Version 1.2



General Certificate of Education (A-level)
June 2012

Chemistry CHEM4

(Specification 2420)

Unit 4: Kinetics, Equilibria and Organic Chemistry

Final

Mark Scheme

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation events which all examiners participate in and is the scheme which was used by them in this examination. The standardisation process ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for standardisation each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, examiners encounter unusual answers which have not been raised they are required to refer these to the Principal Examiner.

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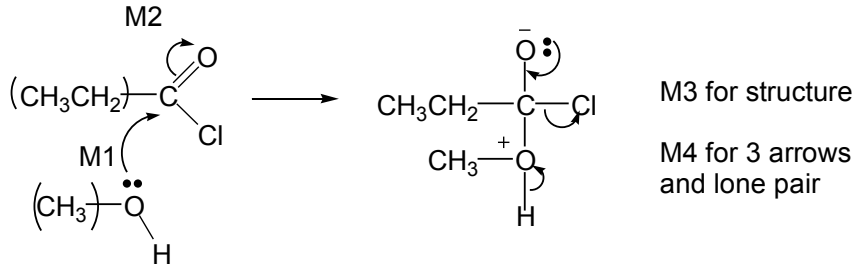
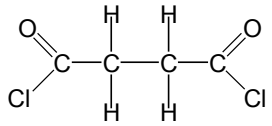
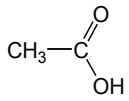
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Question	Marking Guidance		Mark	Additional Guidance
1(a)(i)	mol H_2 = 0.47 mol I_2 = 0.17		1 1	If answers reversed, ie mol H_2 = 0.17 mol I_2 = 0.47 then allow one mark (for second answer).
1(a)(ii)	$\frac{[HI]^2}{[H_2][I_2]}$	Penalise expression containing V But mark on in (a)(iv)	1	**Penalise missing square brackets** in this part (and not elsewhere in paper) but mark on in (a)(iv)
1(a)(iii)	equal number of <u>moles</u> (on each side of equation) ***OR*** equal <u>moles</u> (top and bottom of *K*c expression)		1	
1(a)(iv)	$\frac{[1.94]^2}{[0.38][0.19]}$ = 52(.1)	Ignore V	1 1	If *K*c wrong in (a)(ii) (wrong powers or upside down etc) no marks here
1(b)(i)	**D**		1	
1(b)(ii)	**B**		1	
1(b)(iii)	**A**		1	
1(b)(iv)	**C**		1	

Question	Marking Guidance	Mark	Additional Guidance
2(a)	Exp 2 4.5×10^{-4} Exp 3 4.5×10^{-3} Exp 4 0.043 OR 4.3×10^{-2} OR 0.044 OR 4.4×10^{-2}	1 1 1	Min 2sf If three wrong answers, check their value of *k* in 2(b). They can score all 3 if they have used their (incorrect) value of *k*. see below. Exp 2 rate = $k \times (1.0125 \times 10^{-4})$ Exp 3 [**Q**] = $0.02/k$ Exp 4 [**P**] = $0.0913/\sqrt{k}$
2(b)	$k = \dfrac{5.0 \times 10^{-5}}{(2.5 \times 10^{-2})^2 \times (1.8 \times 10^{-2})}$ = 4.4(4) (allow 40/9) $mol^{-2}dm^{+6}s^{-1}$	1 1 1	Mark is for insertion of numbers into a correctly rearranged rate equ , *k* = etc If upside down, score only units mark from their *k* AE (-1) for copying numbers wrongly or swapping two numbers Any order If *k* calculation wrong, allow units conseq to their *k* expression

