Version 1.1

General Certificate of Education
June 2010

Chemistry CHEM4

Kinetics, Equilibria and Organic Chemistry

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 meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting 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 the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

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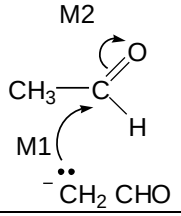
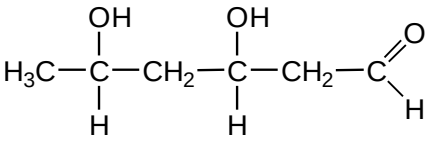
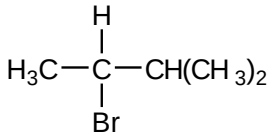
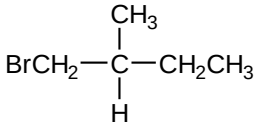
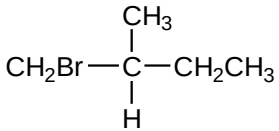
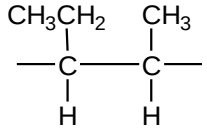
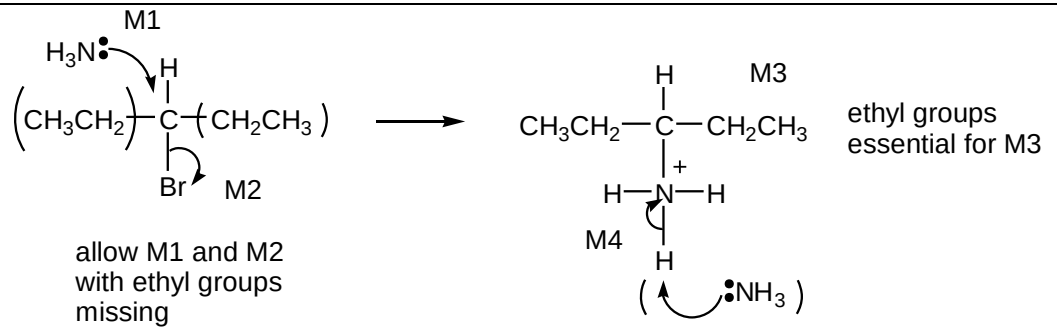
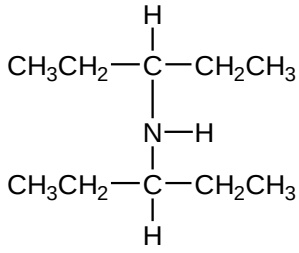
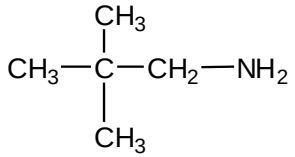
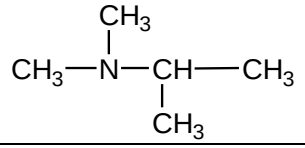
Q	Part	Sub Part	Marking Guidance	Mark	Comments
1	(a)		3-hydroxybutanal ignore number 1 i.e. allow 3-hydroxybutan-1-al	1	not hydroxy**l**
1	(b)		$k = \frac{2.2 \times 10^{-3}}{(0.10)(0.02)}$ $= 1.1$ $mol^{-1}dm^3s^{-1}$	1 1 1	
1	(c)		planar or flat C=O or molecule equal probability of attack from above or below	1 1	allow planar molecule must be equal; not attack of OH^-
1	(d)	(i)	Step 1 if wrong – no mark for explanation. involves ethanal and OH^- or species/"molecules" in rate equation	1 1	
1	(d)	(ii)	(B-L) acid or proton donor	1	not Lewis acid
1	(d)	(iii)	nucleophilic addition	1	QOL
1	(d)	(iv)		2	not allow M2 before M1, but allow M1 attack on C+ after non-scoring carbonyl arrow ignore error in product
1	(e)			1	

