

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 353

Version

1

WEDNESDAY MARCH 9th, 2017

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.

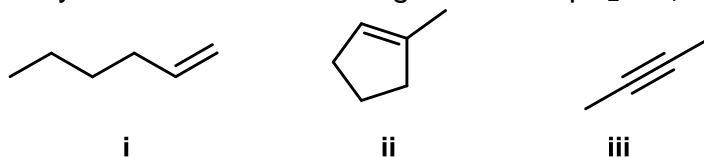
16% **PART 1: RELATIVE PROPERTIES****ANSWER ANY EIGHT (8) OF QUESTIONS 1-10.**

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

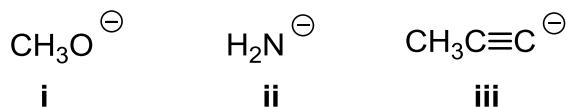
Use the following code to indicate your answers.

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

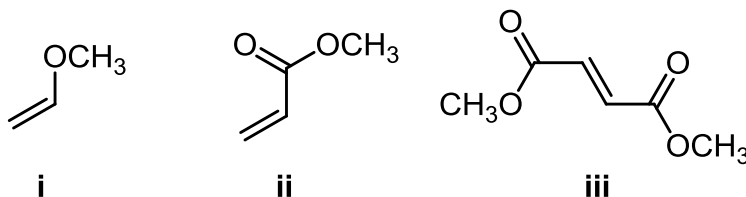
1. The relative reactivity of each of the following towards aq H₂SO₄:



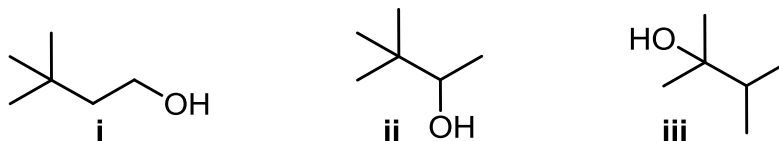
2. The relative basicity of each of the following:



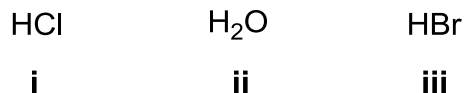
3. The relative reactivity towards 1,3-cyclopentadiene of each of the following:



4. The relative yields of the following products from the reaction of 3,3-dimethylbut-1-ene with aq. H₂SO₄:



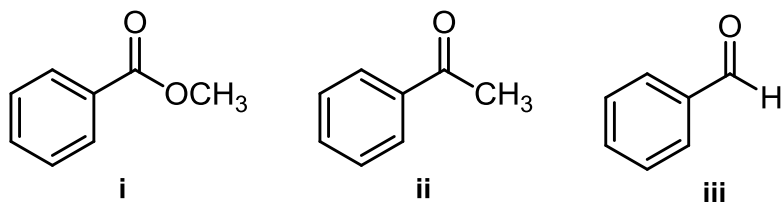
5. The relative reactivity of each of the following towards 2-methylpropene :



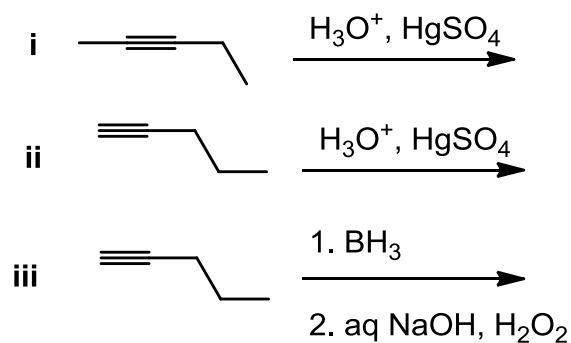
Use the following code to indicate your answers.

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

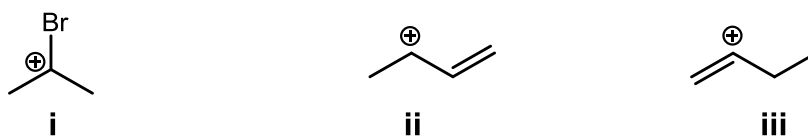
6. The relative reactivity towards sodium borohydride of each of the following:



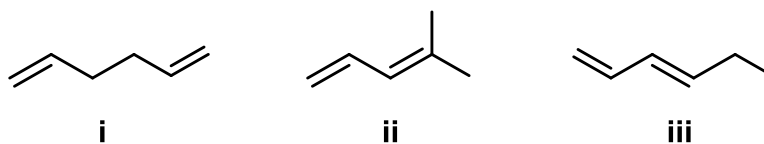
7. The relative yields of pentan-2-one from each of the following reactions:



