UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

November 4th, 2010 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.

PLEASE WRITE THE NUMBER OF YOUR LABORATORY SECTION AT THE TOP OF THE FRONT COVER ON YOUR BLUE ANSWER BOOKLET

18% PART 1: RELATIVE PROPERTIES

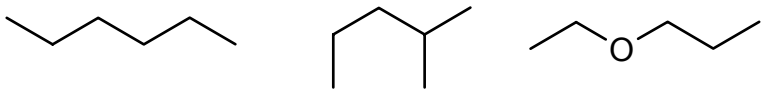
ANSWER ANY NINE (9) of questions 1-10 (2 marks per question)

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.

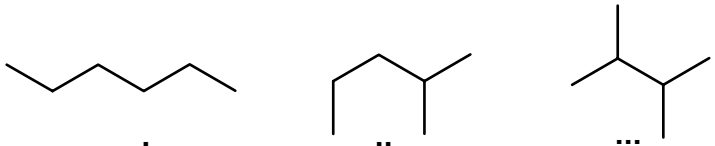
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

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



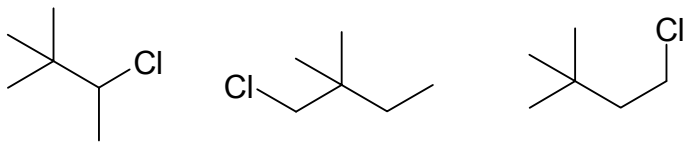
i **ii** **iii**

2. The heats of formation of the following (most exothermic to least exothermic)**:**



i **ii** **iii**

3. The relative yields of the following monochlorinated products from the u.v. light promoted reaction of Cl_2 with 2,2-dimethylbutane:

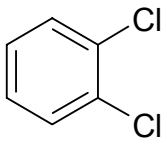


i **ii** **iii**

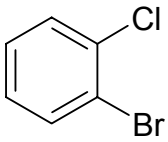
Use the following code to indicate your answers.

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

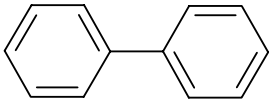
4. The number of peaks in the normal (broadband) ^{13}C-NMR of each of the following:



i

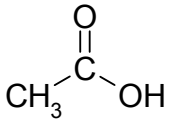


ii

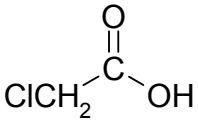


iii

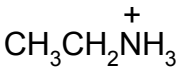
5. The relative acidity of each of the following:



i

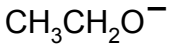


ii

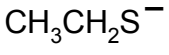


iii

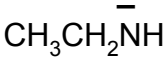
6. The relative basicity of each of the following:



i

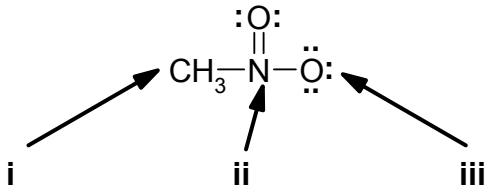


ii



iii

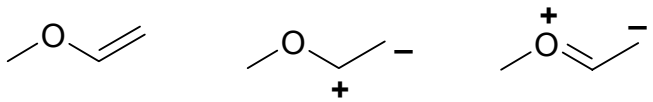
7. The formal charge associated with the atoms indicated (most positive to most negative):



Use the following code to indicate your answers.

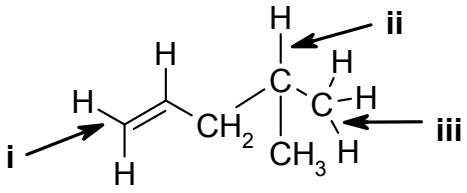
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

