

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 353

Version

1

THURSDAY MARCH 7th, 2024

Time: 2 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON **BOTH** YOUR MULTIPLE CHOICE ANSWER SHEET AND LONG ANSWER SHEET.

ENTER VERSION NUMBER 1 ON THE MULTIPLE CHOICE ANSWER SHEET

The exam consists of **Parts 1 - 7**, each of which should be attempted. 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 APPROPRIATE BOX ON THE LONG ANSWER SHEET PROVIDED**.

A periodic table with atomic numbers and atomic weights and spectroscopic data tables and 2 pages of scrap paper for rough work 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 multiple choice answer sheet. Indicate your answer by completely blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a soft pencil only, **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.

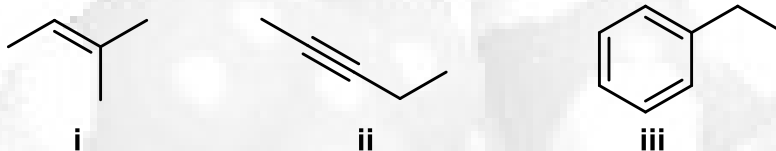
16% PART 1: RELATIVE PROPERTIES**ANSWER ANY EIGHT (8) OF QUESTIONS 1-10.**

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

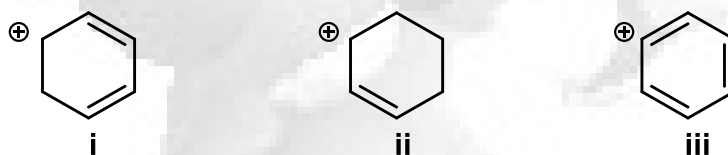
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| 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 aq. H₂SO₄:



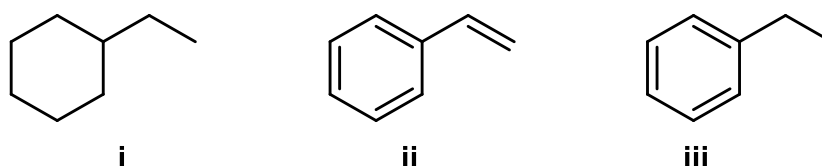
2. The relative stability of the following carbocations:



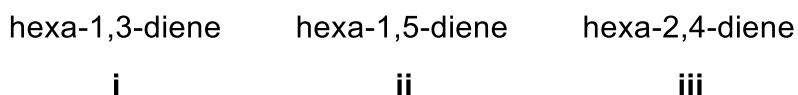
3. The relative pK_a of the most acidic proton in each of the following:



4. The relative yields of each of the following products from the reaction of phenylethyne with H₂ / Pd:



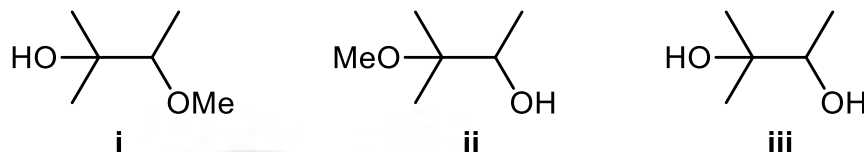
5. The number of possible geometric isomers of each of the following hydrocarbons:



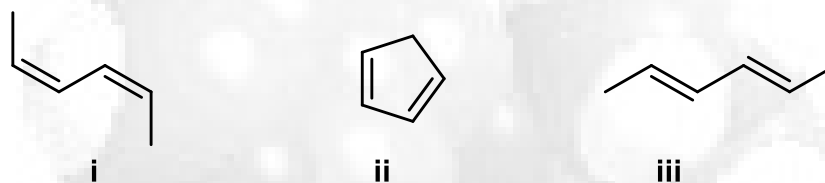
Use the following code to indicate your answers.

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

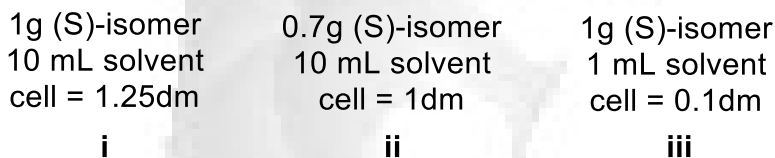
6. The relative yields of each of the following products from the reaction of 2-methyl-2-butene with MCPBA followed by acidic methanol:



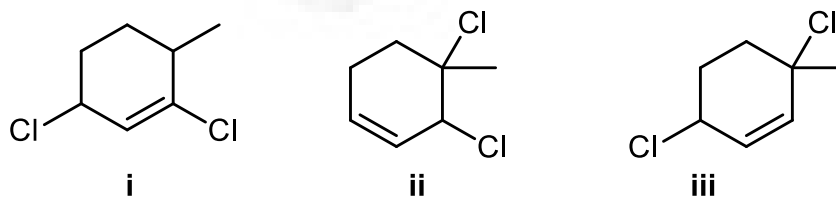
7. The relative reactivity of each of the following dienes towards but-3-en-2-one:



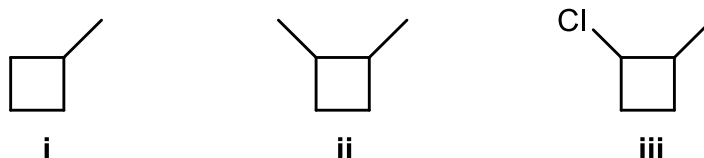
8. The observed optical rotations of the following solutions, given that (S)-2-bromobutane has a specific rotation value $[\alpha]_D = +23^\circ$.