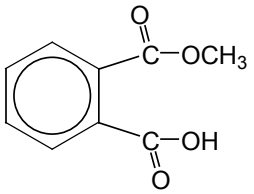
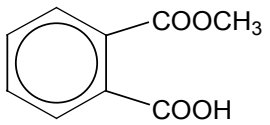
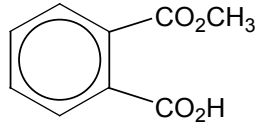
Question		Marking Guidance	Mark	Additional Guidance
3(a)		Proton donor or H^+ donor	1	Allow donator
3(b)(i)		B B	1	Both need to be correct to score the mark
3(b)(ii)		A A	1	Both need to be correct to score the mark
3(b)(iii)		B A	1	Both need to be correct to score the mark
3(c)	M1	$[H^+] = 10^{-1.25}$ OR 0.05623	1	
	M2	mol HCl = $(25 \times 10^{-3}) \times 0.0850$ (= 2.125×10^{-3})	1	Mark for Working
	M3	vol (= $\frac{2.125 \times 10^{-3}}{0.05623}$) = 0.0378 dm^3 or 37.8 cm^3 allow 0.0375 – 0.038 dm^3 or 37.5 –38 cm^3	1	Units and answer tied Lose M3 if total given as (25+ 37.8) = 62.8 cm^3 Ignore "vol added = 12.8cm^3" after correct answer
3(d)(i)		4.52	1	Must be 2dp
3(d)(ii)		$K_a = \frac{[H^+][X^-]}{[HX]}$ ignore = $\frac{[H^+]^2}{[HX]}$ but this may score M1 in d(iii)	1	Must have all brackets but allow ( ) Allow HA etc **NO** mark for 10^{-pKa}
3(d)(iii)		M1 $K_a = \frac{[H^+]^2}{[HX]}$ or with numbers	1	Allow $[H^+] = \sqrt{(Ka \times [HA])}$ for M1
		M2 $[H^+] = (\sqrt{(3.01 \times 10^{-5} \times 0.174)} = \sqrt{(5.24 \times 10^{-6})})$ $= 2.29 \times 10^{-3} - 2.3 \times 10^{-3}$	1	Mark for <u>answer</u> **Allow 1 for correct pH from their wrong $[H^+]$**
		M3 pH = 2.64 (allow more than 2dp but not fewer)	1	If square root forgotten, pH = 5.28 scores 2 for M1 and M3

3(e)	M1	mol OH^- = $(10.0 \times 10^{-3}) \times 0.125 = 1.25 \times 10^{-3}$	1	Mark for answer
	M2	orig mol HX = $(15.0 \times 10^{-3}) \times 0.174 = 2.61 \times 10^{-3}$	1	Mark for answer
	M3	mol HX in buffer = orig mol HX – mol OH^- $= 2.61 \times 10^{-3} - 1.25 \times 10^{-3} = 1.36 \times 10^{-3}$ ($[HX] = 1.36 \times 10^{-3}/25 \times 10^{-3} = 0.0544$)	1	Mark for answer Allow conseq on their (M2 – M1) If no subtraction, max 3 for M1, M2 & M4 (pH = 4.20) If $[H^+] = [X^-]$ & √ used, max 3 for M1, M2 & M3 (pH = 2.89)
	M4	mol X^- in buffer = mol OH^- = 1.25×10^{-3} ($[X^-] = 1.25 \times 10^{-3}/25 \times 10^{-3} = 0.05$)	1	May be scored in M5 expression
	M5	$[H^+]$ $\left(= \frac{Ka \times [HX]}{[X^-]} \right)$ $= \frac{3.01\times10^{-5} \times 1.36\times10^{-3}}{1.25\times10^{-3}}$ OR $\frac{3.01\times10^{-5} \times 0.0544}{0.05}$ $(= 3.27 \times 10^{-5})$	1	If use $K_a = \frac{[H^+]^2}{[HX]}$ no further marks If either value of HX or X^- used wrongly or expression upside down, no further marks
	M6	pH = 4.48 or 4.49 (allow more than 2dp but not fewer)	1	Do **not** allow M6 for correct calculation of pH using their $[H^+]$ - this only applies in 3d(iii) - apart from earlier AE

Question	Marking Guidance	Mark	Additional Guidance
4(a)	 methyl propanoate (**NO** mark for name of mechanism)	4 1	• M2 not allowed independent of M1, but allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • If Cl lost with C=O breaking, max1 for M1 • M3 for correct structure <u>with charges</u> but lp on O is part of M4 • only allow M4 after correct/very close M3 • ignore Cl^- removing H^+
4(b)(i)	pentan<u>e</u>-<u>1,5</u>-diol	1	Second 'e' and numbers needed Allow <u>1,5</u>-pentan<u>e</u>diol but this is not IUPAC name
4(b)(ii)		1	Must show ALL bonds
4(b)(iii)	All three marks are independent M1 (base or alkaline) Hydrolysis (allow close spelling) M2 <u>δ+ C</u> in polyester M3 reacts with OH^- or hydroxide ion	 1 1 1	 Allow (nucleophilic) addition-elimination or saponification Not reacts with NaOH
4(c)(i)		1	Allow CH_3COOH or CH_3CO_2H