Q	Part	Sub Part	Marking Guidance		Mark	Comments
2	(a)	(i)	mol CH_4 = 0.75		1	
			mol H_2O = 1.5		1	
			mol H_2 = 1(.0)		1	
2	(a)	(ii)	0.15 (mol dm^{-3})		1	conseq = (mol CH_4)/5
2	(b)	(i)	$\frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}$	not just numbers	1	do not penalise ( ) If wrong Kc no marks for calc but allow units conseq to their Kc
2	(b)	(ii)	$\frac{(0.15)(0.25)^4}{(0.10)(0.48)^2}$		1	No marks for calc if concs used wrongly or wrong values inserted
			0.025(4)		1	
			$mol^2\ dm^{-6}$		1	allow 1 here for correct units from wrong Kc
2	(c)		increase		1	if wrong, no further marks in (c)
			lower P	M1	1	not “greater volume” for M1 but allow “moves to form a greater volume” for M2
			eqm shifts to side with more moles (Le Chatelier)	M2	1	
2	(d)		(forward reaction is) endothermic or backward reaction is exothermic		1	
			eqm shifts in exothermic direction or to oppose reduction of or change in temp		1	This mark must have reference to temp change or exothermic reaction

Q	Part	Sub Part	Marking Guidance	Mark	Comments
3	(a)	(i)	 must be **branched** and chiral or  or 	1	not allow C_3H_7 allow C_2H_5 bonded to C either way round
3	(a)	(ii)	elimination allow base – elimination	1	but penalise any other qualification
3	(a)	(iii)	Z-pent-2-ene or cis-pent-2-ene either Z or cis is necessary (allow Z-2-pentene or cis-2-pentene)	1	with or without brackets around Z with or without hyphens
3	(b)	(i)	C	1	
3	(b)	(ii)	A	1	
3	(b)	(iii)	B	1	
3	(b)	(iv)	D	1	
3	(c)		 allow C_2H_5 bonded via C or H addition or radical or step or chain growth	1 1	must have both trailing bonds ignore brackets or n QOL not additional

3	(d)	(i)	 allow M1 and M2 with ethyl groups missing ethyl groups essential for M3	4	Allow SN1, i.e M2 first then attack of NH_3 on carbocation. Allow C_2H_5 in M3 bonded either way Allow with or without NH_3 to remove H^+ in M4, but lose mark if Br^- used. ignore $\delta+$ or $\delta-$ unless wrong + on central C instead of $\delta+$ loses M2
3	(d)	(ii)	<u>excess</u> NH_3 ignore reflux	1	allow conc ammonia in sealed tube
3	(d)	(iii)	 NOT $-C_5H_{11}$	1	Allow C_2H_5 bonded either way
3	(e)	(i)		1	
3	(e)	(ii)		1	NOT $(C_2H_5)_2NCH_3$ which is tertiary with 3 peaks but its spectrum has no doublet.

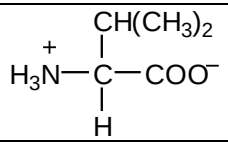
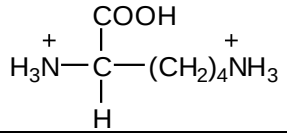
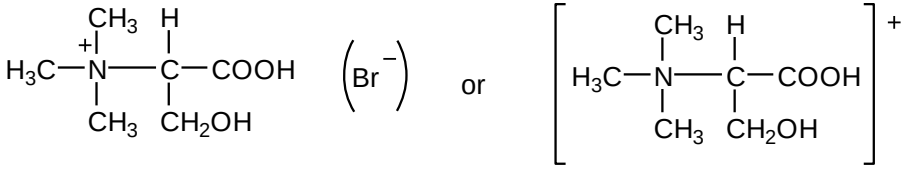
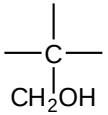
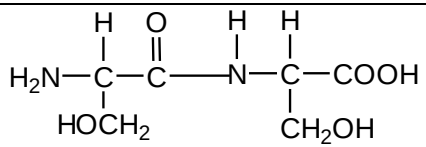
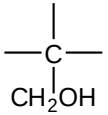
Q	Part	Sub Part	Marking Guidance	Mark	Comments
4	(a)		chromatography (allow GLC TLC GC HPLC)	1	allow any qualification
4	(b)		5 Allow 320(.0) or 322(.0)	1 1	
4	(c)		Use of excess air/oxygen or high temperature (over 800 ^{o}C) or remove chlorine-containing compounds before incineration	1	
4	(d)	(i)	$Si(CH_3)_4$ allow SiC_4H_{12} allow displayed formula and do not penalise sticks	1	Not TMS
4	(d)	(ii)	3	1	