9. The relative yields of each of the following from the reaction of 1-methylcyclohexa-1,3-diene with Cl_2 at 100°C :

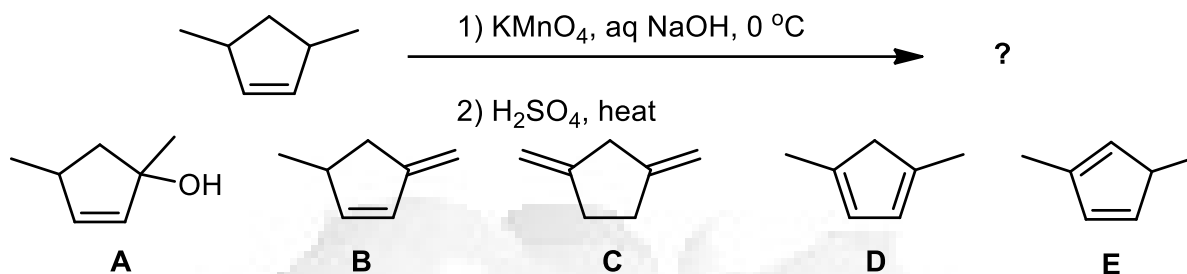


10. The number of configurational isomers of each of the following:

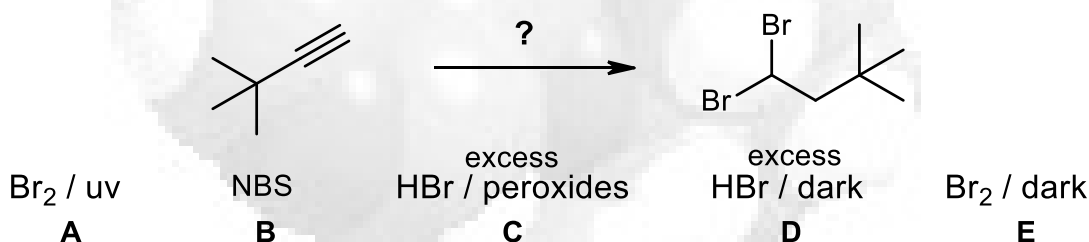


14% **PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS****ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.**For each of questions 11-18 select the **MISSING** component (starting material, product or reagents) required in order to **BEST** complete each reaction scheme.

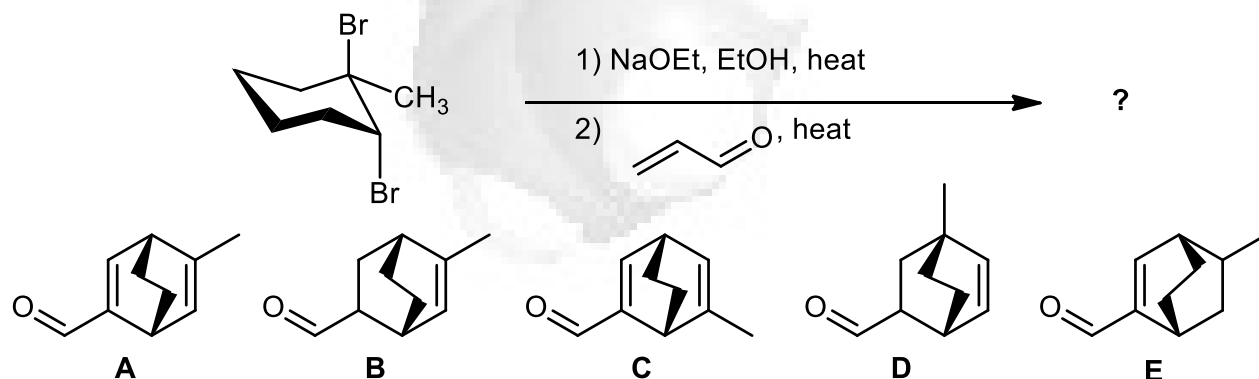
11.



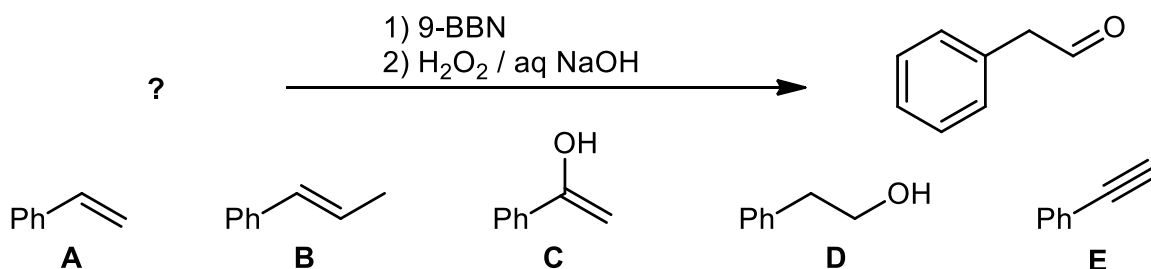
12.



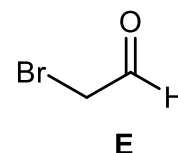
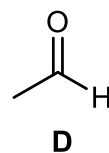
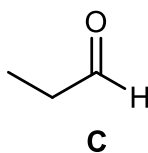
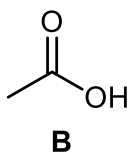
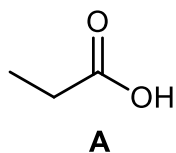
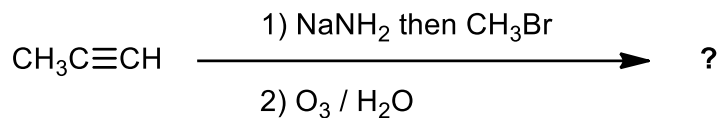
13.