4(c)(ii)	(nucleophilic) addition-elimination OR (nucleophilic) addition followed by elimination	1	Both addition and elimination needed and in that order Do **not** allow electrophilic addition-elimination / esterification Ignore acylation

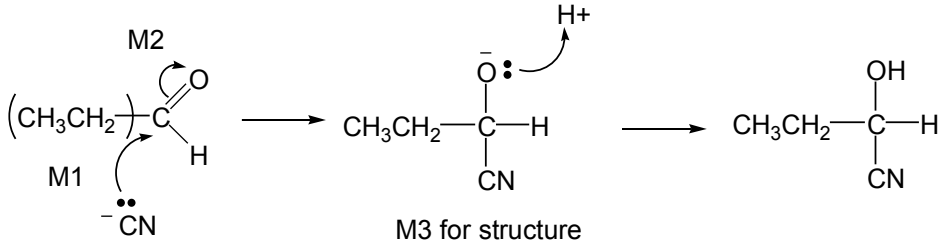
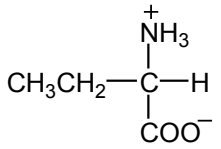
4(c)(iii)	any **two** from: ethanoic anhydride is • less corrosive • less vulnerable to hydrolysis • less dangerous to use, • less violent/exothermic/vigorous reaction OR more controllable rxn • does not produce toxic/corrosive/harmful fumes (of HCl) OR does not produce HCl • less volatile	2 max	**NOT** COST List principle beyond two answers

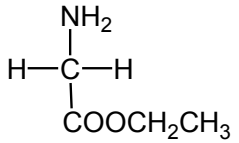
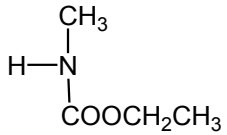
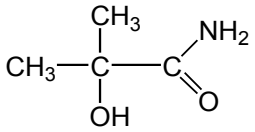
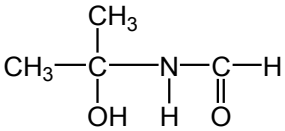
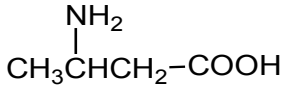
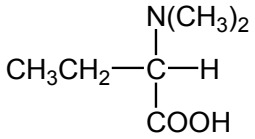
4(d)		1	Allow  or 

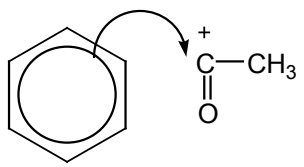
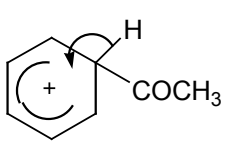
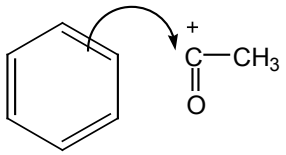
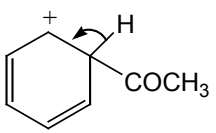
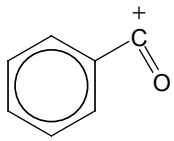
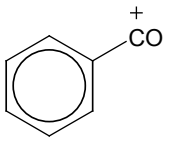
4(e)(i)	ester	1	Do **not** allow ether Ignore functional group/linkage/bond

4(e)(ii)	12 or twelve (peaks)	1	

4(e)(iii)	160 – 185			1	Allow a number or range within these limits Penalize extra ranges given Ignore units
4(f)(i)	sulfuric acid	sodium hydroxide	√	2	4 correct scores 2 3 correct scores 1 2 or 1 correct scores 0
	hydrochloric acid	ammonia	X or blank		
	ethanoic acid	potassium hydroxide	√		
	nitric acid	methylamine	X or blank		
4(f)(ii)	<u>Pink to colourless</u>			1	Allow 'red' OR 'purple' OR 'magenta' instead of 'pink' Do **not** allow 'clear' instead of 'colourless'

