Topics in the June 2008 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2008-J-2:

- Periodic Trends in Aqueous Oxide
- Coordination Chemistry

2008-J-3:

- Strong Acids and Bases
- Kinetics - Catalysis
- Physical States and Phase Diagrams
- Crystal Structures

2008-J-4:

- Coordination Chemistry

2008-J-5:

- Weak Acids and Bases
- Calculations Involving pK_a

2008-J-6:

- Kinetics

2008-J-7:

- Stereochemistry

2008-J-8:

- Alkenes
- Alkynes
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2008-J-9:

- Alkenes
- Alcohols
- Aldehydes and Ketones
- Synthetic Strategies

2008-J-10:

- Representations of Molecular Structure
- Carboxylic Acids and Derivatives

2008-J-11:

- Synthetic Strategies

2008-J-12:

- Structural Determination

2008-J-13:

- Alkenes

Marks

- Explain in terms of their electronic configurations **and** ionisation energies why the alkali metals (Group 1) are powerful *reducing* agents. **2**

The alkali metals have a single electron in an *s*-orbital outside a noble gas full shell. As this electron occupies a new shell and orbits further from the nucleus, it can be removed (*ionized*) much more easily than for the noble gas.

As the alkali metals are in Group 1, they have the smallest nuclear charge in each period, and hence the lowest ionization energy in each period.

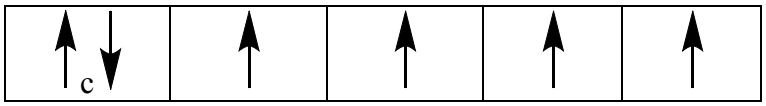
As the alkali metals have low ionization energies for removal of their single valence electron, they are powerful reducing agents – they cause electron gain in substances they react with.

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, explain why most Fe^{2+} and Fe^{3+} compounds are paramagnetic. **2**

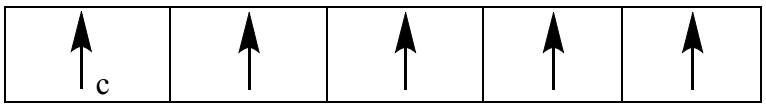
Iron is in Group 8 and thus has 8 valence electrons. Fe^{2+} thus has (8 – 2) = 6 electrons and Fe^{3+} has (8 – 3) = 5 electrons. These electrons occupy the 3*d* orbitals and do so to minimize the number of electron pairs, and thus minimize electron / electron repulsion.

There are five 3*d* orbitals and thus the configurations are:

Fe^{2+} $3d^6$



Fe^{3+} $3d^5$



With 4 and 5 unpaired electrons respectively, both Fe^{2+} and Fe^{3+} are paramagnetic.

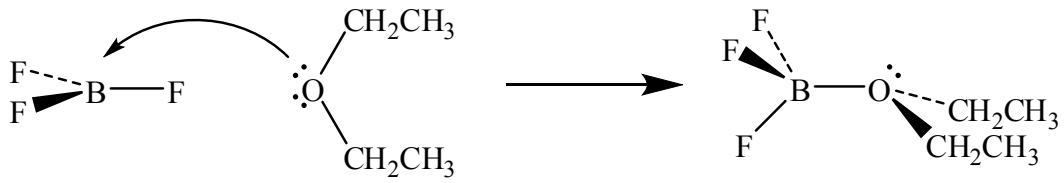
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

- BF_3 is a Lewis acid in its reaction with diethyl ether. Explain what is meant by a Lewis acid and draw the product of this reaction. **2**

A Lewis acid is an electron-pair acceptor.

