

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
FINAL EXAMINATION
CHEMISTRY 351

December 11th 2012

Time: 3 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON **BOTH** YOUR EXAM ANSWER BOOKLET AND COMPUTER ANSWER SHEET.

The examination consists of Parts 1 - 9, each of which should be attempted. Note that some Parts provide you with a choice of questions, *i.e.* answer 4 out of 5. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. Parts 1 - 5 will be computer graded, and Parts 6 - 9 are to be answered in the answer booklet provided. A periodic table with atomic numbers and atomic weights, and spectroscopic tables are appended to this examination paper.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 40, which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a 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

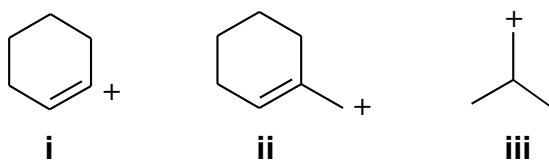
15% **PART 1: RELATIVE PROPERTIES****ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.**

Arrange the items in questions 1-12 in **DECREASING ORDER** (i.e. greatest, most etc. first) with respect to the indicated property.

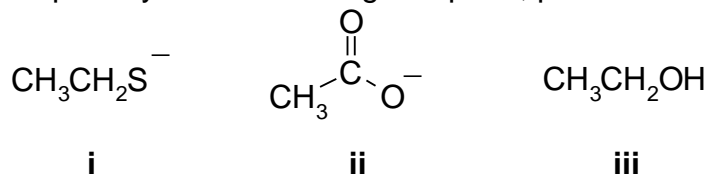
Use the following code to indicate your answers.

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

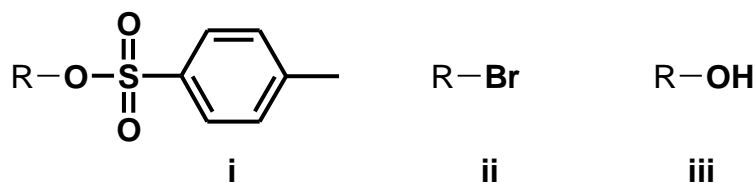
1. The relative stability of the following carbocations:



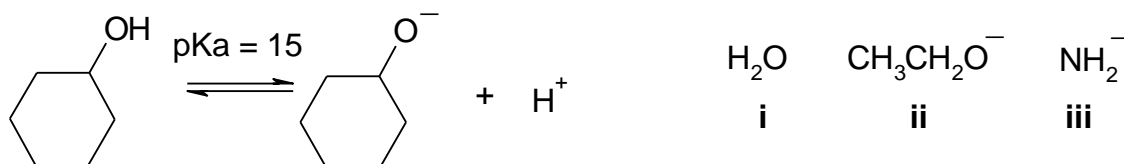
2. The relative nucleophilicity of the following in a polar, protic solvent:



3. The relative leaving group ability of the **bold group** in each of the following:



4. The relative amount of the conjugate base of cyclohexanol formed by the reaction of 1 mole equivalent of each of the following:

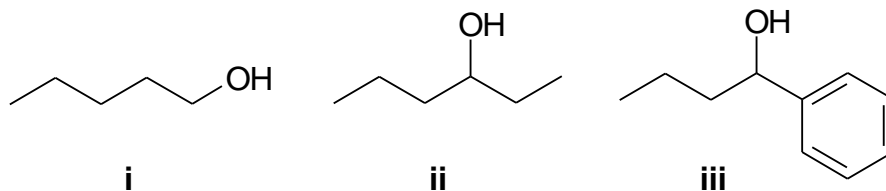


Use the following code to indicate your answers.

A. i > ii > iii
 B. i > iii > ii
 C. ii > i > iii

D. ii > iii > i
 E. iii > i > ii
 AB. iii > ii > i

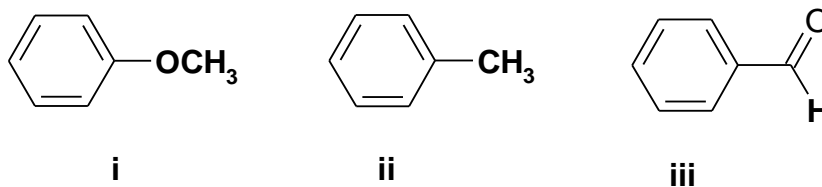
5. The relative rate of reaction of each of the following when treated with HBr:



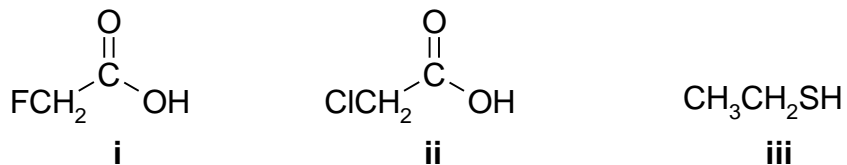
6. The relative rate of reaction of each of the following with AgNO_3 / aq. ethanol :

i 2-Bromopropane
ii 1-Bromopropane
iii Benzyl bromide

7. The $^1\text{H-NMR}$ chemical shifts for the groups shown in **bold** in each of the following structures:



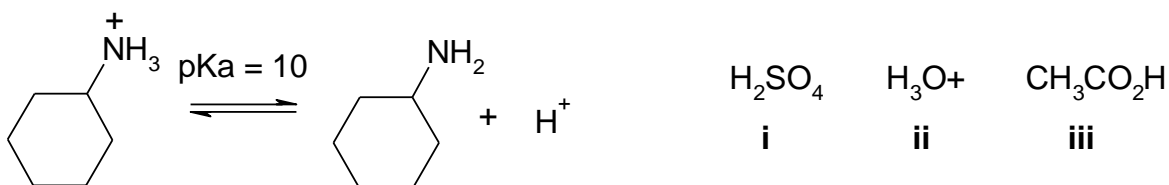
8. The relative acidity of each of the following:



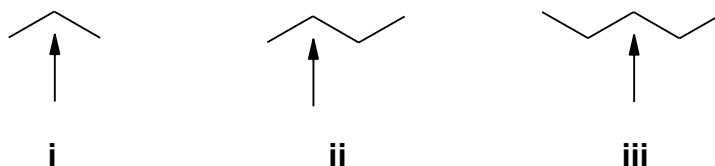
Use the following code to indicate your answers.

