UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

Version 1

WED OCT 30th, 2024 **Time: 2 Hours**

READ ALL THE INSTRUCTIONS CAREFULLY

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

ENTER **VERSION NUMBER 01** ON **BOTH ANSWER SHEETS**

The examination 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 4 out of 5. These will be graded in numerical order until the required number have been graded, regardless of whether they are right or wrong. **Parts 1-4** will be computer graded, and **Parts 5-7** are to be answered **IN BLUE or BLACK INK or DARK PENCIL** (HB or darker) **IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED**.

Parts 1-4 consist of a series of multiple choice questions numbered **1-31** to be answered on the computer answer sheet (no extra time is provided for "bubbling" in). 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 questions. Incorrect answers must be erased ***cleanly***.

A periodic table with atomic numbers and atomic weights and infrared data tables are located on the last two pages

Molecular models and calculators are permitted, ***but NOT programmable calculators***.

Absolutely no other electronic devices are allowed.

14% PART 1: RELATIVE PROPERTIES

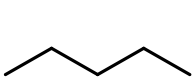
ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

Arrange the items in questions 1-8 in DECREASING ORDER (*i.e.* greatest, most etc. first) with respect to the indicated property.

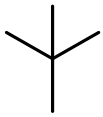
Use the following code to indicate your answers.

A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

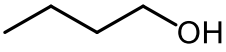
1. The relative boiling points of each of the following**:**



i

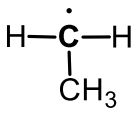


ii

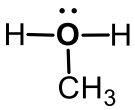


iii

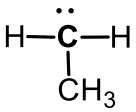
2. The relative formal charge of the **bold atom** in each of following structures (assume all lone pairs are shown, rank most positive to most negative):



i

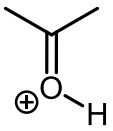


ii

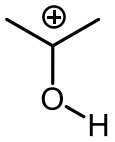


iii

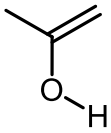
3. The relative importance of each the following resonance contributors of the conjugate acid of 2-propanone (all required charges are shown):



i



ii



iii

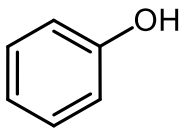
4. The number of different monochlorinated products formed by the reaction of each of the following with Cl_2 / heat:

pentane	cyclohexane	2-methylbutane
i	**ii**	**iii**

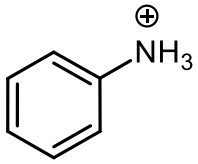
Use the following code to indicate your answers.

A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

5. The relative acidity of the most acidic proton in each of the following:



i



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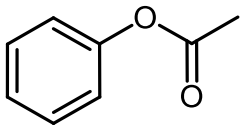


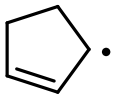
iii

6. The relative number of stereoisomers that each of following has:

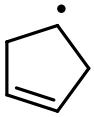
$HOCH_2CH_2CH{=}CHCH_3$ $CH_3CH(OH)CH{=}CHCH_3$ $HOCH_2CH_2CH{=}CH_2$

i **ii** **iii**

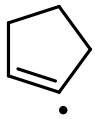
7. The relative radical stability of each the following:



i

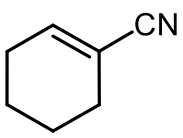


ii

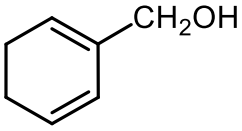


iii

8. The index of hydrogen deficiency (IHD or units of unsaturation) of each of the following:



i



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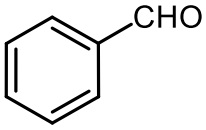


