UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351



December 12th 2017

Time: 3 Hours

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON <u>BOTH</u> YOUR ANSWER BOOKLET AND COMPUTER ANSWER SHEET. ENTER VERSION NUMBER 1 ON THE 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 (this must be completed within the 3hrs). Use a pencil only <u>not ink</u> to completely fill the circle(s). In some cases it is required that you indicate <u>multiple</u> 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 <u>both</u> space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased <u>cleanly</u>.

Molecular models are permitted during the exam; calculators are also permitted, <u>but</u> <u>NOT programmable calculators</u>.

15% PART 1: RELATIVE PROPERTIES

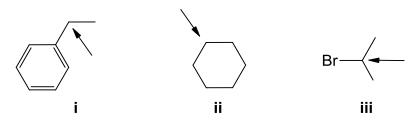
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

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

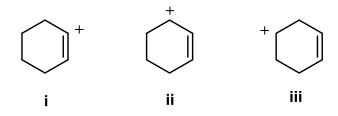
Use the following code to indicate your answers.

Α.	i > ii > iii	D.	ii > iii > i
Β.	i > iii > ii	Ε.	iii > i > ii
С.	ii > i > iii	AB.	iii > ii > i

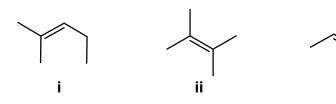
1. The number of lines in the **H-NMR** signals for the H atoms at the positions indicated in each of the following:



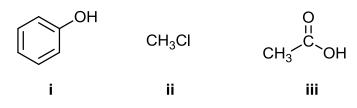
2. The relative stability of each of the following carbocations:



3. The heats of combustion of each of the following (least negative to most negative):



4. The relative acidity of each of the following:



iii

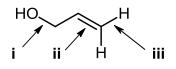
© Dept of Chemistry, University of Calgary

Use the following code to indicate your answers.

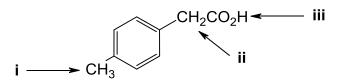
- 5. The relative amount of the conjugate base of ethanoic acid formed by the reaction of1 mole equivalent of each of the following:

 $CH_{3}CO_{2}H \xrightarrow{pKa = 5} CH_{3}CO_{2}^{-} + H^{+} \xrightarrow{CH_{4}} H_{2}O NH_{3}$

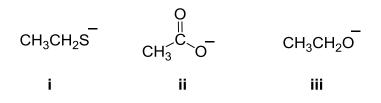
6. The relative frequency for the stretching vibrations of the following bonds :



7. The ¹**H-NMR** chemical shifts for the **H** atoms in the groups indicated by arrows the following structure:



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

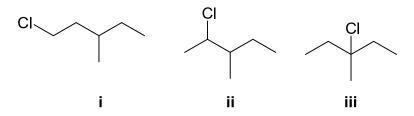


Use the following code to indicate your answers.

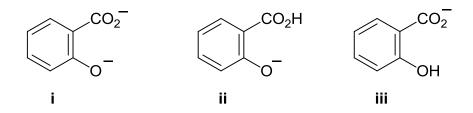
- A.
 i > ii > iii D.
 ii > iii > i

 B.
 i > iii > ii E.
 iii > i > ii

 C.
 ii > i > iii AB.
 iii > ii > i
- The relative amount of the following products formed by the reaction 3methylpentane with Cl₂ / uv light:

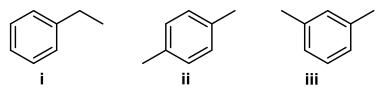


10. The relative amounts of each of the following species of 2-hydroxybenzoic acid present in an aqueous solution of pH = 8:



11. The relative intensity of the electron impact mass spectrum of 2-chloropropane :

- i. m/z = 78 ii. m/z = 79 iii. m/z = 80
- 12. The number of types of hydrogen in each of the following:

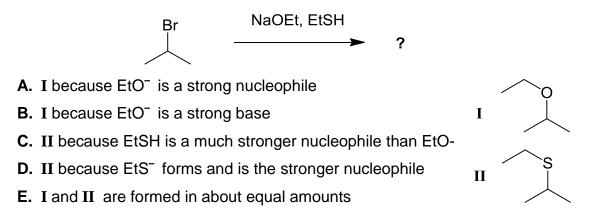


12% PART 2: MOLECULAR PROPERTIES

ANSWER ALL SIX (6) OF THE QUESTIONS 13 TO 18.

