

Question	1-4	5-9	10-13	Total
Mark	/27	/35	/28	/90

CHEMISTRY 112/115 TEST

Tuesday 6 September 2005

Name (Print Clearly):

Student ID number:

Signature:

Instructions:

Attempt **all** questions. Enter answers in the spaces provided.

Total marks: 90

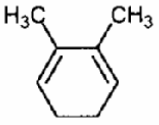
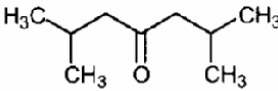
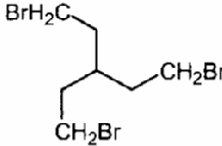
Time allowed: 90 minutes

Periodic Table

1 H 1.008																	2 He 4.00															
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2															
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9															
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8															
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	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	57-71 see below	72 Hf 178.5	73 Ta 181.0	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 (210)	85 At (210)	86 Rn (222)															
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112																					
<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td>57 La 138.9</td> <td>58 Ce 140.1</td> <td>59 Pr 140.9</td> <td>60 Nd 144.2</td> <td>61 Pm (147)</td> <td>62 Sm 150.4</td> <td>63 Eu 152.0</td> <td>64 Gd 157.3</td> <td>65 Tb 158.9</td> <td>66 Dy 162.5</td> <td>67 Ho 164.9</td> <td>68 Er 167.3</td> <td>69 Tm 168.9</td> <td>70 Yb 173.0</td> <td>71 Lu 175.0</td> </tr> </table>																		57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	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
57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	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																		
<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td>89 Ac (227)</td> <td>90 Th 232.0</td> <td>91 Pa (231)</td> <td>92 U 238.1</td> <td>93 Np (237)</td> <td>94 Pu (242)</td> <td>95 Am (243)</td> <td>96 Cm (247)</td> <td>97 Bk (245)</td> <td>98 Cf (251)</td> <td>99 Es (254)</td> <td>100 Fm (253)</td> <td>101 Md (256)</td> <td>102 No (254)</td> <td>103 Lr (257)</td> </tr> </table>																		89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)
89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)																		

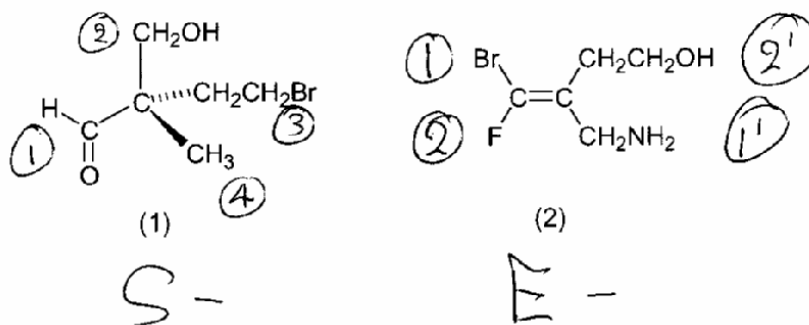
Question 1 (9 marks)

Show the number of signals expected in the ^{13}C and ^1H NMR spectra for each of the compounds shown below. Also give the relative integrals for the peaks in the ^1H NMR spectrum for each compound.

	^{13}C NMR	^1H NMR	Integral ratio
	4	3	3 : 2 : 1
	4	3	6 : 2 : 1
	3	3	6 : 6 : 1

Question 2 (6 marks)

For each of the structures (1) and (2), shown below, give the appropriate priority order of the substituents and the appropriate stereochemical descriptor (R, S, E or Z).

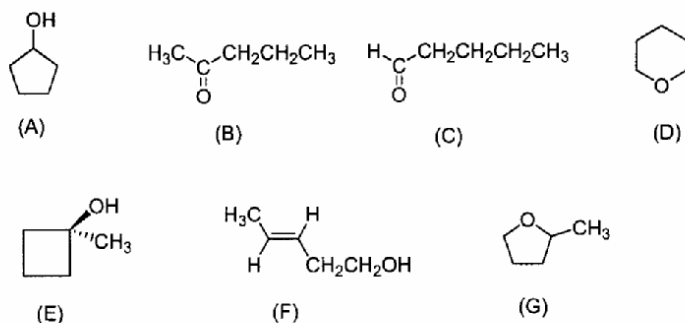


If compound (1) has a specific optical rotation $[\alpha]_{\text{D}}^{25} = +17.4^\circ$, what would be the specific rotation of:

