A' Level Chemistry Year 2



Unit 15: Amines

Summer Examination Revision Pack

The questions in this pack should be attempted AFTER completing all other revision.



Grade Accelerator Recall Definitions Drawing Diagrams Using Equations Drawing Graphs



Condensed Notes Keywords & Definitions Key Concepts Application Key Skills



Quizlet Classes Flashcard Based Games Tests & Quizzes Keyword Spell Checker



Online Forms Take Time to Answer Use Paper & Calculator Work It Out Review Missed Marks

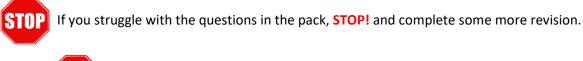
Use the 3 Wave Process when completing these revision packs.



 Complete the questions without assistance (Can't answer a question? Leave it and move on)
 Use your notes to fill any gaps after step 1
 Use the mark scheme to fill in any remaining gaps.

1. Having gaps after step 1 is normal, that's why we are doing revision!

 If your notes don't help during step 2, they are not good enough! (Change your note taking method and try to understand the problem)
 If you don't understand why the mark scheme answer is correct, see Andy.





If you come to a complete dead-end, **STOP!** and speak to **Andy** asap.



1 1 . 2	Amine F can be prepared in a three-step synthesis starting from methylbenzene.
	Suggest the structures of the two intermediate compounds.
	For each step, give reagents and conditions only. Equations and mechanisms are not required.
	[5 marks]
	END OF QUESTIONS
	Turn over ►
	IB/M/Jun17/7405/2

11

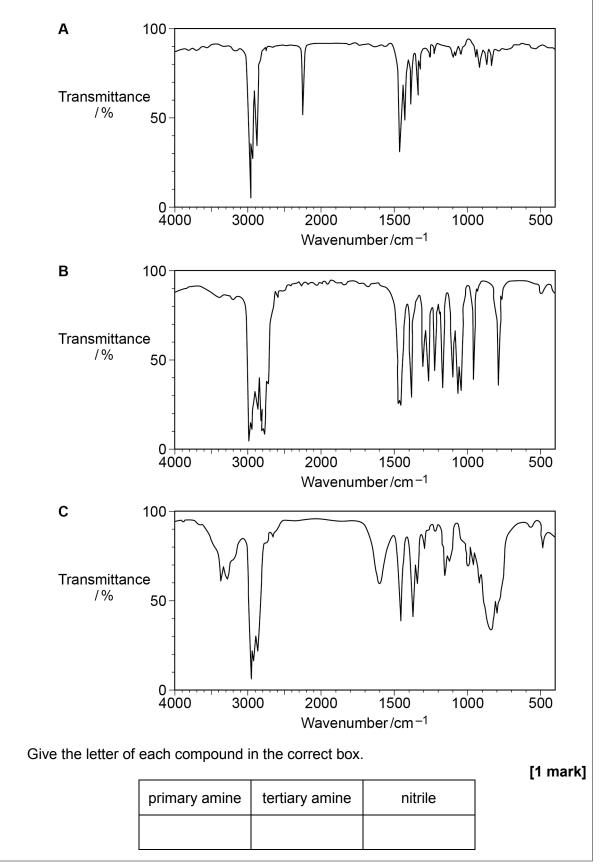
Question	Answers	Mark	Additional Comments/Guidance
	(Strength depends on availability of) lone pair on N (atom)	M1	
	E N (next to ring): (Ip) <u>delocalised</u> into ring	M2	
	(lp) less available (to donate to or to accept a H^+)	M3	
11.1	F or G : N (next to alkyl): (positive) inductive effect/electrons pushed to N	M4	
	(lp) more available (to donate to or to accept a H^{+})	M5	
	order of increasing base strength E <g<f< td=""><td>M6</td><td>Or F is most basic and E is least basic</td></g<f<>	M6	Or F is most basic and E is least basic

	Intermediate compounds		
	Product of step 1 C ₆ H ₅ CH ₂ CI	1	Allow $C_6H_5CH_2Br$
	Product of step 2 C ₆ H ₅ CH ₂ CN	1	In steps 2 and 3, only allow marks for
	Reagents/conditions		reagents/conditions if intermediate compounds are correct or close.
11.2	Step 1 Cl ₂ & UV	1	Allow Br ₂ & UV
	Step 2 KCN alcoholic & aq (both reqd)	1	Ignore temperature
	Step 3 H ₂ / Ni or Pt or Pd	1	Allow LiAlH₄ in (dry) ether – (with acid CE, followed by acid allow) Not NaBH₄ and not Sn/HCl or Fe/HCl
Total		11	



This question is about amines.