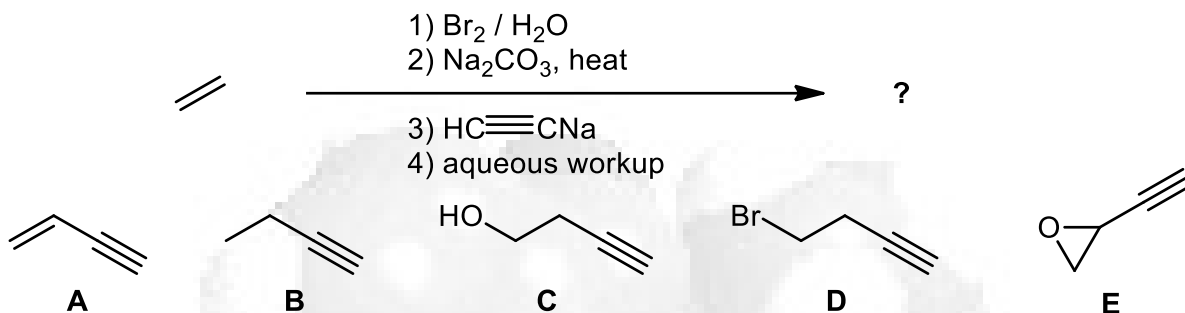
14.



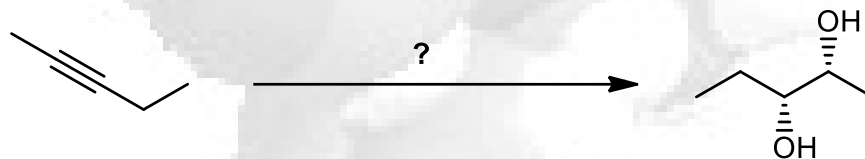
15.



16.

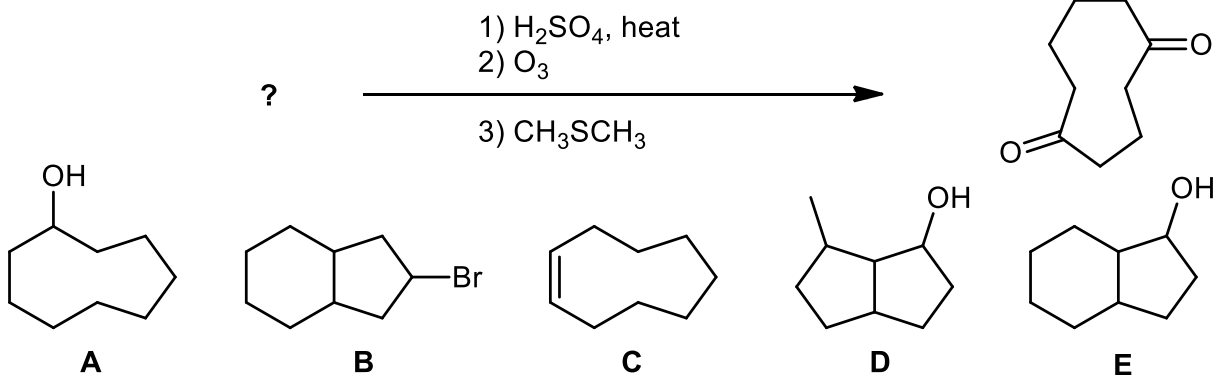


17.



- A.** 1) H_2 , Lindlar's cat. 2) KMnO_4 , aq KOH , 0°C
B. 1) H_2 , Lindlar's cat. 2) MCPBA 3) aq. H_2SO_4
C. 1) Na / NH_3 2) MCPBA 3) aq. H_2SO_4
D. 1) Na / NH_3 2) $\text{Br}_2 / \text{H}_2\text{O}$ 3) Na_2CO_3 , heat
E. 1) NaNH_2 2) aq. H_2SO_4 , HgSO_4

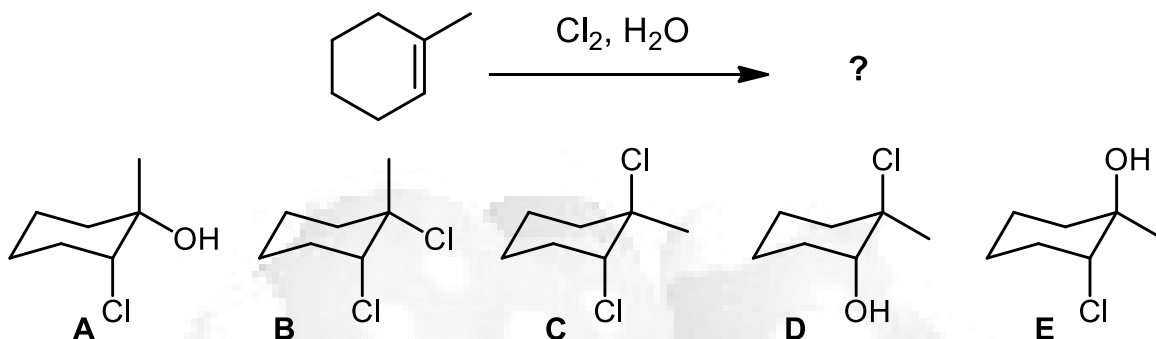
18.



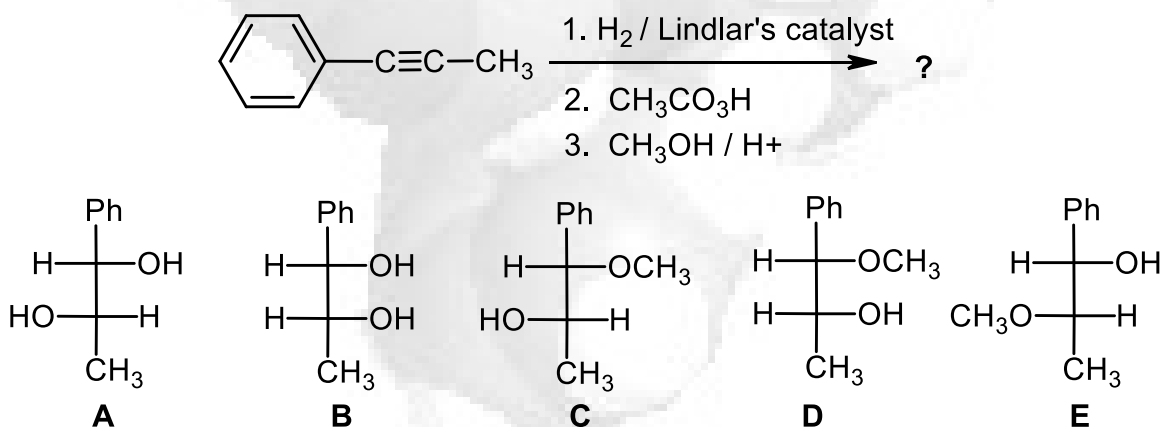
18% **PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS****ANSWER ANY SIX (6) OF QUESTIONS 19-25.**

