

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 351

November 2nd, 2011

Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

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

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 only Parts 5, 6, and 7 are to be answered in the booklet provided. A periodic table with atomic numbers and atomic weights and infrared data tables are located on the last two pages.

Parts 1 - 4 consist of a series of multiple choice questions numbered 1 - 33 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.

18% **PART 1: RELATIVE PROPERTIES**

ANSWER ANY NINE (9) of questions 1-10 (2 marks per question)

Arrange the items in questions 1-10 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

B. i > iii > ii

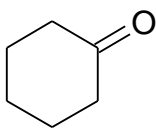
C. ii > i > iii

D. ii > iii > i

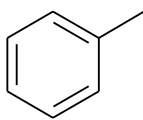
E. iii > i > ii

AB. iii > ii > i

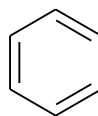
1. The relative acidities of the most acidic H in each of the following:



i

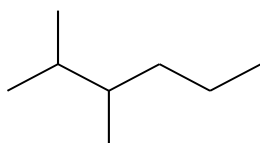


ii

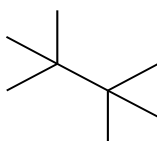


iii

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



i

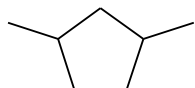


ii



iii

3. The number of types of hydrogen in each of the following:



i



ii



iii

Use the following code to indicate your answers.

A. $i > ii > iii$

B. $i > iii > ii$

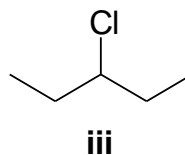
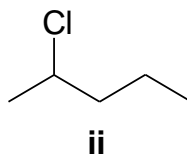
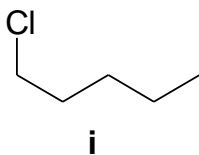
C. $ii > i > iii$

D. $ii > iii > i$

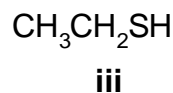
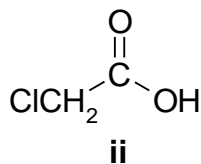
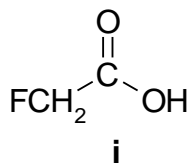
E. $iii > i > ii$

AB. $iii > ii > i$

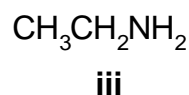
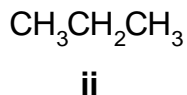
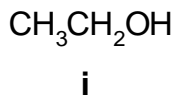
4. The relative yields of the following monochlorinated products from the u.v. light promoted reaction of Cl_2 with pentane:



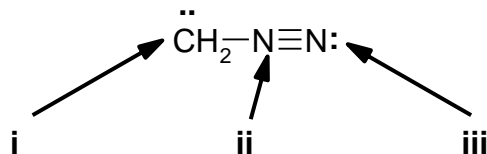
5. The relative acidity of each of the following:



6. The relative basicity of each of the following:



7. The formal charge associated with each of the atoms indicated (most positive to most negative):



Use the following code to indicate your answers.

A. i > ii > iii

B. i > iii > ii

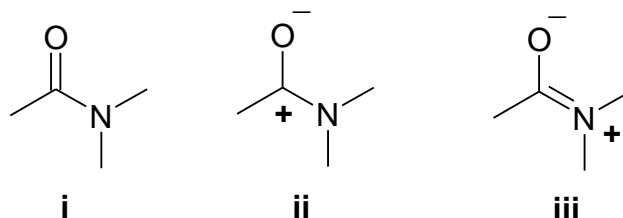
C. ii > i > iii

D. ii > iii > i

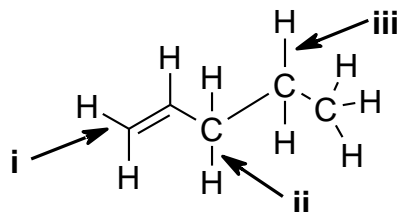
E. iii > i > ii

AB. iii > ii > i

8. The relative importance of the following resonance contributors to the structure shown (all required charges are shown):