In questions 13-17 choose the single option that provides the best answer.

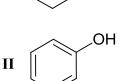
13. Which of the following is the major product of the following reaction ?



14. Which of the following best explains the H-NMR chemical shift difference of the aldehyde H (9-10 ppm) compared to the similar acetal H (about 5 ppm) ?



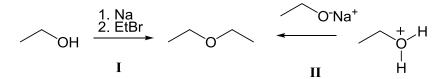
- **A.** Resonance with the pi bond in the aldehyde.
- **B.** Deshielding by the electronegative oxygen atoms.
- C. The high electron density associated with the double bond in the aldehyde
- **D.** It falls in the shielding cone of the magnetic field due to the pi system
- E. It falls in the deshielding area of the magnetic field due to the pi system
- 15. Which of the following is more reactive towards reaction with NaOH?
 - A. I because it forms a less stable primary carbocation
 - **B.** II because it forms a resonance stabilized carbocation
 - C. I because it can undergo an elimination reaction
 - D. II because it forms a resonance stabilized anion
 - E. I and II have about equal reactivity



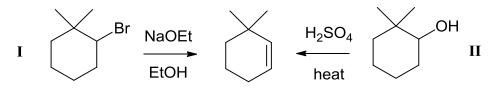
Ι

OH

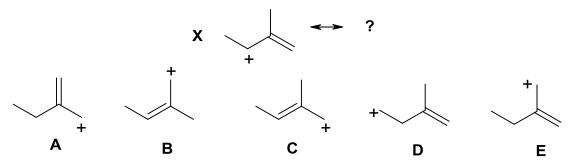
16. Which of the following statements is true regarding to the synthesis of diethyl ether ?



- **A.** Method II is preferred because H_2O is a better leaving group than HO^- .
- **B.** Method **II** is preferred because ethoxide is a better nucleophile than ethanol.
- **C.** Method **I** is preferred because ethanol is a very good nucleophile.
- **D.** Method **I** is preferred because both nucleophile and electrophile are primary.
- E. They are both equally suitable for the synthesis of diethyl ether.
- 17. Which of the following reactions is more efficient for producing the alkene shown ?



- A. I because the reaction is more likely to be E2
- B. II because the reaction is more likely to be E2
- C. I because the reaction is more likely to be E1
- **D.** II because the reaction is more likely to be E1
- E. The routes are equally efficient at producing the alkene
- 18. Which of the following is/are resonance structures of the structure X (select all that apply) ?