- | | |
|---|--------------------|
| (i) its enantiomer? | Ans: -17.4° |
| (ii) a racemic mixture of (1) and its enantiomer? | Ans: 0° |
| (iii) the product of reaction of (1) with NaBH_4 ? | Ans: 0° |
| (iv) compound (2)? | Ans: 0° |

Question 3 (8 marks)

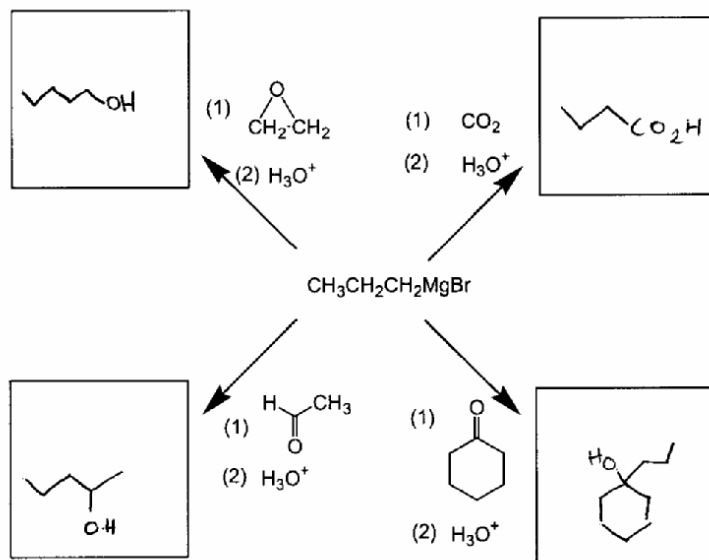
Shown below are the structures (A – G) of seven isomers with the formula $C_5H_{10}O$.



- (a) How many peaks would be in the 1H NMR spectrum of isomer F? Ans: **6**
- (b) Which two isomers would show three peaks in their ^{13}C NMR spectra? Ans: **A and D**
- (c) Which isomer is a secondary alcohol? Ans: **A**
- (d) Which isomers would show neither a C=O nor an O-H stretch in their infrared spectra? Ans: **D and G**
- (e) Which isomers would react with $K_2Cr_2O_7/H^+$? Ans: **A and F**
- (f) Which isomer could exist as two diastereoisomers? Ans: **F**
- (g) Which isomer could exist as two enantiomers? Ans: **G**
- (h) Which isomer would rapidly react with bromine? Ans: **F**

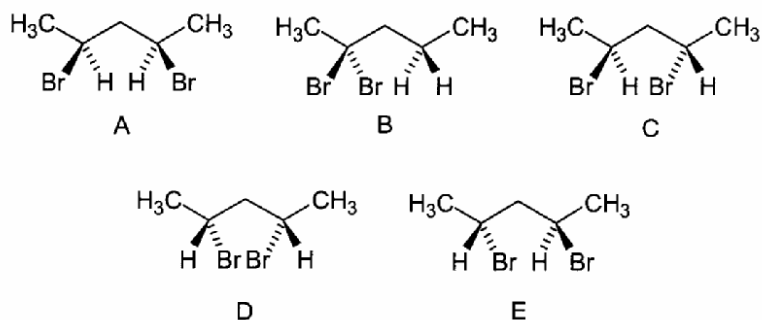
Question 4 (4 marks)

Draw the structures of the organic products from the following reactions.



Question 5 (5 marks)

Shown below are the structures (A – E) of several dibromopentanes



List two which are:

(a) constitutional isomers

Ans: B and any other

(b) enantiomers

Ans: C and E

(c) diastereoisomers

Ans: A and C (other possible)

(d) identical

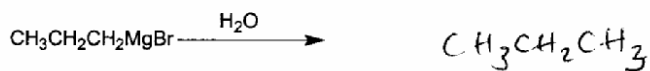
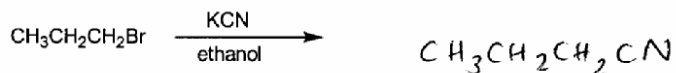
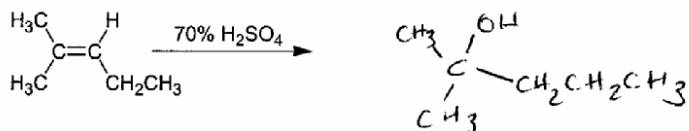
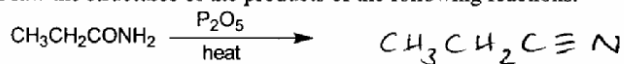
Ans: A and D

Which structures depict a *meso* compound?