9. The relative strength of the C-H bonds indicated:



10. The relative energies of the following orbitals on a C atom:

2p

i

sp²

ii

sp³

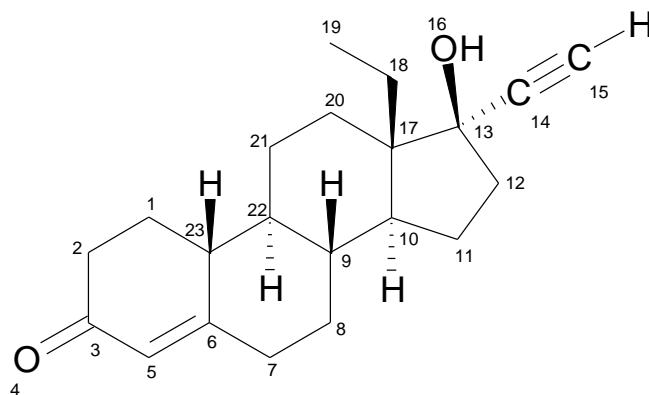
iii

18% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 11 – 19 (2 marks per question)

For each of the questions 11-19 select the appropriate answer from the answers provided. In some cases more than one selection may be required for full credit.

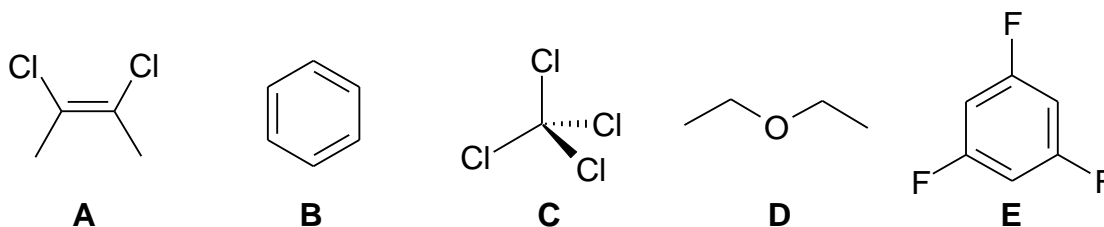
Questions 11 to 15 all refer to Norgestrel (structure shown below), a steroidal ingredient in oral contraceptives.



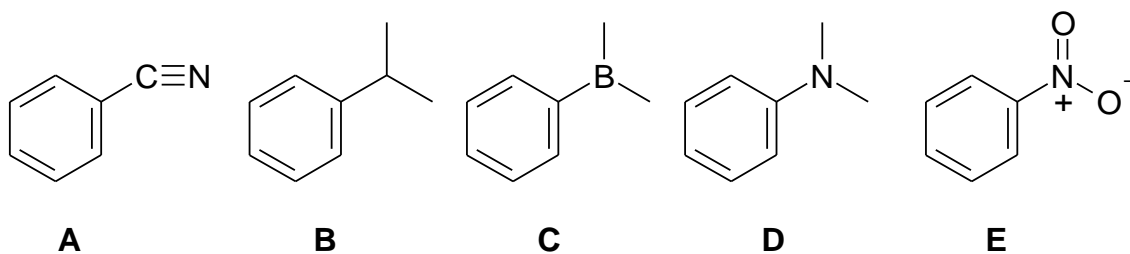
11. Which functional group(s) are present in Norgestrel ?
 A. Alcohol B. Alkene C. Alkyne D. Ester E. Ketone
12. How many π -bonds are present in Norgestrel ?
 A. 0 B. 1 C. 2 D. 3 E. 4 AB. 5 AC. More than 5
13. Which atom is the most acidic hydrogen in Norgestrel bonded to ?
 A. C2 B. C5 C. C15 D. O16 E. C23
14. Which of the following atoms in Norgestrel is / are sp^2 hybridized ?
 A. C3 B. O4 C. C15 D. O16 E. C20
15. Which bond in Norgestrel is the longest among those listed below ?
 A. C3-O4 B. C5-C6 C. C7-C8 D. C13-C14 E. C14-C15

For each of the questions 16-19 select the appropriate answer from the answers provided. In some cases more than one selection may be required for full credit.

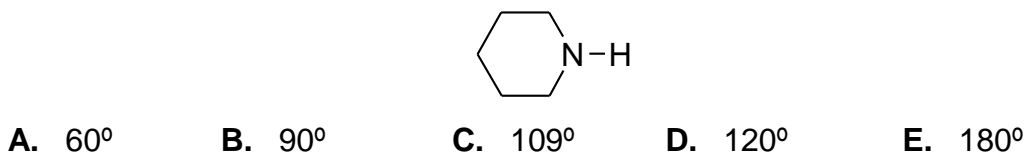
16. Which of the following molecules have a net dipole ?