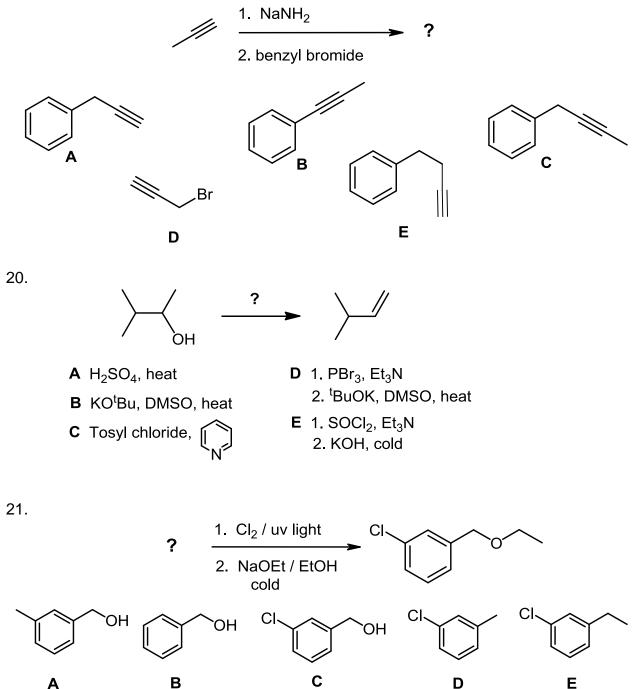


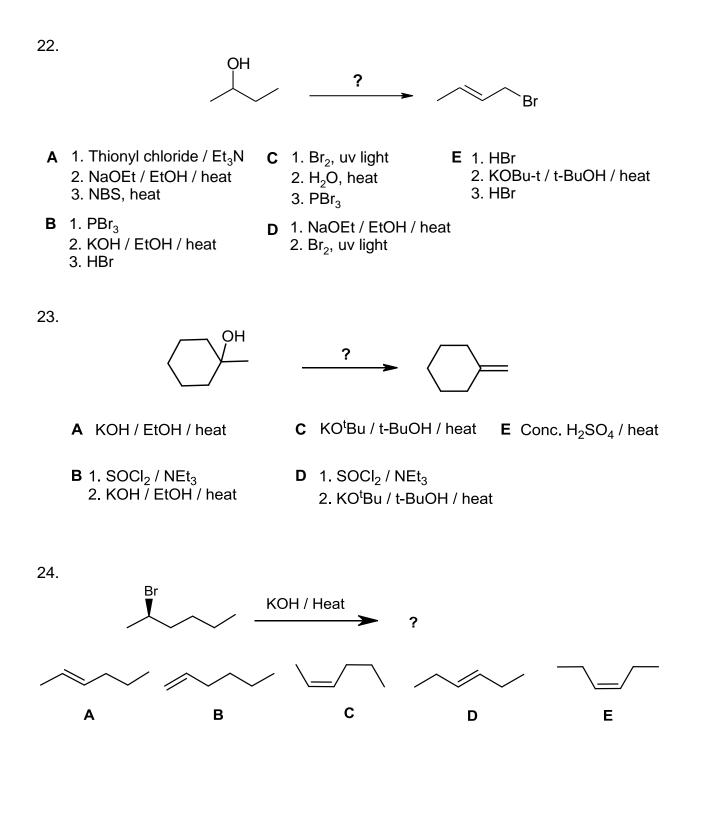
14% PART 3: REACTIONS

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

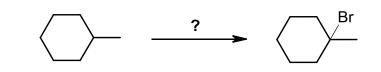
For each of questions 19-26 select the MISSING component (the best starting material, the major product or the best reagents) required in order to BEST complete each of the reaction schemes.

19.



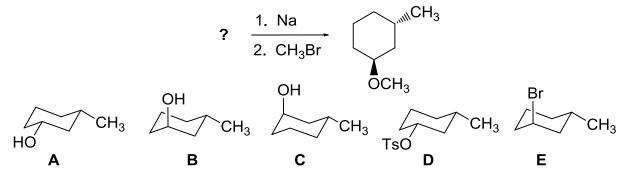


25.



A HBr **B** PBr_3 / Et_3N **C** Br_2 **D** 1. Br_2 / uv **E** $NaBr / H_2SO_4$

26.

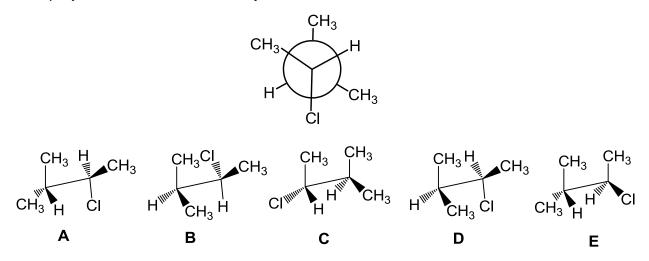


9% PART 4: CONFORMATIONAL ANALYSIS

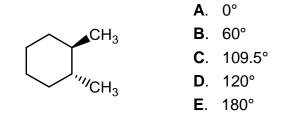
ANSWER ANY SIX (6) OF THE QUESTIONS 27 TO 34.

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.

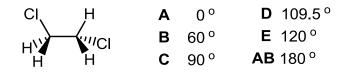
- 27. How many equatorial hydrogens are there in the most stable conformation of trans-1,3-dimethylcyclohexane.
 - **A** 12 **B** 10 **C** 6 **D** 5 **E** 4 **AB** 3
- 28. Which of the following representations is the same conformation as the Newman projection of 2-chloro-3-methylbutane structure shown below:



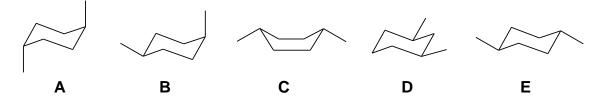
29. What is the torsional angle between the two methyl groups in the *trans*-1,2dimethylcyclohexane (shown below) in its most stable conformation ?



