CHEM 2OA3 FINAL EXAM December 17, 2008 VERSION 1

NAME (First & Last): _____ ID#:_____

Lab Station: _____ (Print 'E' if you are exempt from the labs)

Please circle your lab section in the table below.

Group	Monday	Tuesday	Wednesday	Thursday	Friday
I	L01	L02	L03	L04	L05
II	L06	L07	L08	L09	L10

Duration: 180 minutes Instructor: Harald Stöver

Instructions: This examination paper consists of 27 pages, containing 20 (twenty) multiple choice (MC) questions, and 6 short-answer questions. You are responsible for ensuring your copy of the question paper is complete. A mini-periodic table and spectral correlation charts are provided on the last two pages. Feel free to detach these last pages for easier use.

Answer all the MC questions on optical scan sheets. Each MC question is worth two marks and you will not be penalized for incorrect answers. Follow the instructions on the optical scan sheets, and the University rules for OMR exams which are reproduced on page 2. Failure to follow instructions may result in loss of credit.

You are responsible for ensuring all answers are in the correct place, and that you follow the correct procedure for filling out the scan sheet.

Mark your student number in the space provided on the sheet on Side 1 AND FILL IN THE CORRESPONDING BUBBLES UNDERNEATH. Now enter your version number, which can be found on the top right hand corner of this page, by filling in the BUBBLE in the "version" column provided. You MUST sign the sheet in the space provided.

All McMaster rules and procedures relating to **Academic Dishonesty and Academic Integrity** apply to this exam; **all violations will result in a penalty**. Students **must** do their own work. A program designed to detect similar answers will be used for this exam.

You MUST also complete ALL the information at the top of this page.

MC	Written Section						
	Q21	Q22	Q23	Q24	Q25	Q26	Written Tot.
/40	/15	/12	/10	/5	/10	/8	/60

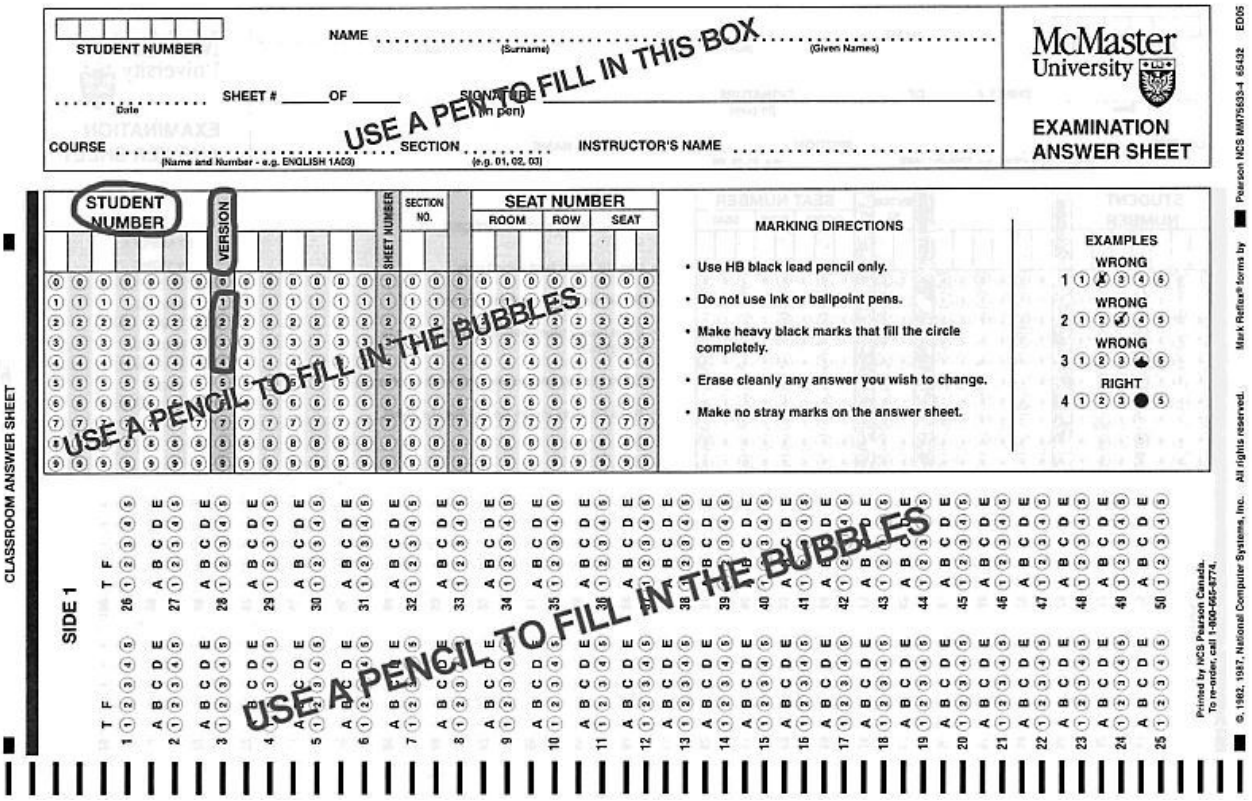
 Continued on next page

OMR EXAMINATION – STUDENT INSTRUCTIONS

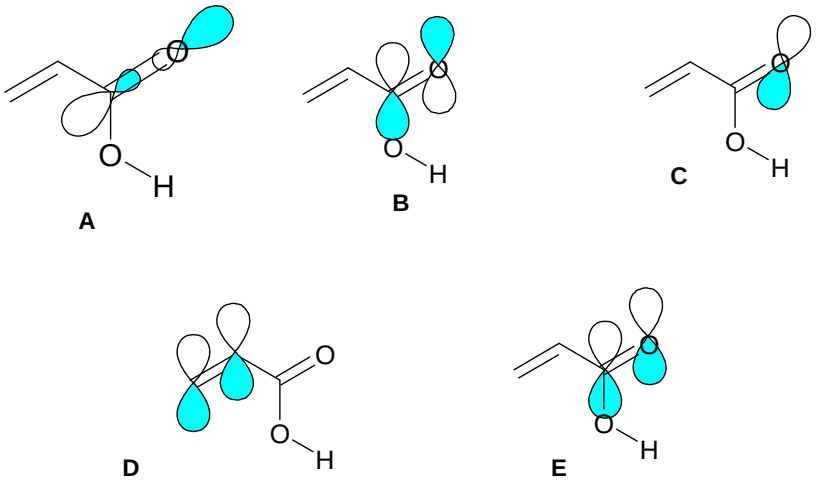
NOTE: IT IS YOUR RESPONSIBILITY TO ENSURE THAT THE ANSWER SHEET IS PROPERLY COMPLETED. YOUR EXAMINATION RESULT DEPENDS UPON PROPER ATTENTION TO THESE INSTRUCTIONS.