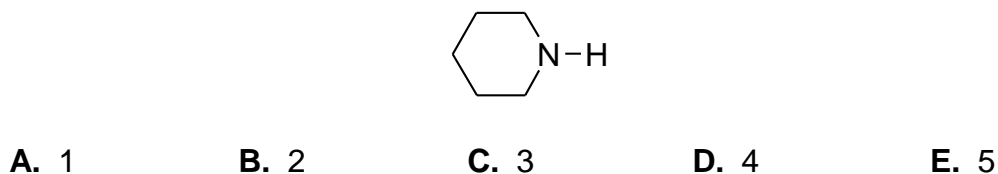
17. Which of the following species contains an atom with an incomplete octet of electrons in its valence shell ?



18. What is the C-N-C bond angle in piperidine (structure shown below) ?



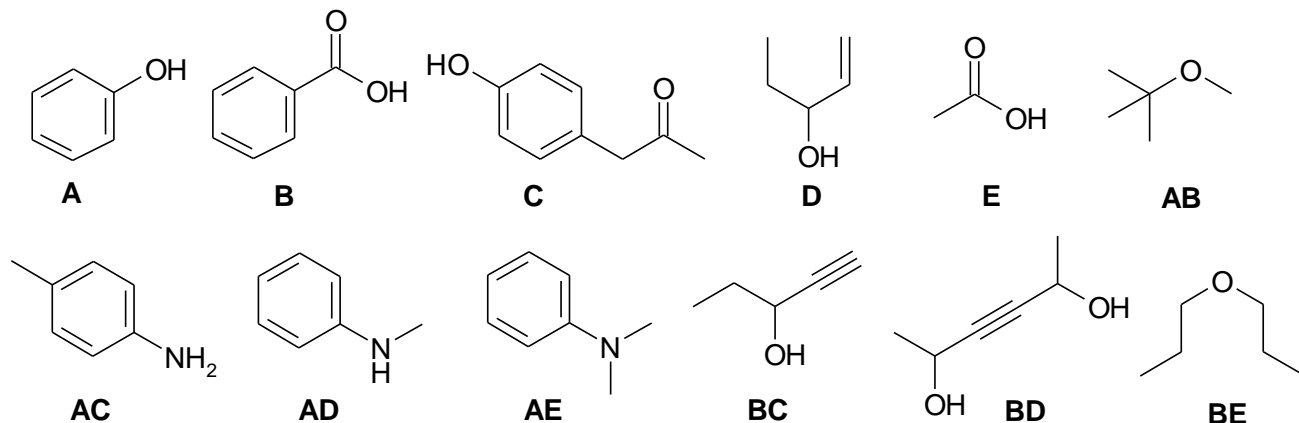
19. How many types of carbon are there in piperidine (shown below) ?



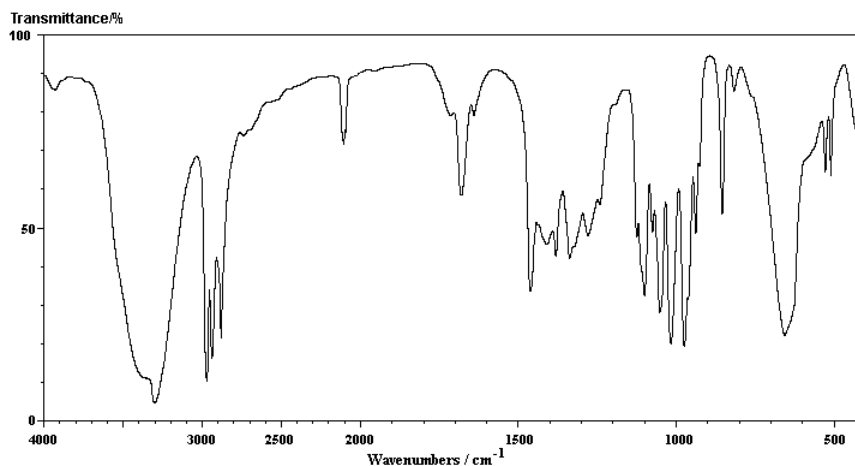
15% **PART 3: SPECTROSCOPY**

ANSWER ALL SIX (6) OF QUESTIONS 20 – 25 (2.5 marks per question).