30. What is the **torsional** angle between the bonds to the two chlorine atoms in the conformation of 1,2-dichloroethane shown below ?



31. Which of the following structures represents the lowest energy conformation of *cis*-1,4-dimethylcyclohexane ?



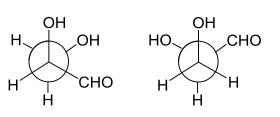
32. Which of the following terms **best** describes the relative position of the two highlighted bonds in the conformation of the molecule shown below?



A eclipsedB staggeredC anti

D gauche E syn AB trans

33. 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

34. Which of the following cycloalkanes has the least angle strain?

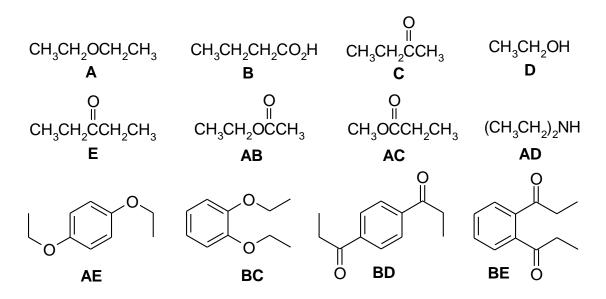
A cyclopropaneB bicyclo[2.1.1]hexaneC cyclopentaneD cyclohexaneE cycloheptaneAB spiro[2.3]hexane

12% PART 5: SPECTROSCOPY

ANSWER ALL SIX (6) OF QUESTIONS 35 TO 40.

For each of questions 35-40 select the compound from the list provided that corresponds BEST with the spectroscopic data provided.

- ¹H NMR : δ/ppm 1.1 (t, 3H), 2.1 (s, 3H), 2.4 (q, 2H)
 ¹³C-NMR: δ/ppm 7.9, 29.4, 36.9, 209.3
 IR : 1718 cm⁻¹
- ¹H NMR : δ/ppm 1.2 (t, 3H), 2.3 (q, 2H), 3.7 (s, 3H)
 ¹³C-NMR: δ/ppm 9.2, 27.5, 51.5, 174.9
 IR : 1741 cm⁻¹
- ¹H NMR : δ/ppm 1.1 (t, 3H), 2.4 (q, 2H)
 ¹³C-NMR: δ/ppm 7.9, 35.5, 212.1
 IR : 1716 cm⁻¹
- ¹H NMR : δ/ppm 1.4 (t, 3H), 4.0 (q, 2H), 6.9 (m, 2H)
 ¹³C-NMR: δ/ppm 14.9, 64.6, 114.0, 121.1, 149.0
- ¹H NMR : δ/ppm 1.3 (t, 3H), 2.0 (s, 3H) 4.1 (q, 2H)
 ¹³C-NMR: δ/ppm 14.3, 21.0, 60.4, 171.0
 IR : 1743 cm⁻¹
- 40. ¹H-NMR: δ/ppm 1.0 (t, 3H), 1.7 (sextet, 2H), 2.3 (t, 2H), 11.5 (s, 1H, D₂O exchange)
 ¹³C-NMR: δ/ppm 13.7, 18.4, 36.2, 180.7
 IR: 2700-3300, 1712 cm⁻¹