The scanner, which reads the sheets, senses the bubble shaded areas by their non-reflection of light. **A heavy mark must be made, completely filling the circular bubble, with an HB pencil.** Marks made with a pen will **NOT** be sensed. Erasures must be thorough or the scanner will still sense a mark. Do **NOT** use correction fluid on the sheets. Do **NOT** put any unnecessary marks or writing on the sheet.

1. On SIDE 1 (**red side**) of the form, in the top box, print your student number, name, course name, and the date in the spaces provided, *in pen*. Then you **MUST** write your signature, in the space marked SIGNATURE.
2. In the second box, mark your **student number** and **test or exam version number (1, 2, 3 …)** by filling in the corresponding bubbles underneath, *in pencil*.
3. Answers: mark only **ONE** choice from the alternatives (A,B,C,D,E) provided for each question. The question number is to the left of the bubbles. Make sure that the number of the question on the scan sheet is the same as the number on the test paper. Begin answering Question # 1 using the first set of bubbles, marked "1". Do Not use Side 2.



1. Which orbital drawing best represents the carbonyl bonding π molecular orbital of propenoic acid (acrylic acid)?



2. Rank the following intermolecular interactions in order of increasing strength.

i. van der Waals interaction
ii. ionic interactions
iii. hydrogen bonding
iv. dipole - dipole interactions

A. i < ii < iii < iv
B. i < iv < iii < ii
C. ii < iii < i < iv
D. iv < i < ii < iii
E. iii < ii < i < iv

Continued on next page

3. Identify the correct rankings of acid strengths in the pairs of compounds listed below

i. propanol > propane

ii. ethanol > aminoethane

iii. ethene > ethyne

iv. 2-chloro acetic acid > 2-fluoro acetic acid

A. i, ii

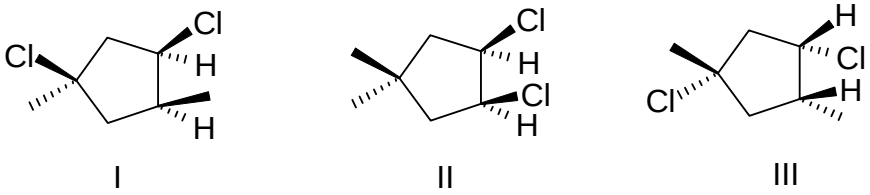
B. i, iii

C. ii, iii

D. ii, iv

E. iii, iv

4. The three structures below all represent dichloro-dimethylcyclopentane. Indicate the correct statements with respect to these structures.



I II III

A. i and ii are enantiomers, while iii is a *meso* compound

B. i and iii are enantiomers, while ii is a *meso* compound

C. ii and iii are enantiomers, while i is a *meso* compound

D. ii and iii are identical compounds, while i is a *meso* compound

E. i and iii are all identical structures, while ii is a *meso* compound

Continued on next page

5. Indicate the correct statements below:

i. S_N2 reactions, due to their bimolecular nature, are always faster than S_N1 reactions

ii. In E2 and S_N2 reactions, the properties of the leaving group plays an important role

iii. E1 reactions often lead to mixtures of products, and are hence rarely desirable.

iv. In order to avoid eliminations, S_N1 reactions are best carried out with excess nucleophile and at low temperature.

A. i, ii

B. ii, iii, iv

C. ii, iv

D. iii

E. iii, iv

6. Indicate the correct statement regarding S_N1 reactions of alkyl halides.

A. The rate of an S_N1 reaction depends on the concentration of the alkyl halide.

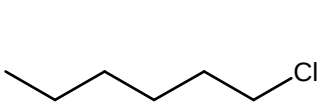
B. The rate of an S_N1 reaction depends on the concentration of the nucleophile.

C. S_N1 reactions of alkyl halides are faster in polar aprotic solvents than in polar protic solvents

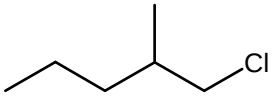
D. Answers A and C only are true.

E. Answers A, B and C are true.

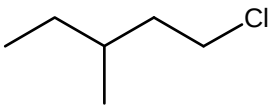
7. Which one of these primary alkyl chlorides is essentially unreactive in S_N2 reactions?



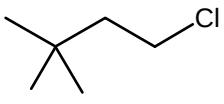
A



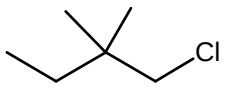
B



C



D



E

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8. Which product(s) would be formed in appreciable amount(s) when *trans*-1-bromo-2-methylcyclohexane undergoes dehydrohalogenation (E2) by treatment with sodium ethoxide in ethanol?

I II III IV

A. I

B. II

C. III

D. IV

E. More than one of these

9. Indicate the correct statement(s) below:

i. Bimolecular eliminations proceed through an anti-coplanar transition state

ii. Stronger bases tend to favour E2 over E1 reactions

iii. Dehydrohalogenation with strong, unhindered bases tends to give the more highly substituted alkene product, where possible.

iv. On secondary substrates, small unhindered bases/nucleophiles can give S_N2 product, while larger, hindered bases/nucleophiles tend to give E2 products.

A. i, iii, iv

B. ii, iii

C. ii, iii, iv

D. iii, iv

E. All of the above

Continued on next page

10. A mixture of two compounds is injected onto a Gas Chromatograph. Compound A elutes before compound B. You know that both of these compounds were formed through a substitution mechanism (either S_N1 or S_N2). What does the order of elution tell you about the mechanism by which the compounds were formed?