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

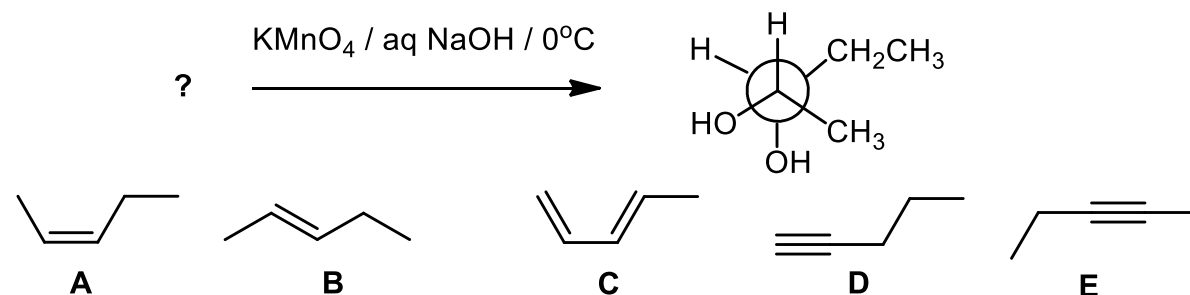
19.



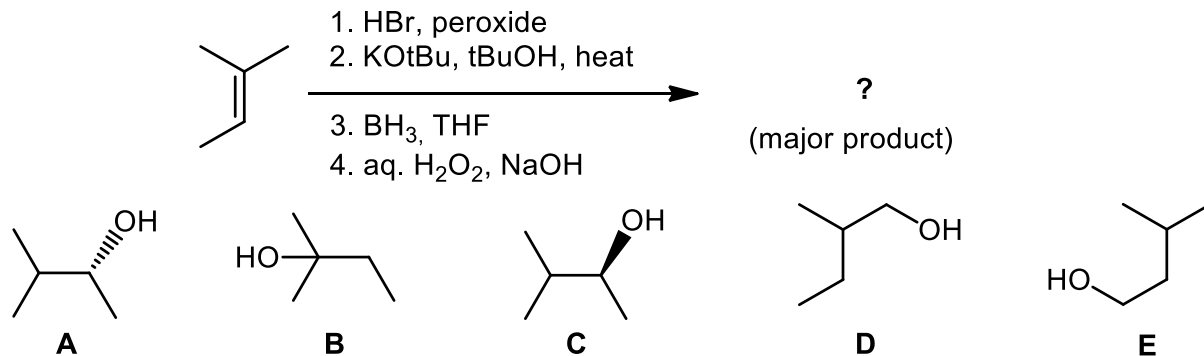
20.



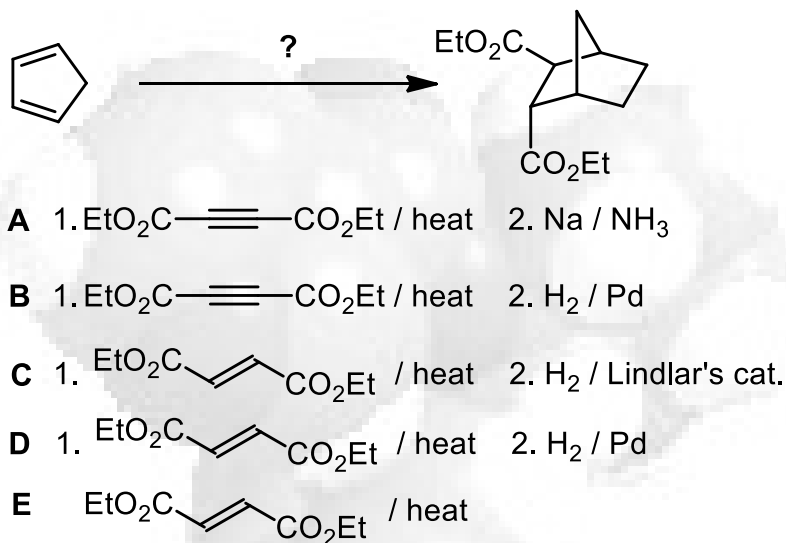
21.



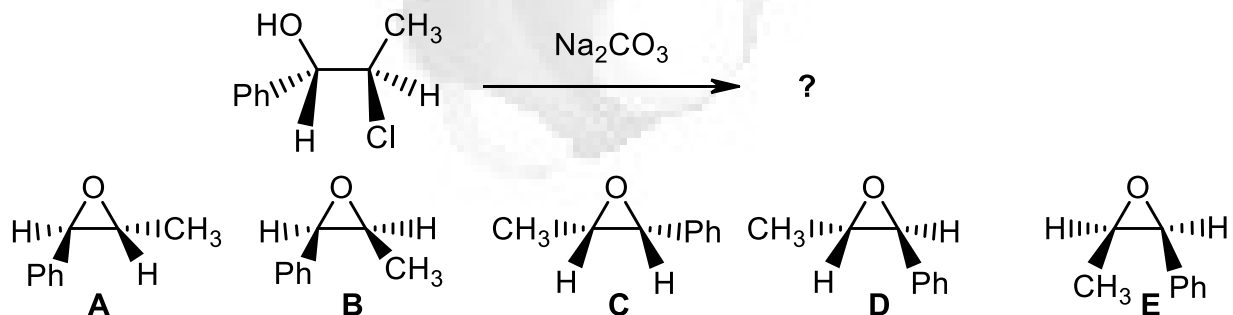
22.



