

Full Name:

Student ID #:

UNIVERSITY OF CANTERBURY

End-of-Year Examinations 2008

Prescription Number(s):	CHEM 112 CHEM 115
Paper Title:	General Chemistry B General Chemistry C

Time Allowed: 2¹/₂ HOURS

Number of pages: EIGHTEEN

Before commencing work, read the instructions on this page.

1. This is both your examination paper and your answer book. You may use the blank page opposite for any additional working pertaining to that question.
2. Please ensure that your name has been entered in the appropriate spaces above.
3. ANSWER ALL QUESTIONS.

Total marks = 120

NOTE: There is a periodic table on p18.

Please write your answers in the spaces provided

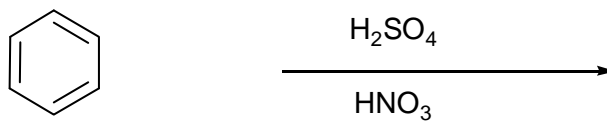
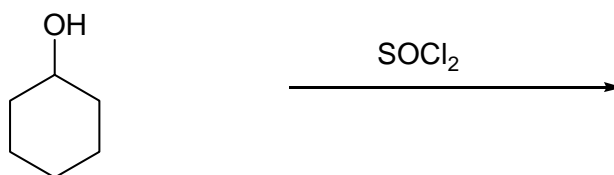
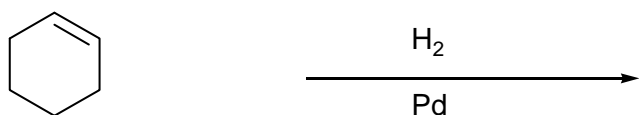
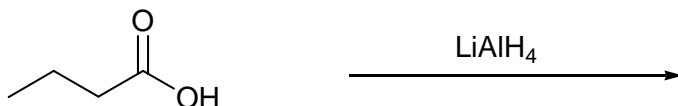
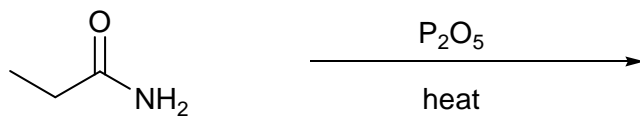
For examiners use only

1-6	7-9	10-13	TOTAL

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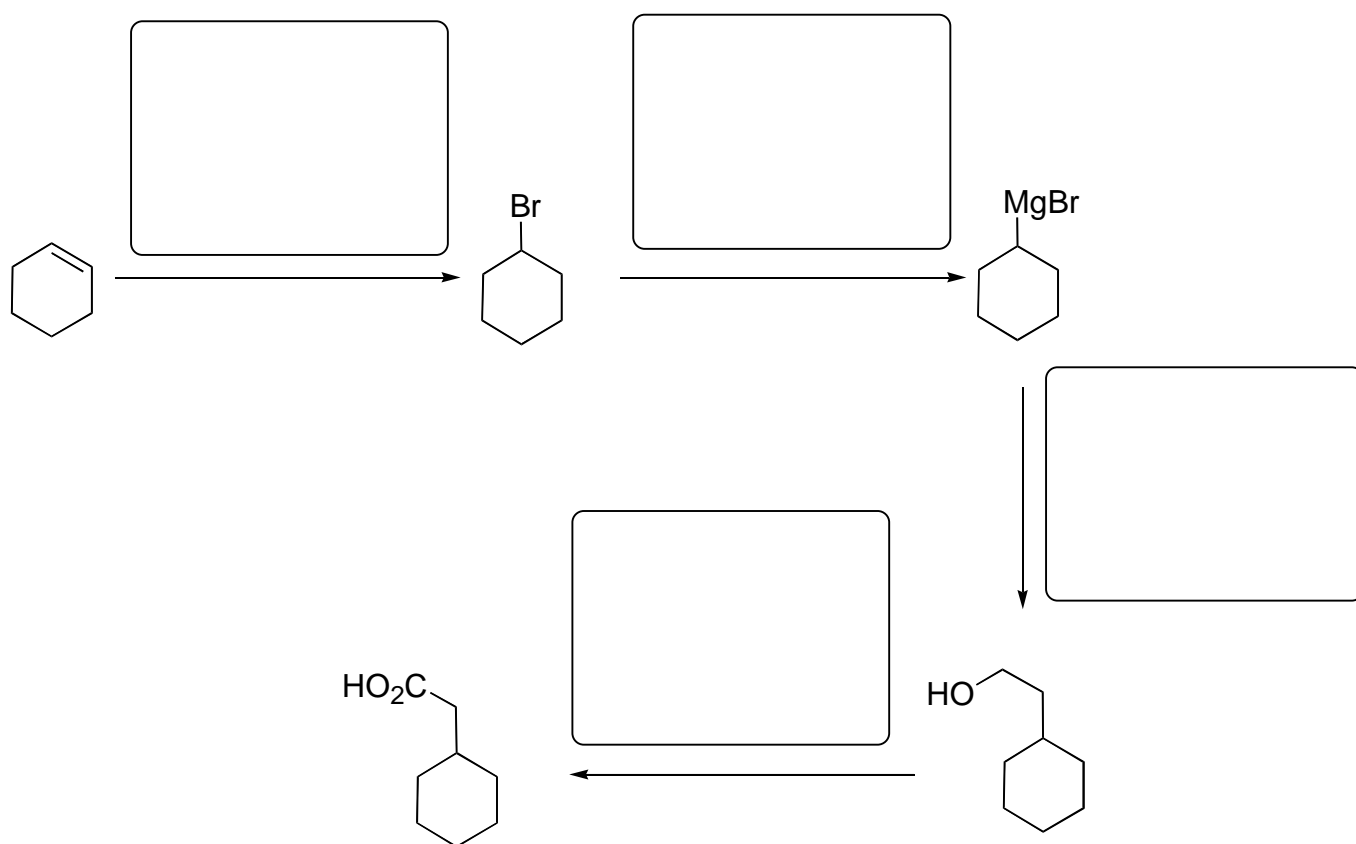
Question 1 (6 marks)