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

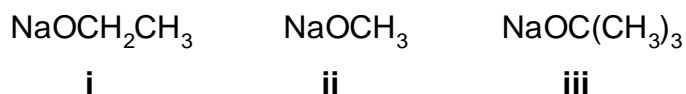
9. The relative amount of the conjugate acid of cyclohexylamine formed by the reaction of 1 mole equivalent of each of the following:



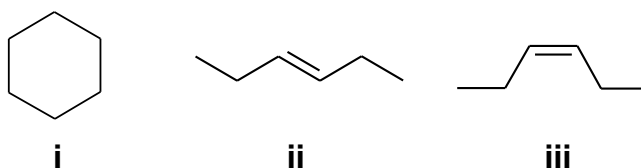
10. The number of lines in the H-NMR signals for the H atoms at the positions indicated in each of the following :



11. The relative yields of the anti-Zaitsev product (also known as the Hoffman product) produced by the reaction of 2-bromo-2,3-dimethylbutane with each of the following:



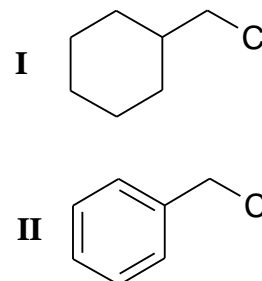
12. The relative heats of combustion of the following isomers (least exothermic to most exothermic):



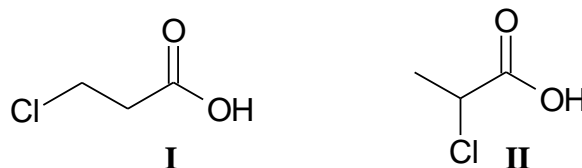
10% **PART 2: MOLECULAR PROPERTIES****ANSWER ANY FIVE (5) OF THE QUESTIONS 13 TO 18.****CHOOSE THE SINGLE OPTION THAT PROVIDES THE BEST ANSWER.**

13. Which of the following is more reactive under SN1 conditions ?

- A. **I** because it forms a less stable primary carbocation
 B. **II** because it forms a less stable primary carbocation
 C. **I** because it is less sterically hindered
 D. **II** because it is less sterically hindered
 E. **II** because it forms a resonance stabilized carbocation



14. Which of the following is the strongest acid ?



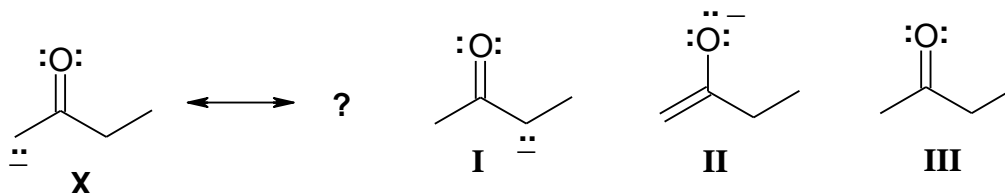
- A. **I** because there is less of a steric effect due to the large Cl atom
 B. **II** because there is a greater steric effect due to the large Cl atom
 C. **I** because of the greater inductive effect of the more distant Cl atom
 D. **II** because of the greater inductive effect of the closer Cl atom
 E. There is no difference because both are carboxylic acids

15. Which of the following is the conjugate base of ethanal ?



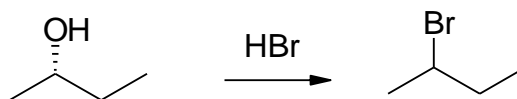
- A. **I** because the -ve charge can be delocalised
 B. **II** because the -ve charge can be delocalised
 C. **I** because the negative charge is further from the electronegative oxygen
 D. **II** because the negative charge is closer to the more electronegative oxygen
 E. **II** because it has the lower pKa

16. Which of the following is/are resonance structures of the structure **X** ?



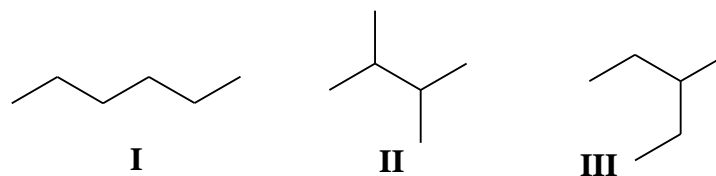
- A.** None of **I**, **II** or **III** are resonance structures of **X**
B. **I** only **C.** **II** only **D.** **III** only **E.** **I** and **II** only
AB. All of **I**, **II** and **III** are resonance structures of **X**

17. In the following reaction, stereochemistry:



- A.** Is lost because the reaction is $\text{S}_{\text{N}}1$ and takes place with inversion
B. Is reversed because the reaction is $\text{S}_{\text{N}}2$ and takes place with inversion.
C. Is lost because the reaction is $\text{S}_{\text{N}}1$ and occurs via a carbocation intermediate.
D. Is lost because the reaction is neither $\text{S}_{\text{N}}1$ nor $\text{S}_{\text{N}}2$
E. Is irrelevant because the alcohol does not have a chirality center

18. Which of the following isomers has the highest boiling point ?



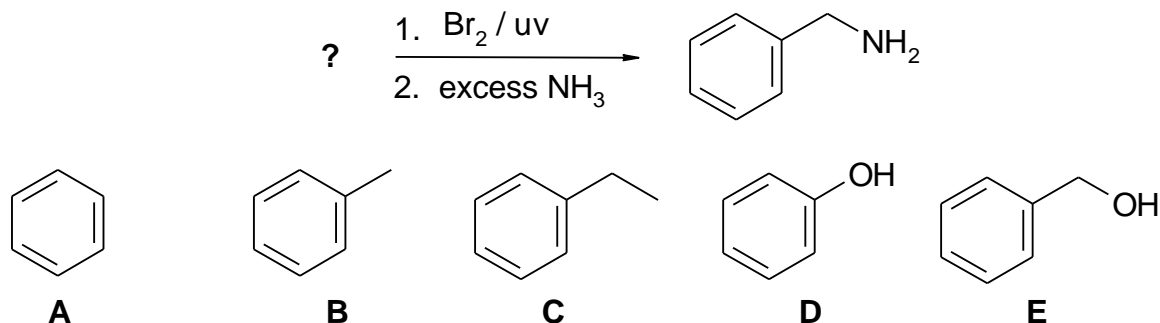
- A.** **I** because it is the most thermodynamically stable
B. **II** because it is the most thermodynamically stable
C. **III** because it is the most thermodynamically stable
D. **I** because it has more surface area
E. **II** because it is more branched