The infrared spectra **A**, **B** and **C** are those of a primary amine, a tertiary amine and a nitrile, but not necessarily in that order.





10.2	There are three secondary amines that contain four carbon atoms per molecule.
	Draw the skeletal formulas of these three secondary amines. [2 marks]
10.3	Primary amines can be prepared by the reaction of halogenoalkanes with ammonia or by the reduction of nitriles.
	Justify the statement that it is better to prepare primary amines from nitriles rather
	than from halogenoalkanes. [2 marks]
10.4	Draw the structure of a primary amine with four carbon atoms that cannot be formed from a nitrile.
	[1 mark]



Turn over ►

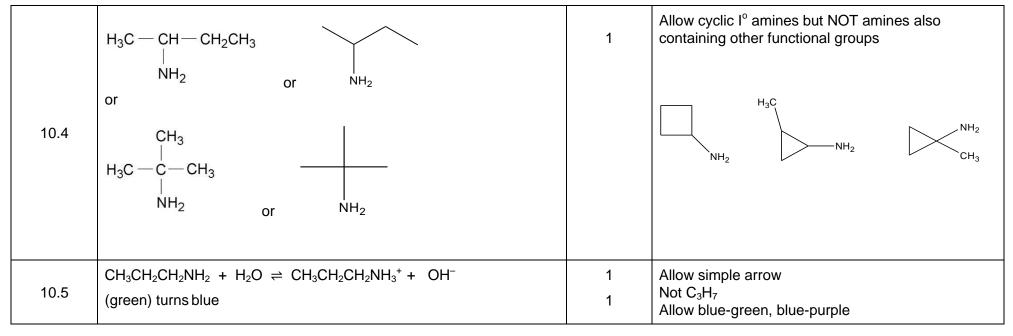
1 0.5	A student dissolves a few drops of propylamine in 1 cm ³ of water in a test tube.	
	Give an equation for the reaction that occurs. Describe what is observed when Universal Indicator is added to this solution. [2 marks]	
	Equation	
	Observation	
10.6	Phenylamine can be prepared by a process involving the reduction of nitrobenzene using tin and an excess of hydrochloric acid.	
	Give an equation for the reduction of nitrobenzene to form phenylamine. Use [H] to represent the reducing agent. Explain why an aqueous solution is obtained in this reduction even though phenylamine is insoluble in water.	
	[2 marks]	
	Equation	
	Explanation	
		10



MARK SCHEME – A-LEVEL CHEMISTRY – 7405/2 – JUNE 2018

Question	Answers	Mark	Additional Comments/Guidance
A 10.1	<u>CBA</u> this order only	1	
	Any three from		Must be skeletal – allow with or without H on N
	N or H		All 3 correct score 2 (or one if not skeletal) Any two correct score 1 (or zero if not skeletal)
	N OR H	2	Allow cyclic II ^o amines but NOT amines also containing other functional groups
10.2			
	N OR H		
			N H

	With halogenoalkane: further reaction (of primary amines)	1	Ignore bi-product / yield
	OR		
	Impure product/mixture of products/lower atom economy		
10.3			
	With nitriles		
	No further reaction	1	
	OR		
	Single product / higher atom economy		



	$\begin{array}{rcl} C_6H_5NO_2 &+& 6[H] &\rightarrow C_6H_5NH_2 &+& 2H_2O \\ \\ OR \end{array}$	1	Not H ₂ Not molecular formulae
10.6	$NO_2 + 6[H] \longrightarrow NH_2 + 2H_2O$		
	$C_6H_5NH_2$ present as ionic salt OR $C_6H_5NH_3^+$ (Cl ⁻) OR phenyl ammonium (chloride)	1	Allow present as an ion But not phenylammonium hydroxide
Total		10	

	D
Answer all questions in the spaces provided.	Do not write outside the box
This question is about amines.	
Give an equation for the preparation of 1,6-diaminohexane by the reaction of 1,6-dibromohexane with an excess of ammonia. [2 marks]	
Complete the mechanism for the reaction of ammonia with 6-bromohexylamine to form 1,6-diaminohexane.	
Suggest the structure of a cyclic secondary amine that can be formed as a by-product in this reaction. [4 marks]	
Mechanism	
NH ₃	
Br NH2	

Cyclic secondary amine



0 1

1.