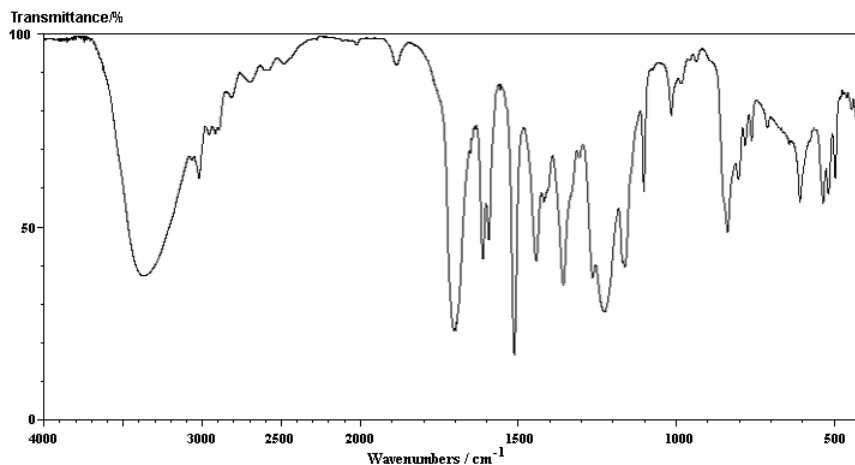
For each of the questions 20-25, use the spectroscopic data (and any additional experimental data) provided to match with a structure from the list below:

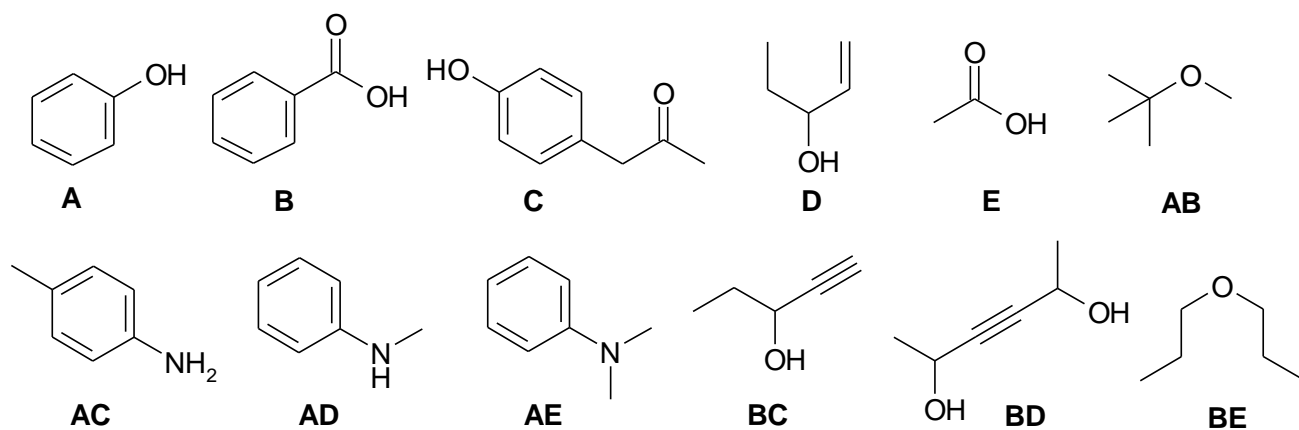


20. 5 types of hydrogen
IR spectrum:

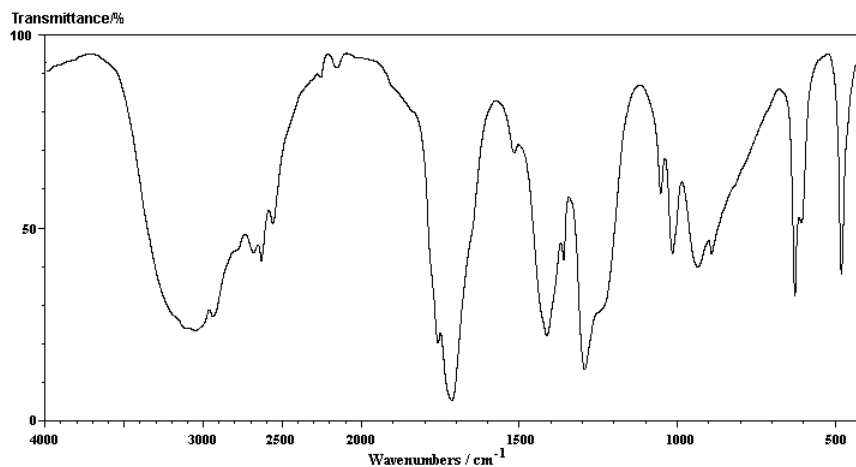


21. Positive ferric
chloride test (purple
colour)
IR spectrum:

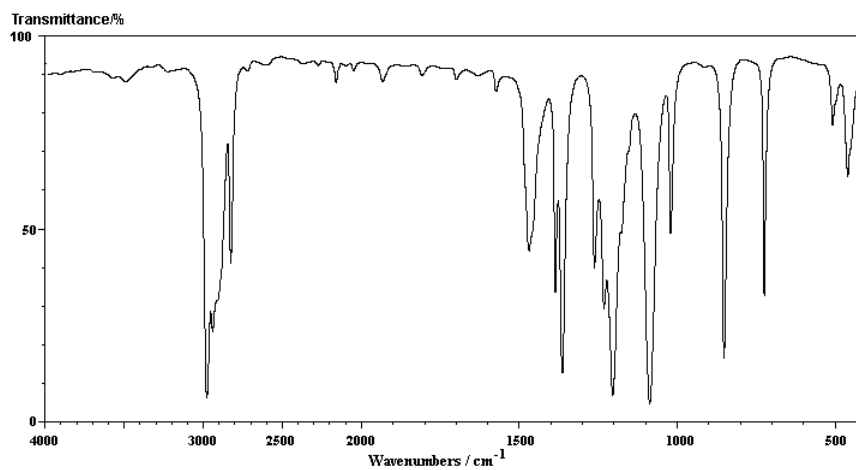


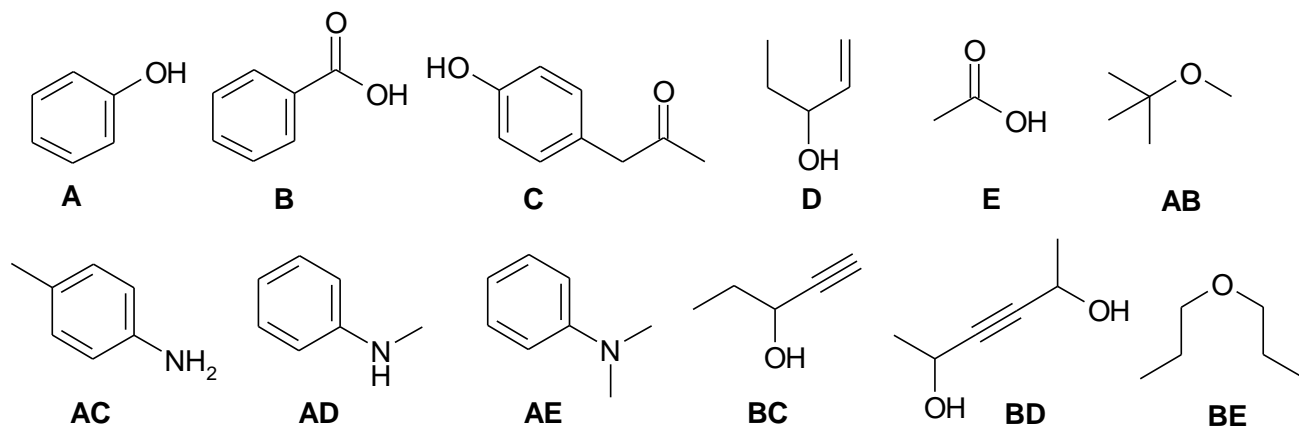


22. Soluble in:
 aq. 5% NaOH
 and
 aq. 5% NaHCO₃
 IR spectrum:

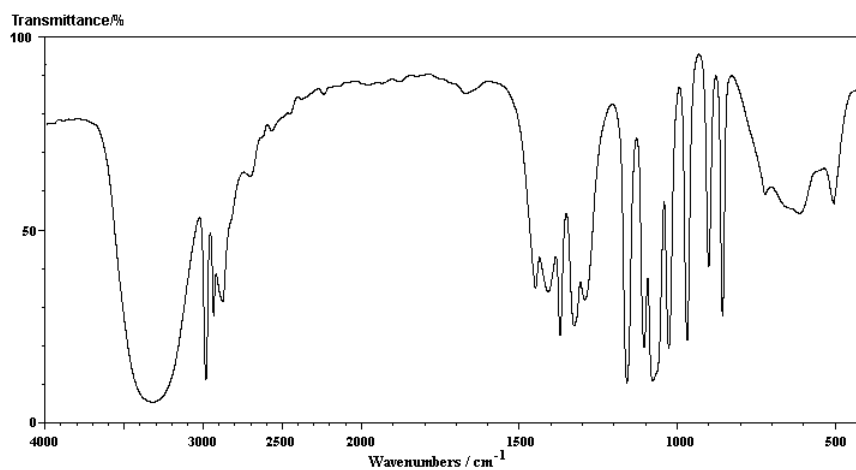


23. 2 types of hydrogen
 IR spectrum:

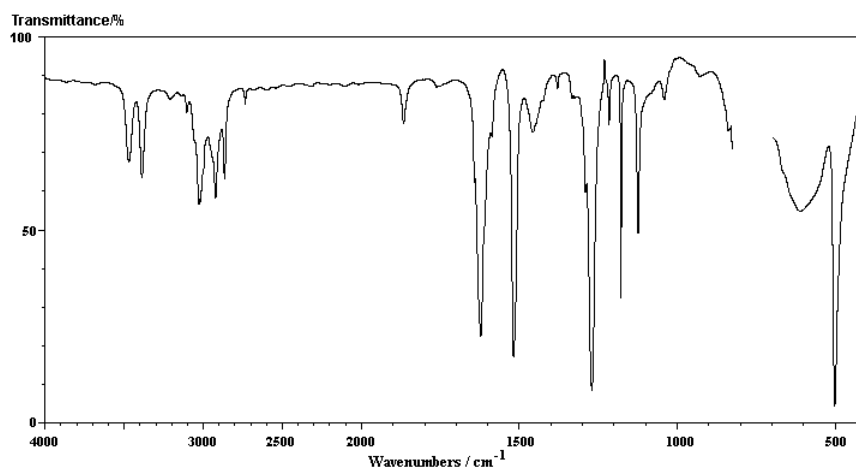




24. 3 types of hydrogen
IR spectrum:



25. Soluble in aq. 5%
HCl solution
IR spectrum:

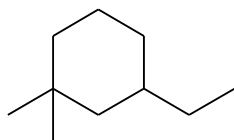


14% **PART 4: NOMENCLATURE**

ANSWER ANY SEVEN (7) of the questions 26-33 (2 marks per question).

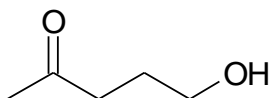
For each of questions 26 to 29, select the correct IUPAC name for the compound shown:

26



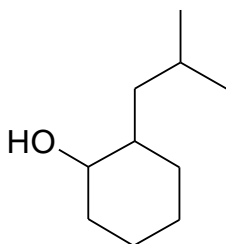
- A. 3,3-dimethyl-1-ethylcyclohexane
- B. 1,1-dimethyl-3-ethylcyclohexane
- C. 3-ethyl-1,1-dimethylcyclohexane
- D. 1-ethyl-3,3-dimethylcyclohexane
- E. 5-ethyl-1,1-dimethylcyclohexane

27



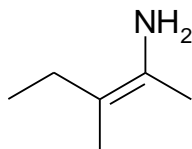
- A. 5-hydroxypentan-2-one
- B. 1-hydroxypentan-4-one
- C. 2-oxopentan-5-ol
- D. 4-oxopentan-1-ol
- E. 1-hydroxy-4-methylbutan-4-al

28



- A. 2-isobutylcyclohexan-1-ol
- B. 2-(2-methylethyl)cyclohexan-1-ol
- C. 2-2-methylethylcyclohexan-1-ol
- D. 1-(2-methylpropyl)cyclohexan-2-ol
- E. 1-butylcyclohexan-2-ol