14% **PART 3: REACTIONS**

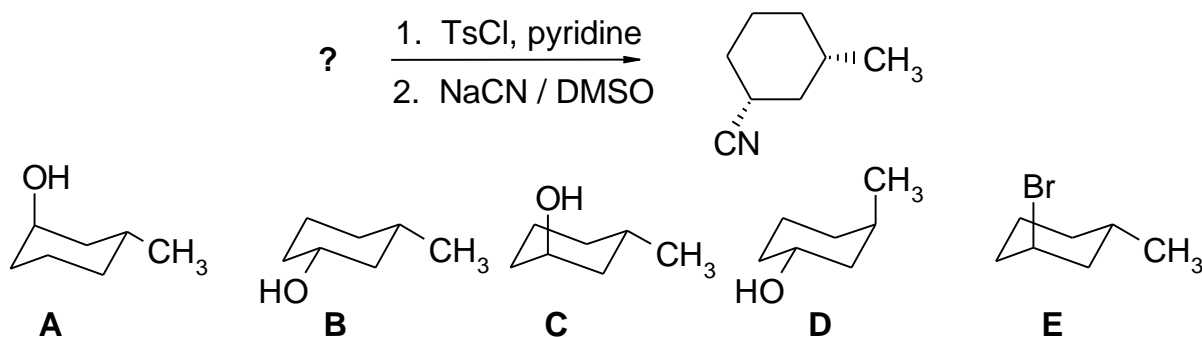
ANSWER ANY SEVEN (7) OF QUESTIONS 19 TO 26.

For each of questions 19-26 select the **MISSING** component (the best starting material, the major product or the best reagents) required in order to **BEST** complete each of the reaction schemes.

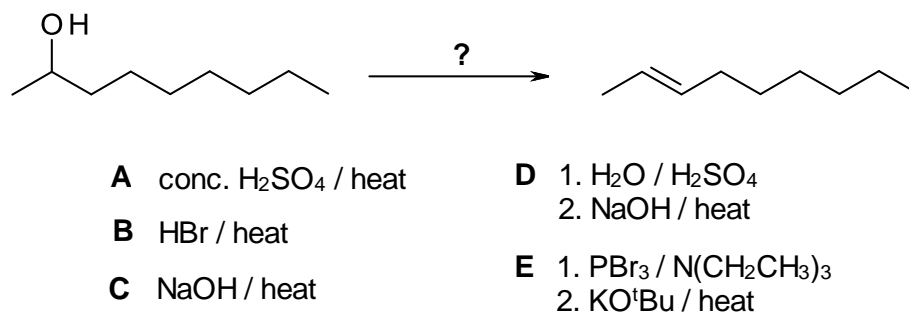
19.



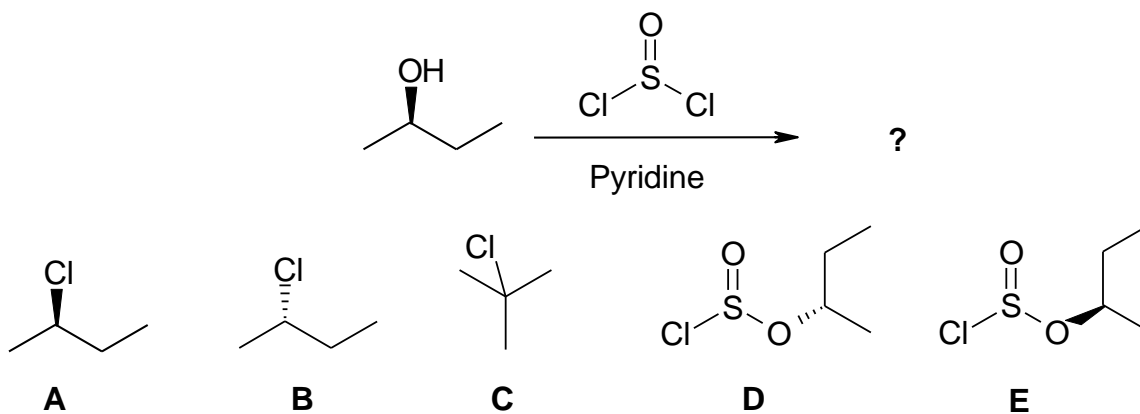
20.



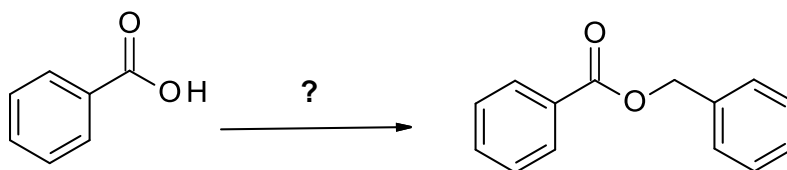
21.



22.

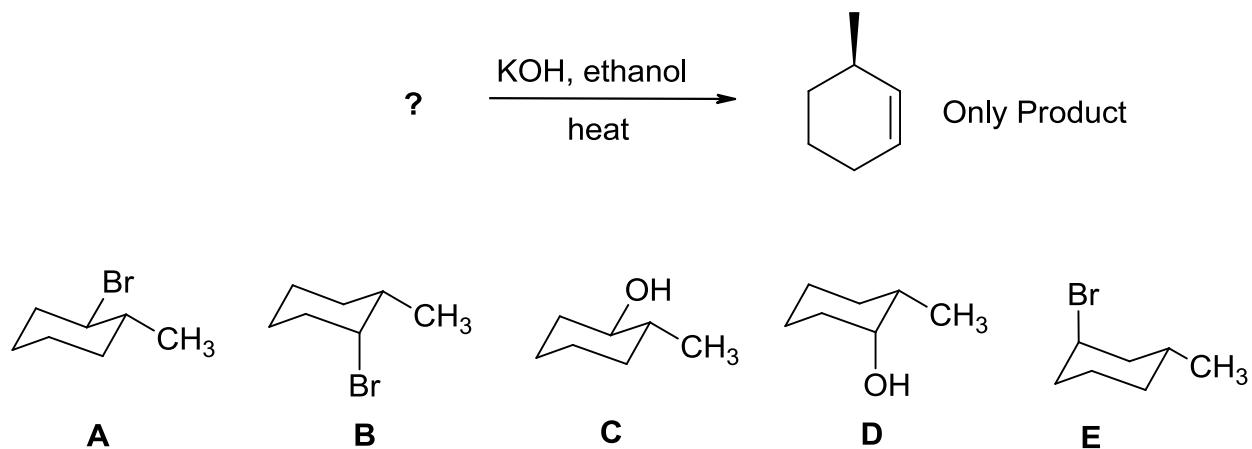


23.