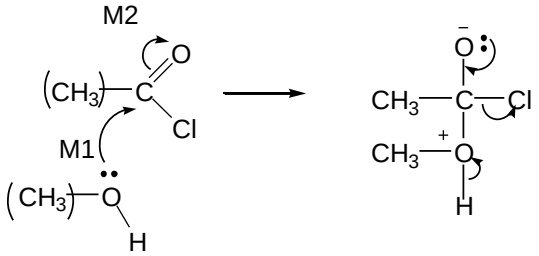
Q	Part	Sub Part	Marking Guidance		Mark	Comments
5	(a)	(i)	$-\log[H^+]$		1	penalise missing [ ] here **and not elsewhere**
5	(a)	(ii)	$[H^+][OH^-]$		1	
5	(b)	(i)	$[H^+] = 2.34 \times 10^{-7}$ pH = 6.63 *Penalise fewer than 3 sig figs but allow more than 2 dp*		1 1	
5	(b)	(ii)	$[H^+] = [OH^-]$		1	
5	(b)	(iii)	$[H^+] = K_w/[OH^-]$ $(= 5.48 \times 10^{-14} / 0.140) = 3.91 \times 10^{-13}$ pH = 12.4(1) *Penalise fewer than 3 sig figs but allow more than 3 sfs* *For values above 10, allow 3sfs - do not insist on 2 dp.* *For values below 1, allow 2dp – do not insist on 3 sig figs*	M1 M2 M3	1 1 1	if upside down or CE, allow M3 only for correct use of their $[H^+]$ not 12.40 (AE from 12.407)
			Not allow pH = 14 – pOH but can award M3 only for pH = 13.1(46) Can award all three marks if $pK_w = 13.26$ is used			

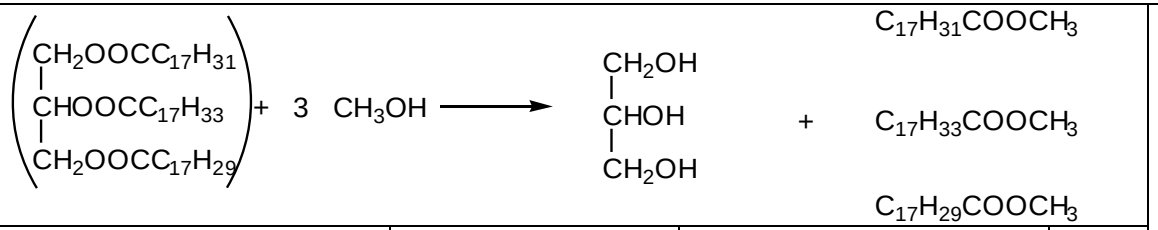
5	(c)		mol NaOH = mol OH^- = $(30\times10^{-3}) \times 0.20 = 6.0 \times 10^{-3}$	M1	1	mark for answer
			mol H_2SO_4 = $(25\times10^{-3}) \times 0.15 = 3.75\times10^{-3}$	M2	1	mark for answer
			mol H^+ = $(25\times10^{-3}) \times 0.15 \times 2 = 7.5\times10^{-3}$ OR XS mol H_2SO_4 = 0.75×10^{-3}	M3	1	if factor of 2 missed or used wrongly, CE - lose M3 and next mark gained. In this case they must then use K_w to score any more. see examples below
			XS mol H^+ = 1.5×10^{-3}	M4	1	
			$[H^+]$ = $(1.5\times10^{-3}) \times (1000/55) = 0.0273$	M5	1	if no use or wrong use of volume, lose M5 and M6 except if 1000 missed AE -1 (pH = 4.56)
			pH = 1.56 *Penalise fewer than 3 sig figs but allow more than 3 sfs* *For values above 10, allow 3sfs - do not insist on 2 dp.* *For values below 1, allow 2dp – do not insist on 3 sig figs*	M6	1	