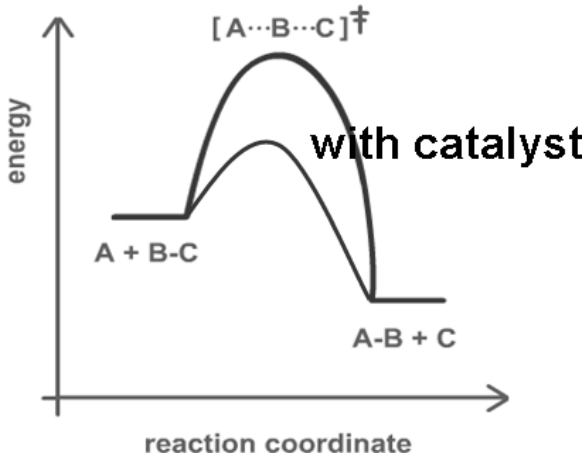
Thus, in its reaction with diethyl ether, BF_3 accepts a pair of electrons from the oxygen atom to form a B-O coordinate (dative) bond:



- What is a catalyst and, in general terms, how does it work? Make reference to an energy level diagram in your answer. **2**

A catalyst increases the rate of a reaction and is not consumed by the reaction. Catalysts provide an alternative reaction pathway with a lower activation energy.

For the reaction A + BC → AB + C, the energy level diagram below shows the lower activation energy associated with the reaction involving a catalyst.



- The gas methane, CH_4, has a critical point at –82 °C and 46 atm. Can methane be liquefied at 25 °C? Explain your answer. **2**

The critical point is the temperature above which a substance cannot be liquefied by increasing the pressure. The boundaries between the gas and liquid phases disappear.

Thus, above -82 °C, methane cannot be liquefied – it cannot be liquefied at 25 °C.

- Define what is meant by an "allotrope". Give an example of a pair of allotropes involving (i) phosphorus and (ii) a pair not involving phosphorus. **2**

Allotropes are different structural forms of the same element.

(i) Phosphorus exists as a number of allotropes, including white, red and black phosphorus. The most common forms are white and red phosphorus which are based on P_4 tetrahedra and linked P_4 tetrahedra respectively. Black phosphorus consists of layers of puckered 6-membered rings.

(ii) Other elements showing allotropes include:

- **carbon – diamond, graphite and fullerenes**
- **oxygen – O_2 and O_3 molecules**
- **sulfur – S_n rings with n = 6 – 20.**

- Complete the following table. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$) **Marks 9**

Formula	$(NH_4)_2[CoCl_4]$	$[Cr(NH_3)_5(H_2O)]Cl_3$	*cis*-$[PtCl_2(en)_2]$
Oxidation state of transition metal ion	**+2 (II)**	**+3 (III)**	**+2 (II)**
Coordination number of transition metal ion	**4**	**6**	**6 (2 × Cl and 4 × N from 2en)**
Number of *d*-electrons in the transition metal ion	**7 (Co is in Group 9 so Co^{2+} has 9 – 2= 7)**	**3 (Cr is in Group 6 so Co^{2+} has 6 – 3= 3)**	**8 (Pt is in Group 10 so Pt^{2+} has 10 – 2= 8)**
Charge of the complex ion	**-2 $[CoCl_4]^{2-}$**	**+3 $[Cr(NH_3)_5(OH_2)]^{3+}$**	**0 $[PtCl_2(en)]$**
Geometry of the complex ion	**tetrahedral**	**octahedral**	**octahedral**
List all the ligand donor atoms	**4 × Cl^-**	**5 × N and 1 × O**	**2 × Cl^- and 4 × N**

Marks

- Calculate the pH of a 0.20 M solution of potassium fluoride. The pK_a of HF is 3.17. **3**

As F^- is a weak base, $[OH^-]$ must be calculated by considering the equilibrium:

	F^-	H_2O	$\rightleftharpoons$	OH^-	HF
initial	**0.20**	**large**		**0**	**0**
change	**-*x***	**negligible**		**+*x***	**+*x***
final	**0.20 – *x***	**large**		***x***	***x***

The equilibrium constant K_b is given by:

$$K_b = \frac{[OH^-][HF]}{[F^-]} = \frac{x^2}{0.20 - x}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 3.17 = 10.83$$

As $pK_b = 10.83$, $K_b = 10^{-10.83}$. K_b is very small so $0.20 - x \sim 0.20$ and hence:

$$x^2 = 0.20 \times 10^{-10.83} \quad \text{or} \quad x = 0.0000017 \text{ M} = [OH^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = -\log_{10}[0.0000017] = 5.76$$

Finally, pH + pOH = 14.00 so

$$pH = 14.00 - 5.76 = 8.24$$

Answer: **pH = 8.24**

- A 300.0 mL solution of HCl has a pH of 1.22. Given that the pK_a of iodic acid, HIO_3, is 0.79, how many moles of sodium iodate, $NaIO_3$, would need to be added to this solution to raise its pH to 2.00? **3**