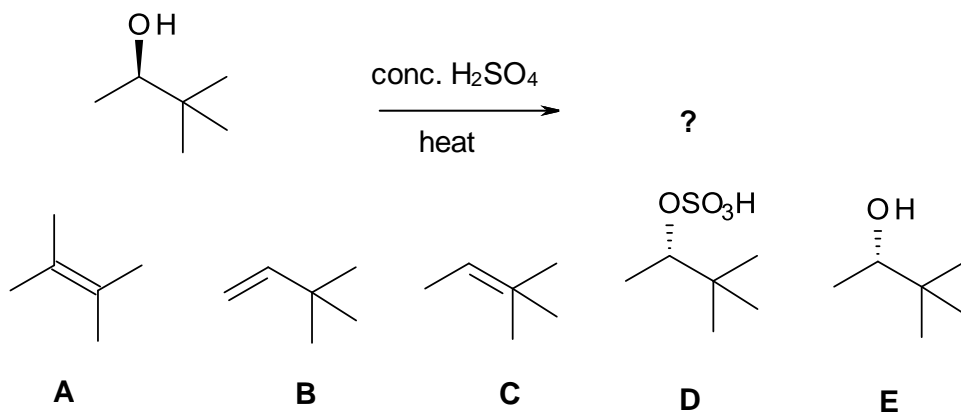


- | | |
|--|---|
| <p>A Phenol / Pyridine</p> <p>B Benzyl alcohol / Pyridine</p> <p>C Benzyl chloride / Pyridine</p> | <p>D 1. PBr_3 / $\text{N}(\text{CH}_2\text{CH}_3)_3$
2. Phenol / Pyridine</p> <p>E 1. TsOH / $\text{N}(\text{CH}_2\text{CH}_3)_3$
2. Chlorobenzene / Pyridine</p> |
|--|---|

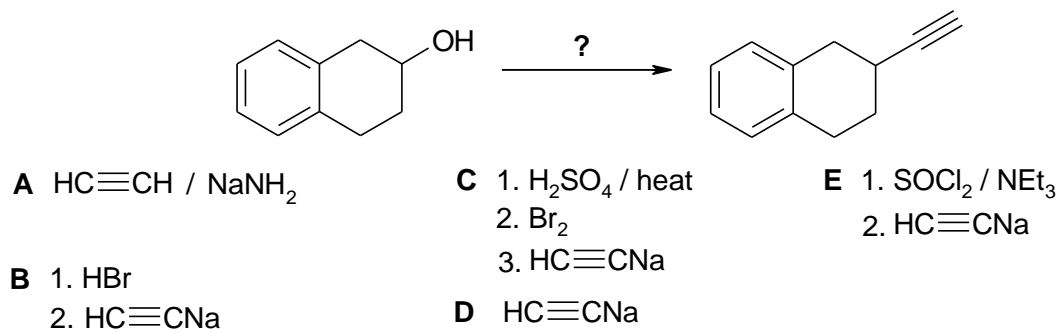
24.



25.



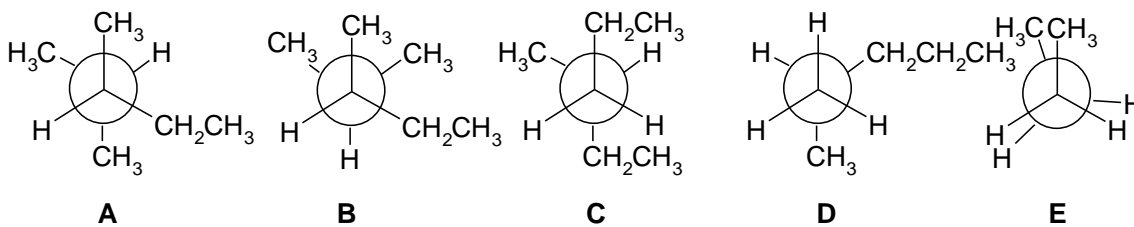
26.



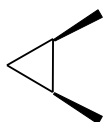
12% **PART 4: CONFORMATIONAL ANALYSIS****ANSWER SIX (6) OF THE QUESTIONS 27 TO 34.**

For each of the questions 27-34 select the answer(s) from those provided. In some cases more than one answer may be correct in which case all correct answers should be selected for full marks.

27. Which of the Newman projections shown represent conformations of 2-methylpentane ?

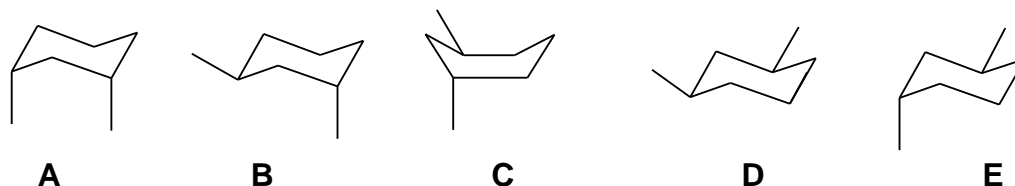


28. What is the **torsional** angle between the two methyl groups in the most stable conformation of the substituted cyclopropane shown below ?

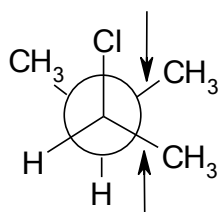


- | | |
|--------------|-----------------|
| A 0° | D 109.5° |
| B 60° | E 120° |
| C 90° | AB 180° |

29. Which of the following structures represent conformations that can be adopted by *cis*-1,3-dimethylcyclohexane ? (Indicate **all that apply**)

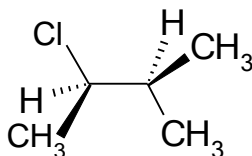
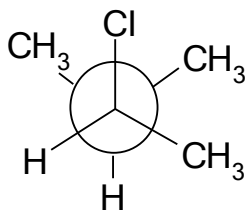


30. Which of the following terms **best** describes the relative position of the two indicated bonds in the conformation of the molecule shown below?



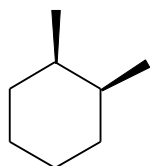
- | | |
|--------------------|-----------------|
| A eclipsed | E gauche |
| B staggered | AB trans |
| C anti | AC cis |
| D syn | |

31. Which of the following terms **best** describes the relationship between the two molecules shown below ?



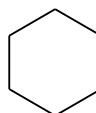
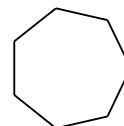
- A** constitutional isomers
B identical
C conformational isomers
D enantiomers
E diastereomers
AB meso
AC not isomers

32. What term(s) associated with types of strain can be used to describe the molecule shown below in its most stable conformation ?