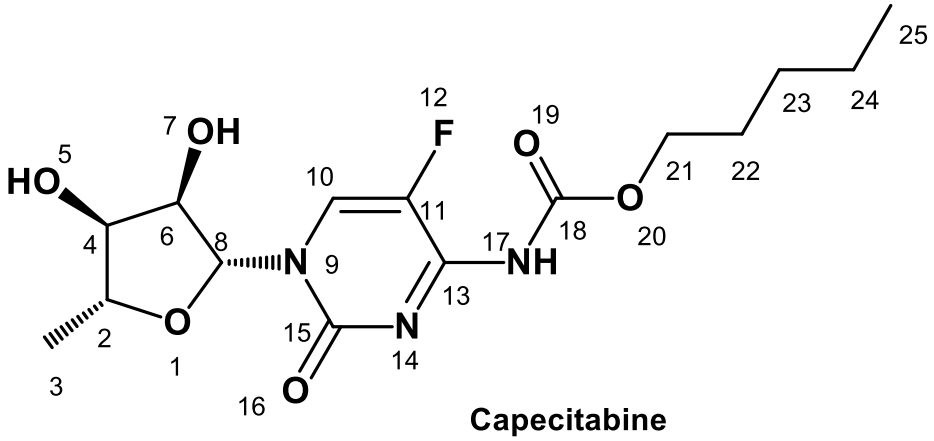
iii

18% PART 2: MOLECULAR PROPERTIES

ANSWER ALL of the questions 9 – 17

For each of the questions 9 - 17 select the appropriate answer(s) from the answers provided. In some cases more than one selection may be required for full credit.

Capecitabine is an anticancer medication used to treat breast cancer, gastric cancer and colorectal cancer. Use the structure **below** to answer questions **9** - **17**



Capecitabine

9. Which of the following best represents the **C2-O1-C8** bond angle in a molecule of Capecitabine ?

A. 72° **B**. 90° **C**. 109.5° **D**. 120° **E**. 180°

10. What are the hybridizations of **O1** and **N9** respectively ?

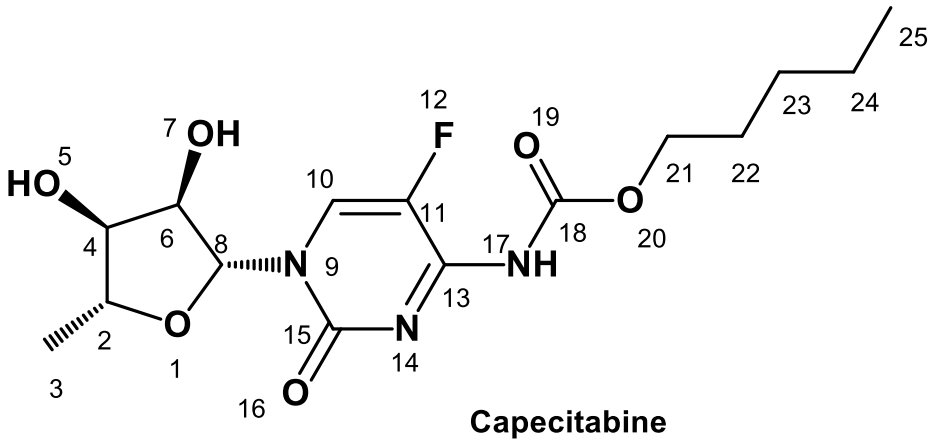
A. sp^3,sp^3 **B**. sp^3,sp^2 **C**. sp,sp **D**. sp^2,sp **E**. sp^3,sp