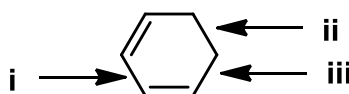
8. The relative stability of the following carbocations as drawn:



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



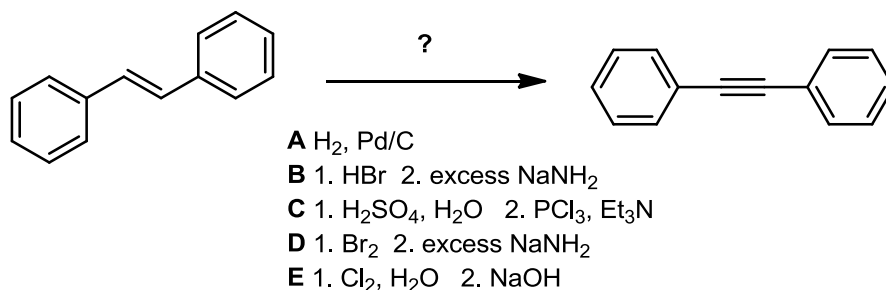
10. The relative strengths of the indicated **CC** bonds:



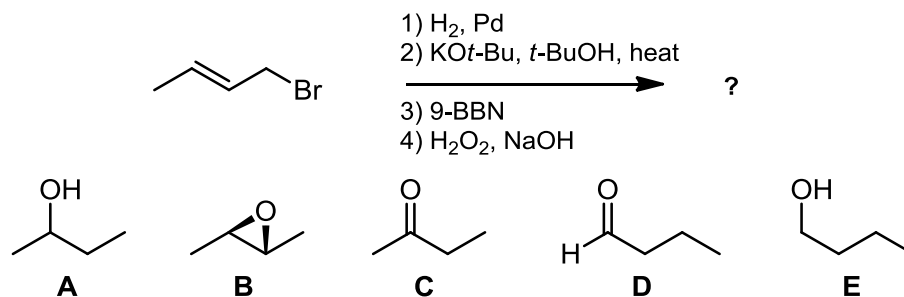
14% PART 2: STARTING MATERIALS, REAGENTS AND PRODUCTS**ANSWER ANY SEVEN (7) OF QUESTIONS 11-18.**

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.

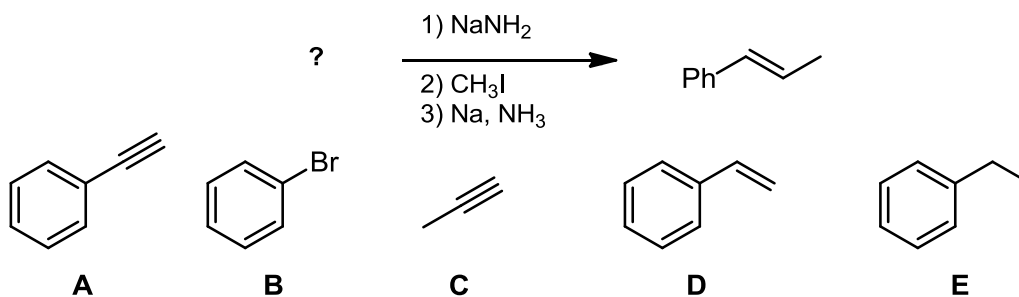
11.



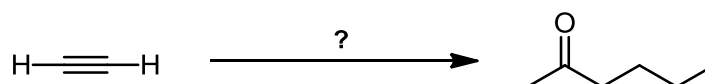
12.



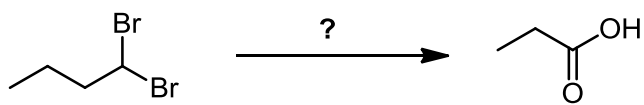
13.



14.