A. Compound A was formed by S_N2; Compound B by S_N1

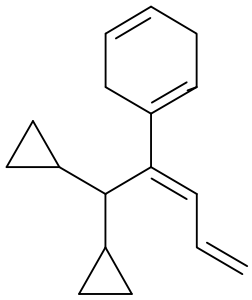
B. Compound B was formed by S_N2, Compound A by S_N1

C. Both were formed by S_N2 mechanisms

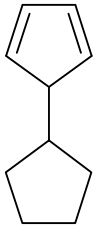
D. Both were formed by S_N1 mechanisms

E. Elution time tells you nothing about the mechanisms

11. You are asked to test the following molecules for unsaturation, using acidic permanganate:



1



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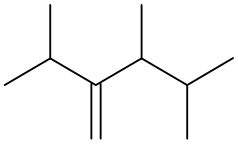
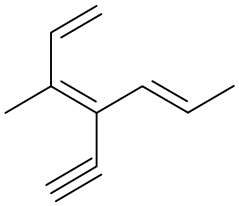


3



4

Rank the molecules in order of smallest to largest amount of permanganate decolorized per millimole of compound.

A. 1 < 2 < 3 < 4

B. 3 < 2 < 1 < 4

C. 3 < 2 < 4 < 1

D. 2 < 3 < 1 < 4

E. 2 < 1 < 4 < 3

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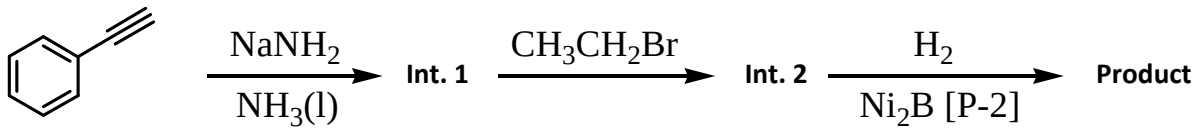
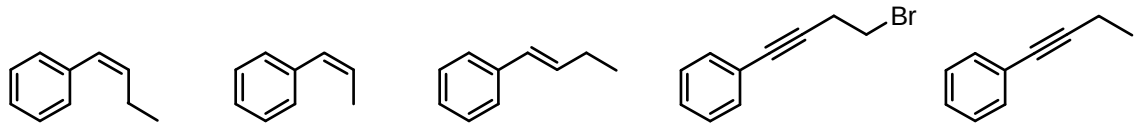
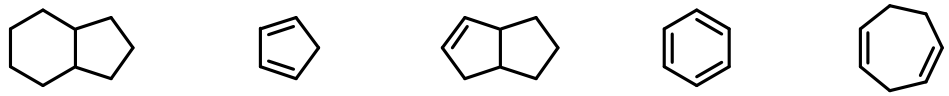
12. Indicate the likely product of the following sequence of reactions:





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

13. Which of the compounds below has an index of hydrogen deficiency of three, and absorbs one molar equivalent of hydrogen when treated with hydrogen over a platinum catalyst?



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

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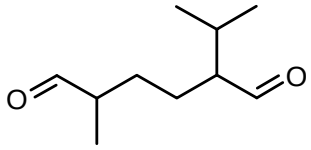
14. An alkene with the molecular formula $C_{10}H_{18}$ is treated with ozone and then with zinc and acetic acid. The only product isolated from these reactions is the dialdehyde shown on the right:



What is the structure of the alkene?

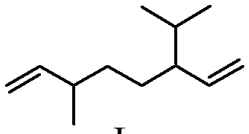
A. I

B. II

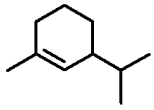
C. III

D. IV

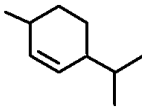
E. V



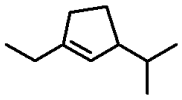
I



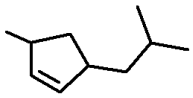
II



III

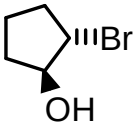


IV

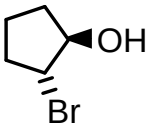


V

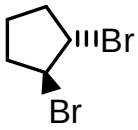
15. Which of these compounds are formed **to at least some extent** when cyclopentene is reacted with an aqueous solution of bromine?



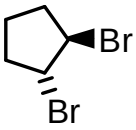
I



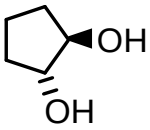
II



III



IV



V

A. I, II, V

B. I, II, III, IV

C. III, IV,

D. I, II, V

E. I, II

Continued on next page

16. Which reaction would give a *meso* compound as the product?

A. Cyclopentene + Br_2/CCl_4

B. Cyclopentene + OsO_4, then $NaHSO_3$

C. Cyclopentene + RCO_3H, then H_3O^+

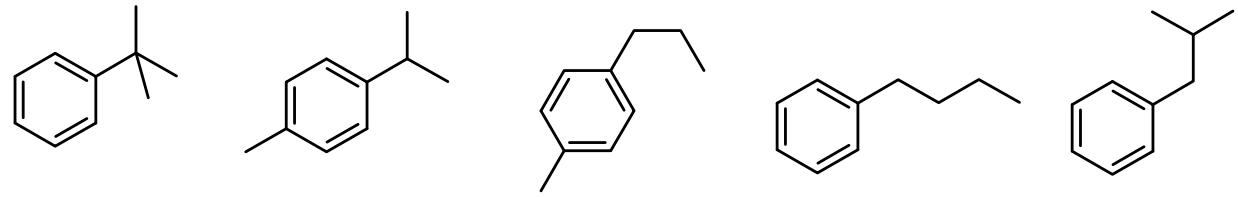
D. Cyclopentene + Cl_2, H_2O

E. More than one of these

17. A compound with the molecular formula $C_{10}H_{14}$ gave the following ^1H NMR spectrum:

doublet at 1.2 ppm; singlet at 2.3 ppm; septet at 2.8 ppm; multiplet at 7.1 ppm

Select a possible structure for the compound:



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

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18. The intensity data below, taken from the molecular ion region of the mass spectrum of a halogen-containing compound, are consistent with the presence of what halogen(s) in the original compound?