Using $pH = -\log_{10}[H^+(aq)]$,

$$[H^+(aq)]_{initial} = 10^{-1.22} = 0.060 \text{ M}$$

$$[H^+(aq)]_{final} = 10^{-2.00} = 0.010 \text{ M}$$

ANSWER CONTINUES ON THE NEXT PAGE

The change of (0.060 – 0.010 M) = 0.050 M occurs due to the reaction with IO_3^-(aq) to produce HIO_3(aq). If [IO_3^-(aq)] = *x*, the reaction table is:

	H^+(aq) +	IO_3^-(aq)	$\rightleftharpoons$	HIO_3(aq)
initial	**0.060**	***x***		**0**
change	**-0.050**	**-0.050**		**+0.050**
final	**0.010**	***x* – 0.050**		**0.050**

As pK_a = 0.79 = -$\log_{10}K_a$:

$$K_a = \frac{[H^+(aq)][IO_3^-(aq)]}{[HIO_3(aq)]} = \frac{(0.010)\times(x-0.050)}{0.050} = 10^{-0.79}$$

Thus, *x* = 0.86 M = [IO_3^-(aq)]$_{initial}$. This concentration corresponds to a 300.0 mL solution so the number of moles that have been added is:

number of moles = concentration × volume
= (0.86 M) × (0.3000 L) = 0.26 mol

Answer: **0.26 mol**

Marks 5

- Nitric oxide, a noxious pollutant, and hydrogen react to give nitrous oxide and water according to the following equation.

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

The following rate data were collected at 225 °C.

Experiment	$[NO]_0$ (M)	$[H_2]_0$ (M)	Initial rate (d[NO]/dt, M s^{-1})
1	6.4×10^{-3}	2.2×10^{-3}	2.6×10^{-5}
2	1.3×10^{-2}	2.2×10^{-3}	1.0×10^{-4}
3	6.4×10^{-3}	4.4×10^{-3}	5.1×10^{-5}

Determine the rate law for the reaction.

Between experiments (1) and (2), $[H_2]_0$ is constant whilst $[NO]_0$ doubles. This causes the rate to increase by a factor of (1.0×10^{-4} / 2.6×10^{-5}) = 3.8 ~ 4. The reaction is second order with respect to NO.

Between experiments (1) and (3), $[NO]_0$ is constant whilst $[H_2]_0$ doubles. This causes the rate to increase by a factor of (5.1×10^{-5} / 2.6×10^{-5}) = 2.0. The reaction is first order with respect to H_2.

Thus, overall, rate = $k[NO]^2[H_2]$

Calculate the value of the rate constant at 225 °C.

Using experiment (1), the rate – 2.6×10^{-5} M s^{-1} when $[NO]_0 = 6.4 \times 10^{-3}$ M and $[H_2]_0 = 2.2 \times 10^{-3}$ M. Hence, inserting these values into the rate equation gives

$$(2.6 \times 10^{-5}\ \text{M s}^{-1}) = k \times (6.4 \times 10^{-3}\ \text{M})^2 \times (2.2 \times 10^{-3}\ \text{M}) \quad \text{so } k = 290\ \text{M}^{-2}\ \text{s}^{-1}$$

The units of *k* are obtained by ensuring that the units on the left and right-hand side of the equation balance.

Answer: **290 M^{-2} s^{-1}**

Calculate the rate of appearance of N_2O when $[NO] = [H_2] = 6.6 \times 10^{-3}$ M.