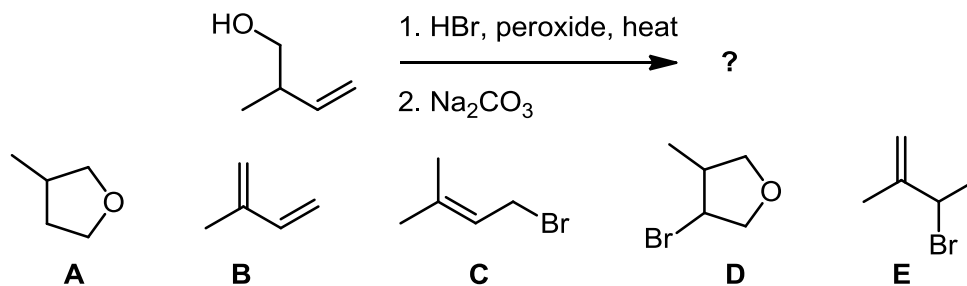


- A** 1. NaNH₂ 2. 1-bromobutane 3. O₃ then Zn/H⁺
B 1. NaNH₂ 2. 1-bromobutane 3. BH₃, THF 4. aq H₂O₂, NaOH
C 1. O₃ then H₂O 2. NaNH₂ 3. 1-bromobutane
D 1. NaNH₂ 2. 1-bromobutane 3. aq. acid, Hg(OAc)₂
E 1. Na, NH₃ 2. NaNH₂ 3. 1-bromobutane 4. aq. H₂SO₄

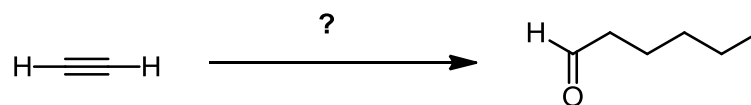


- A** 1. excess NaNH_2 , 2. aq KMnO_4 , NaOH , 0°C
B 1. KOt-Bu 2. NaNH_2 3. O_3 then Zn , acetic acid
C 1. O_3 then Zn , H_2O 2. NaNH_2 3. Na , NH_3
D 1. NaNH_2 2. Na , NH_3
E 1. excess NaNH_2 then H_2O 2. O_3 then H_2O_2

16.

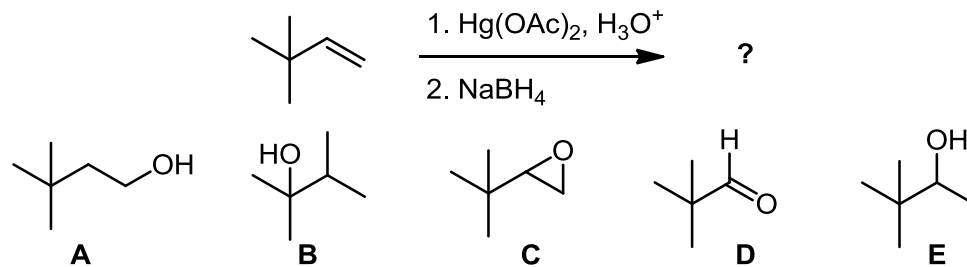


17.



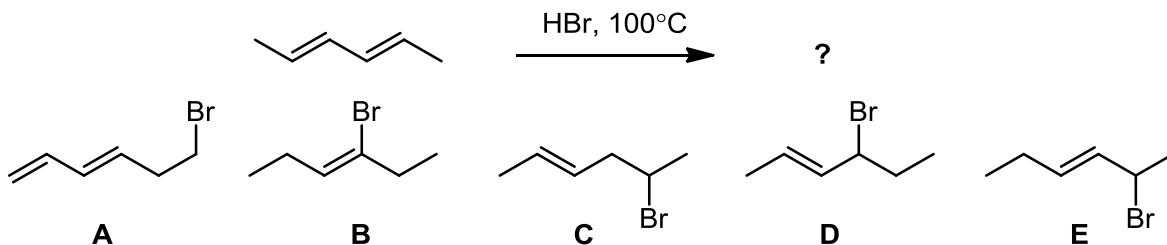
- A** 1. NaNH_2 2. 1-bromobutane 3. O_3 then Zn/H^+
B 1. NaNH_2 2. 1-bromobutane 3. BH_3 , THF 4. aq H_2O_2 , NaOH
C 1. O_3 then H_2O 2. NaNH_2 3. 1-bromobutane
D 1. NaNH_2 2. 1-bromobutane 3. aq. acid, $\text{Hg}(\text{OAc})_2$
E 1. Na , NH_3 2. NaNH_2 3. 1-bromobutane 4. aq. H_2SO_4

18.