Question	Marking Guidance	Mark	Additional Guidance
5(a)	nucleophilic addition M4 for lp and arrow to H^+  M3 for structure	1 4	• allow :CN^- • M2 not allowed independent of M1, but • allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • M3 is for correct structure including minus sign but lone pair is part of M4 • Allow C_2H_5 • M1 and M4 for lp and curly arrow
5(b)	2-bromobutanenitrile	1	Allow 2-bromobutane-1-nitrile
5(c)	**M1** ammonia or NH_3 **M2** excess (ammonia) excess tied to NH_3 and may score in M1 unless contradicted **M3** nucleophilic substitution	1 1 1	Ignore temp or pressure Ignore concentrated or sealed container, Acid loses conditions mark Allow close spelling
5(d)(i)	 	1	Allow C_2H_5 Allow $-CO_2^-$ Allow $^+NH_3-$ Don't penalize position of + on NH_3
5(d)(ii)	**M1** electrostatic forces between ions in **X** **QOL** Marks independent **M2** (stronger than) hydrogen bonding between $CH_3CH_2CH(OH)COOH$	1 1	Allow ionic bonding. **CE** mention of molecules of **X** or inter molecular forces between **X** loses both marks

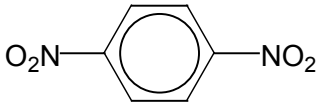
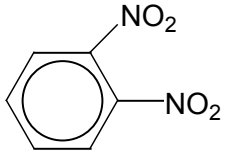
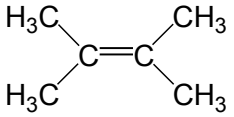
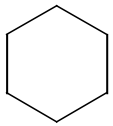
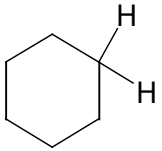
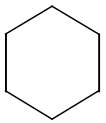
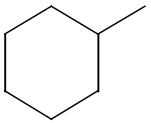
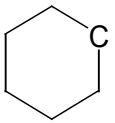
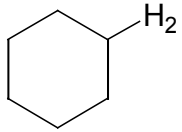
5(e)(i)	 OR 	1	Isomer of $C_4H_9NO_2$ Allow NH_2–
5(e)(ii)		1	Isomer of $C_4H_9NO_2$ allow NH_2– Allow 
5(e)(iii)	$H_2N—CH_2CH_2CH_2—COOH$ or $H_2N—(CH_2)_3—COOH$ OR 	1	Isomer of $C_4H_9NO_2$ allow NH_2– Do **not** allow $–C_3H_6-$ Beware – do not credit **X** itself
5(f)		1	Answer has 6 carbons so **NOT** isomer of **X** Allow C_2H_5 Must have bond from C to N not to methyl group

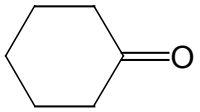
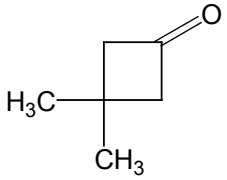
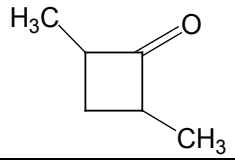
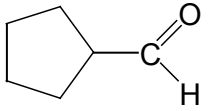
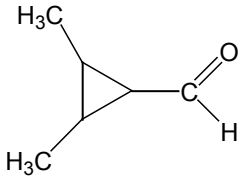
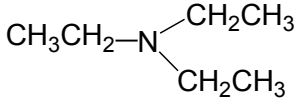
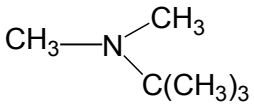
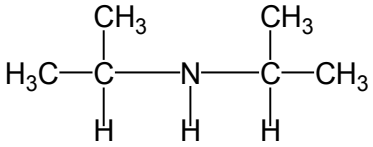
Question	Marking Guidance	Mark	Additional Guidance
6(a)	$CH_3COCl + AlCl_3 \longrightarrow CH_3CO^+ + AlCl_4^-$	1	Allow RHS as $CH_3-C^{\delta+}(=O)\cdots Cl\cdots AlCl_3^{\delta-}$ Allow + on C or O in equation but + must be on C in mechanism below Ignore curly arrows in equation even if wrong.
	$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$	1	
	M1  M3  M2 OR M1  M3  M2	3	• M1 arrow from within hexagon to C or to + on C • + must be on C of RCO in mechanism • + in intermediate not too close to C1 • gap in horseshoe must be centred approximately around C1 • M3 arrow into hexagon unless Kekule • allow M3 arrow independent of M2 structure • ignore base removing H for M3 • **NO** mark for name of mechanism
	Phenylethanone ignore 1 in name, penalise other numbers	1	Note: this is the sixth marking point in 6a
6(b)	 or 	1	+ must be on C But allow $[C_6H_5CO]^+$