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

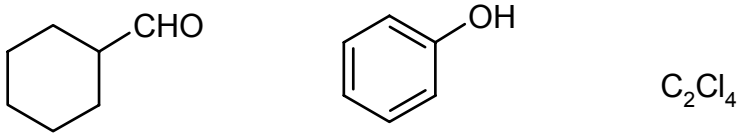


i **ii** **iii**

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



10. The relative IHD (index of hydrogen deficiency or units of unsaturation) of the following molecules:

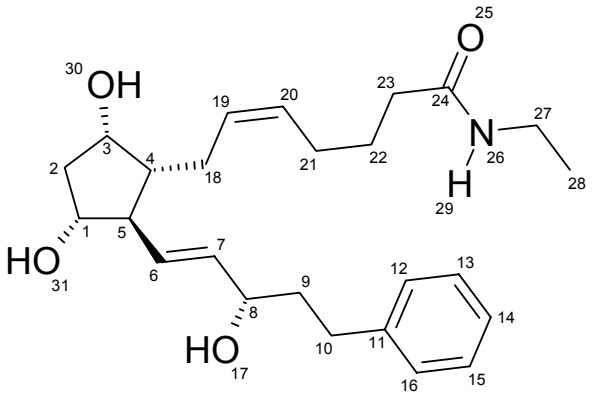


i **ii** **iii**

18% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 11 - 19.

Bimatoprost is a drug used to treat glaucoma, a leading cause of blindness. It is structurally similar to a group of lipid compounds called prostaglandins that have important functions in the animal body.



Bimatoprost

11. What is the IHD of Bimatoprost ?

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

12. What are the hybridizations of **O17** / **O25** respectively ?

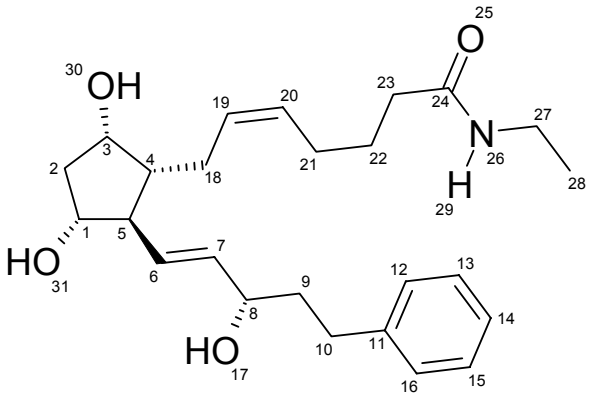
A. sp^3,sp^3 B. sp^3,sp^2 C. sp^2,sp^2 D. sp^2,sp E. sp^3,sp

13. What is the closest value to the **C9-C10-C11** bond angle ?

A. 90° B. 112° C. 109.5° D. 120° E. 180°

14. On which of the following atoms in Bimatoprost is the most acidic hydrogen atom ?

A. **C6** B. **C23** C. **C27** D. **N26** E. **O30**



Bimatoprost

15. Which C-H bond is the weakest among those listed below ?
    A. **C2-H** B. **C6-H** C. **C10-H** D. **C13-H** E. **C28-H**

16. Among the bonds listed below, which one is the shortest ?
    A. **C4-C18** B. **C11-C12** C. **C14-C15** D. **C19-C20** E. **C22-C23**

17. What type of orbital does the lone pair of **N26** occupy ?
    A. s B. p C. sp D. sp^2 E. sp^3

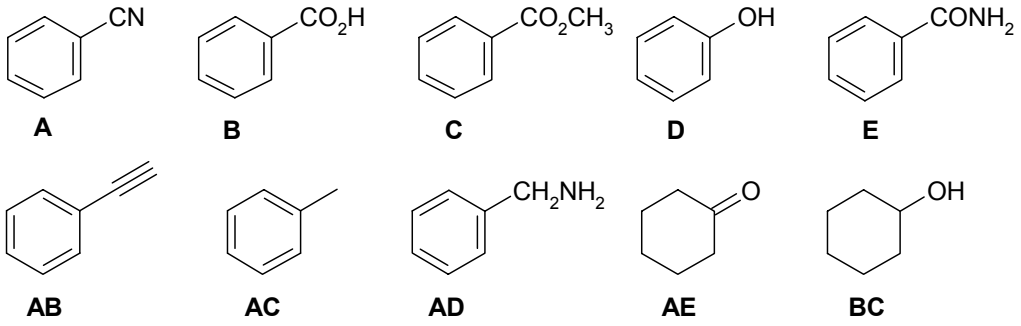
18. What functional groups are present in Bimatoprost?
    A. alcohol B. aldehyde C. amide D. amine E. ketone