11. What is the index of hydrogen deficiency (IHD) of Capecitabine ?

A. 4 **B**. 5 **C**. 6 **D**. 7 **E**. 8

12. What is the oxidation state of **C11** in Capecitabine ?

A. +3 **B**. +2 **C**. +1 **D**. 0 **E**. -1 **AB**. -2 **AC** -3



Capecitabine

13. Among the bonds listed below, which one is the shortest ?

A. **C4-O5** **B**. **C2-C3** **C**. **C3-H** **D**. **C22-H** **E**. **C10-H**

14. How many types of sp^3 **C** are there in Capecitabine ?

A. 3 **B**. 6 **C**. 8 **D**. 10 **E**. 12 **AB**. none of these

15. Excluding any halogens, how many types of sp^2 **heteroatoms** are there in Capecitabine ?

A. 3 **B**. 6 **C**. 8 **D**. 9 **E**. 10 **AB**. none of these

16. What configuration descriptors can be used for **C6 & C8** centers, respectively ?

A. R,R **B**. R,S **C**. S,R **D**. S,S **E**. none of these

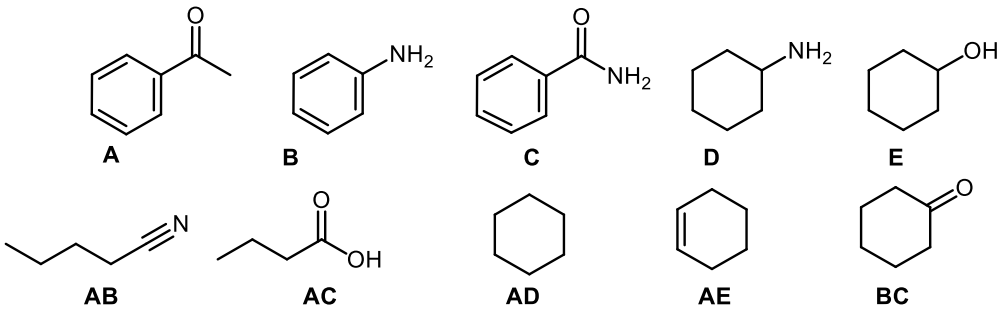
17. What orbitals do the two lone pairs of **O20** occupy ?

A. sp^3, sp^3 **B**. sp^2, sp^2 **C**. sp^3, p **D**. sp^2, p **E**. p, p

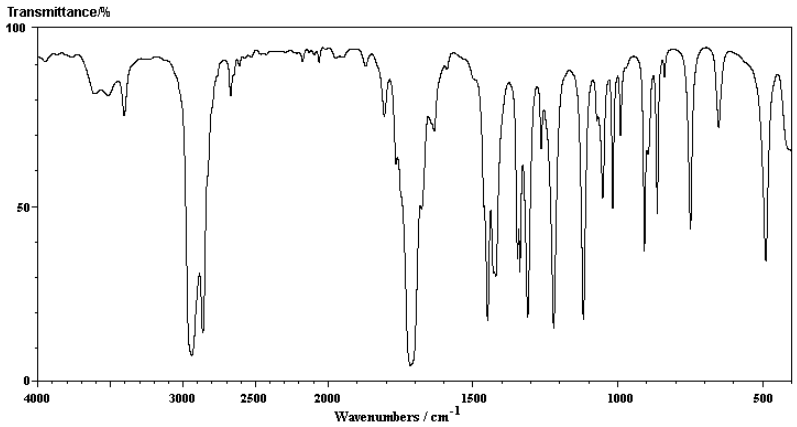
15% PART 3: SPECTROSCOPY

ANSWER ALL SIX (6) OF QUESTIONS 18 – 23 (2.5 marks per question).

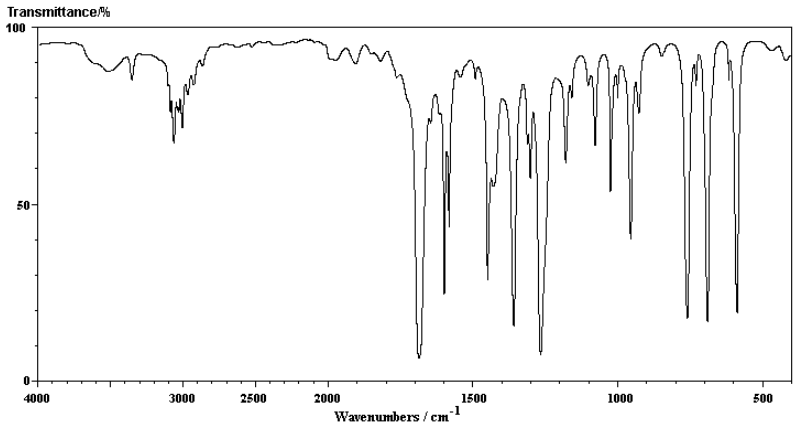
For each of the questions 18-23, match the IR spectra to a structure in the list below:



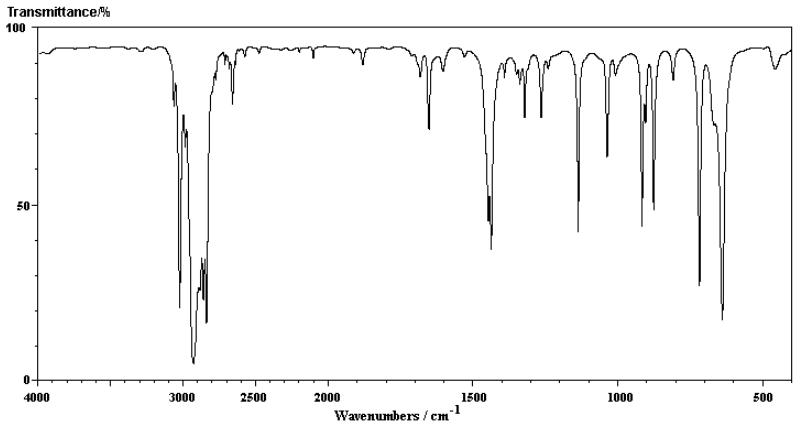
18.

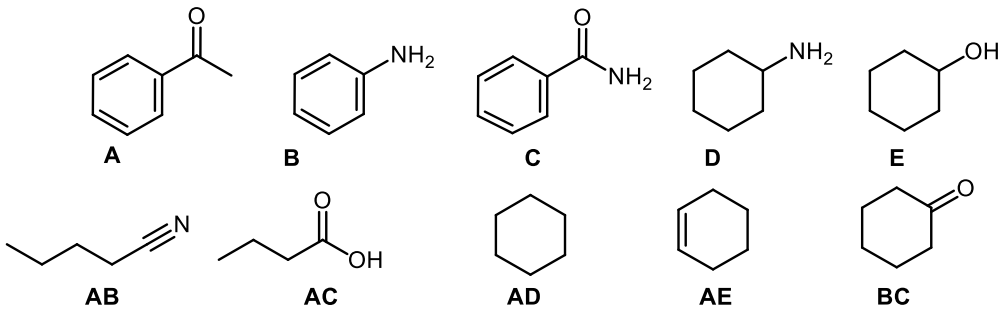


19.

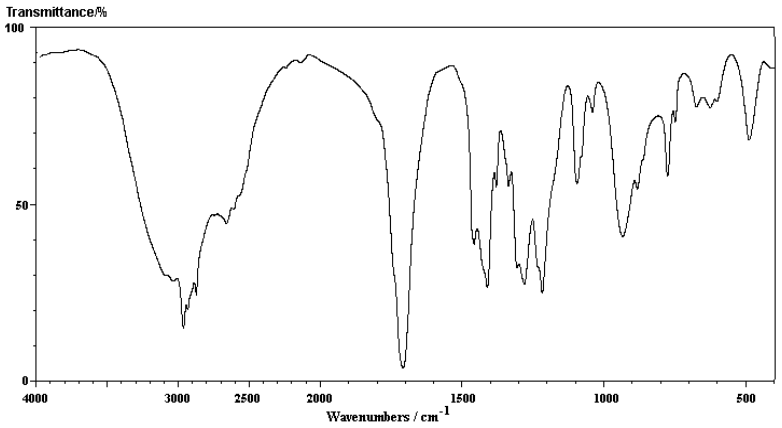


20.