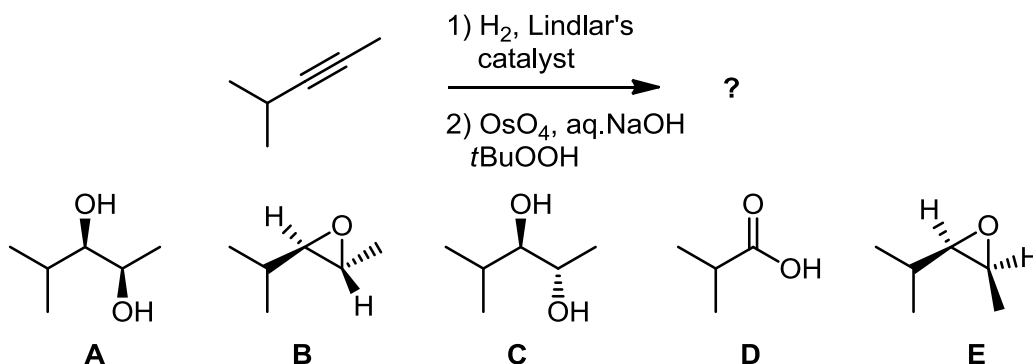


18% PART 3: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS**ANSWER ANY SIX (6) OF QUESTIONS 19-25.****For each of the questions 19-25, select the structure required to BEST complete the reaction shown.**

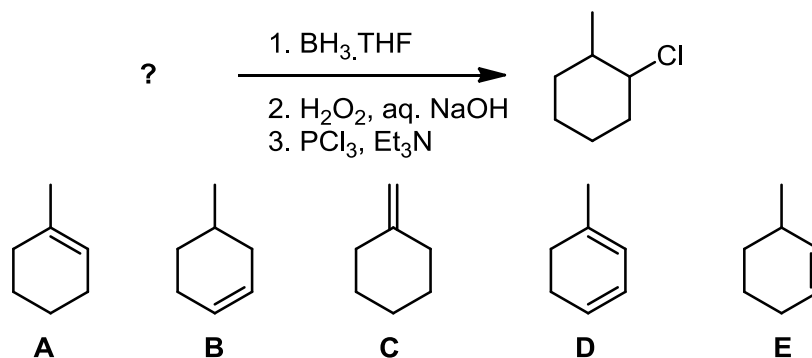
19.



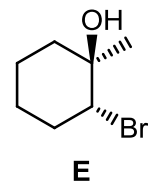
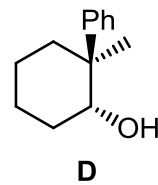
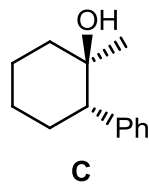
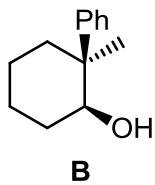
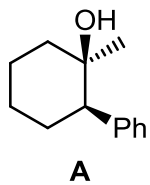
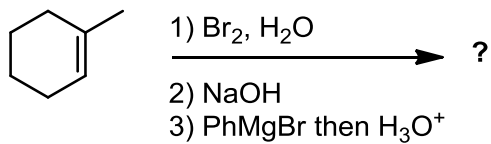
20.



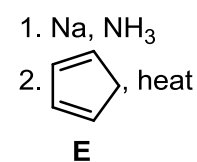
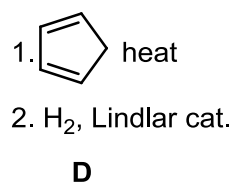
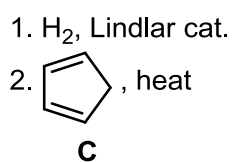
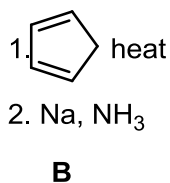
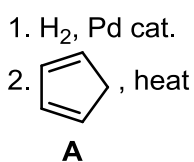
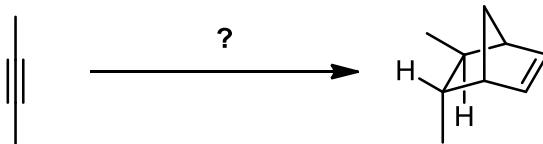
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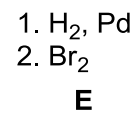
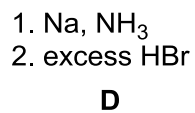
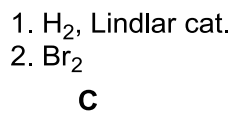
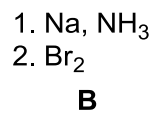
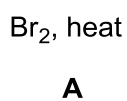
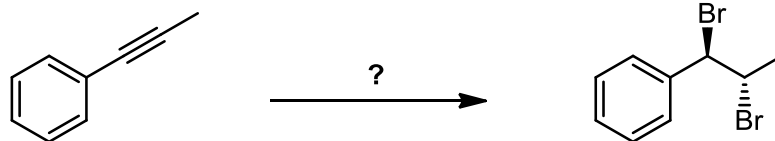
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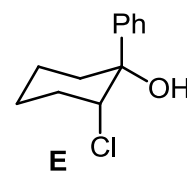
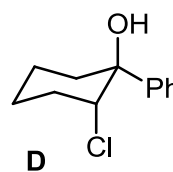
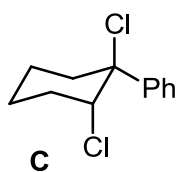
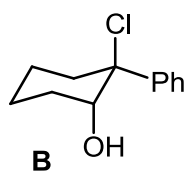
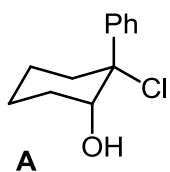
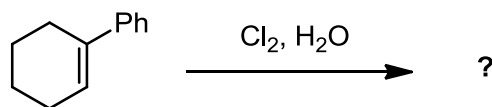
23.