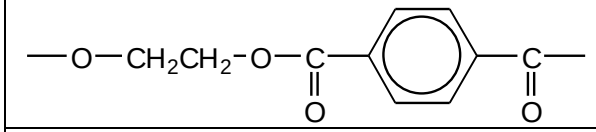
5	(d)	(i)	$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$	Must have all 3 brackets but don't penalize ( ) see note to Q5(a)(i)	1	not HA This mark could score in (d) (ii)

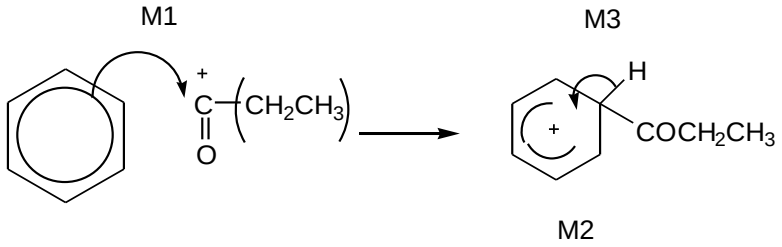
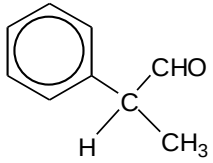
5	(d)	(ii)	$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers or $[H^+] = [CH_3COO^-]$		1	allow HA here This mark could score in (d) (i)
			$[H^+]$ =($\sqrt{(1.74\times10^{-5} \times 0.136)} = \sqrt{(2.366\times10^{-6}} =) 1.54\times10^{-3}$		1	mark for answer if 1.5×10^{-3} penalise here if miss √ but it is shown, AE -1 so allow 2 for pH = 5.63
			pH = 2.81 can give three marks here for (d)(ii) *Do not insist on 2 dp* *Penalise fewer than 3 sig figs but allow more than 3 sfs* *For values below 1, allow 2dp – do not insist on 3 sig figs*		1	allow pH = 2.82 conseq

Q	Part	Sub Part	Marking Guidance	Mark	Comments
6	(a)	(i)	hydrolysis	1	not hydration
6	(a)	(ii)	2-aminopropanoic acid	1	ignore alanine QoL
6	(a)	(iii)		1	allow $-CO_2^-$ allow $^+NH_3-$ don't penalize position of + on NH_3
6	(a)	(iv)		1	allow $-CO_2H$ allow $^+NH_3-$ don't penalize position of + on NH_3
6	(b)	(i)		1	allow $-CO_2H$ allow limit as  + on N or outside [ ]
6	(b)	(ii)		1	allow $-CO_2H$ allow $-CONH-$ or $-COHN-$ allow NH_2- allow limit as 

Q	Part	Sub Part	Marking Guidance		Mark	Comments
7	a		$CH_3CH_2CH_2COOH$	M1	1	not C_3H_7COOH
			CH_3CH_2OH or C_2H_5OH	M2	1	
			$\rightarrow CH_3CH_2CH_2COOCH_2CH_3 + H_2O$	M3	1	allow $C_3H_7COOC_2H_5$ penalise M3 for wrong products and unbalanced equation
			H_2SO_4 or HCl or H_3PO_4 conc or dil or neither	M4	1	not HNO_3
7	b		$CH_3CH_2CH_2CH_2OH$	M1	1	not C_4H_9OH
			$(CH_3CO)_2O$	M2	1	
			$\rightarrow CH_3COOCH_2CH_2CH_2CH_3 + CH_3COOH$	M3	1	allow $CH_3COOC_4H_9$ penalise M3 for wrong products and unbalanced equation
7	c		(nucleophilic) addition-elimination  		5	not acylation alone M2 not allowed indep of M1 but allow M1 for correct attack on C+ +C=O loses M2 only allow M4 after correct or v close M3 ignore Cl^- removing H^+