From the chemical equation, *one* N_2O is made by the reaction of *two* NO. The rate of appearance of N_2O is one half of the rate of disappearance of NO:

rate = $0.5 \times k[NO]^2[H_2] = 0.5 \times (290\ \text{M}^{-2}\ \text{s}^{-1}) \times (6.6 \times 10^{-3}\ \text{M})^2 \times (6.6 \times 10^{-3}\ \text{M})$

$= 4.2 \times 10^{-5}$ M s^{-1}

Answer: **4.2×10^{-5} M s^{-1}**

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

As collisions of three molecules is *very* unlikely, a possible reaction mechanism involves a fast equilibrium follow by the rate determining step:

Mechanism:

$$NO(g) + NO(g) \rightleftharpoons N_2O_2(g) \quad \text{fast equilibrium}$$

$$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O \quad \text{slow}$$

The second step is the slowest and is rate determining. It involves the reaction of one N_2O_2 molecule with one H_2 molecule so its rate law is first order with respect to each:

$$\text{rate of reaction} = \text{rate of step 2} = k_2[N_2O_2(g)][H_2(g)]$$

However, the rate law as written contains $[N_2O_2(g)]$. The concentration of this highly reactive reaction intermediate cannot be controlled or measured. To test the rate law experimentally, it should contain only species whose concentrations can be changed. N_2O_2 molecules are generated by the first step.

If the first step is in equilibrium,

$$K_{eq} = \frac{[N_2O_2(g)]}{[NO(g)]^2} \quad \text{or } [N_2O_2(g)] = K_{eq}[NO(g)]^2$$

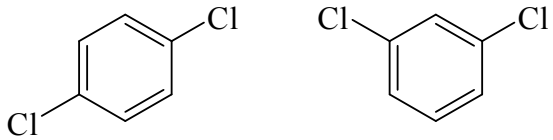
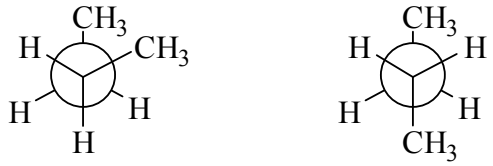
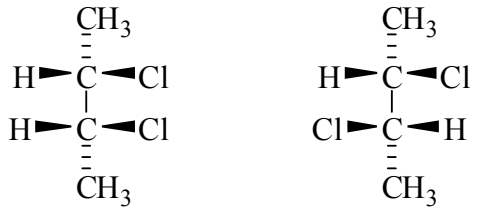
Putting this expression into the rate law for the rate determining step (step 2) gives:

$$\text{rate} = k_2[N_2O_2(g)][H_2(g)] = k_2\, K_{eq}[NO(g)]^2\, [H_2(g)] = k[NO(g)][H_2(g)]$$

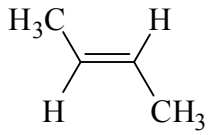
This mechanism gives the same rate law as found experimentally. It is thus a *possible* mechanism.

Marks 8

- Consider the following pairs of compounds. Indicate the isomeric relationship that exists between the compounds in each set.

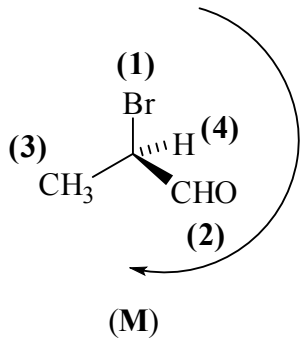
	**Constitutional isomers.** **They differ in the interatomic connectivity.**
	**Conformational isomers.** **They differ only be rotation about the central C-C bond.**
 (**L**)	**Diastereomers.** **They differ in the arrangement of the atoms in space. They are *not* mirror-image stereoisomers.**
 (**M**)	**Identical.** **They are superimposable mirror images of each other.**
 (**N**)	**Diastereomers.** **They differ in the arrangement of the atoms in space. They are *not* mirror-image stereoisomers.**

Give the name of compound (**L**) that unambiguously describes its stereochemistry.

 (**L**)	**(*E*)-but-2-ene** **The two CH_3 groups on either end of the double bond have higher priority than the two H groups. As they are located on opposite sides of the double bond, the stereochemistry is designated as (*E*).**

ANSWER CONTINUES ON THE NEXT PAGE

Give the name of compound (**M**) that unambiguously describes its stereochemistry.



(**M**)

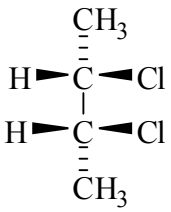
(*R*)-2-bromopropanal

The priority of the groups is Br > CHO > CH_3 > H. With the lowest priority (H) at the back, the path from highest to lowest ((1)-(2)-(3)) is clockwise. The stereochemistry is designed as (*R*).