M^+ 51.0

$M^+ + 2$ 100.0

$M^+ + 4$ 49.0

A. One Br

B. One Cl

C. One Br and one Cl

D. Two Br

E. Two Cl

19. For which of the following gas-phase reactions would the E^{act} be equal to dH°?

A. Cl–Cl → 2Cl·

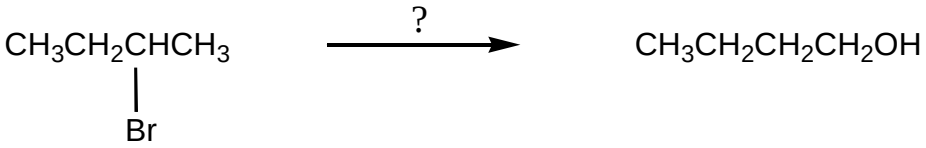
B. 2 Cl· → Cl–Cl

C. Cl· + CH_4 → CH_3· + H–Cl

D. CH_3· + CH_3· → CH_3–CH_3

E. CH_3· + Cl–Cl → CH_3–Cl + Cl·

20. Which would be the best way to carry out the following synthesis?



A. (1) HA, heat; (2) H_3O^+, H_2O, heat

B. (1) $(CH_3)_3COK$ / $(CH_3)_3COH$; (2) BH_3:THF, then H_2O_2, OH^-

C. (1) $(CH_3)_3COK$ / $(CH_3)_3COH$; (2) H_3O^+, then H_2O, heat

D. (1) KOH, C_2H_5OH; (2) BH_3:THF, then H_2O_2, OH^-

E. (1) KOH, C_2H_5OH; (2) HA, heat; (3) H_3O^+, H_2O, heat

Continued on next page

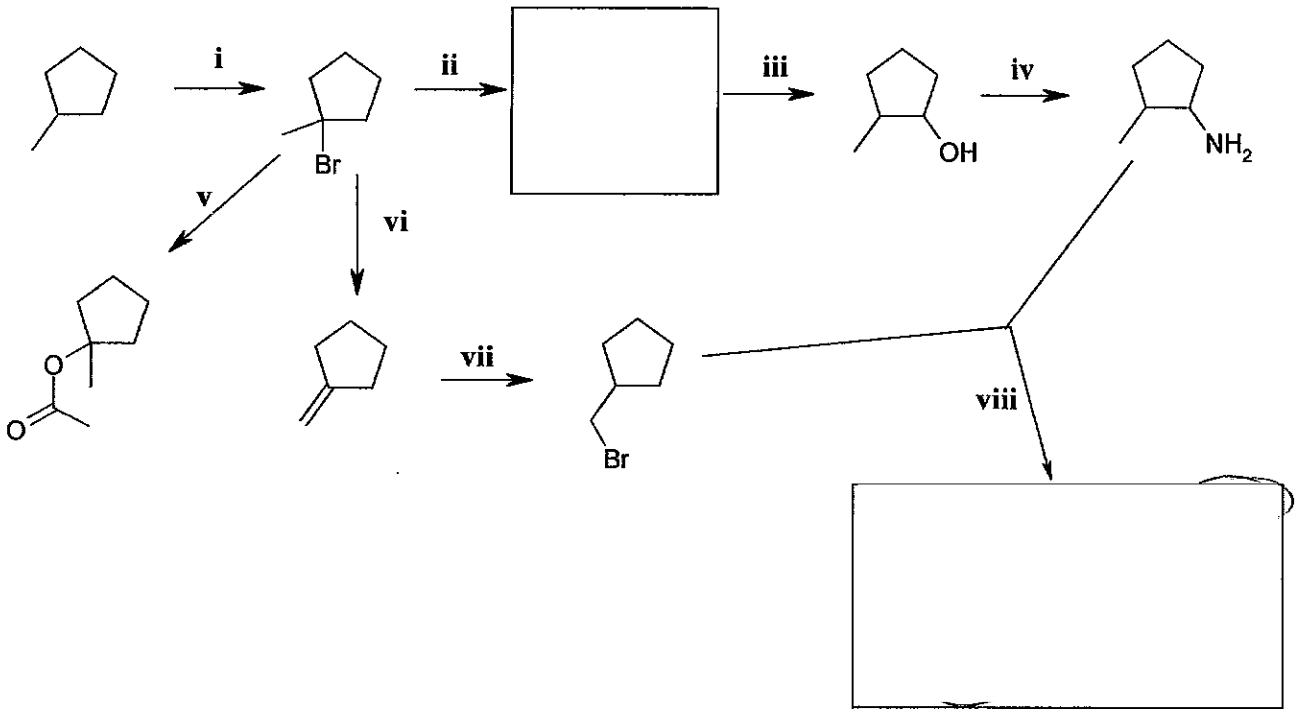
MC Answers 2OA3 Exam 2008

Version1
1. E
2. B
3. A
4. B
5. B
6. A
7. E
8. B
9. E
10. E
11. B
12. A
13. C
14. C
15. B
16. B
17. B
18. D
19. A
20. B

Note: on some questions there is more than one correct answer. Reasonable alternate answers will get full or part marks.

SHORT ANSWER SECTION: (6 questions, total 60 pts)

21. [15] This question concerns reactions starting from methylcyclopentane:



A. For reaction steps i to viii, write the most suitable reagents, and the mechanism (i.e. E2, S_N2, Markovnikov addition, Oxidation, etc), for each of the eight reactions shown in the scheme above. If multiple steps are required, separate them accordingly as in 1. and 2., etc.