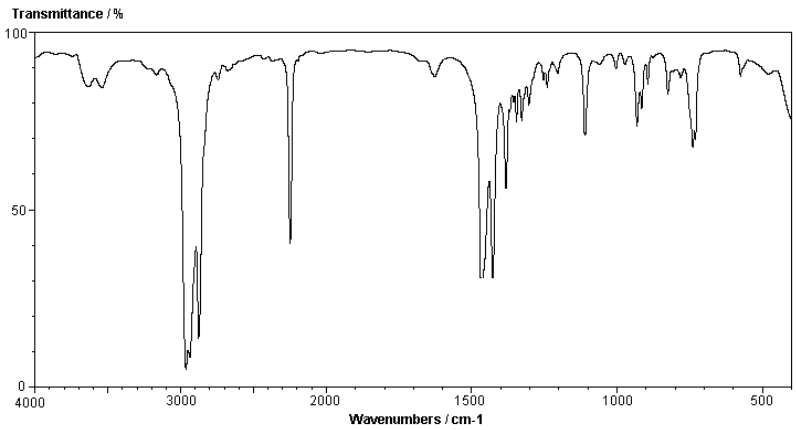



O
NH2
O
NH2
NH2
OH
A
B
C
D
E
N
O
OH
O
AB
AC
AD
AE
BC

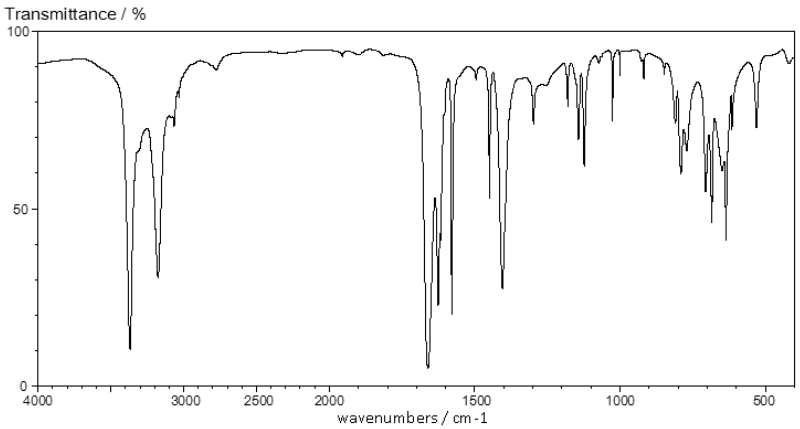
21.


Transmittance/%
100
50
0
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

22.


Transmittance / %
100
50
0
4000
3000
2000
1500
1000
500
Wavenumbers / cm-1

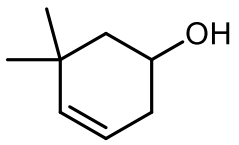
23.


Transmittance / %
100
50
0
4000
3000
2500
2000
1500
1000
500
wavenumbers / cm-1

14% **PART 4: NOMENCLATURE**

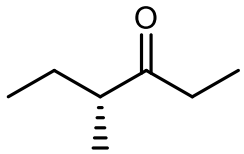
ANSWER ANY SEVEN (7) of the questions 24-31 (2 marks per question). For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



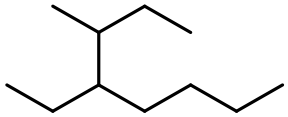
A. 3,3-dimethylcyclohex-1-en-5-ol
B. 2,2-dimethylcyclohex-1-en-4-ol
C. 5,5-dimethylcyclohex-3-en-1-ol
D. 3,3-dimethylcyclohex-4-en-1-ol
E. 1-hydroxy-5,5-dimethylcyclohex-3-ene
AB. 1-hydroxy-3,3-dimethylcyclohex-4-ene

25.



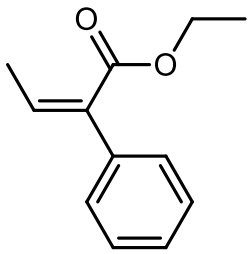
A. (R)-4-methylhexan-3-one
B. (S)-4-methylhexan-3-one
C. (R)-3-methylhexan-4-one
D. (S)-3-methylhexan-4-one
E. 4-methylhexan-3-one
AB. 3-methylhexan-4-one

26.



A. 3-(2-butyl)-heptane
B. 3-isobutylheptane
C. 3-sec-butylheptane
D. 2,3-diethylheptane
E. 4-ethyl-3-methyloctane
AB. 3-methyl-4-ethyloctane

27.

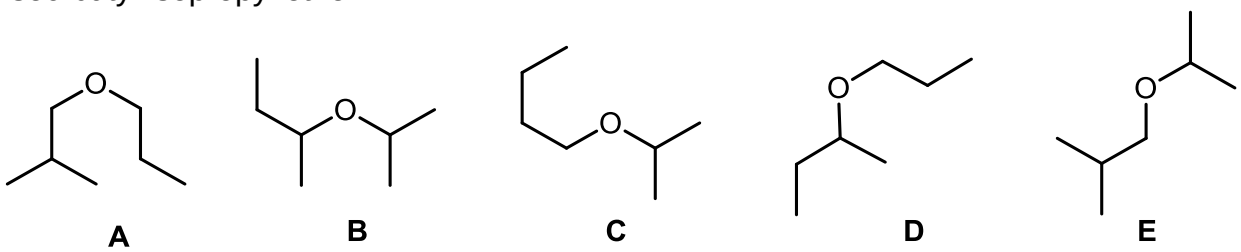


A. methyl (Z)-2-phenylbut-2-enoate
B. methyl (E) 2-phenylbut-2-enoate
C. methyl (E) 3-phenylbut-2-enoate
D. ethyl (E)-3-phenylbut-2-enoate
E. ethyl (Z)-2-phenylbut-2-enoate
AB. ethyl (E)-2-phenylbut-2-enoate