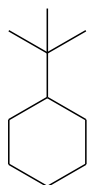
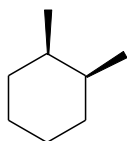
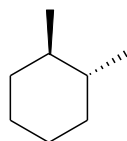
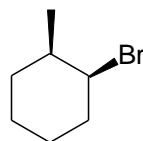
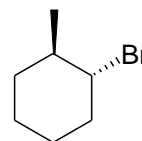


- A** Van der Waals
B torsional (eclipsing)
C 1,3-diaxial
D flagpole
E ring

33. Which of the following molecules would have the least exothermic heat of combustion per methylene (-CH₂-) unit ?

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

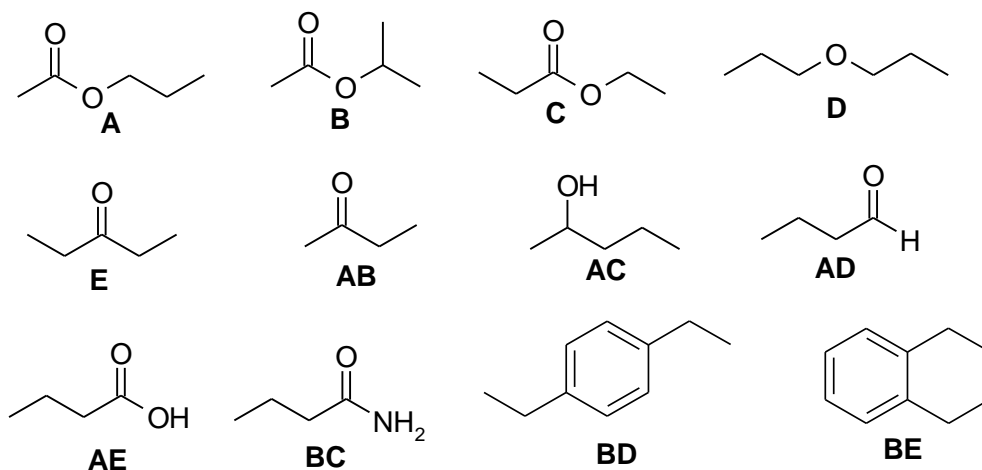
34. Which of the following structures have two chair conformations of equal energy

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

12% PART 5: SPECTROSCOPY**ANSWER ALL SIX (6) OF QUESTIONS 35 TO 40.**

For each of questions 37-42 select the compound from the list provided that corresponds **BEST** with the spectroscopic data provided. The following common abbreviations have been used s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet.

35. $^1\text{H-NMR}$: δ/ppm 1.0 (t, 3 H), 1.6 (sextet, 2 H), 2.0 (s, 3 H), 4.1 (t, 2 H).
 $^{13}\text{C-NMR}$: δ/ppm 10.4, 20.9, 22.1, 66.1, 171
 IR = 1745 cm^{-1}
36. $^1\text{H-NMR}$: δ/ppm 1.22 (t, 3H), 2.64 (q, 2H) 7.14 (m, 2H)
 $^{13}\text{C-NMR}$: δ/ppm 15.4, 25.5, 126, 128.3, 141.6
 IR: $1489, 1461\text{ cm}^{-1}$
37. $^1\text{H-NMR}$: δ/ppm 1.0 (t, 3H), 2.4 (q, 2H)
 $^{13}\text{C-NMR}$: δ/ppm 7.9, 35.5, 212
 IR: 1720 cm^{-1}
38. $^1\text{H-NMR}$: δ/ppm 0.9 (t, 3H), 1.2 (d, 3H), 1.32-1.48 (m, 4H), 2.6 (s, 1H, D_2O exchange), 3.8 (sextet, 1H)
 $^{13}\text{C-NMR}$: δ/ppm 14.1, 19.0, 23.4, 41.6, 67.7
 IR: $3100\text{-}3500\text{ cm}^{-1}$
39. $^1\text{H-NMR}$: δ/ppm 0.9 (t, 3H), 1.5 (sextet, 2H), 2.0 (t, 2H), 6.7 (s, 1H), 7.2 (s, 1H)
 $^{13}\text{C-NMR}$: δ/ppm 13.7, 19.0, 37.9, 176.4
 IR: $3356, 3184, 1660\text{ cm}^{-1}$
40. $^1\text{H-NMR}$: δ/ppm 1.0 (t, 3H), 1.7 (sextet, 2H), 2.3 (t, 2H), 11.5 (s, 1H, D_2O exchange)
 $^{13}\text{C-NMR}$: δ/ppm 13.7, 18.4, 36.2, 180.7
 IR: $2700\text{-}3300, 1712\text{ cm}^{-1}$

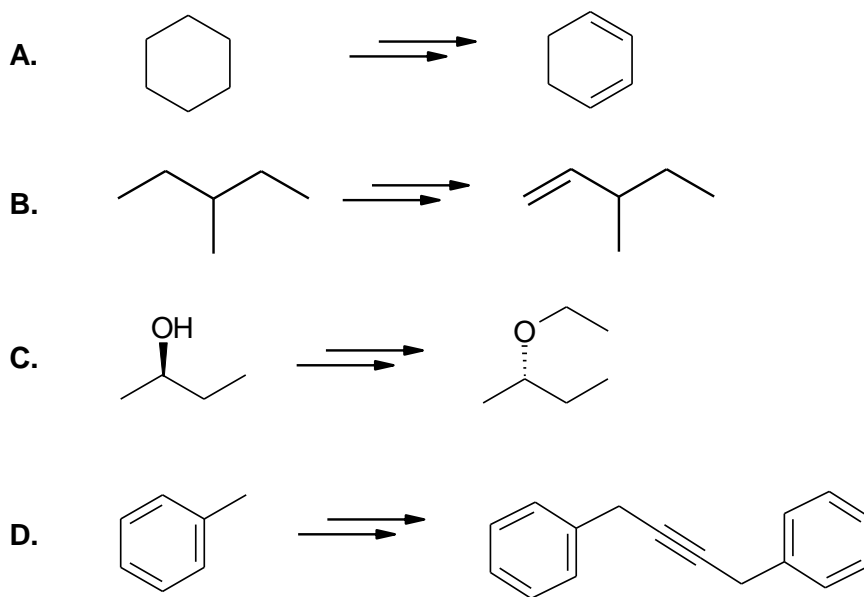


8% PART 6: SYNTHESIS

DESIGN EFFICIENT SYNTHESSES OF ANY TWO (2) of the following target molecules from the indicated starting materials. In addition, you are allowed to use any hydrocarbon with three or fewer carbon atoms, any solvents or inorganic reagents, and any organic reagents that do not contribute carbon atoms to the carbon skeleton in the product. More than one step will be required for each synthesis. Clearly show the required reagents and the product of each step.

WRITE YOUR ANSWERS IN THE EXAM BOOKLET PROVIDED.

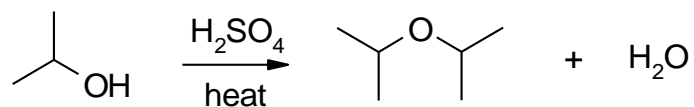
DO NOT SHOW MECHANISMS.