Ans: A and D

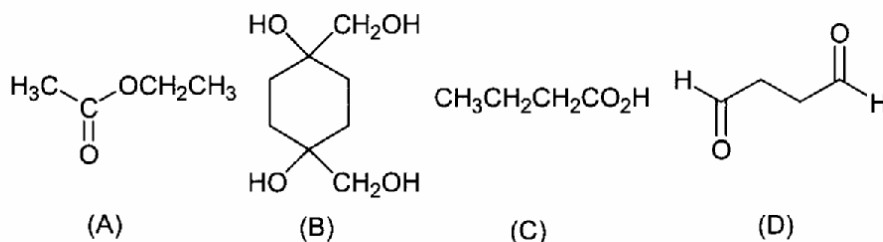
Question 6 (6 marks)

Draw the structures of the products of the following reactions.



Question 7 (5 marks)

Consider the four structures shown below.



(a) Which of these structures would show a different elemental (combustion) analysis to the other three? Ans: D

(b) Which two structures would produce molecular ions of the same mass in their mass spectra? Ans: A and C

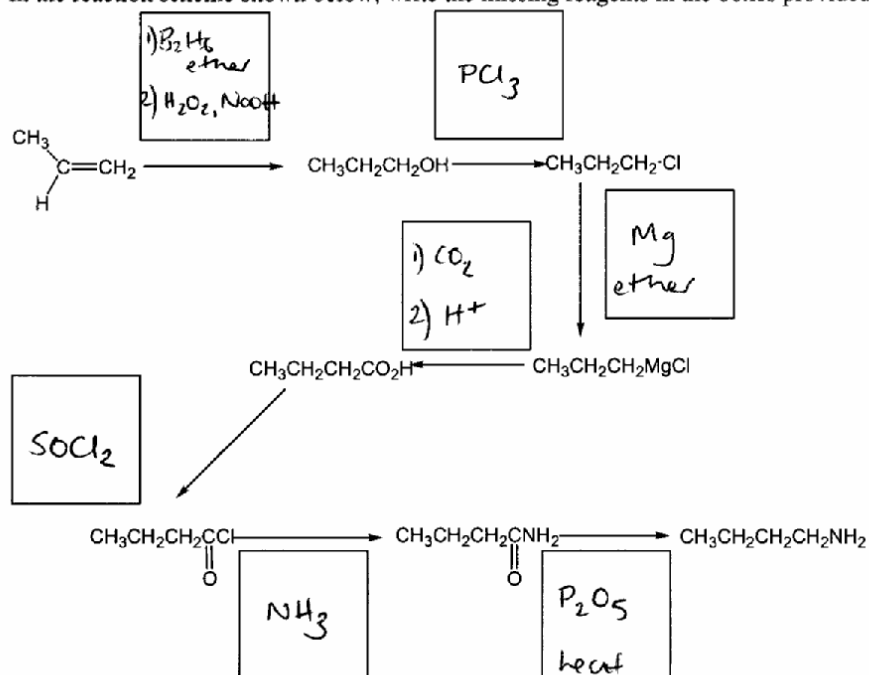
(c) List one feature that would appear in the infrared spectrum of (A) but not (B). Ans: C=O stretch

(d) List one feature that would appear in the infrared spectrum of (B) but not (A). Ans: O-H stretch