19. What term(s) can be used to best describe **C1** ?
    A. primary B. secondary C. tertiary D. allylic E. benzylic

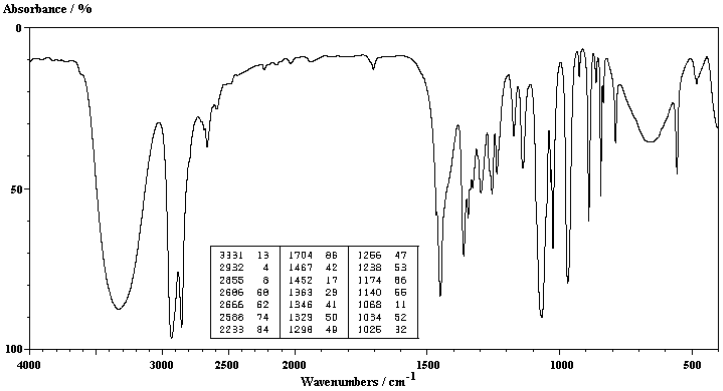
15% **PART 3: SPECTROSCOPY**

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

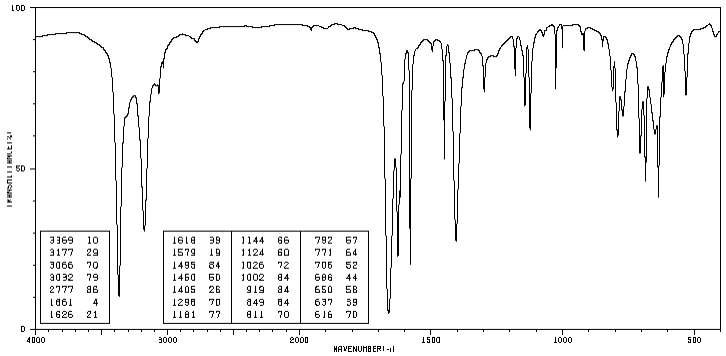
For each of the questions 20-25, match the IR spectra to a structure from the list provided below:



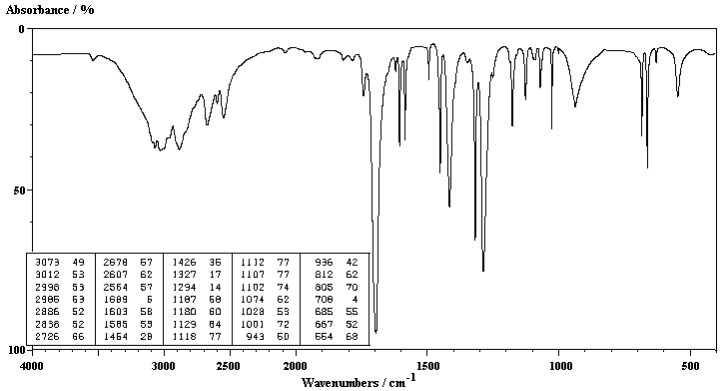
20

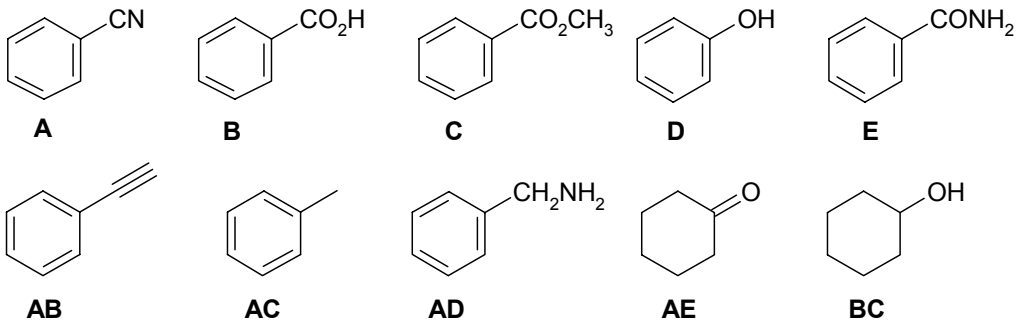


21

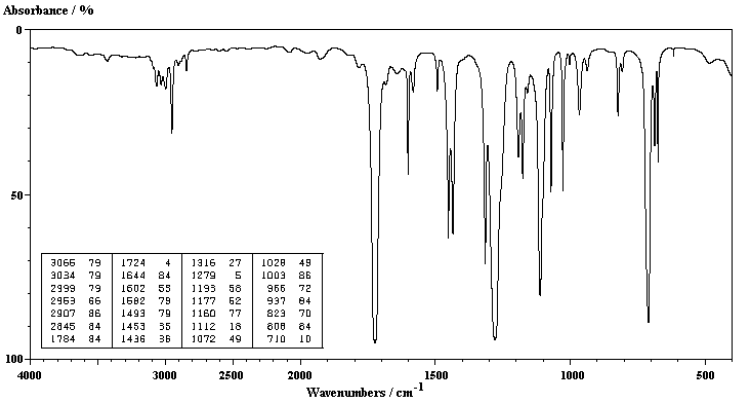


22

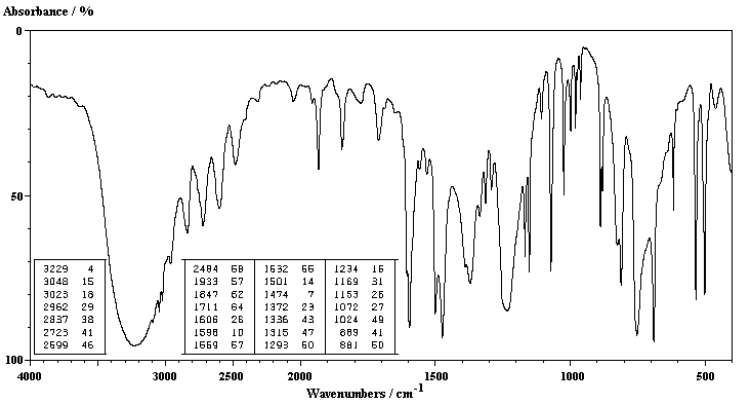



CN
CO2H
CO2CH3
OH
CONH2
A
B
C
D
E
CH2NH2
O
OH
AB
AC
AD
AE
BC

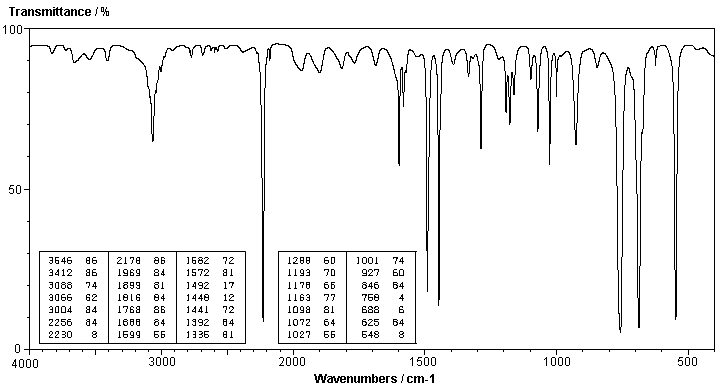
23


Absorbance / %
Wavenumbers / cm-1

24


Absorbance / %
Wavenumbers / cm-1

25

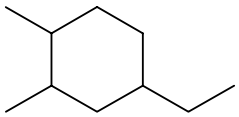

Transmittance / %
Wavenumbers / cm-1

14% **PART 4: NOMENCLATURE**

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

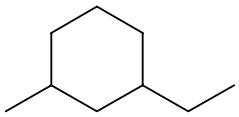
For each of questions 26 to 27, select the correct name for the compound shown:

26



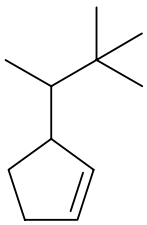
A. 1-ethyl-3,4-dimethylcyclohexane
B. 1,2-dimethyl-4-ethylcyclohexane
C. 4-ethyl-1,2-dimethylcyclohexane
D. 3-ethyl-1,6-dimethylcyclohexane
E. 5-ethyl-1,2-dimethylcyclohexane

27



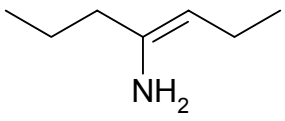
A. 1-ethyl-3-methylcyclohexane
B. 3-ethyl-1-methylcyclohexane
C. 1-methyl-3-ethylcyclohexane
D. 1-methyl-5-ethylcyclohexane
E. 5-ethyl-1-methylcyclohexane

28



A. 3-(1,2,2-trimethylpropyl)cyclopentene
B. 3-(2,2 dimethylbutyl)cyclopentene
C. 2-(2,2 dimethylbutyl)cyclopentene
D. 1-(1,2,2-trimethylpropyl)cyclopent-2-ene
E. 1-(1,1,2-trimethylpropyl)cyclopent-2-ene

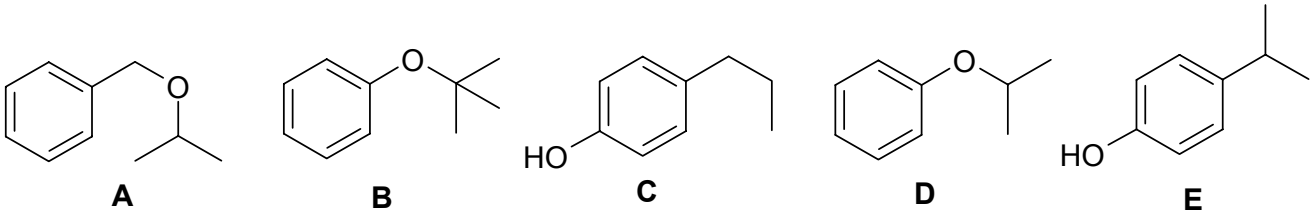
29



A. (Z)-4-aminohept-3-ene
B. (E)-4-aminohept-3-ene
C. (Z)-4-aminohept-4-ene
D. (E)-4-aminohept-4-ene
E. cis-4-aminohept-4-ene

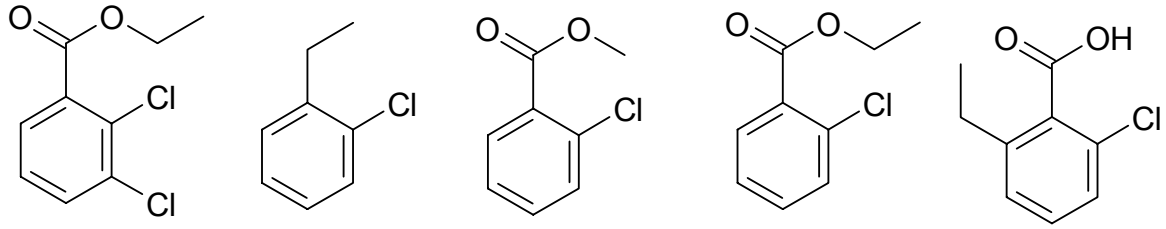
For each of questions 30 to 33, select the correct structure for the name provided:

30. isopropyl phenyl ether



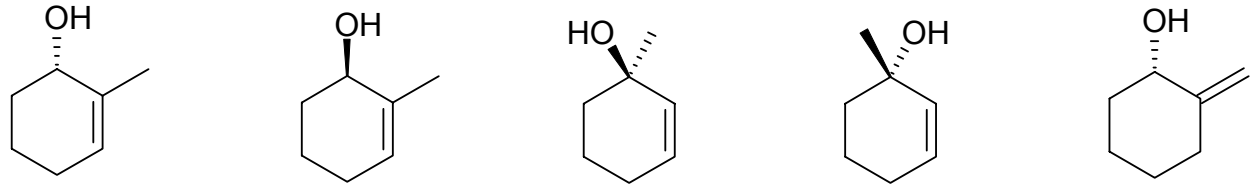
A **B** **C** **D** **E**

31. ethyl *ortho*-chlorobenzoate :