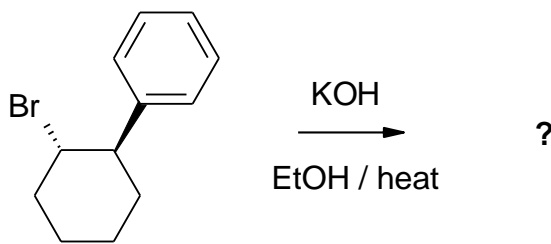
9% **PART 7: MECHANISMS****WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

Use curly arrows to show the mechanism in order to explain **ANY TWO** of the following:

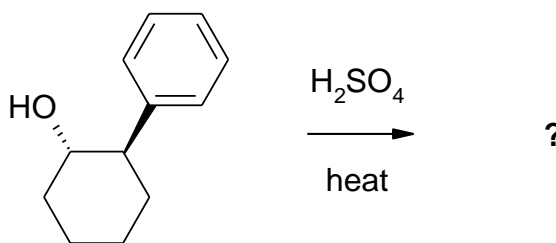
- A** Draw the reaction mechanism for the reaction of propan-2-ol to give diisopropyl ether.



- B** Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



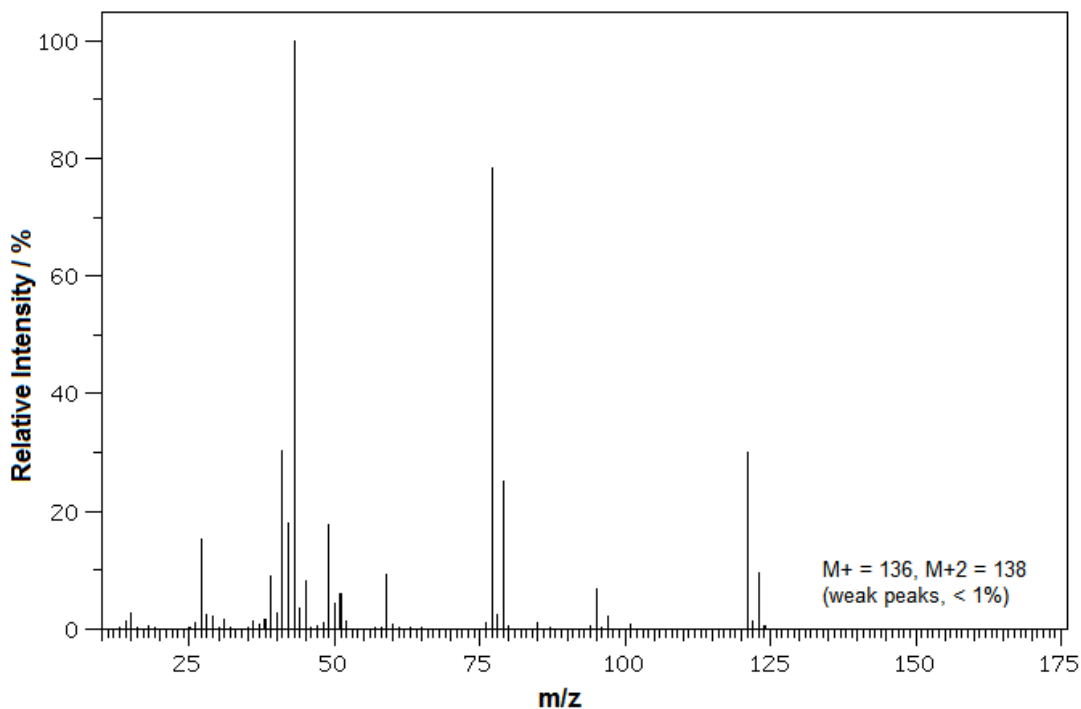
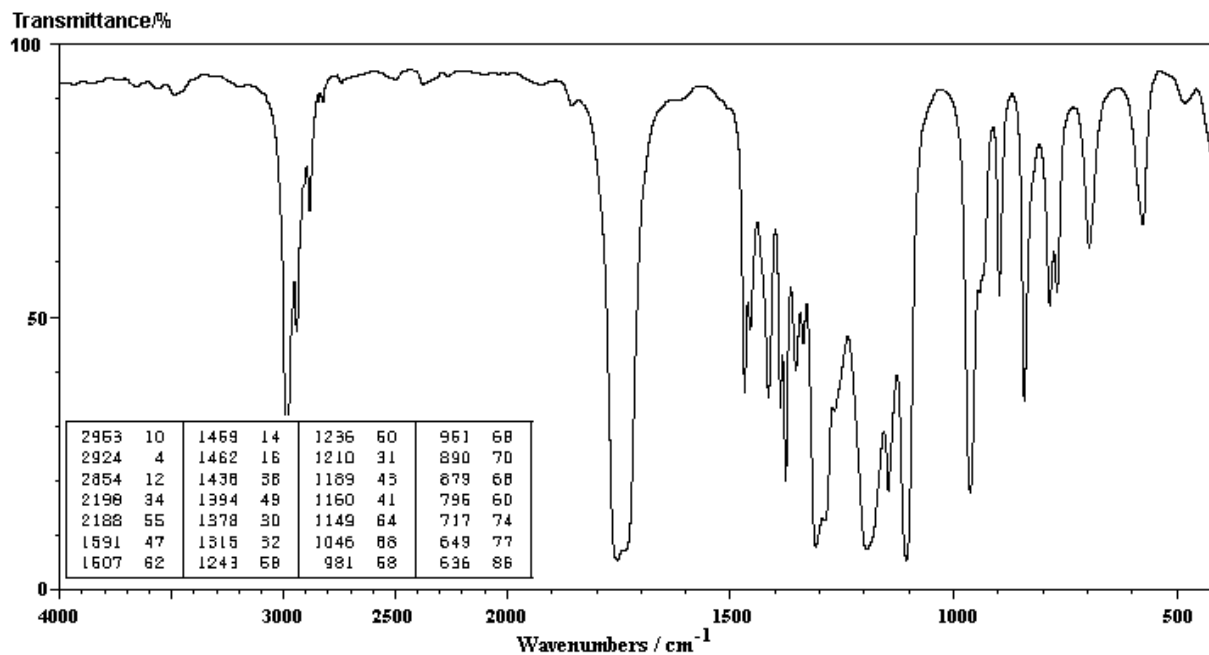
- C** Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