(e) Which two structures are constitutional isomers? Ans: A and C

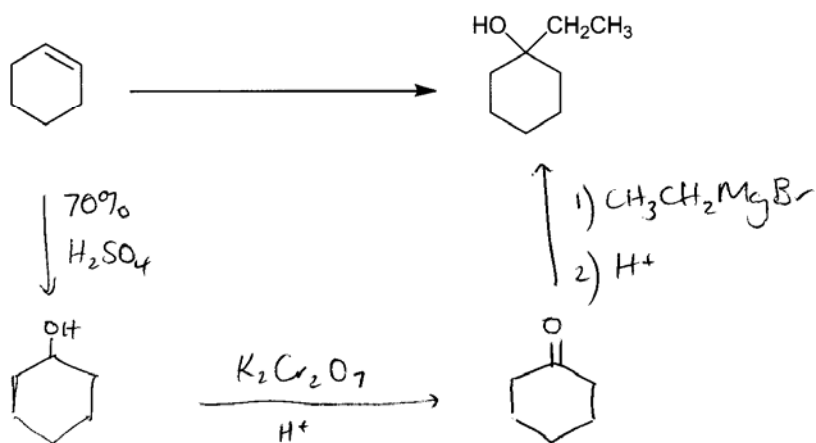
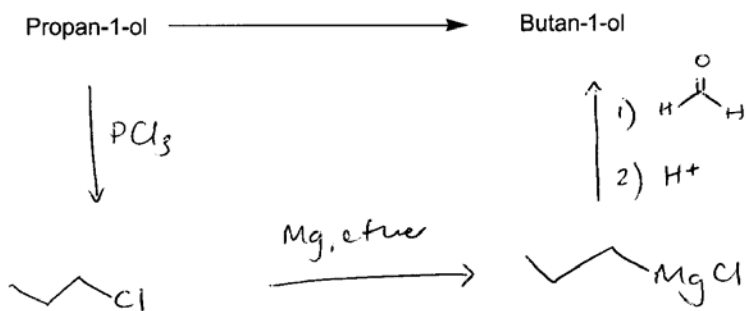
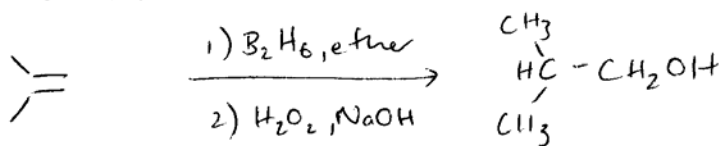
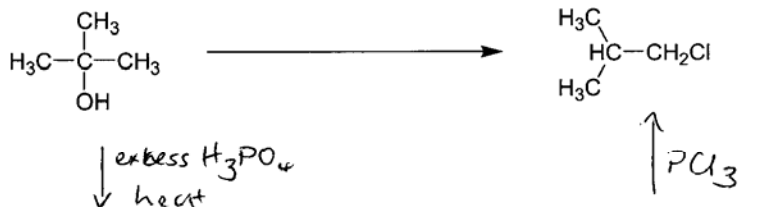
Question 8 (7 marks)

In the reaction scheme shown below, write the missing reagents in the boxes provided.



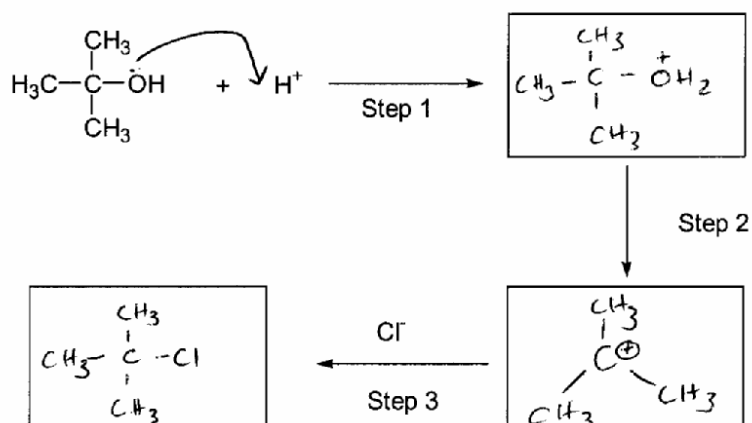
Question 9 (12 marks)

For each of the following transformations draw a reaction scheme that could be used to convert the starting material to the final product. For each step of the reaction sequence specify all necessary reagents and reaction conditions.



Question 10 (8 marks)

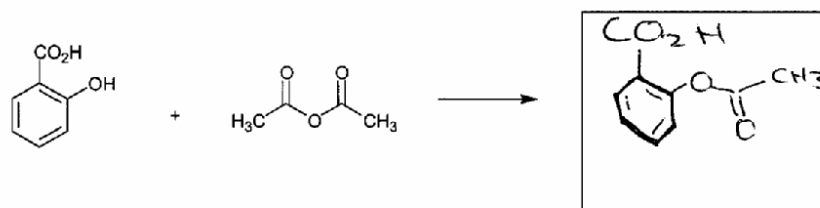
Shown below is the reaction of a tertiary alcohol with aqueous HCl.