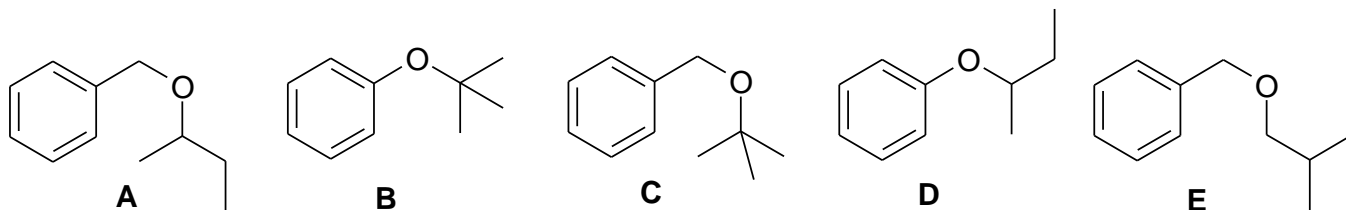
29



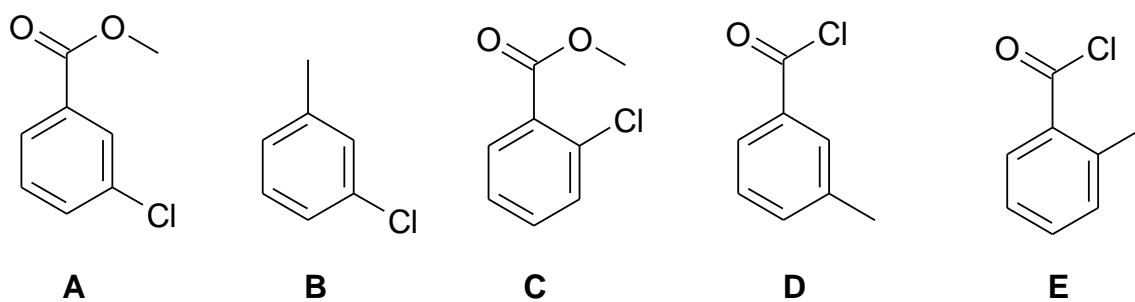
- A. (Z)-4-amino-3-methylpent-3-ene
- B. (E)-4-amino-3-methylpent-3-ene
- C. (Z)-2-amino-3-methylpent-2-ene
- D. (E)-2-amino-3-methylpent-2-ene
- E. cis-4-amino-3-methylpent-3-ene

For each of questions 30 to 33, select the correct structure for the IUPAC name provided:

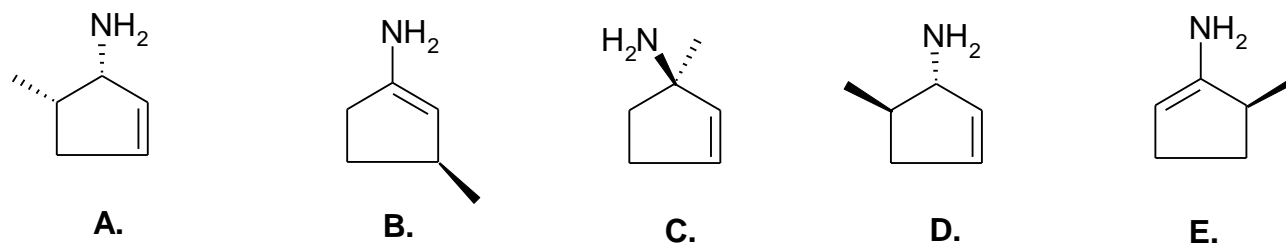
30. benzyl sec-butyl ether



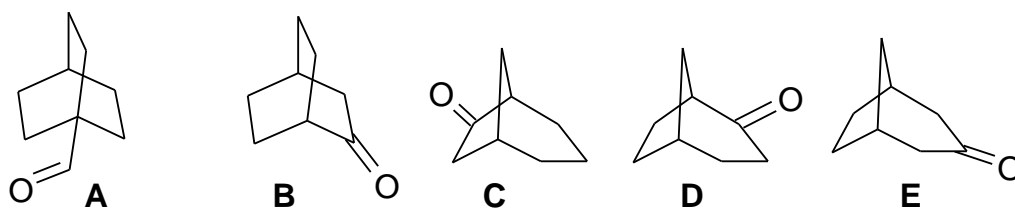
31. methyl *meta*-chlorobenzoate :



32. (S)-5-methylcyclopent-1-en-1-amine :



33. Bicyclo[3.2.1]octan-3-one:



12% **PART 5: STRUCTURE DETERMINATION**

Write your answer in the booklet provided. For FULL marks you MUST show your work. PARTIAL marks will be awarded.