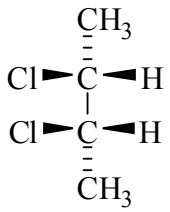
Is compound (**N**) optically active? Give a reason for your answer.

Compound (N) is meso and is *not* optically active. It is superimposable on its mirror image. Simple rotation of the mirror image on the right generates the molecule on the left.

(N) possesses an internal mirror plane (between the carbon atoms) and is thus not chiral.

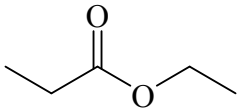
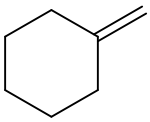
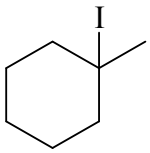
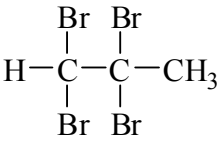
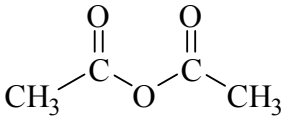
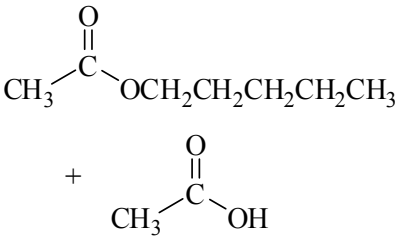
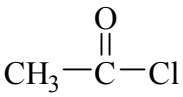
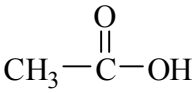
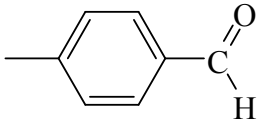
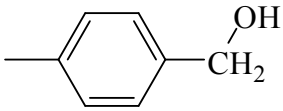
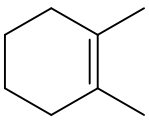
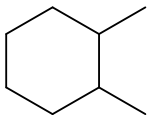


(**N**)



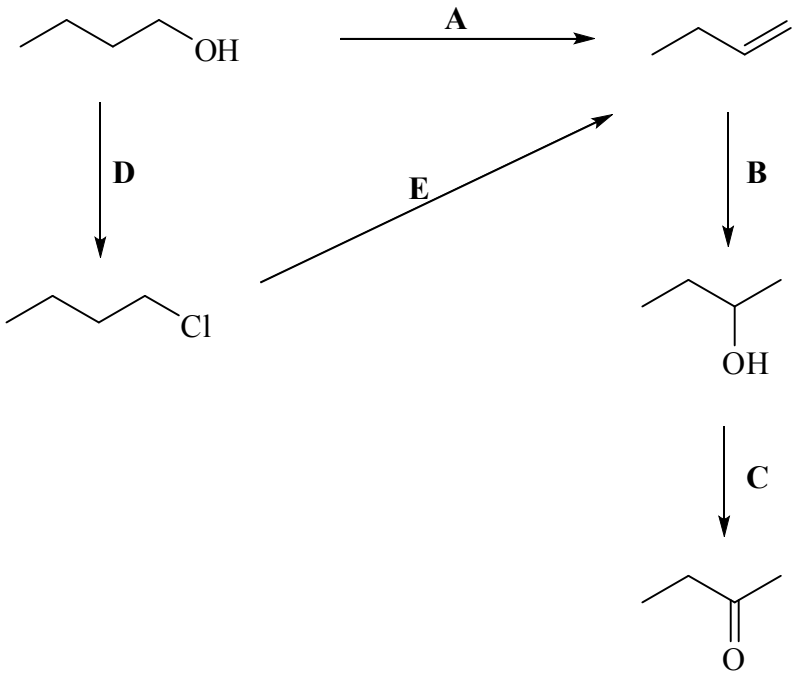
- Complete the following table. Make sure you indicate any relevant stereochemistry.

Marks 7

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
CH_3CH_2COOH	1. $SOCl_2$ 2. CH_3CH_2OH	**$CH_3CH_2COOCH_2CH_3$** 
	dry HI	 **(Markovnikov addition)**
$H-C\equiv C-CH_3$	excess Br_2 in CCl_4 solvent	
$CH_3CH_2CH_2CH_2CH_2OH$		
	H_2O	
	1. $LiAlH_4$ / dry ether 2. $H^{\oplus}$/ H_2O	
	H_2 / Pd / C	

Marks 5

- Consider the following reaction sequence.