(Reagents) **(Mechanism)**

[1] i. Reagents / mechanism are:

[1] ii. Reagents / mechanism are:

[2] iii. Reagents / mechanism are:

[2] iv. Reagents / mechanism are:

Continued on next page

(Question 21 continued...) **(Reagents)** **(Mechanism)**

[1] v. Reagents / mechanism are

[1] vi. Reagents / mechanism are

[2] vii. Reagents / mechanism are:

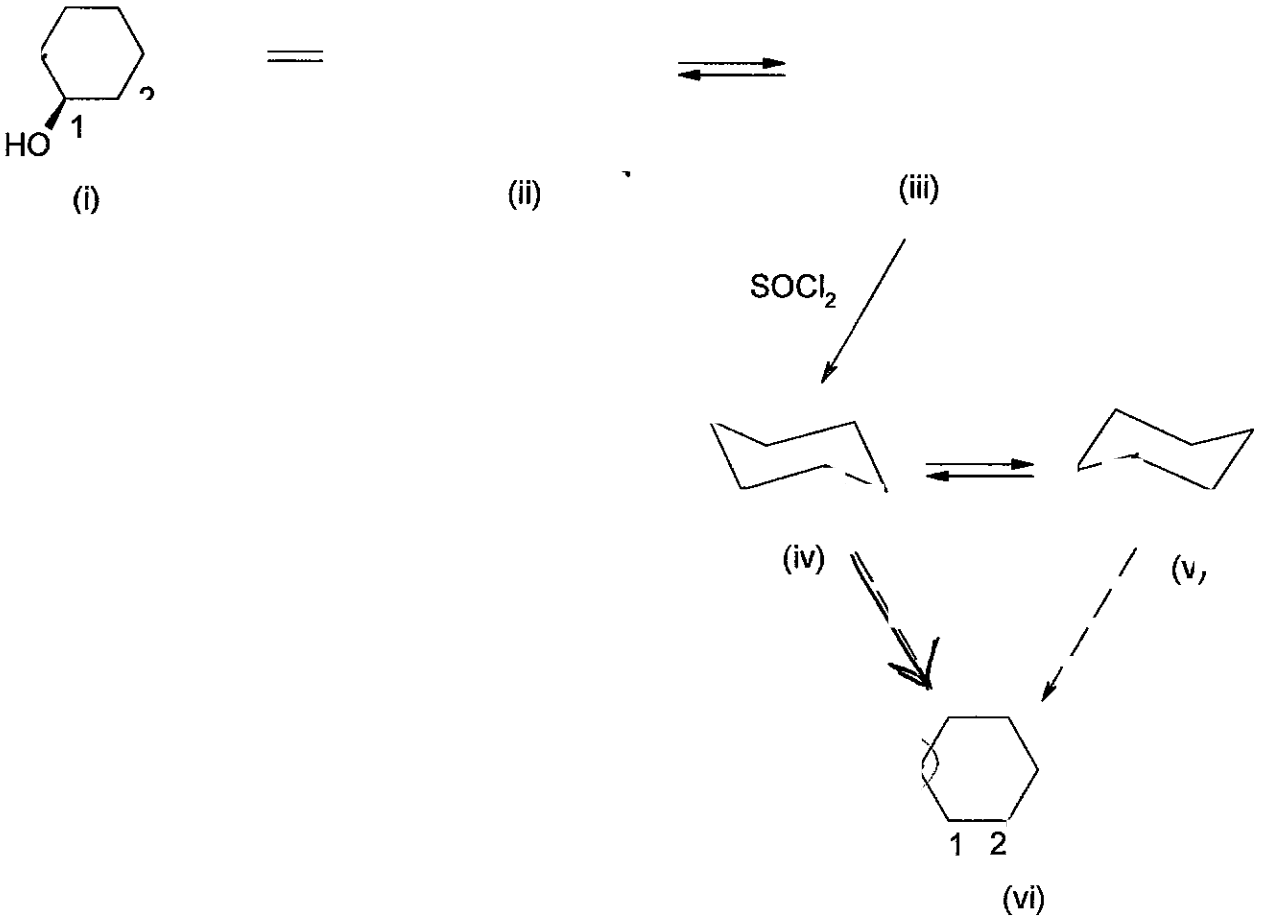
[1] viii. Mechanism is:

[2] **B.** Draw the two missing compounds into the two boxes provided in the above scheme.

[2] **C.** Draw below the complete mechanism for step v, including intermediate(s).

Continued on next page

22. [12] Answer the questions below, using dashed / wedged bonds, and equatorial / axial bonds, as appropriate, to show stereochemistry on the two types of template provided. Check each step to avoid propagating errors. Follow the carbon numbering indicated.



[2] i. Complete the cyclohexane template (i) to reflect (1*S*, 2*S*, 6*S*)-2-ethyl-6-methyl-cyclohexanol. Show the stereochemistry using dashed and wedged bonds.

[3] ii. Redraw the starting material in the chair template (ii), using axial and equatorial bonds.

[1] iii. Show the product of a chair-to-chair interconversion to the more stable conformation.

[2] iv. Show the product obtained by reacting (iii) with $SOCl_2$ / pyridine.

[1] v. Show the product of a chair-to-chair interconversion of (iv).

[3] vi. Indicate, by redrawing the correct dashed arrow, which one of (iv) or (v) would react with $NaOCH_3$ in methanol by E2 to form alkene (vi), and complete the alkene (vi).

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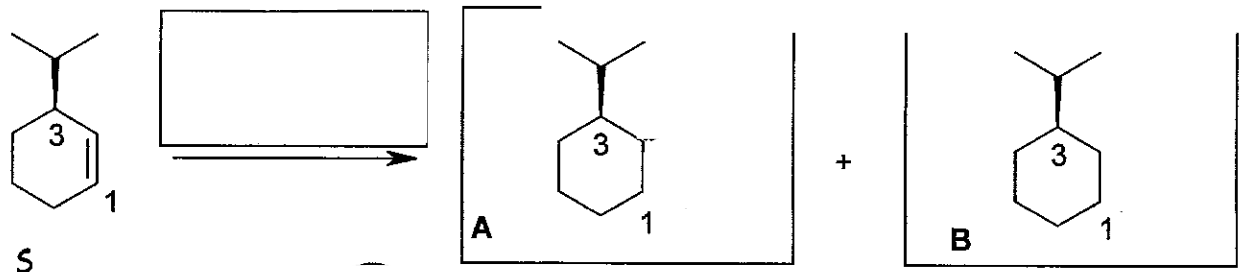
23. [10] This question concerns reactions on substituted cyclohexenes. Follow the carbon numbering indicated.