24.



25.

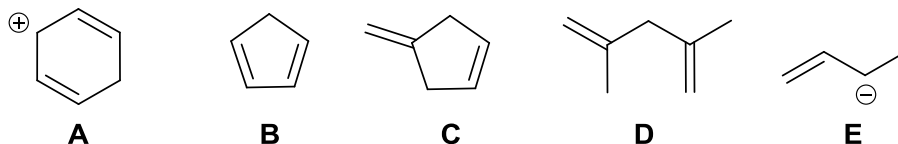


16% **PART 4: PI SYSTEMS**

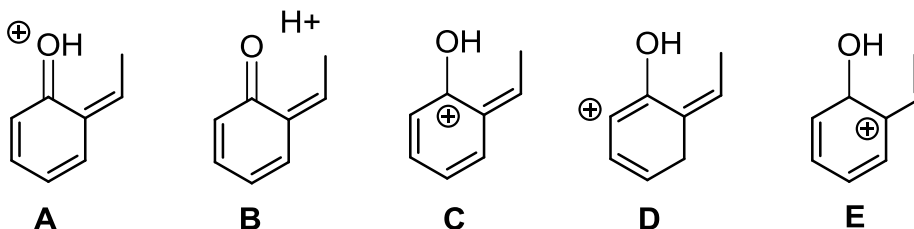
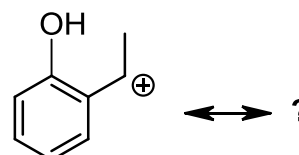
ANSWER ANY EIGHT (8) of the questions 26 - 34.

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.

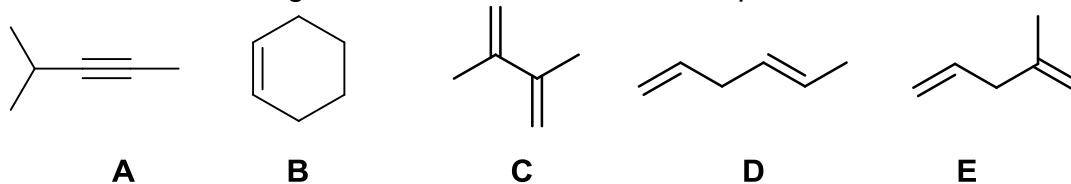
26. Which of the following contain conjugated systems? **(select all that apply)**



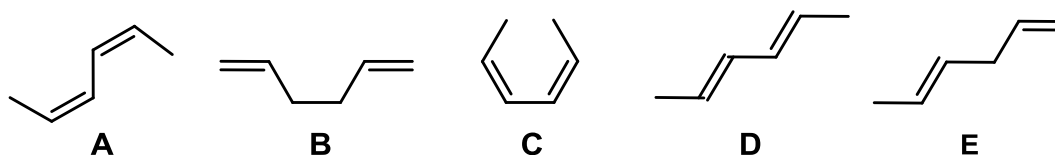
27. Which of the following systems are resonance contributors of the cation shown to the right? **(select all that apply)**



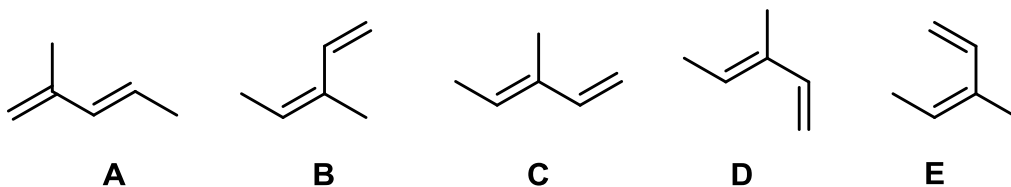
28. Which of the following isomers reacts **fastest** with aq. H_2SO_4 ?