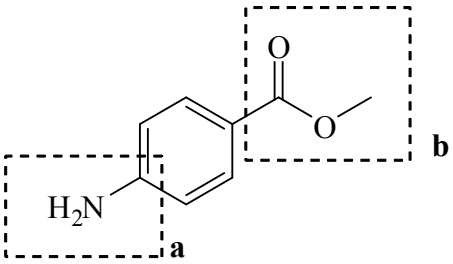
Clearly state the reagents required (including conditions and solvent where appropriate) for each of the steps.

A: **hot, concentration H_2SO_4(aq) (dehydration)**
B: **cold, dilute H_2SO_4(aq) (acid catalysed addition of H-OH)**
C: **$K_2Cr_2O_7$(aq) / H_2SO_4(aq) (oxidation of secondary alcohol to ketone)**
D: **hot, concentrated HCl(aq) or SOCl (nucleophilic substitution of water soluble alcohol)**
E: **hot, concentrated KOH in ethanol (elimination – heat and solvent prevents substitution)**

Marks 5

- The structure of methyl 4-aminobenzoate, (**E**), is given below.

(**E**)



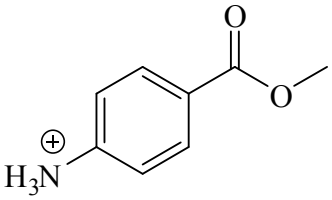
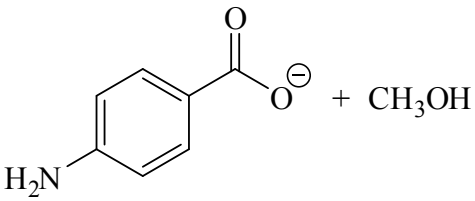
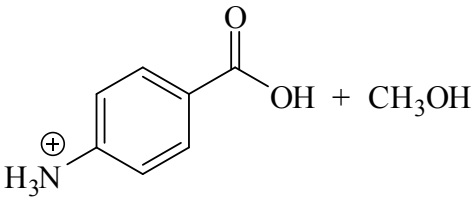
Give the molecular formula of compound (**E**).

$C_8H_9NO_2$

Name the functional groups in molecule (**E**) indicated by the boxes "**a**" and "**b**".