(3S)-3-isopropyl-cyclohexene

( )-1,2-dihydroxy-3-isopropyl-cyclohexane

( )-1,2-dihydroxy-3-isopropyl-cyclohexane

[1] i. Write, into the box above the reaction arrow, reagents and reaction conditions required to convert the above (3S)-3-isopropyl-cyclohexene into two ***cis* diols, A** and **B**:

[1] ii. Complete the structures for the two resulting diols in the boxes labeled A and B, using the same molecular orientation as in the starting material. Indicate stereochemistry with wedged and dashed bonds. Use the lead provided in **A**, and do not show hydrogens.

[1] iii. Complete the names of **A** and **B** by writing the correct stereochemical designations into the brackets provided in front of the two names.

[1] iv. Circle the correct stereochemical relationship between **A** and **B:**

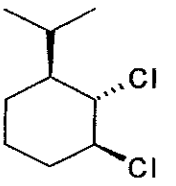
enantiomers diastereomers *meso* compounds different constitutional isomers

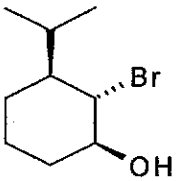
[1] v. One of the two products **A** and **B** above will likely be produced in slight excess. Which one would it be, and in one sentence, explain why:

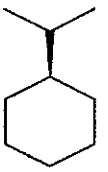
Continued on next page

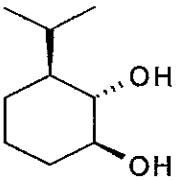
(Question 23 cont...)

[5] vi. Write the reagents/conditions needed to convert the above (3S)-3-isopropyl-cyclohexene starting material into the following 4 products (ignore stereo or regio isomers), into the boxes below:









[1]	[1]	[1]	[2]
			1.
			2.

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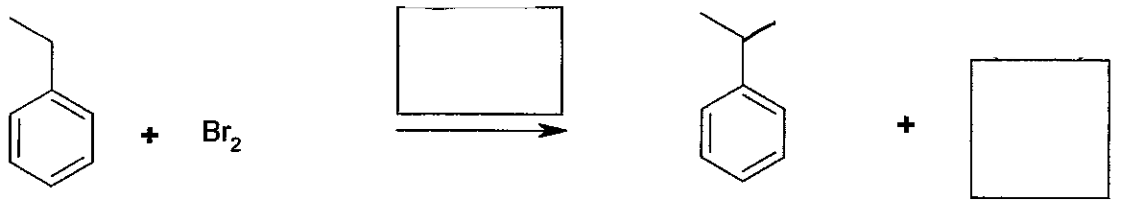
24. [5] This question relates to the monobromination of ethylbenzene by a chain reaction.



[1] i. Complete the above reaction scheme by writing the reaction conditions, and the missing product, into the two boxes provided.

[1] ii. Complete the structure of the bromoethylbenzene product above, by drawing one bromine into the most likely position on the ethylbenzene template above (see BDE table, ignore stereochemistry).

[1] iii. Carefully draw the reaction mechanism for the initiation step, using curly arrows:

[1] iv. Draw the reaction mechanisms for the propagation steps:

[1] v. Draw the mechanism for any one of the three possible termination reactions:

Continued on next page

Answer the questions below, concerning unknown **A**:

i. What are all of the oxygen containing groups possibly present in **A**, according to the IR (ignore ethers):

ii. From the ^{13}C-NMR data, indicate the number of types of carbon present:

iii. Estimate the total (integer) number of carbons present in the molecule, based on the **relative** intensities of the M^+ and $M^+ +1$ peaks (Intensities of 14.4 : 1.2, or 100 : 8.3):

iv. Are bromine or chlorine are present in the molecule?

v. [2] The ^{1}H-NMR shows three signals, *a* through *c*, from left to right in the spectrum. In the first row of the table below, write the (minimum) **number of protons** for each of these signals. In the second row, write the number of protons **coupling** to each of these signals.

	a 2.36ppm	*b* 1.59ppm	*c* 0.9ppm
Minimum number of protons in this set of protons			
Number of protons **coupling** to this set of protons			

vi. [2] Draw the structure of the unknown **A twice, once in each box.**

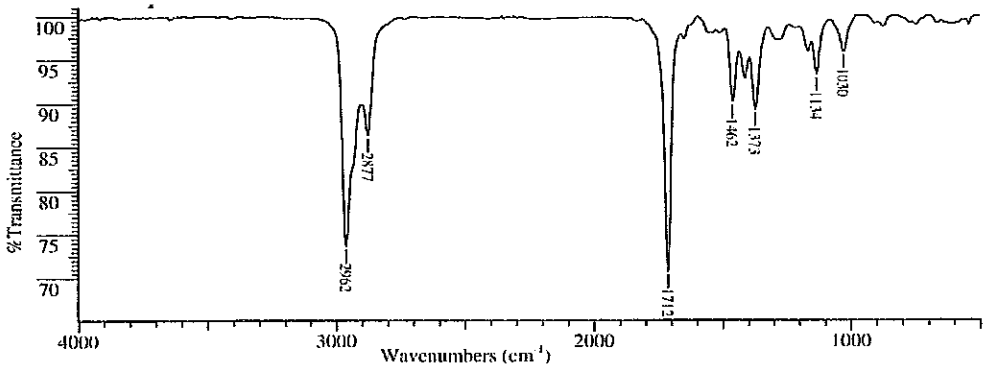
Label with a, b, c	Label with 1, 2, 3, 4

vii. [2] Label the structures of **A** with ***a*** to ***c***, and ***1*** to ***4***, as in the ^{1}H and ^{13}C NMR spectra.