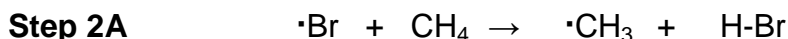
An organic molecule was determined to have a molecular formula of $C_{11}H_{16}$.

- a) What is the index of hydrogen deficiency for this molecule?
- b) Draw two possible isomers that would fit the molecular formula and would meet the criteria below:
- Isomer 1: contains at least one ring, and would react rapidly with Br_2 *without* requiring the presence of a catalyst or uv light. What is the name of this type of reaction with Br_2 ?
 - Isomer 2: contains at least one C-H bond that would be more easily deprotonated than the other C-H bonds in the molecule, with a pK_a value around 25. Briefly mention what makes this C-H bond acidic.
- c) Using the two isomers you drew in part (b), what spectroscopic technique could you use to tell these two isomers apart? How would this technique allow you to tell them apart?
- d) Isomer 3 of $C_{11}H_{16}$ shows a sharp stretch in its IR spectrum at 1609 cm^{-1} , has only 4 types of hydrogen, and when reacted with Br_2 and uv light gives only a single product with a molecular formula of $C_{11}H_{15}Br$.
- What isomer of $C_{11}H_{16}$ fits these data?
 - What is the product ($C_{11}H_{15}Br$) formed when this isomer reacted with Br_2 and uv light?
 - If the reaction was performed by mixing 1.00g of the $C_{11}H_{16}$ isomer with an excess of Br_2 and 0.80 g of the product ($C_{11}H_{15}Br$) was obtained, what was the percent yield of this reaction?

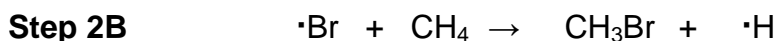
11% **PART 6: THERMODYNAMICS**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

Three steps (1A to 3A) in the radical bromination of methane are shown below:



- a) Write a balanced stoichiometric equation for the radical bromination of methane.
- b) Calculate the heat of reaction for the bromination of methane in either kJ or kcal/mol given the following bond dissociation energies:
- | | |
|---|--|
| C-H: 413 kJ mol ⁻¹ (98 kcal mol ⁻¹) | Br-Br: 193 kJ mol ⁻¹ (46 kcal mol ⁻¹) |
| C-Br: 288 kJ mol ⁻¹ (69 kcal mol ⁻¹) | H-Br: 366 kJ mol ⁻¹ (87 kcal mol ⁻¹) |
- c) Using your calculated answer from "part b" above, state whether the reaction is **exothermic** or **endothermic** ?
- d) Calculate the enthalpy change (ΔH) associated with **step 2A**.
- e) Steps (1B to 3B) of an *alternative* pathway for the radical bromination of methane are shown below:



Why is **mechanism B** less plausible than **mechanism A**?

- f) Suggest a reason why it would be unwise to use a large excess of bromine in the production of bromomethane ?

12% **PART 7: MECHANISM**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

a) Draw a mechanistic sequence using double headed (*i.e.* electron pair) curly arrows that represents the **single reaction sequence** described verbally by the following points in which an alkyne, but-1-yne, is alkylated using ethyl iodide in the presence of a base, sodium amide, to give hex-3-yne.

Step 1. An acid / base reaction of the amide ion from sodium amide where it deprotonates but-1-yne to give a nucleophilic carbanion and ammonia.

Step 2. Reaction of the nucleophilic carbanion with the electrophilic carbon in ethyl iodide to form a new carbon – carbon bond with the simultaneous loss of an iodide ion as a leaving group to give hex-3-yne and sodium iodide.

b) Draw the structure of another base that could be used to deprotonate but-1-yne for this reaction.

Answer parts c) – e) based on the above sequence:

c) What reagents could be used to synthesise hex-2-yne ?

d) What reagents could be used to synthesise 2-methylhex-3-yne ?

e) Could the analogous reaction of but-1-ene with ethyl iodide be used to prepare hex-3-ene ? Briefly justify your answer.

**** THE END ****

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	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 **