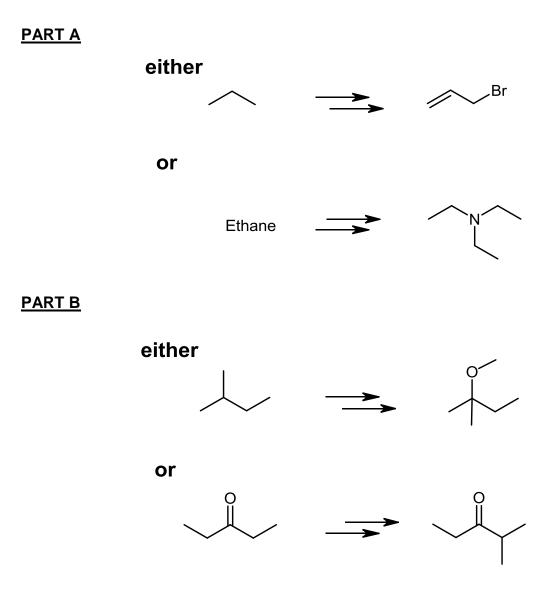


8% PART 6: SYNTHESIS

DESIGN TWO(2) EFFICIENT SYNTHESES, <u>ONE</u> from PART A and <u>ONE</u> from PART B of the following target molecules from the indicated starting material. In addition, you are allowed to use <u>any hydrocarbon with three or fewer carbon atoms</u>, any solvents or inorganic reagents, and any organic reagents that do not contribute carbon atoms to the <u>carbon</u> skeleton in the <u>product</u>. More than one step will be required for each synthesis. Clearly show the <u>required reagents</u> and the <u>product of each step</u>.

WRITE YOUR ANSWERS IN THE EXAM BOOKLET PROVIDED.

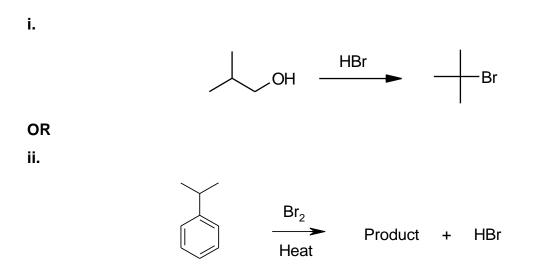
DO NOT SHOW MECHANISMS.



10% PART 7: MECHANISMS

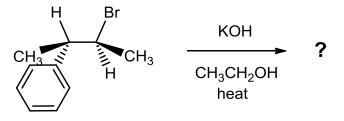
WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED ANSWER TWO (2) QUESTIONS, <u>ONE</u> from PART A and <u>ONE</u> from PART B. NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED.

(5%) PART A: Use a curly arrow mechanism to explain ONE of the following reactions:



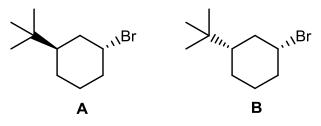
(5%) PART B: Use a curly arrow mechanism to explain ONE of the following reactions:

i. Draw the reaction mechanism for the formation of **the MAJOR** product in the following reaction.



OR

ii. Which of the two isomers shown below reacts at a faster rate when heated with potassium t-butoxide ? Provide a clear and detailed mechanistic explanation (with curly arrows) of your reasoning.



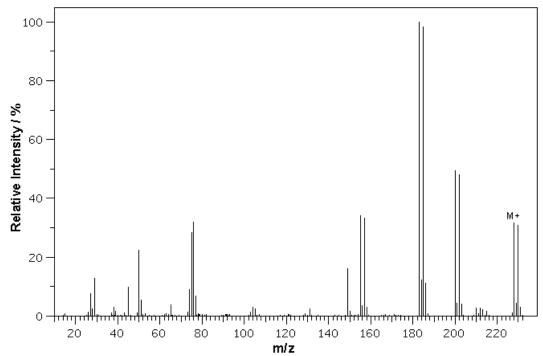
10% PART 8: SPECTROSCOPY

WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED.

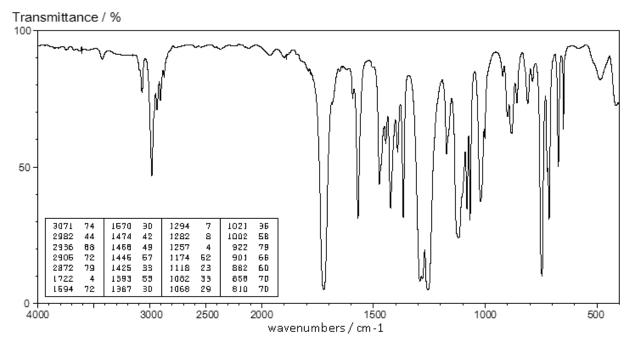
Show your workings as PARTIAL marks will be given.