Draw the structures of the products of the following reactions.



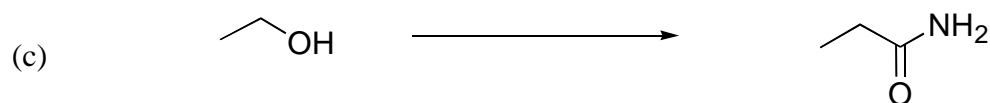
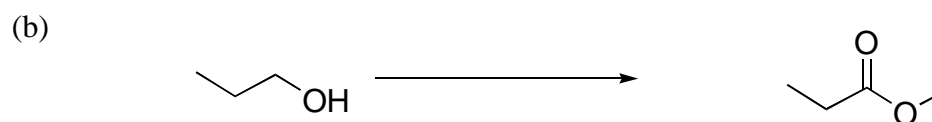
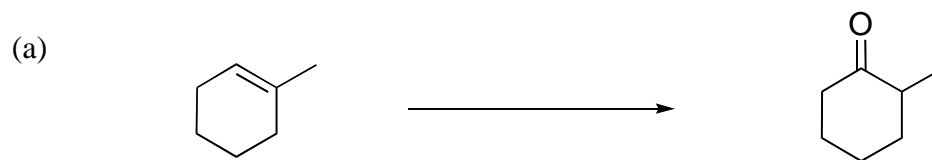
Question 2 (4 marks)

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



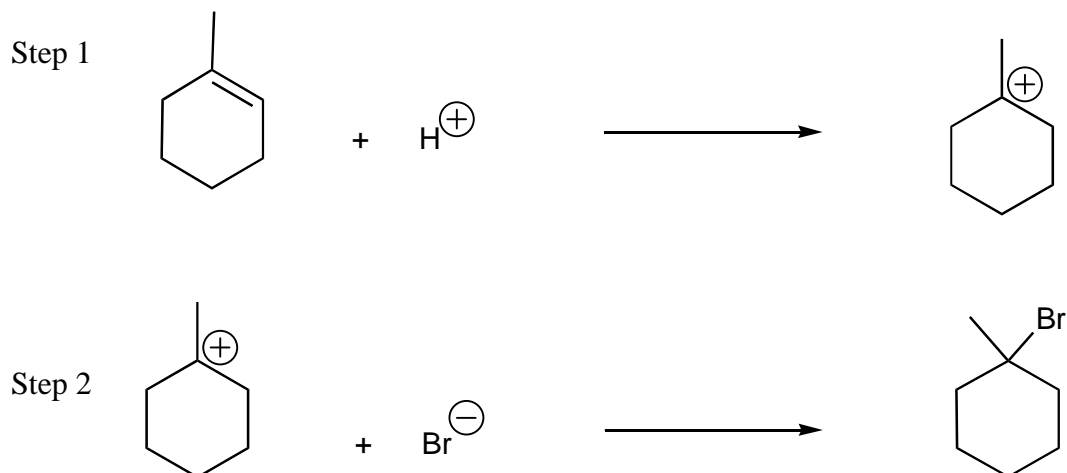
Question 3 (12 marks)

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 4 (9 marks)

Shown below is the mechanism for the electrophilic addition of HBr to 1-methylcyclohexene.