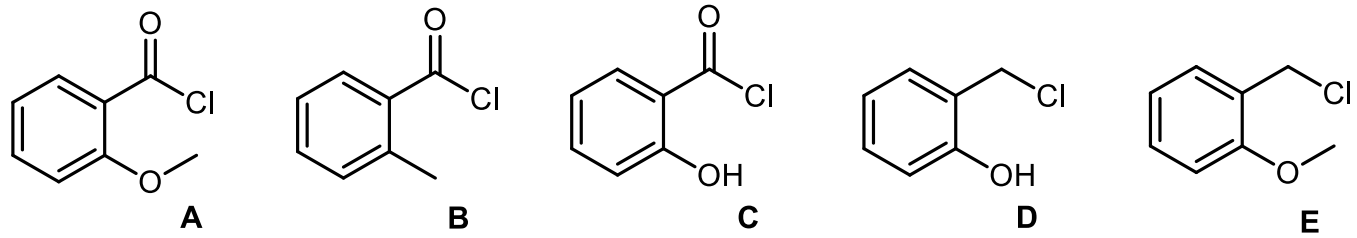
ANSWER ANY SEVEN (7) of the questions 24-31 (2 marks per question).

For each of questions 28 to 31, select the correct structure for the name provided:

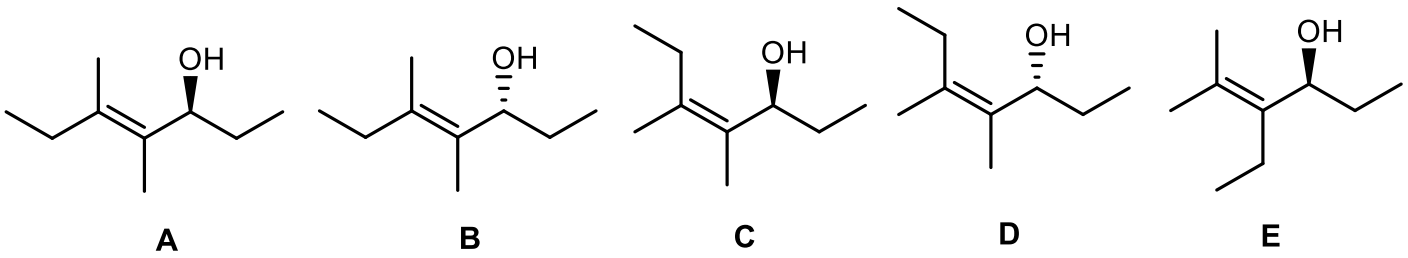
28. sec-butyl isopropyl ether



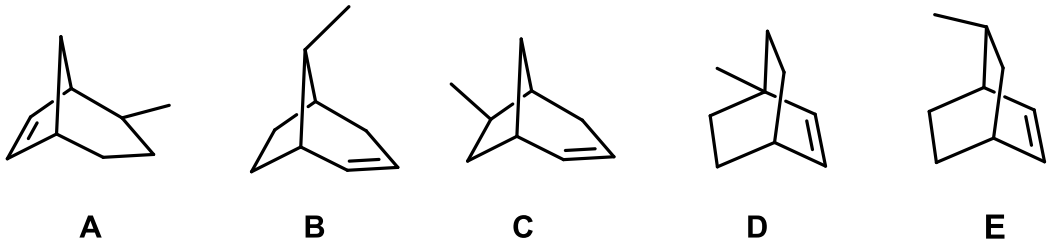
29. *o*-methoxybenzyl chloride



30. (3S,4Z)-4,5-dimethylhept-4-en-3-ol



31. 8-methylbicyclo[3.2.1]oct-2-ene:



13% PART 5: STRUCTURE DETERMINATION

Write your answer in the APPROPRIATE BOX on the ANSWER SHEET provided.
Show your work as PARTIAL marks may be awarded.