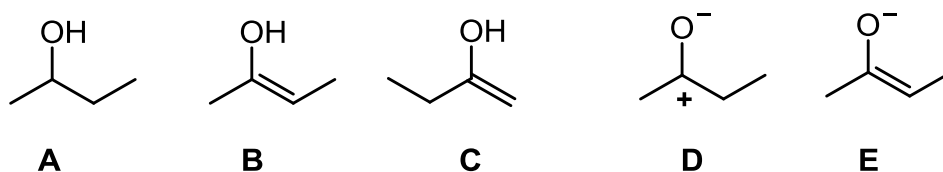
29. Which of the following isomers is the **most** stable as drawn?



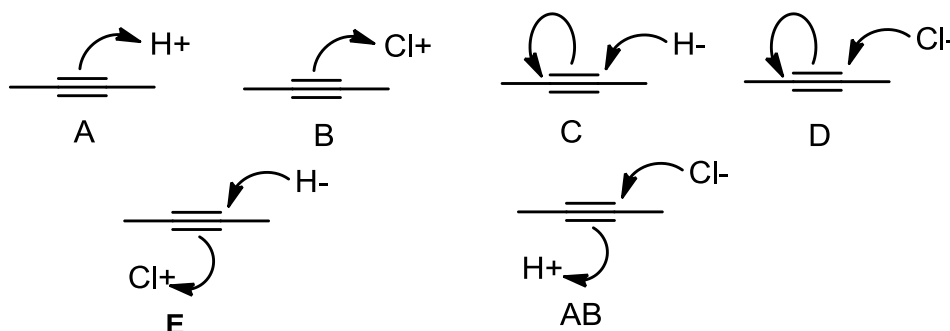
30. Which of the following molecules is the *s-trans* form of (3E)-3-methylpenta-1,3-diene ? **(select all that apply)**



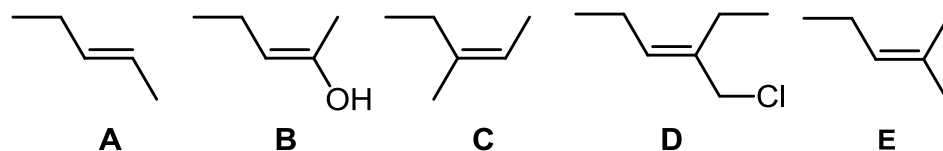
31. Which of the following systems are tautomers of butan-2-one ? **(select all that apply)**



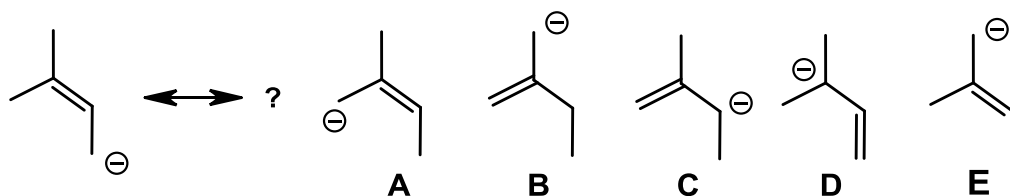
32. Which of the following **best** represents the mechanism of the reaction of an alkyne with HCl ?

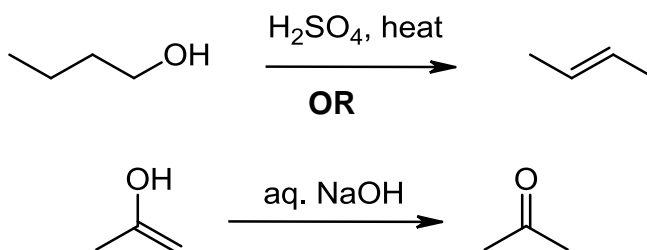
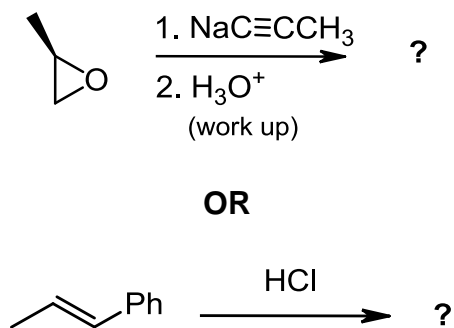