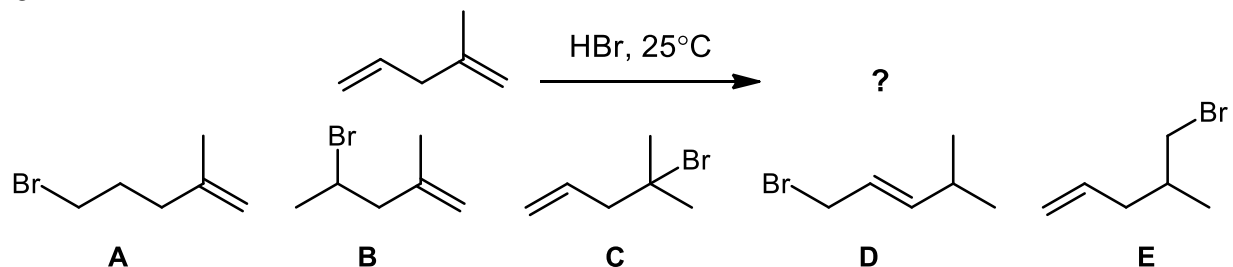
23.



24.



25.

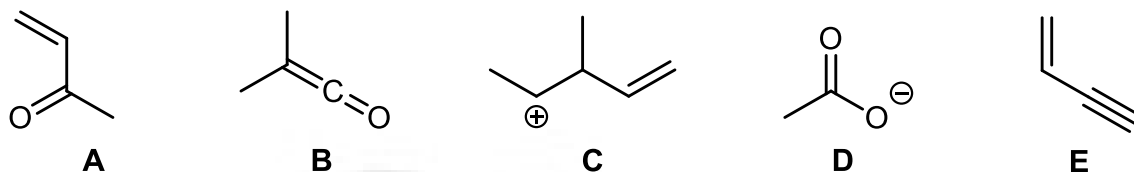


16% **PART 4: PI SYSTEMS**

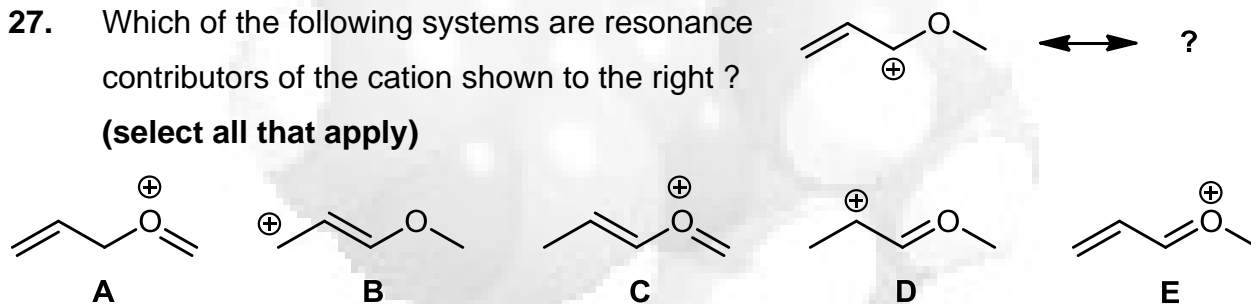
ANSWER ANY EIGHT (8) of the questions 26 - 34.

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

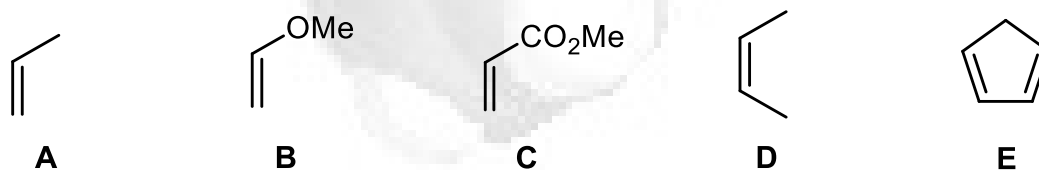
26. Which of the following contain conjugated systems? (select all that apply)



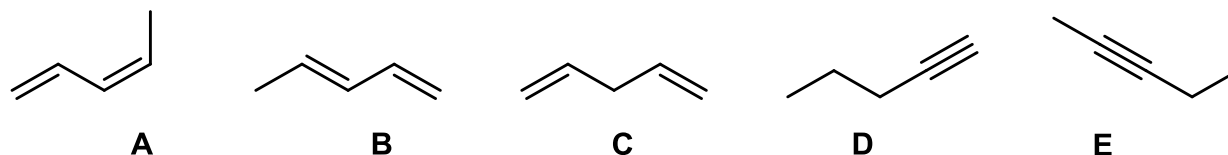
27. Which of the following systems are resonance contributors of the cation shown to the right? (select all that apply)



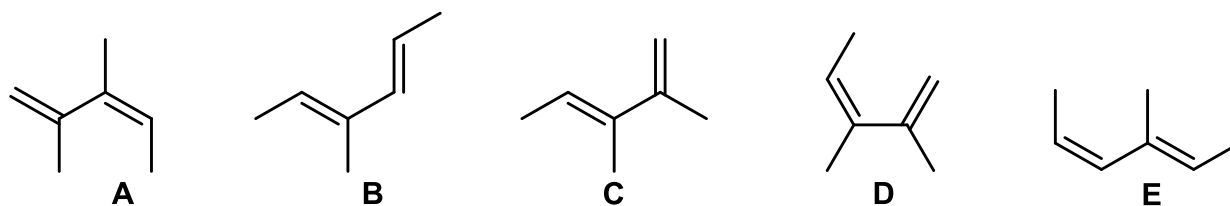
28. Which of the following is the **most** reactive towards 1,3-butadiene:



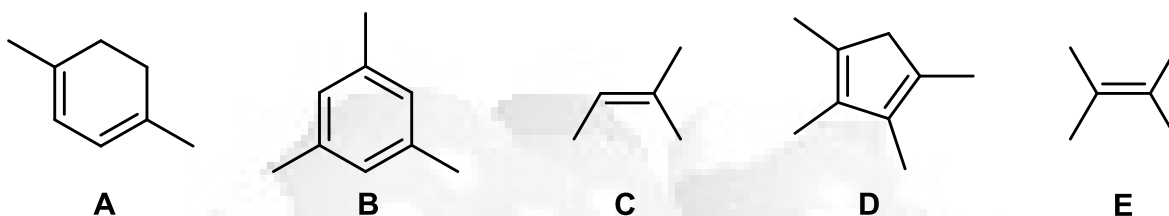
29. Which of the following isomers has the **most exothermic** heat of hydrogenation?