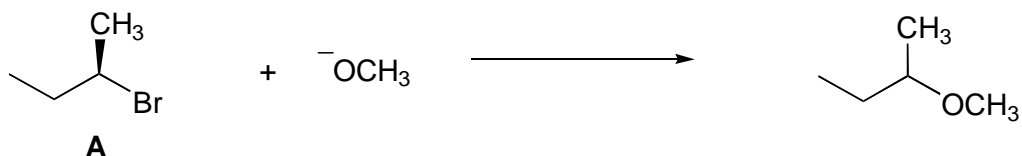


- (a) For each step above, draw an arrow to indicate the movement of electrons.
- (b) Which step of the mechanism is the rate-determining step?
- (c) In Step 1, which species is the electrophile?
- (d) In Step 2, which species is the nucleophile?
- (e) In Step 1, the H^{\oplus} forms a bond with the least-substituted carbon, consistent with Markovnikov's rule. Explain why this happens.

- (f) Draw a reaction energy profile diagram for this reaction. Indicate the position of the starting materials, products and any transition states or intermediates on your diagram.

Question 5 (9 marks)

The following optically active alkyl halide undergoes nucleophilic substitution by an S_N2 mechanism.

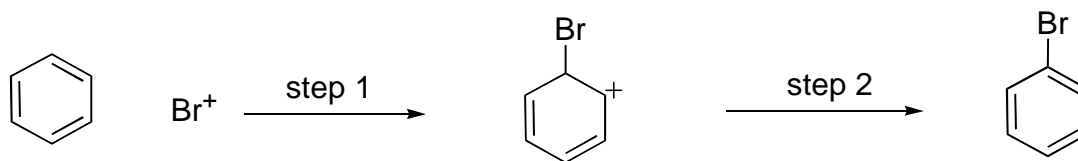


- (a) Use arrows to give the mechanism of this reaction.
- (b) Which species is the electrophile?
- (c) Redraw the product, showing its stereochemistry.
- (d) Predict what would happen to the rate of this S_N2 reaction when the following changes are made to the reaction. In each case explain your answer.
- (i) The concentration of $^-OCH_3$ is doubled

- (ii) Compound A is changed to:

Question 6 (5 marks)

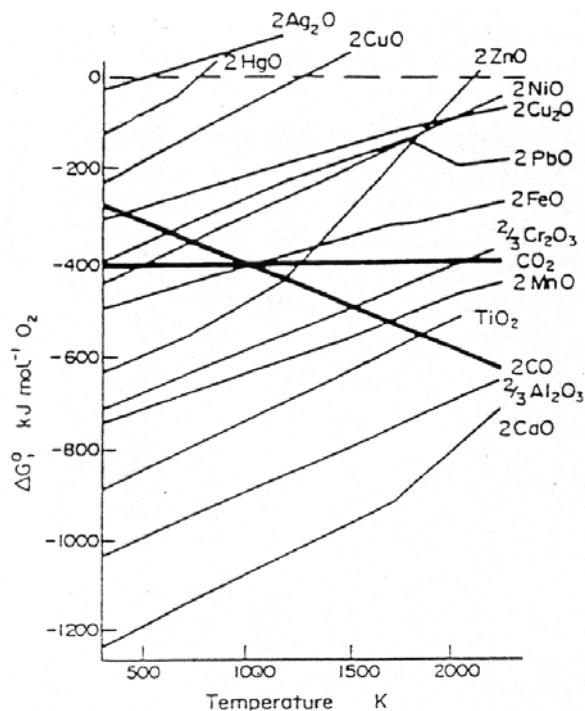
Benzene undergoes a substitution reaction to give bromobenzene



- (a) In Step 1, which species is the electrophile?
- (b) What reagent is required to react with Br_2 in order to produce the Br^+ required in this reaction?
- (c) Use arrows to give the mechanism of both steps of this reaction.

Questions 7 (10 marks)

The Ellingham diagram shown below will be useful for answering this question.



- (a) Explain, in detail, why thermal decomposition is a practical method for extraction of copper from CuO, whereas reduction with carbon, rather than thermal decomposition, is a practical method for extraction of iron.
- (b) Above what temperature can copper metal be produced from CuO by thermal decomposition?
- (c) Calculate ΔG° for the reduction of FeO by carbon at 2000 K (assume carbon is converted to CO₂).

- (d) (i) Estimate ΔG° for the reduction of Cr_2O_3 by Al.
- (ii) The reaction in (i) is thermodynamically spontaneous at all temperatures. Explain why mixtures of Cr_2O_3 and Al do not, however, spontaneously react at all temperatures.