- (a) For the first step above, draw an arrow to indicate the movement of electrons.
(b) Draw the structures of the intermediates and final product in the empty boxes above.
(c) In step 1, which species is the electrophile? Ans: H⁺
(d) In step 3, which species is the nucleophile? Ans: Cl⁻
(e) Is this an S_N1 or S_N2 reaction mechanism? Ans: S_N1
(f) Which step is the rate determining step? Ans: Step 2

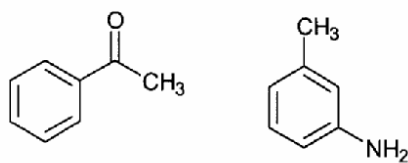
Question 11 (4 marks)

In the CHEM 112/115 laboratory you prepared aspirin by the reaction shown below.

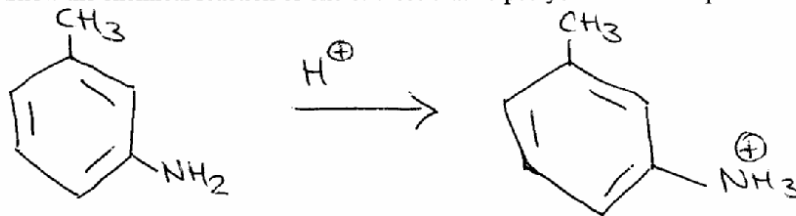


- (a) Draw the structure of aspirin the the box above.
(b) What technique was used to purify the aspirin? Ans: Recrystallisation

In another experimental you separated the two compounds shown below.



(c) Show the chemical reaction of one of these that helped you to do this separation.

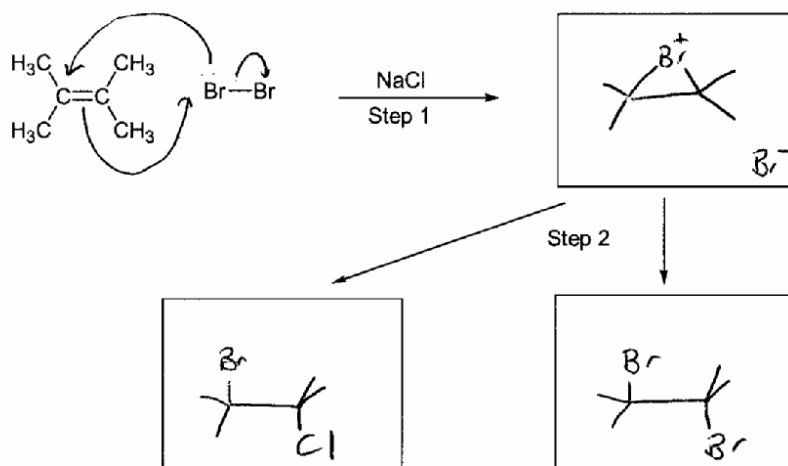


(d) What property of the above compound was altered by this reaction?

Ans: Solubility in water

Question 12 (6 marks)

The reaction of an alkene with bromine in the presence of added sodium chloride is depicted below.



(a) For the first step above, draw arrows to indicate the movement of electrons.

(b) In the empty box draw the structure of the intermediate formed in step 1.

(c) What is the name given to this type of intermediate?

Ans: Bromonium ion

(e) In the boxes draw the structures of the two products formed in step 2.

(d) Is this a substitution, elimination, addition, reduction or oxidation reaction?

Ans:

Question 13 (10 marks)

For each of the following statements **circle** the correct description (True or False).

- (a) R-enantiomers always rotate plane polarized light in a clockwise direction.
True **False**
- (b) All molecules found in nature rotate the plane of plane-polarised light.
True **False**
- (c) Alkenes only show geometrical isomerism if they have four different substituents attached to the C=C double bond.
True **False**
- (d) A meso compound is superimposable on its mirror image.
True False
- (e) Constitutional isomers produce different elemental (combustion) analyses.
True **False**
- (f) Tertiary alcohols are readily oxidised by acidified potassium dichromate.
True **False**
- (g) Reaction of cyclohexene with 70% H₂SO₄ gives the same alcohol as that produced by reaction with B₂H₆ followed by H₂O₂/NaOH.
True False
- (h) Markovnikov's rule only applies to the additions of unsymmetrical reagents to unsymmetrical alkenes.
True False
- (i) S_N1 reactions occur with inversion of configuration of the reacting carbon.
True **False**
- (j) S_N2 reaction of a racemic alkyl halide produces a racemic product.
True False

END OF PAPER