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

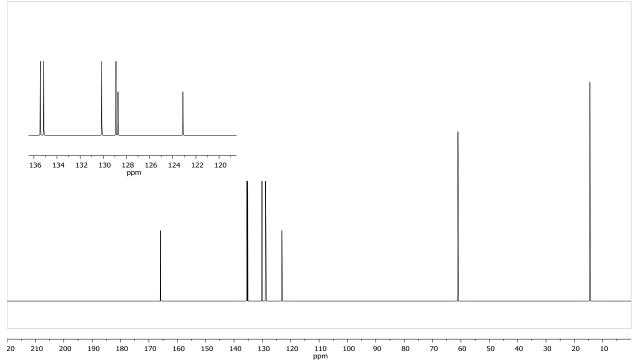
Mass Spectrum:



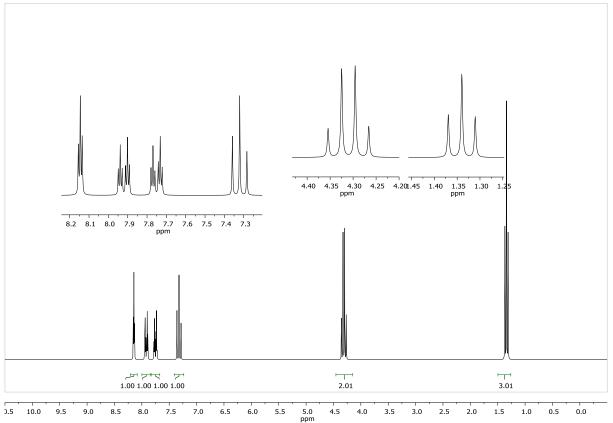
IR Spectrum:



¹³C-NMR:



¹H-NMR:



10% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED

An alkyl bromide **A**, $C_5H_{11}Br$, which contains a chiral centre, was found to react at a moderate rate with Nal / acetone and a moderate rate with aq. ethanolic AgNO₃. When **A** was reacted with aqueous Na₂CO₃ solution, it give **B** $C_5H_{12}O$ (IR : 3500cm⁻¹, broad) as the major product.

Reaction of **B** with HBr gave **C** a constitutional isomer of **A**. **C** was found to react slowly with Nal / acetone and rapidly with aq. ethanolic AgNO₃. When **C** was heated with KOH / ethanol, the major product was **D**, C_5H_{10} (IR : 1650cm⁻¹). **C** could also be obtained on reaction of 2-methylbutane with bromine / uv light.

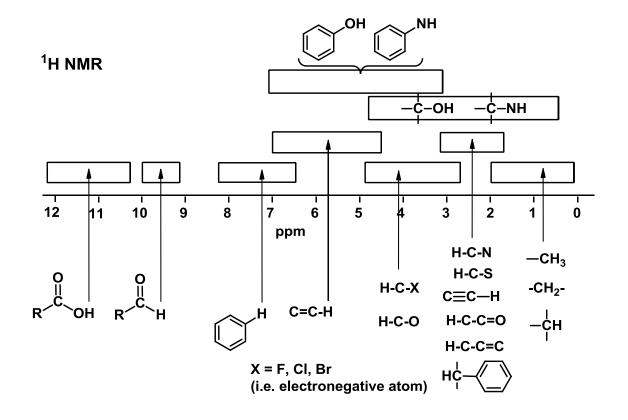
In contrast, reaction of **A** with KOtBu / t-butanol/ heat gave **E**, which was a constitutional isomer of **D**. Reaction of **C** with KOtBu / t-butanol/ heat gave **F**, another constitutional isomer of **D**

- i. Identify **A-F** (only structures are needed)
- ii. Indicate how many types of carbon are present in the structures you have drawn for
 A, D and F
- **iii.** Give the complete name of one enantiomer of **A** and a structure to show the stereochemistry.