0 1.2

1

0

0 1.3	1,6-Diaminohexane can also be formed in a two-stage synthesis starting from	Do not write outside the box
	1,4-dibromobutane. Suggest the reagent and a condition for each stage in this alternative synthesis.	
	[3 marks] Stage 1 reagent and condition	
	Stage 2 reagent and condition	
0 1.4	Explain why 3-aminopentane is a stronger base than ammonia. [2 marks]	
0 1 . 5	Justify the statement that there are no chiral centres in 3-aminopentane. [1 mark]	
		12
	Turn over for the next question	



Question	Answers	Additional Comments/Guidelines	Mark
01.1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	 M1 both organic compounds correct (not molecular formulae) Allow one correct structural formula and the other correct molecular formula of type XC₆H₁₂X M2 balanced 	2
	M1 arrow & lone pair Br H H H H H M2 structure	Or with structural formulae, $Br(CH_2)_6NH_2$ etc Allow $S_N 1$ Penalise incorrect partial charges in M1	3
01.2	(:NH ₃ $)$ M3 arrow NH ₃ removal need not be shown but penalise Br ⁻ removal Impurity	allow	
	(or as structural formula)		1

	M1 Stage 1 reagent KCN or NaCN	Not HCN this loses M1 and M2 Any mention of acid loses M1 & M2	1
	M2 Stage 1 condition aqueous alcohol	M2 dependent on correct M1 (allow condition if only CN^{-} ions)	1
01.3	M3 Stage 2 reagent & condition H_2 and Ni or Pt or Pd	M3 only accessible if a cyanide is used in stage 1	1
01.0		Allow LiAlH ₄ (in dry ether) – acidic/aqueous = CE, but allow followed by acid. NOT NaBH ₄ NOT Sn/HCl or Fe/HCl	
		Ignore heat and reflux and pressure Apply list principle to incorrect reagents/conditions	
	In 3-aminopentane	Allow converse for ammonia	
01.4	Lone pair on N more available or Lone pair on N accepts H⁺ better	Or greater stability of protonated N	1
	because of alkyl electron pushing /inductive effect	Mark independently	1
01.5	No carbon (atom is) attached to 4 different groups	Allow central carbon has two alkyl groups Allow symmetrical molecule	1

1 0	This question is about the reaction scheme shown.		
	$\begin{array}{c} CH_{3} \\ step 2 \\ NO_{2} \\ NH_{2} \\ Mine A \end{array} \xrightarrow{\begin{array}{c} CH_{3} \\ step 3 \\ NH_{2} \\ NHCOCH_{3} \end{array}} \xrightarrow{\begin{array}{c} CH_{3} \\ CH_{3} \\ NHCOCH_{3} \\ CH_{3} \\ $		
	$\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$		
10.1	State the reagents needed for step 1 and the reagents needed for step 2 . [3 marks]		
	step 1		
	step 2		
10.2	Give the name of the mechanism for the reaction in step 3 . [1 mark]		



1 0 . 3	Name the reagent for step 4 .		Do not write outside the box
	State a necessary condition for step 4 .		
	Reagent	[2 marks]	
	Condition		
10.4	Amine A is formed in step 2 and amine B is formed in step 5 .		
	Explain why the yield of B in step 5 is less than the yield of A in step 2 .	[2 marks]	
10.5	Explain why amine B is a stronger base than amine A .	[2 marks]	
		[2 marks]	
			10
	END OF QUESTIONS		



Question	Answers	Additional Comments/Guidelines	Mark
	Step 1 Conc HNO ₃		M1
10.1	Step 1 Conc H ₂ SO ₄	If conc missing in both allow 1 for HNO_3 and H_2SO_4	M2
10.1	Step 2 Sn and HCl	Allow Fe and HCl or Ni and H_2	M3 (3 x AO1)

Question	Answers	Additional Comments/Guidelines	Mark
10.2	(nucleophilic) addition-elimination		1 (AO1)

Question	Answers	Additional Comments/Guidelines	Mark
	Chlorine	Allow Cl ₂	M1
10.3	UV (light)	Allow sunlight / High temp (above 300°c)	M2 (2 x AO1)

Question	Answers	Additional Comments/Guidelines	Mark
10.4	In Step 5 further substitution / gives other amine products		1
	In Step 2 only one amine		1 (2 x AO3)

Question	Answers	Additional Comments/Guidelines	Mark
10.5	In B Alkyl group is electron donating or positive inductive effect	Or in A lone pair (on N partially) delocalised	1
	Lone pair <u>on N</u> more available	Lone pair <u>on N</u> less available	1 (2 x AO2)