33. Which of the following molecules would be named as *trans*? **(select all that apply)**



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



10% PART 5: MECHANISMS**ANSWER TWO (2) QUESTIONS, ONE FROM PART A and ONE FROM PART B****WRITE YOUR ANSWER IN THE BOOKLET PROVIDED****Draw curly arrow mechanisms to explain the following reactions / observations.****No other reagents are required.****A.** Show the mechanism for **one** of the following reactions:**AND****B.** Show the mechanism for **one** of the following reactions. Briefly justify your choice:

15% PART 6: SYNTHESIS

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

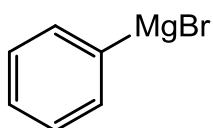
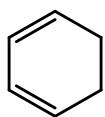
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

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)

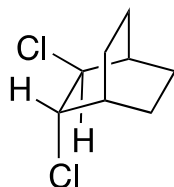
Allowed starting materials and reagents:



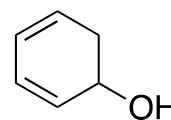
Any hydrocarbons with 4 or less C atoms

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

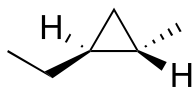
A



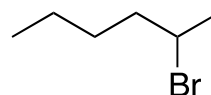
or



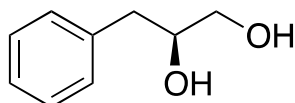
B



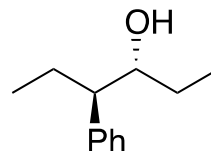
or



C



or



11% PART 7: STRUCTURE DETERMINATION**WRITE YOUR ANSWER IN THE BOOKLET PROVIDED****Use the information in the following paragraph to answer the questions below.**

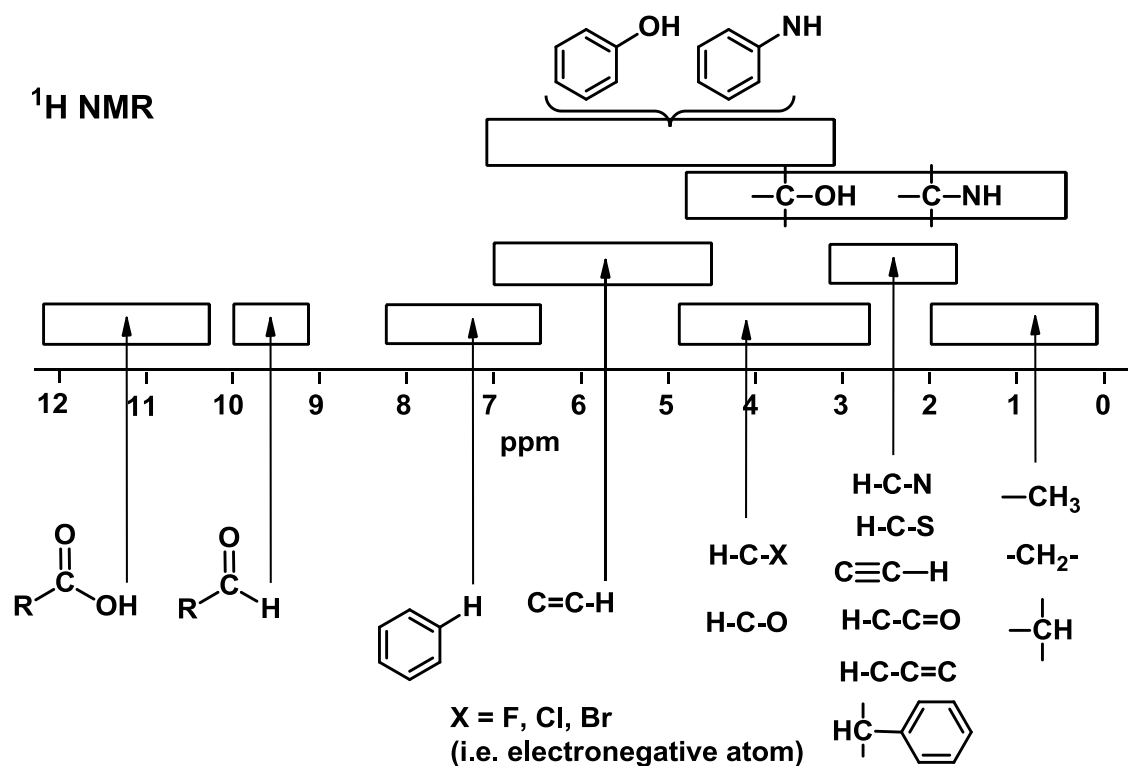
Compound **A** (C_8H_{14}) was reacted with excess H_2 over Pd to give a mixture of isomers **B** and **C** (C_8H_{16}). Compound **B** was found to be optically inactive while **C** had an S configuration. When **A** was reacted with HBr (in N_2 , dark) the major product **D** was obtained as a pair of diastereomers.