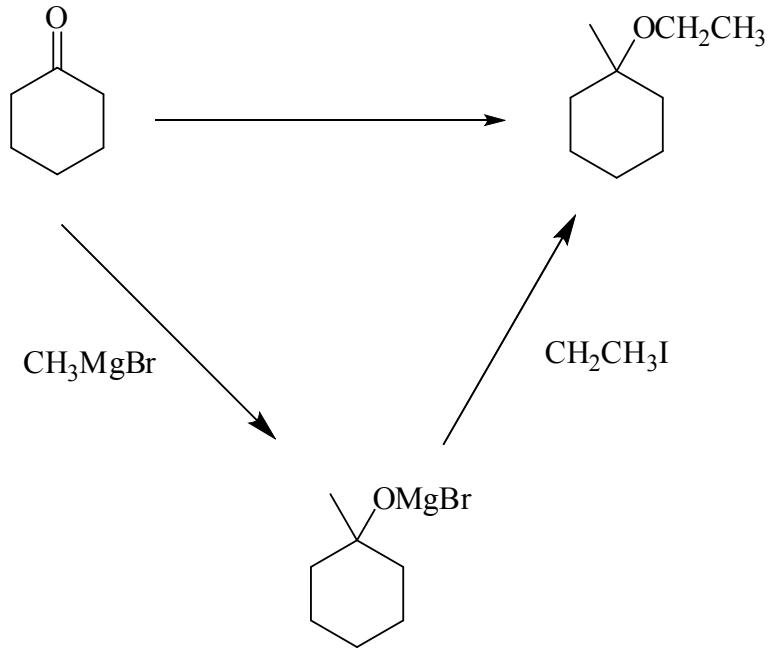
a: **amine**	**b**: **ester**

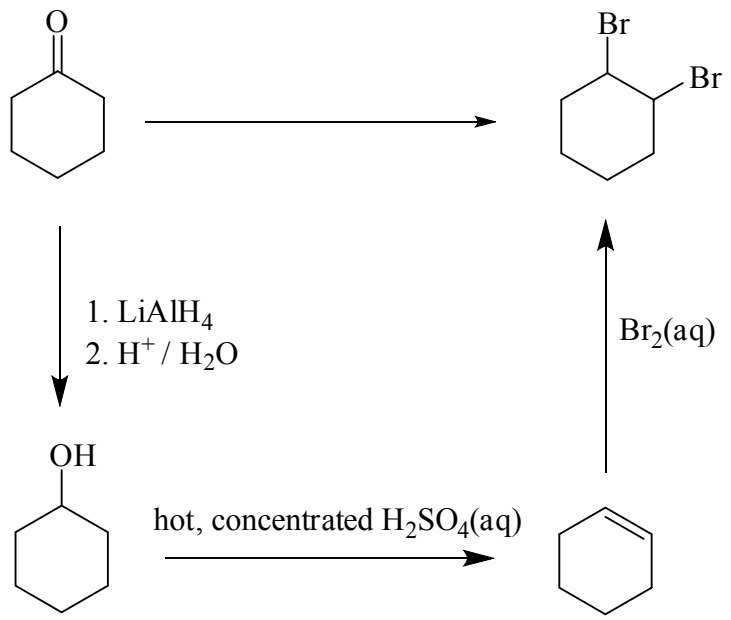
Give the structure(s) of all organic products formed when compound (**E**) is treated with the following reagents. If no reaction occurs, write "NO REACTION".

cold HCl (1 M)	**No hydrolysis of the ester under these conditions. The amine group will be protonated by the strong acid.** 
hot NaOH (4 M)	**Treatment with base will lead to hydrolysis of the ester. In the basic solution, the carboxylic acid will be deprotonated and the amine will not be protonated.** 
hot HCl (4 M)	**Hydrolysis of ester. In acidic conditions, the carboxylic acid will not be deprotonated and the amine group will be protonated.** 

- Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step may be required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

Marks 6

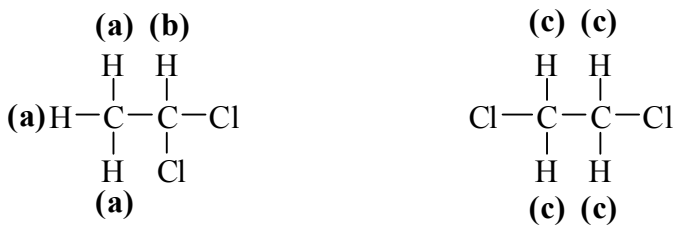




Marks 6

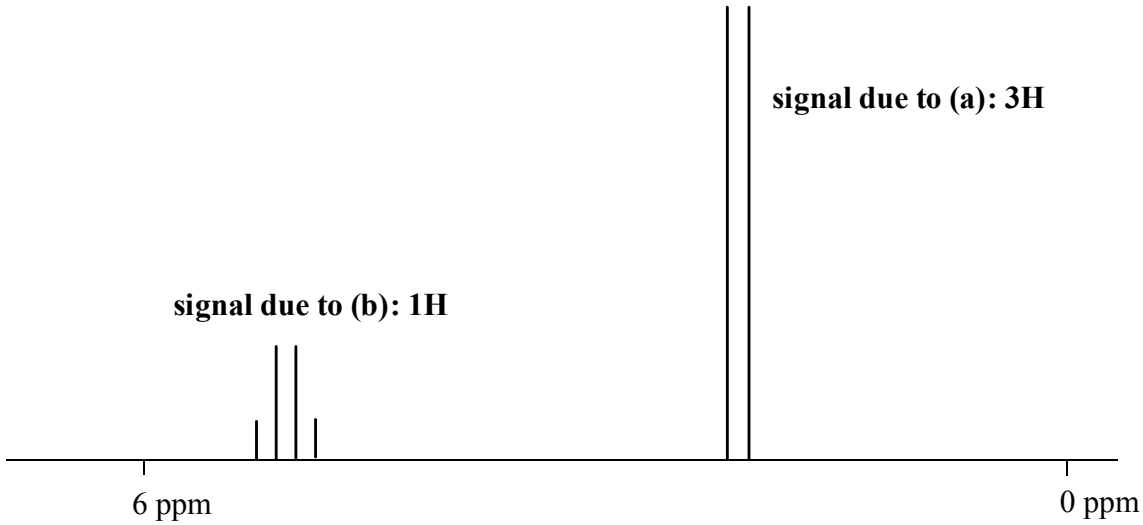
- Consider the isomers 1,1-dichloroethane and 1,2 dichloroethane, which can be readily identified by their ^{1}H NMR spectra.