Question 8 (15 marks)

- (a) For each set of atoms/ions given below, circle the smallest:

- (i) F F^- Li^+
(ii) N Be F
(iii) Cl Br Sb
(iv) K^+ Sc^{3+} Ca^{2+}
(v) S^{2-} Cl^- Ar

- (b) Describe how the effective nuclear charge (Z_{eff}) impacts on ionization potential, electron affinity and electronegativity.

- (c) Explain why a C–O bond (351 kJ/mol) is stronger than both a C–C bond (347 kJ/mol) and an O–O bond (142 kJ/mol).
- (d) A C=C double bond (682 kJ/mol) is approximately twice as strong as a C–C single bond (345 kJ/mol).
- (i) Explain why the strength of an N=N double bond (450 kJ/mol) is much more than twice that of an N–N single bond (167 kJ/mol).
- (ii) Explain why the strength of a P=P double bond (310 kJ/mol) is much less than twice that of a P–P single bond (200 kJ/mol).

Question 9 (13 marks)

- (a) The most common oxidation state of Al is +III and for Si it is +IV.
- (i) Give the most common oxidation state of:
- (A) Tl;
- (B) Pb.
- (ii) Explain your answers to part (i).
- (iii) Give the formulae for TWO tin chlorides.
- (b) Write a balanced equation for the reaction of Cl_2 with hot aqueous NaOH to give $\text{NaClO}_3(\text{aq})$ and $\text{NaCl}(\text{aq})$. Indicate the oxidation state of Cl in the reactant and products.
- (c) (i) An example of a covalent hydride is:
- (ii) An example of a metallic hydride is:
- (iii) The oxidation state of H in CaH_2 is:
- (iv) CaH_2 is frequently used to dry organic solvents. Write a balanced equation for its reaction with water.

Question 10 (14 marks)

- (a) Define the term **transition metal**.
- (b) Give the electron configurations of the following species in their ground electronic state (note you should start from the configuration of the appropriate noble gas, e.g. [Ar].....):
- Cr(0):
- Fe(II):
- Rh(III):
- (c) For the complex $[\text{Co}(\text{EDTA})]^{2-}$:
- What is the oxidation state (oxidation number) of Co?
 - What is the coordination number of Co?
 - What are the donor atoms?
 - What is the geometry of the complex?
- (d) (i) Give the formula and colour of the nickel species that forms when NiCl_2 is dissolved in water.

Formula:

Colour:

- (ii) Give the colour, overall charge and geometry of the nickel dimethylglyoxime (dmg) species that forms when dmg and dilute ammonia solution are added to the solution in part (i).

Colour:

Charge of complex:

Geometry:

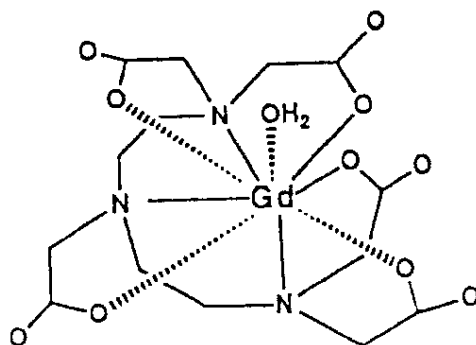
Question 11 (6 marks)

An example of the chelate effect is the higher stability of $[\text{Ni}(\text{en})_3]^{2+}$ compared with $[\text{Ni}(\text{NH}_3)_6]^{2+}$. (Note: en is ethylenediamine or ethane-1,2-diamine).

Use entropy arguments to account for the relative stabilities of $[\text{Ni}(\text{en})_3]^{2+}$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$.

Question 12 (10 marks)

A gadolinium(III) complex used as a contrast agent for diagnostic magnetic resonance imaging (MRI) is shown below.



- (a) Explain why MRI contrast agents commonly incorporate the Gd(III) ion.

- (b) Outline the properties of the DTPA complex of Gd(III) which make it an effective contrast agent.

Question 13 (7 marks)

- (a) Explain the terms **weak-field** ligand and **strong-field** ligand.

- (b) Use d orbital splitting diagrams to explain why the Fe(II) (d^6) complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is paramagnetic whereas $[\text{Fe}(\text{CN})_6]^{4-}$ (also an Fe(II), d^6 , complex) is diamagnetic. Your answer should indicate the role of the ligands in determining whether the Fe(II) complex is paramagnetic or diamagnetic.

END OF PAPER
(Periodic Table on following page)

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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						

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
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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)
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