6(c)	M1 about electrons	methyl group has (positive) inductive effect OR increases electron density on benzene ring OR pushes electrons OR is electron releasing	1	Ignore reference to delocalisation
	M2 about attraction	electrophile attracted more or benzene ring better nucleophile	1	Allow intermediate ion stabilised **M2 only awarded after correct or close M1**

Question	Marking Guidance							Mark	Additional Guidance
7(a)	**If 2 stage test for one compound, award no marks for that compound, eg no mark for ROH or RX to alkene then Br_2 test. If reagent is wrong or missing, no mark for that test; if wrong but close/incomplete, lose reagent mark but can award for correct observation. In each test, penalise each example of wrong chemistry, eg $AgCl_2$**								
	propan-1-ol	M1	acidified potassium dichromate	sodium	Named acid + conc H_2SO_4	named acyl chloride	PCl_5	1	
		M2	(orange) turns green	effervescence	Sweet smell	Sweet smell /misty fumes	Misty fumes	1	
	propanal	M3	add Tollens or Fehlings / Benedicts	acidified potassium dichromate	Bradys or 2,4-dnph			1	if dichromate used for alcohol cannot be used for aldehyde
		M4	Tollens: silver mirror or Fehlings/ Benedicts: red ppt	(orange) turns green	Yellow or orange ppt			1	
	propanoic acid	M5	Named carbonate/ hydrogencarbonate	water and UI (paper)	Named alcohol + conc H_2SO_4	sodium or magnesium	PCl_5	1	if sodium used for alcohol cannot be used for acid
		M6	effervescence	orange/red	Sweet smell	effervescence	Misty fumes	1	if PCl_5 used for alcohol cannot be used for acid
	1-chloro propane	M7	NaOH then acidified $AgNO_3$	$AgNO_3$				1	If acidification missed after NaOH, no mark here but allow mark for observation
		M8	white ppt	white ppt				1	

7(b)	M1 oxidation (of alcohol by oxygen in air) M2 absorption at 1680 -1750 (due to C=O) M3 – comparison of polarity of molecules or correct imf statement: propanone is less polar OR propan-2-ol is more polar OR propanone has dipole-dipole forces OR propan-2-ol has hydrogen bonding M4 - about attraction to stationary phase or solubility in moving phase Propan-2-ol has greater affinity for stationary phase or vice versa OR propanone is more soluble in solvent/moving phase or vice versa I	1 1 1 1 	Must refer to the spectrum

Question	Marking Guidance		Mark	Additional Guidance
8(a)	**F**	**G**		Penalize –O_2N once Penalise missing circle once Don't penalise attempt at bonding in NO_2
			1, 1	
8(b)	**H**	**J**		If **both H** and **J** correct but reversed, award one mark
			1, 1	
	A carbon in saturated ring structures should be shown as  OR  but not  OR  OR 			

Question	Marking Guidance		Mark	Additional Guidance
8(c)	**K**	**L**		
	 OR  OR 	 OR 	1, 1	
8(d)	**M**	**N**		
	 OR 		1, 1	Allow C_2H_5 but NOT allow C_4H_9 or C_3H_7

General principles applied to marking CHEM4 papers by CMI+ (June 2012)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**
-

A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a candidate gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

N.B. Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip.
For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

N.B. Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (**QoL**) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the candidate to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.
For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $Ag(NH_3)_2^+$ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a candidate provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