  On the structures below, write the letters **a**, **b**, **c**, *etc*. as necessary to identify each **unique** hydrogen environment giving rise to a signal in the ^{1}H NMR spectra of these compounds.



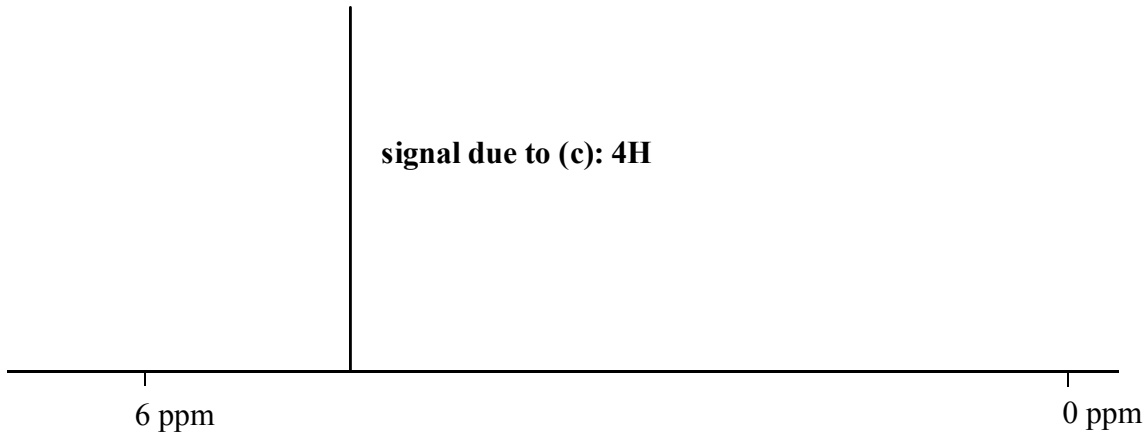
Sketch the ^{1}H NMR spectrum of each compound. Label each signal in the spectra with **a**, **b**, **c**, *etc.* to correspond with your assignments on the diagram above. Make sure you show the splitting pattern (number of fine lines) you expect to see for each signal. Also write the relative number of hydrogens you expect above each signal.

Spectrum of 1,1-dichloroethane

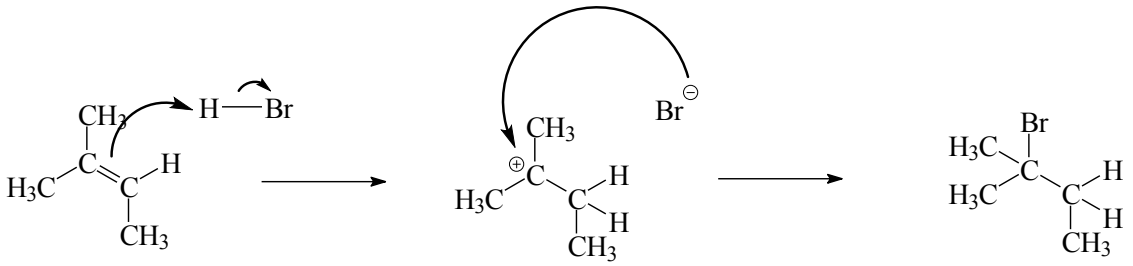


b

Spectrum of 1,2-dichloroethane



	Marks
• The incomplete proposed mechanism for the reaction of 2-methyl-2-butene with HBr is shown below. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place.	2



Which one of the two reactants is the electrophile?	**HBr is the electrophile.**