**** THE END ****

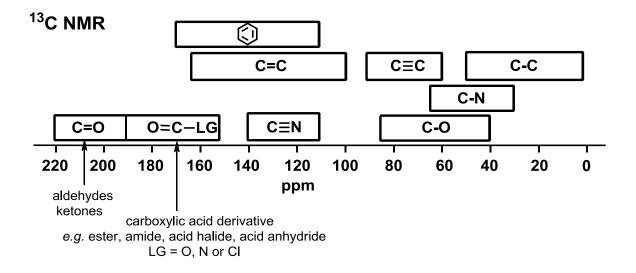
ASC / IRH / CCL 2017

SPECTROSCOPIC TABLES

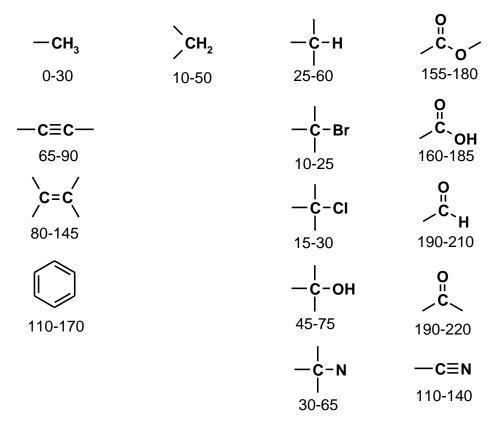


¹H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

R =	e methyl	methylene	methyne					
	$-CH_3$	-CH ₂ -	–¢н	other				
R-C-	0.9	1.4	1.5	sp³C -OH	1-5			
R, /				sp ³ C -NH	1-3			
)C=C	1.6	2.3	2.6	С≡сн	2.5			
	2.1	2.4	2.5)c=c_H	4.5-6.5			
R-N	2.2	2.5	2.9	н-{	6.5-8			
R-	2.3	2.7	3.0	0 " R ^{/C} \H	9-10			
R–Br	2.7	3.3	4.1	0 0				
R–CI	3.1	3.4	4.1	^{к_с} ,он	9-12			
R-0—	3.3	3.4	3.7					



¹³C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

	1	TYPE OF VIBRATION	FREQUENCY (cm ⁻¹)	<u>WAVELENGTH</u> (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 ac	id	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–0	Alcohols, Ethe	ers, Esters,			
	Carboxylic ac	ids	1300-1000	7.69-10.0	S
O–H	Alcohols, Phe	enols			
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic ac	ids (2)	3300-2500	3.03-4.00	m
N–H	Primary and s	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, Iodi	de	<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	4											5	6	7	8	9	10
Li	Be											В	С	Ν	0	F	Ne
6.941	9.012											10.81	12.01	14.01	16.00	19.00	20.18
11	12	2	4	_	(-	0	0	10	11	10	13	14 G	15	16 G	17	18
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
22.99 19	24.31 20	21	22	23	24	25	26	27	28	29	30	26.98 31	28.09 32	30.97 33	32.07 34	35.45 35	39.95 36
K			Ti	23 V													
	Ca	Sc		·	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.10 37	40.08 38	44.96 39	47.88 40	50.94 41	52.00 42	54.94 43	55.85 44	58.93 45	58.69 46	63.55 47	65.38 48	69.72 49	72.59 50	74.92 51	78.96 52	79.90 53	83.80 54
Rb	Sr	Y	Zr	Nb	Mo	Тс	Ru	Rh	Pd		Cd	In	Sn	Sb	Te	I	Xe
85.47	87.62	∎ 88.91	91.22	92.91	95.94	(98)	101.1	102.9	106.4	Ag 107.9	112.4	114.8	118.7	121.8	127.6	∎ 126.9	AC 131.3
55	56	57*	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Та	w	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.9	137.3	138.9	178.5	180.9	183.9	186.2	190.2	192.2	195.1	197.0	200.6	204.4	207.2	209.0	(209)	(210)	(222)
87	88	89**	104	105	106	107	108	109	110	111							
Fr	Ra	Ac	Rf	На	Sg	Ns	Hs	Mt	Uun	Uuu							
(223)	226.0	(227)	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)							
	-			58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Lant	hanic	des *	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
			140.1	140.9	1 NU 144.2	(145)	5111 150.4	152.0	Gu 157.3	158.9	Dу 162.5	164.9	167.3	168.9	10 173.0	175.0	
				140.1	140.9	144.2	(143)	150.4	152.0	157.5	150.9	102.5	104.9	107.5	100.9	175.0	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)