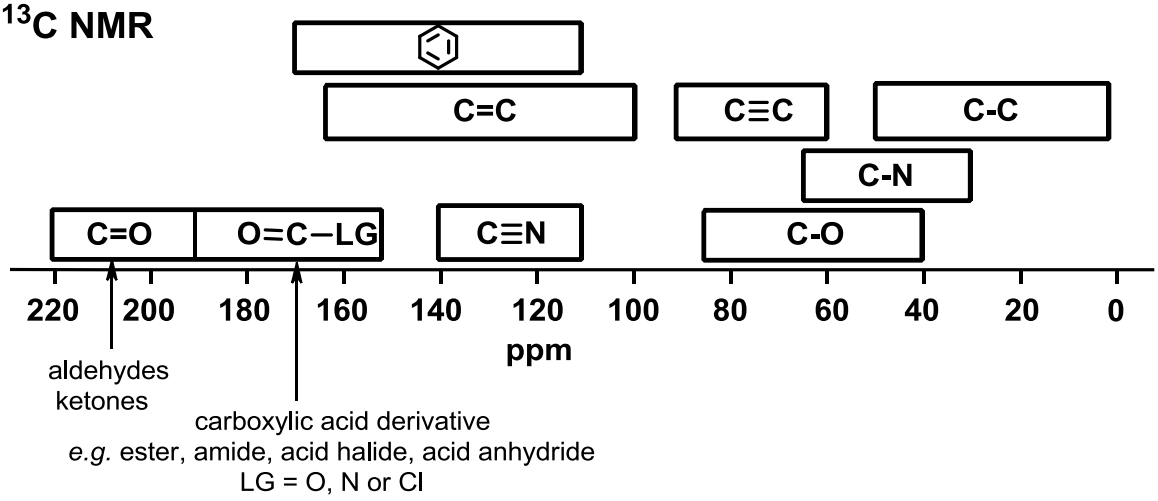
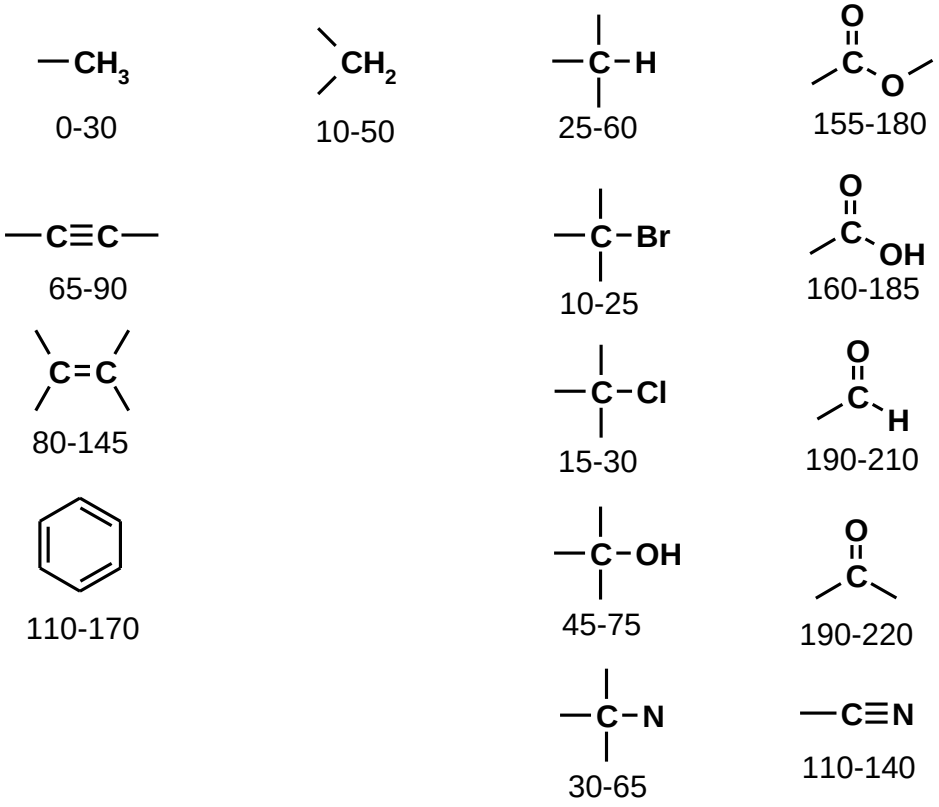
^{13}C NMR



^{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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