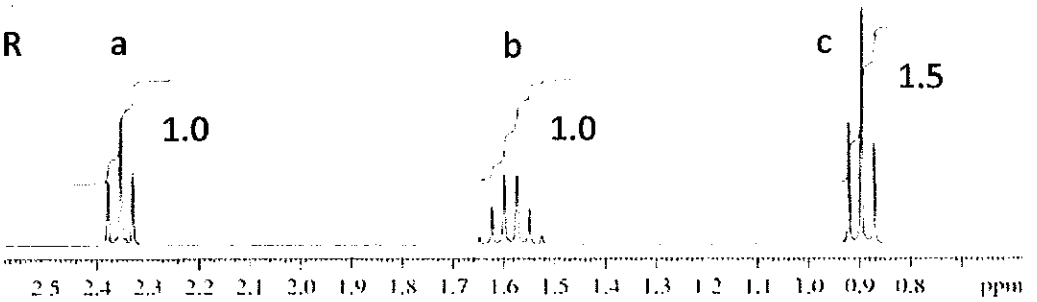
Continued on next page

25. [10] Elucidate the structure of the unknown **A** by examining its spectra, shown below.

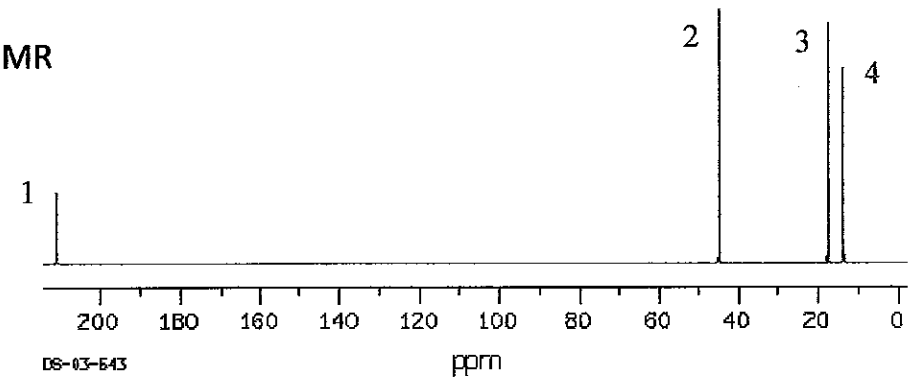
IR



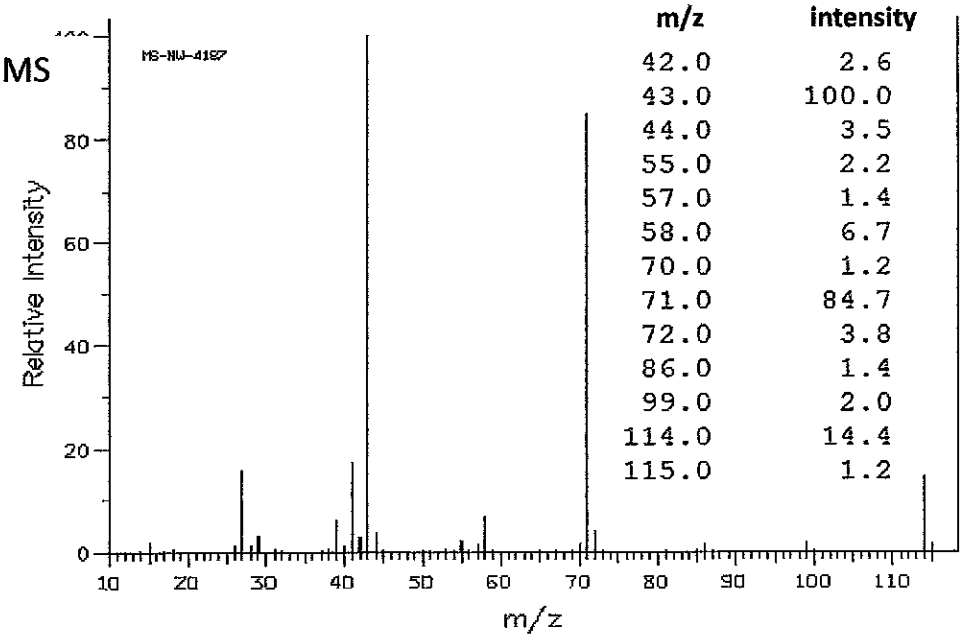
^{1}H-NMR



^{13}C-NMR



MS



m/z	intensity
42.0	2.6
43.0	100.0
44.0	3.5
55.0	2.2
57.0	1.4
58.0	6.7
70.0	1.2
71.0	84.7
72.0	3.8
86.0	1.4
99.0	2.0
114.0	14.4
115.0	1.2