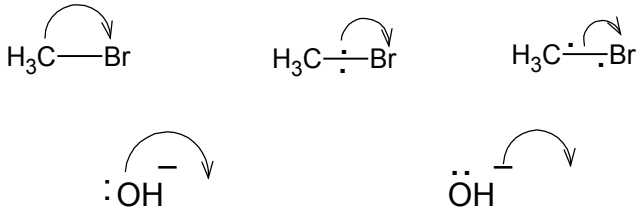
G. Marking calculations

In general

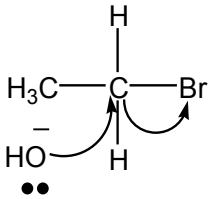
- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.
The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

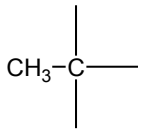
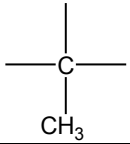
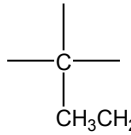
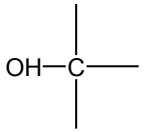
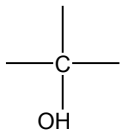
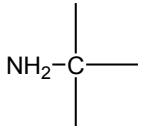
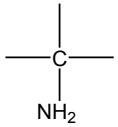
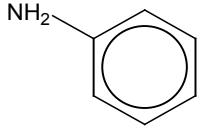
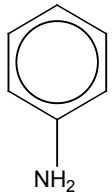
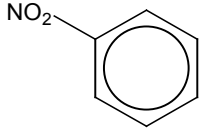
- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

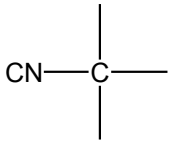
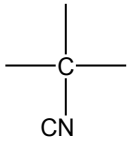
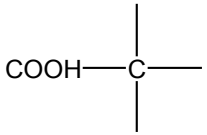
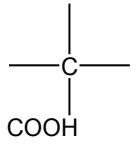
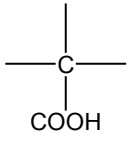
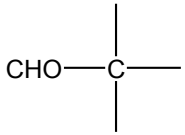
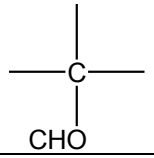
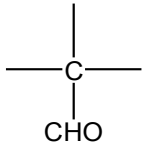
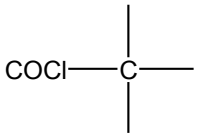
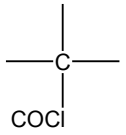
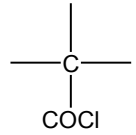
In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

I. Organic structures

In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if candidates show the alcohol functional group as C ─ HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C ─ C bonds in alkyl groups, given that CH_3─ is considered to be interchangeable with H_3C─ even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH_2─ C will be allowed, although H_2N─ C would be preferred.
- Poor presentation of vertical C ─ CH_3 bonds or vertical C ─ NH_2 bonds should **not** be penalised. For other functional groups, such as ─ OH and ─ CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.
  By way of illustration, the following would apply.

				
allowed	**allowed**	not allowed	not allowed	not allowed
				
allowed	**allowed**	**allowed**	**allowed**	not allowed

					
not allowed	not allowed	not allowed	not allowed	not allowed	
					
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

- In most cases, the use of "sticks" to represent C ─ H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C ─ H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH_3COH	for	ethanal
CH_3CH_2HO	for	ethanol
$OHCH_2CH_3$	for	ethanol
C_2H_6O	for	ethanol
CH_2CH_2	for	ethene
$CH_2.CH_2$	for	ethene
$CH_2:CH_2$	for	ethane

N.B. Exceptions <u>may</u> be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
$CH_3CHOHCH_3$	for	propan-2-ol, $CH_3CH(OH)CH_3$

J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit.
Some illustrations are given here.

but-2-ol	should be **butan-2-ol**
2-hydroxybutane	should be **butan-2-ol**
butane-2-ol	should be **butan-2-ol**
2-butanol	should be **butan-2-ol**
ethan-1,2-diol	should be **ethane-1,2-diol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan	should be **3-methylpentane**
3-mythylpentane	should be **3-methylpentane**
3-methypentane	should be **3-methylpentane**
propanitrile	should be **propanenitrile**
aminethane	should be **ethylamine** (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be **2-bromo-3-methylbutane**
3-bromo-2-methylbutane	should be **2-bromo-3-methylbutane**
3-methyl-2-bromobutane	should be **2-bromo-3-methylbutane**
2-methylbut-3-ene	should be **3-methylbut-1-ene**
difluorodichloromethane	should be **dichlorodifluoromethane**