7	d		 (1) (1) (1)	3	ignore errors in initial triester First mark for $3CH_3OH$ Third mark for all three esters

7	e		not – C_2H_4 –  First mark for correct ester link second mark for the rest including trailing bonds	2	If ester link wrong, lose second mark also
			Adv reduces landfill saves raw materials lower cost for recycling than making from scratch reduces CO_2 emissions by not being incinerated	1	not allow cost without qualification ignore energy uses
			Disad difficulty/cost of collecting/sorting/processing product not suitable for original purpose, easily contaminated	1	not allow cost without qualification ignore energy uses

Q	Part	Sub Part	Marking Guidance	Mark	Comments
8	a		CH_3CH_2COCl OR CH_3CH_2CClO OR propanoyl chloride OR $(CH_3CH_2CO)_2O$ OR propanoic anhydride penalize contradiction in formula and name e.g. propyl chloride	1	could score in equation
			$AlCl_3$ or $FeCl_3$ or names	1	could score in equation
			$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$ Allow RCOCl in equation but penalise above	1	allow + on C or O in equation
8	b			3	M1 arrow from circle or within it to C or to + on C Horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure Ignore base removing H in M3
8	c		Tollens or ammoniacal silver nitrate	1	penalise wrong formula
				1	

General principles applied to marking CHEM4 papers by CMI+ June 2010

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

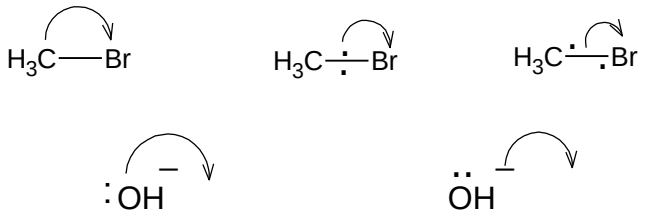
In general

- 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.

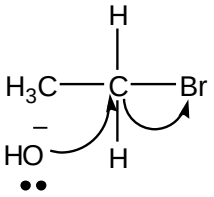
H. Organic reaction mechanisms

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

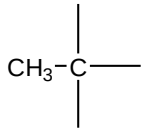
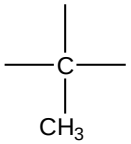
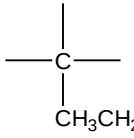
In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

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.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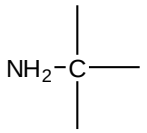	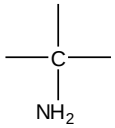	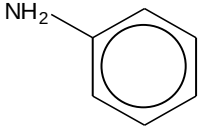	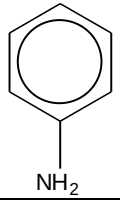	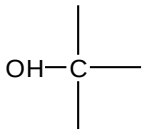	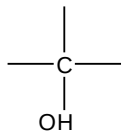
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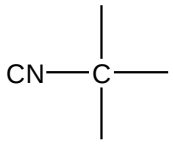	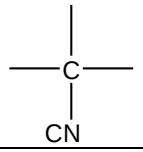	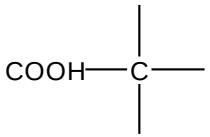	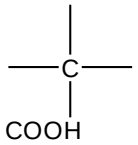	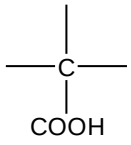	
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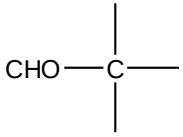	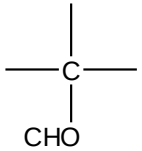	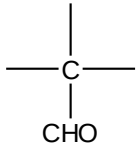	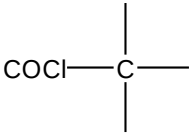	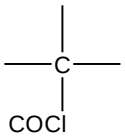	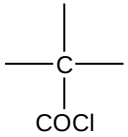
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- In most cases, the use of "sticks" to represent C — H bonds in a structure should not be penalised. The exceptions will include structures in mechanisms when the C — H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed 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	ethene

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

- 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**
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**