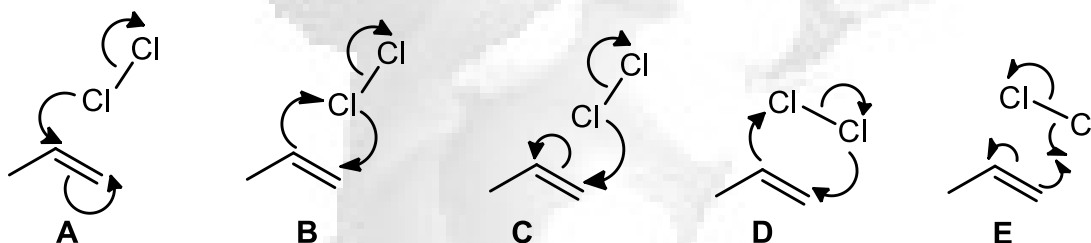
30. Which of the following molecules is the *s-cis* form of (3Z)-2,3-dimethylpenta-1,3-diene?



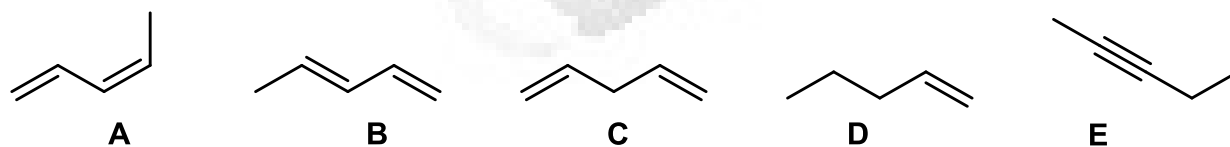
31. Which of the following molecules has the **most** allylic hydrogens ?



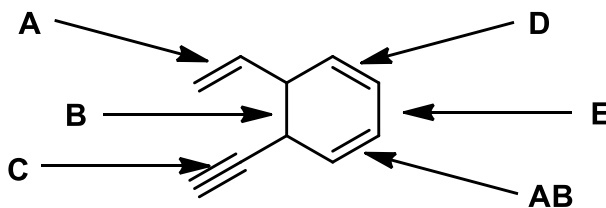
32. Which of the following **best** represents a step in the mechanism of the reaction of propene with Cl_2 at 0°C ?



33. Which of the following systems react with Na / NH_3 (select all that apply) ?



34. Which of the **CC** bonds indicated below is the **longest** ?



15% PART 5: SYNTHESIS

WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE LONG ANSWER SHEET PROVIDED

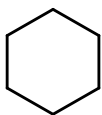
ANSWER THREE (3) QUESTIONS, ONE FROM EACH OF 5.1, 5.2 AND 5.3

Design an efficient synthesis of 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)

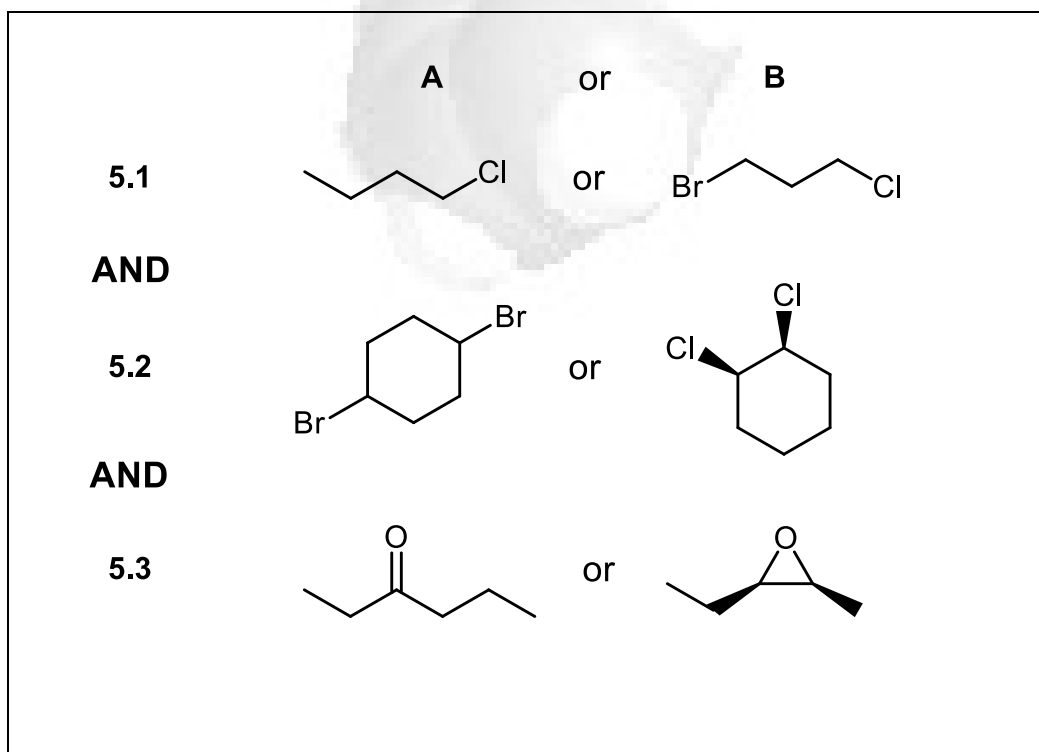
Allowed starting materials and reagents:



and / or

Any hydrocarbons with 4 or less C atoms

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



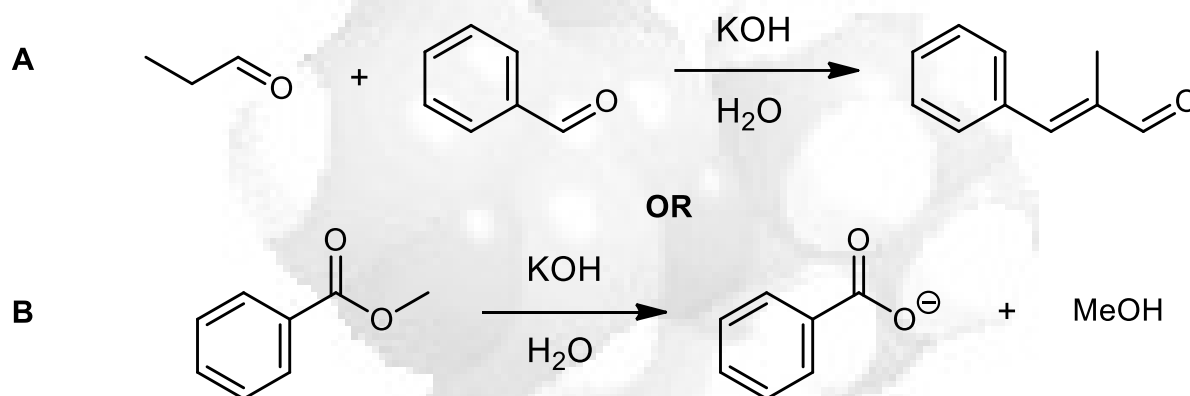
10% **PART 6: MECHANISMS**

WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE LONG ANSWER SHEET PROVIDED

ANSWER TWO (2) QUESTIONS, ONE FROM PART 6.1 AND ONE FROM PART 6.2

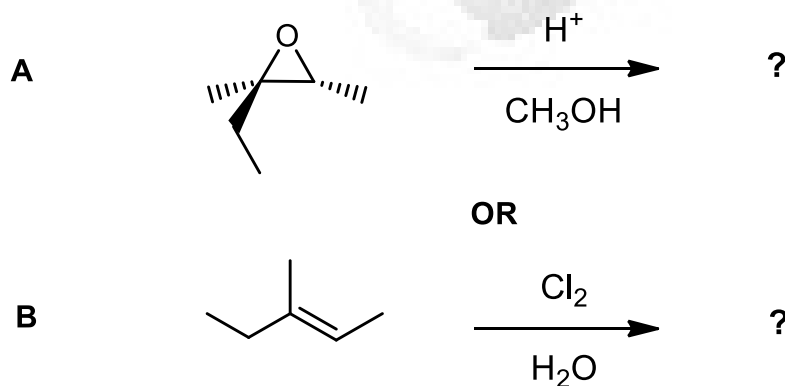
Draw curly arrow mechanisms to explain the following reactions / observations. No other reagents are required.

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



AND

6.2. Show the mechanism for **one** of the following reactions to predict the major product :



11% PART 7: STRUCTURE DETERMINATION

WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE LONG ANSWER SHEET PROVIDED

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

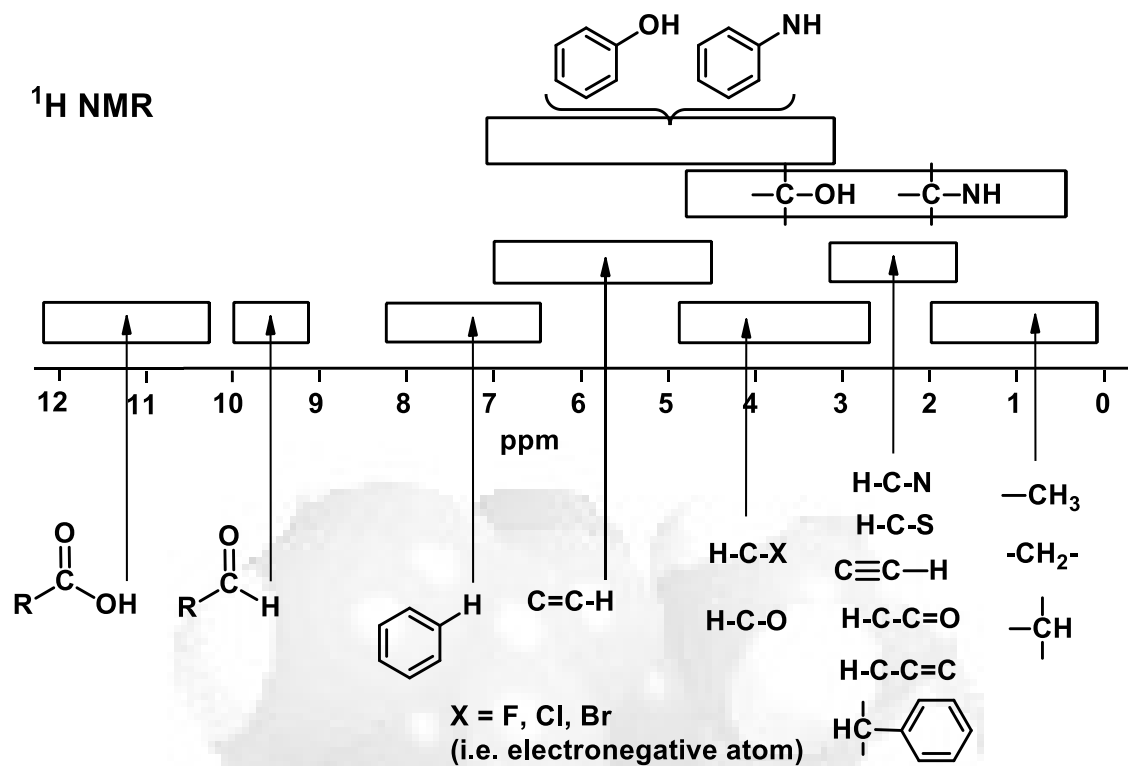
Compound **A** (C_6H_{10}) was reacted with sodium in liquid ammonia to give **B**. Subsequent reaction of **B** with bromine gave **C** which was found to exist as a single configurational isomer and optically inactive. When **C** was then heated with KOH / EtOH, the major product was **D**, an isomer of **A**.