When Compound **D** was heated with KOH / EtOH it gave **E**, an isomer of **A**, as the major product. In contrast when **D** was heated with KOtBu/t-BuOH, **A** was the major product.

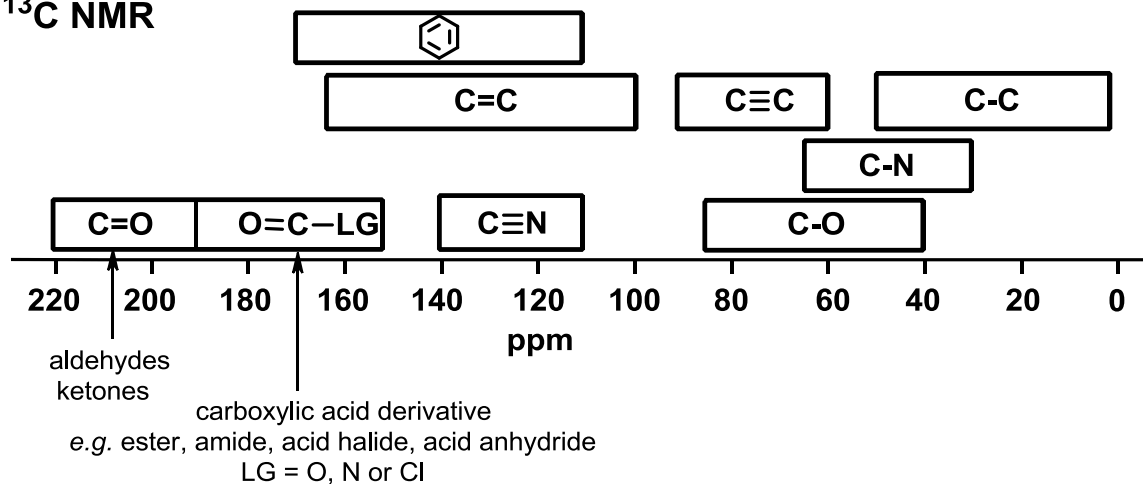
When Compound **E** was reacted with excess H_2 over Pd to give it gave **B** as the sole product. The ^{13}C NMR of **E** showed just 4 peaks. Reaction of **E** reacted with O_3 followed by work up with zinc in acid or H_2O_2 gave a single product, **F** $C_8H_{14}O_2$ (IR 1715 cm^{-1}). In contrast reaction of **A** with O_3 followed by work up with zinc in acid gave 2-methylcyclohexanone and methanal.

**Draw the structures of A to F. Include 3D stereochemistry where appropriate.
Make sure to show both diastereomers of D.**

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

SPECTROSCOPIC TABLES **^1H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

	R = methyl	methylene	methyne	other
$\text{R}-\text{C}-$	$-\text{CH}_3$ 0.9	$-\text{CH}_2-$ 1.4	$-\text{CH}$ 1.5	$\text{sp}^3\text{C}-\text{OH}$ 1-5
$\text{R}-\text{C}=\text{C}$	1.6	2.3	2.6	$\text{sp}^3\text{C}-\text{NH}$ 1-3
$\text{R}-\text{C}(=\text{O})-$	2.1	2.4	2.5	$\text{C}\equiv\text{CH}$ 2.5
$\text{R}-\text{N}$	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
$\text{R}-\text{O}-$	3.3	3.4	3.7	

^{13}C NMR **^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

—CH_3 0-30	>CH_2 10-50	—C—H 25-60	—C(=O)—O— 155-180
$\text{—C}\equiv\text{C—}$ 65-90	>C=C< 80-145	—C—Br 10-25	—C(=O)OH 160-185
 110-170		—C—Cl 15-30	—C(=O)H 190-210
		—C—OH 45-75	—C(=O)— 190-220
		—C—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											18 8A
1 H 1.008													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
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 **