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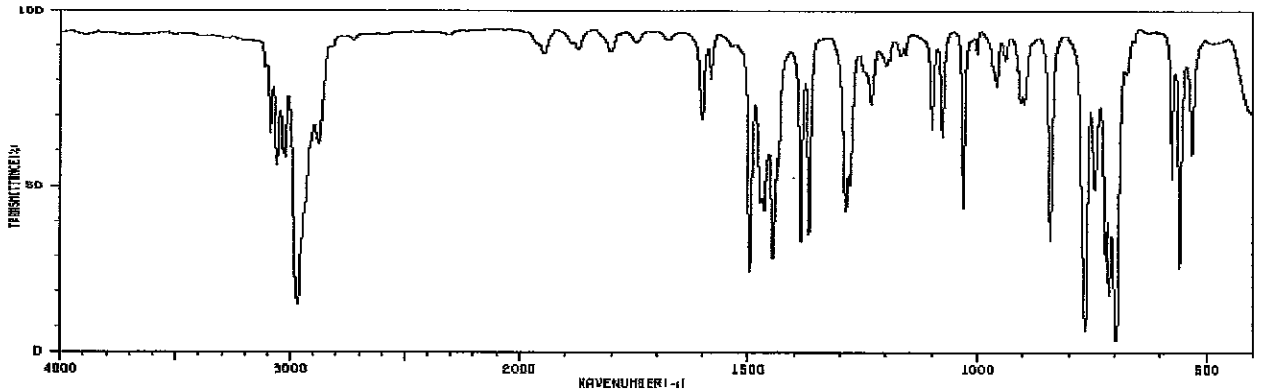
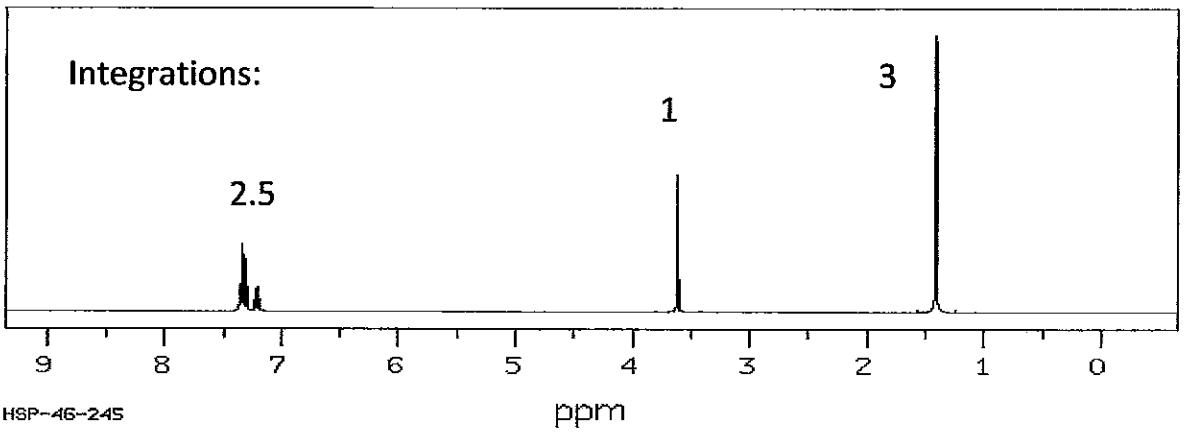
26. [8] Answer the following questions about unknown **B**, based on its spectra below:

IR



^{1}H-NMR



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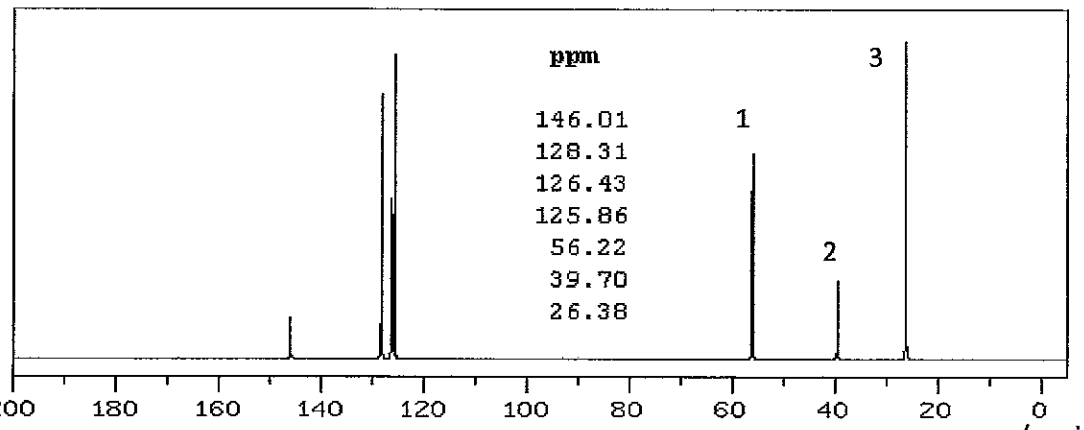
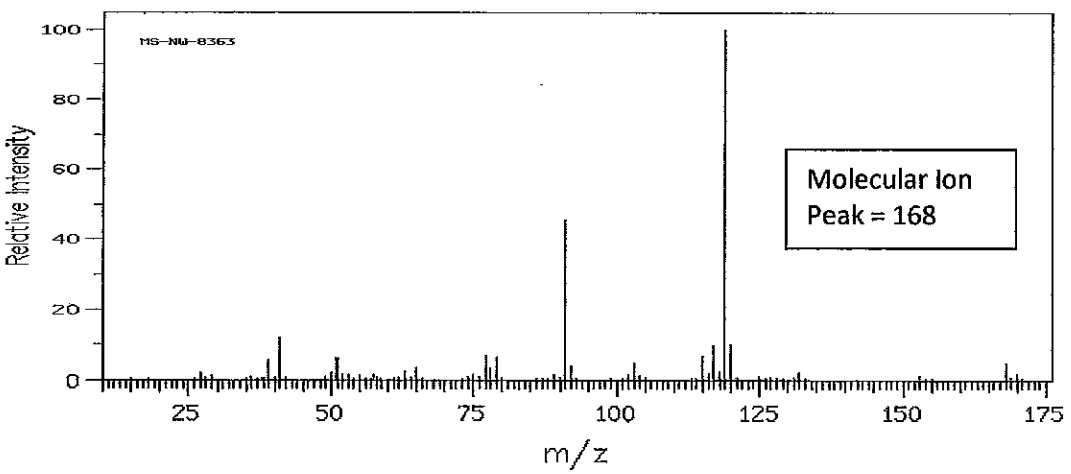
^{13}C-NMR



MS



m/z	intensity
91.0	45.7
92.0	3.7
102.0	1.3
103.0	4.5
104.0	1.0
115.0	6.4
116.0	1.6
117.0	9.6
118.0	2.1
119.0	100.0
120.0	10.0
132.0	1.8
153.0	1.0
168.0	4.7
170.0	1.54

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i. In the table below, list all available evidence for the presence of an aromatic ring.

IR	^{1}H NMR	^{13}C NMR	MS

0.5 0.5 0.5 0.5

ii. How many different types of carbons are present in the molecule?

[0.5]

iii. How many protons are likely present in the molecule?

[0.5]

iv. Which halide is present, and what is the evidence?

[1]

v. What is the total number of carbons present, given that the M^+ +1 peak intensity (at 169 m/z, not shown) is 11.35 % of the M^+ peak intensity?

[1]

vi. [2] Draw the structure of the unknown **B**

[2]

Label with 1, 2, 3

[1] vii. Label all aliphatic carbons in structure **B** with the numbers on the ^{13}C NMR, from 1 to 3.

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