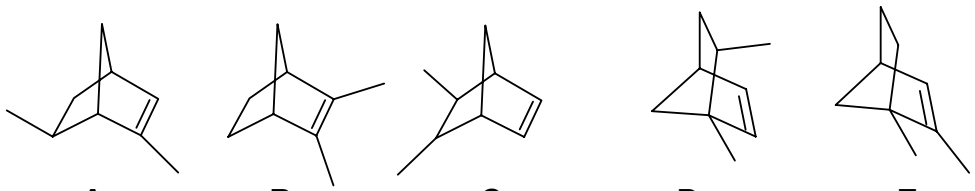
A **B** **C** **D** **E**

32. (S)-2-methylcyclohex-2-en-1-ol :



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

33. 1,2-dimethylbicyclo[2.2.1]hept-2-ene:



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

11% PART 5: STRUCTURE DETERMINATION

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

Elemental analysis on an organic molecule was found to have 88.2% carbon and 11.8% hydrogen by weight. The mass spectrum revealed a molecular ion at *m/z* 68.

a) What is the empirical formula ?

b) What is the molecular formula ?

c) What is the index of hydrogen deficiency ?

d) **Draw** a structure that matches the above data and has two types of hydrogen and four types of carbon.

e) **Draw** a structure that matches the above data and has two types of hydrogen and three types of carbon.

f) **Draw** a structure that matches the above data and has one type of hydrogen and two types of carbon.

12% **PART 6: THERMODYNAMICS**

2,2-Dimethylhexane and 2,2,3,3-tetramethylbutane are structural (constitutional) isomers.

a) Write a balanced equation for the combustion of these C_8H_{18} isomers.

b) One of these isomers has a heat of combustion (ΔH_C^o) = -1303.0 kcal mol^{-1}. Calculate ΔH_f^o, for this isomer using the following heats of combustion:

ΔH_C^o, C (graphite) = -93.9 kcal mol^{-1}

ΔH_C^o, H_2 (gas) = -68.4 kcal mol^{-1}

c) If the other C_8H_{18} isomer has a heat of formation (ΔH_f^o) = + 30.4 kcal mol^{-1}, which of the above named isomers correspond to which heat of formation ? STATE which isomer is more stable and justify your choice.

d) When 2,2,3,3-tetramethylbutane was treated with an equimolar amount of chlorine and irradiated with ultraviolet light, it produced a single monochlorinated derivative. Calculate the heat of reaction given the following bond dissociation energies:

C-H: 105 kcal $mole^{-1}$

C-Cl: 84 kcal $mole^{-1}$

Cl-Cl: 58 kcal $mole^{-1}$

H-Cl: 103 kcal $mole^{-1}$

e) Is the reaction exothermic or endothermic ?

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 a carboxylic acid, benzoic acid, is alkylated using 1-bromopropane in the presence of a base, ammonia, to yield propyl benzoate.

Step 1. Deprotonation of benzoic acid by ammonia to create the conjugate base of benzoic acid (which is a carboxylate ion).

Step 2. Attack of the carboxylate ion as a nucleophile on the electrophilic carbon of 1-bromopropane producing propyl benzoate with the simultaneous loss of a bromide ion as the leaving group.

(b) NAME another base that could be used to deprotonate benzoic acid for this reaction.

(c) Based on the above sequence, what reagents could be used to synthesize isopropyl benzoate ?

(d) Based on the above sequence, what reagents could be used to prepare phenyl propyl ether ?

(e) Is a phenol more or less acidic than a carboxylic acid ? Briefly explain why.

**** THE END ****

ASC / IRH / TGB Nov 2010

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
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
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)