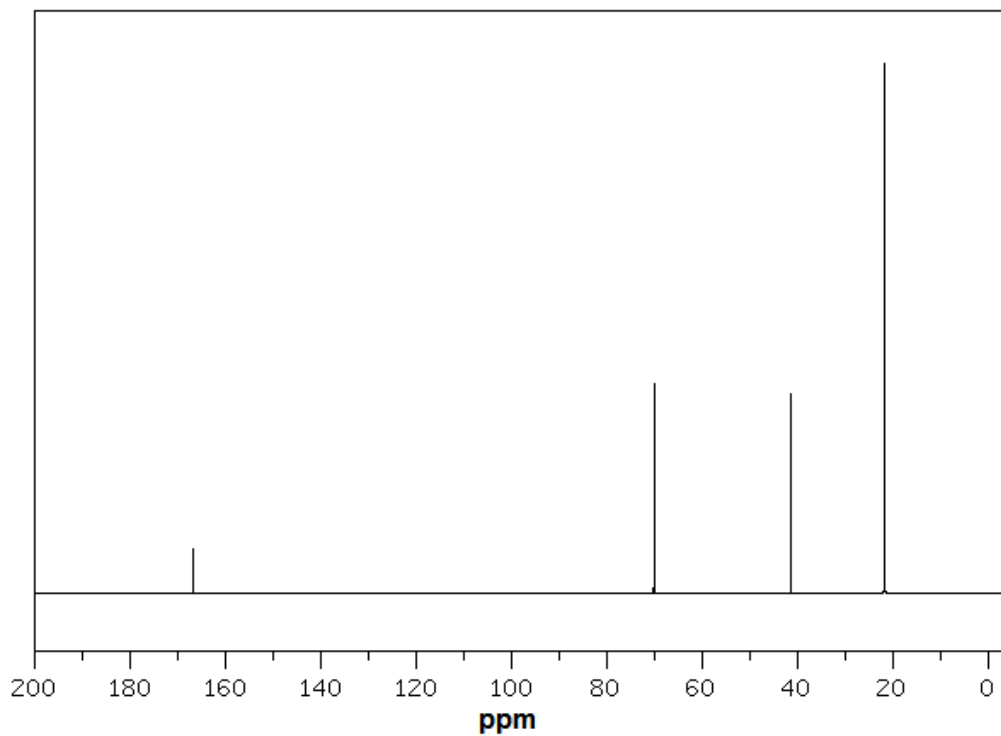
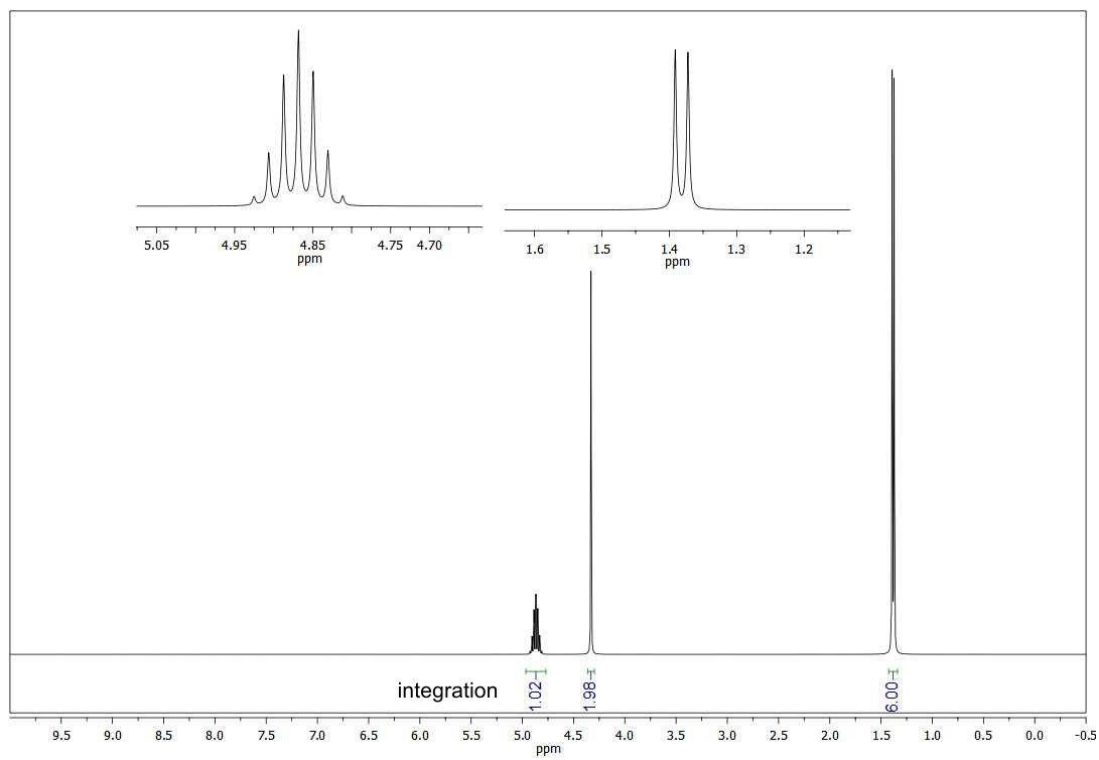
10% PART 8: SPECTROSCOPY

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

From the spectral data provided below, identify the structure of the "unknown" molecule.

Mass Spectrum:**IR Spectrum:**

Cont'd -->

^{13}C -NMR: **^1H -NMR:**

Cont'd -->

10% PART 9: STRUCTURE DETERMINATION**WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

A chiral alkyl bromide, **A** $C_6H_{13}Br$ was determined to have an R configuration. **A** was observed to react at a moderate rate with either aqueous ethanolic silver nitrate or with sodium iodide in acetone. When **A** was reacted with either KOH / heat or KOtBu / DMSO / heat it gave the same product, **B**, C_6H_{12} (IR: $1650cm^{-1}$). The H NMR of **B** showed the following peaks: 1.2 ppm, 9H, singlet; 5.0 ppm, 2H multiplet; 5.7 ppm, 1H, doublet of doublets; The normal ^{13}C NMR of **B** had 4 peaks.