All questions in this section are to be answered using the molecular formula $C_4H_5FO_2$.

a) What is the molecular weight of $C_4H_5FO_2$?

b) What is the index of hydrogen deficiency (IHD, units of unsaturation) for this molecular formula ?

c) Draw a structure **C** with a *cis*-alkene and is soluble in aqueous $NaHCO_3$.

d) **i.** Draw a structure **D** that is an ester, but is not an alkene, and has a chirality center. Show the 3D arrangement of the groups at the chirality center using a wedge-hash representation).

ii. Assign the Cahn-Ingold-Prelog priority to the groups around the chirality center in part **d i** above.

iii. What is the chirality of the structure you have drawn in part **d i** above ?

13% **PART 6: THERMODYNAMICS**

Write your answer IN THE APPROPRIATE BOX on the ANSWER SHEET provided.
Show your work as PARTIAL marks may be awarded.

All questions in this section are based on three constitutional isomers **X**, **Y**, **Z** of C_5H_8.

a) Write a balanced reaction equation for the complete combustion of one isomer.

b) Given the thermodynamic data below, calculate the heat of formation for isomer **X** and the heat of combustion for isomer **Y** using the following heats of combustion: ΔH_c^o (graphite) = -94.05 kcal mol^{-1}, ΔH_c^o (H_2) = -68.32 kcal mol^{-1}.

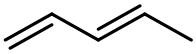
	Thermodynamic data in kcal mol^{-1}	
Compound	**ΔH_c^o**	**ΔH_f^o**
Isomer X	-766.95	**?**
Isomer Y	**?**	19.33
Isomer Z	**-**744.57	1.04

c) Draw an energy diagram (with clearly labeled reactants, products, **X**, **Y** and **Z**, and all ΔH values) to illustrate the relative energy difference between the three isomers.

d) On your energy diagram, compare the three isomers by **clearly labeling** the three isomers **X**, **Y**, **Z**. Indicate which is the most stable and which is the least stable.

e) The three constitutional isomers are:

i



ii

iii

Using bonding theory knowledge, match each of these three isomers **i-iii** to **X**, **Y**, **Z**, and briefly explain your reasoning

f). Draw another constitutional isomer (**iv**) of C_5H_8, with a C-H bond that is certainly weaker than every C-H bond in **i-iii.** Clearly label which C-H bond in your new structure is the weakest.

13% **PART 7: MECHANISM**

Write your answer in the APPROPRIATE BOX on the ANSWER SHEET provided. Show your work as PARTIAL marks may be awarded.

a) Draw a mechanistic sequence using double headed (*i.e.* electron pair) curly arrows that represents the reaction sequence described verbally by the following points in which an alkene, 1-methylcyclohex-1-ene, is hydrated using aqueous acid.

Step 1. Protonation of the alkene in 1-methylcyclohex-1-ene by a hydronium ion to make an organic carbocation and a water molecule.

Step 2. Attack of water as a nucleophile on the most electrophilic carbon of the organic carbocation to create a new C-O bond and an oxonium ion.

Step 3. Removal of a proton from the oxonium ion by a water molecule to regenerate the acidic catalyst to form 1-methylcyclohexan-1-ol.

b) If the carbocation in **step 2** (above) was reacted with methanol as the nucleophile instead of water, and then deprotonated with a base, **B:**, draw the structure of the organic product formed (mechanism not required) and give its systematic IUPAC name.

c) If the 1-methylcyclohexan-1-ol formed above in **step 3** was deprotonated using NaH to form an alkoxide (a nucleophile), then treated with methyl iodide to undergo a nucleophilic substitution, draw the structure of the organic product formed (mechanism not required).

**** THE END ****

 Cont'd

INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
$-CH_3$		(bend)	1450 and 1375	6.90 and 7.27	m
$-CH_2-$		(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		3500-3100	2.86-3.23	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

Cont'd

PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)