When compound **D** was heated with ethene in a sealed vessel, **E**, was the major product. When compound **E** was reacted with excess H_2 over Pd gave *cis*-1,4-dimethylcyclohexane as the major product.

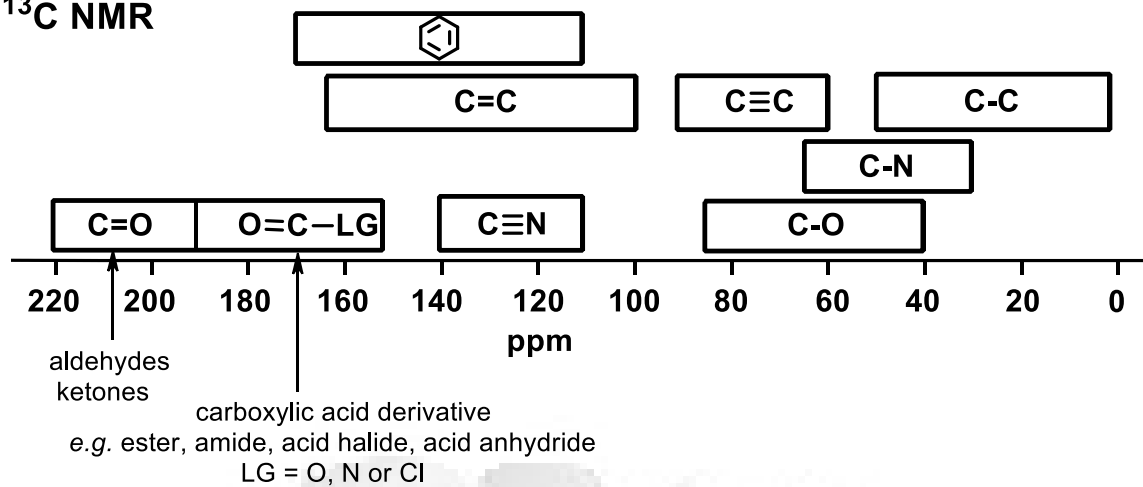
Draw the structures of A to E. Include 3D stereochemistry where appropriate.

What is the IUPAC name for D ?

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

SPECTROSCOPIC TABLES **$^1\text{H NMR}$ CHARACTERISTIC CHEMICAL SHIFTS / ppm**

	R = methyl	methylene	methyne	other
$\text{R}-\text{C}-\text{CH}_3$	0.9	1.4	1.5	$\text{sp}^3\text{C}-\text{OH}$ 1-5
$\text{R}-\text{C}=\text{C}-\text{H}$	1.6	2.3	2.6	$\text{sp}^3\text{C}-\text{NH}$ 1-3
$\text{R}-\text{C}(=\text{O})-\text{H}$	2.1	2.4	2.5	$\text{C}\equiv\text{CH}$ 2.5
$\text{R}-\text{N}-\text{H}$	2.2	2.5	2.9	$\text{C}=\text{C}-\text{H}$ 4.5-6.5
$\text{R}-\text{C}_6\text{H}_5$	2.3	2.7	3.0	$\text{H}-\text{C}_6\text{H}_5$ 6.5-8
$\text{R}-\text{Br}$	2.7	3.3	4.1	$\text{R}-\text{C}(=\text{O})-\text{H}$ 9-10
$\text{R}-\text{Cl}$	3.1	3.4	4.1	$\text{R}-\text{C}(=\text{O})-\text{OH}$ 9-12
$\text{R}-\text{O}-\text{H}$	3.3	3.4	3.7	

¹³C NMR**¹³C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

$-\text{CH}_3$ 0-30	CH_2 10-50	$-\text{C}-\text{H}$ 25-60	$-\text{C}-\text{O}-\text{C}-$ 155-180
$-\text{C}\equiv\text{C}-$ 65-90	$\text{C}=\text{C}$ 80-145	$-\text{C}-\text{Br}$ 10-25	$-\text{C}-\text{OH}$ 160-185
Benzene ring 110-170	$-\text{C}-\text{Cl}$ 15-30	$-\text{C}-\text{OH}$ 45-75	$-\text{C}-\text{H}$ 190-210
	$-\text{C}-\text{N}$ 30-65	$-\text{C}-\text{N}$ 30-65	$-\text{C}\equiv\text{N}$ 110-140

INFRA-RED GROUP ABSORPTION FREQUENCIES

	<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm⁻¹)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>	
C-H	Alkanes (stretch)	3000-2850	3.33-3.51	s	
	-CH ₃ (bend)	1450 and 1375	6.90 and 7.27	m	
	-CH ₂ - (bend)	1465	6.83	m	
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne (stretch)	ca. 3300	ca.3.03	s	
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C-C	Alkane	not usually useful			
C=C	Alkene	1680-1600	5.95-6.25	m-w	
	Aromatic	1600-1400	6.25-7.14	m-w	
C≡C	Alkyne	2250-2100	4.44-4.76	m-w	
C=O	Aldehyde	1740-1720	5.75-5.81	s	
	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												13 3A					14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.008	2 He 4.003											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18				
3 Li 6.941	4 Be 9.012	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
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)

Actinides **

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