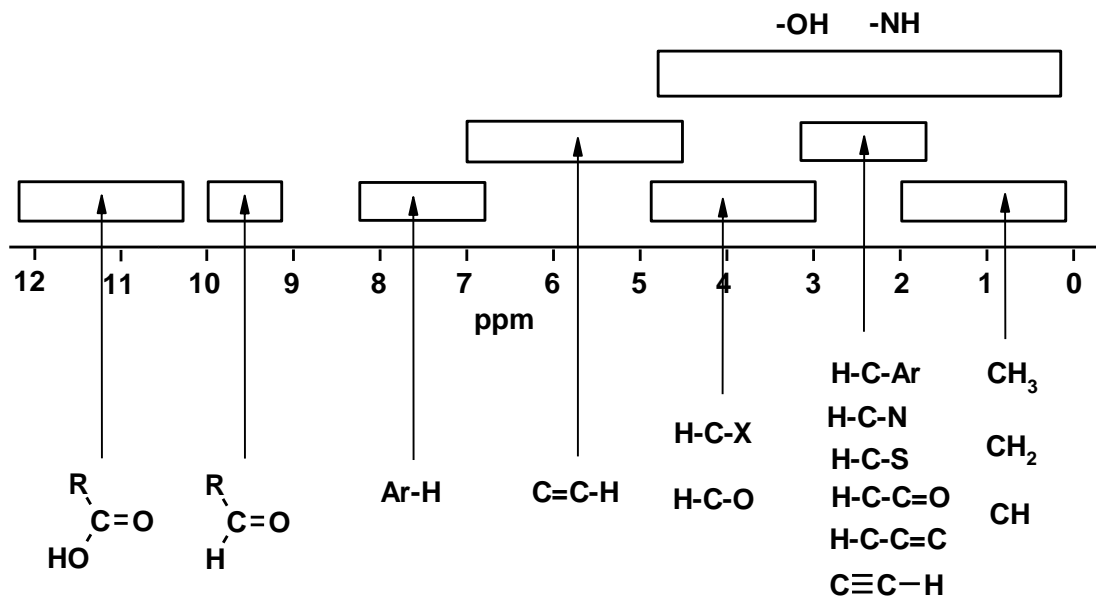
When **A** was reacted with cold NaOH solution the major product was a chiral compound **C**, $C_6H_{14}O$ (IR: $3500cm^{-1}$, broad).

When **C** was reacted with PBr_3 / Et_3N , **A** was obtained but when **C** was treated with HBr the reaction gave an achiral product, **D** as the major product. **D** was observed to react rapidly with aqueous ethanolic silver nitrate but very slowly (if at all) with sodium iodide in acetone. **D** was found to be a constitutional isomer of **A**. **D** could also be obtained on reaction of 2,3-dimethylbutane with bromine / uv light.

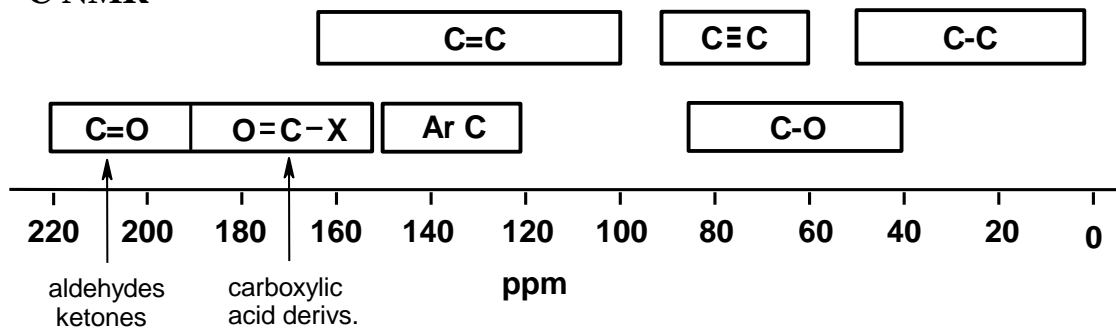
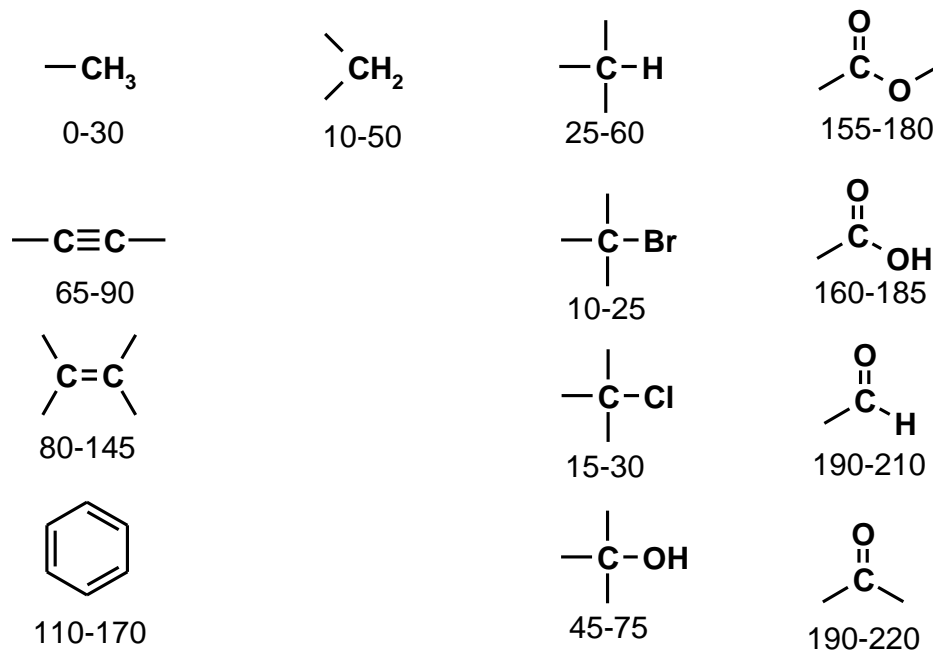
When **C** was heated with conc. H_2SO_4 , the major product was **E**, a constitutional isomer of **B**. The normal ^{13}C NMR spectrum of **E** had only 2 peaks. **E** was also formed as the major product of the reaction of **D** with hot ethanolic KOH.

- **Identify A-E (only structures are needed)**
- **Draw a structure showing the stereochemistry and give the complete name of one enantiomer of C.**

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

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

	methyl CH ₃ -	methylene -CH ₂ -	methyne CH	other	
$\begin{array}{c} \\ \text{R}-\text{C}- \\ \end{array}$	0.9	1.4	1.5	-OH	1-5
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \end{array}$	1.6	2.3	2.6	-NH	1-3
$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C} \end{array}$	2.1	2.4	2.5	C≡CH	2.5
$\begin{array}{c} \diagdown \\ \text{R}-\text{N} \\ \diagup \end{array}$	2.2	2.5	2.9	$\begin{array}{c} \text{H} \\ \\ \text{C}=\text{C} \\ \diagdown \end{array}$	5.5
R-Ar	2.3	2.7	3.0	Ar-H	7.3
R-Br	2.7	3.3	4.1	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{H} \end{array}$	10
R-Cl	3.1	3.4	4.1	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{OH} \end{array}$	9-12
R-O-	3.3	3.4	3.7		

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

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											18						
1A											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
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 **