



Examiners' Report June 2010

GCE Chemistry 6CH05





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Introduction

This paper produced some excellent answers with the best candidates able to show that they could use the information provided to draw conclusions in circumstances they had not previously met. There were also significant opportunities for weaker candidates to show what they knew and could do, particularly in the question on transition metal chemistry which was very well answered across the board.

The paper contained a significant amount of structural chemistry and it is clear that some candidates do not sufficiently practise writing skeletal and 3-D formulae. It is too late to try and deal with the conventions in an exam - some candidates do not realise that the symbols used do have conventions if they are to be meaningful.

Calculations were generally set out well, although there remains a minority of answers that are very hard to follow because candidates do not think that words are necessary.

Although, some questions proved challenging there was no evidence that candidates were pressed for time.

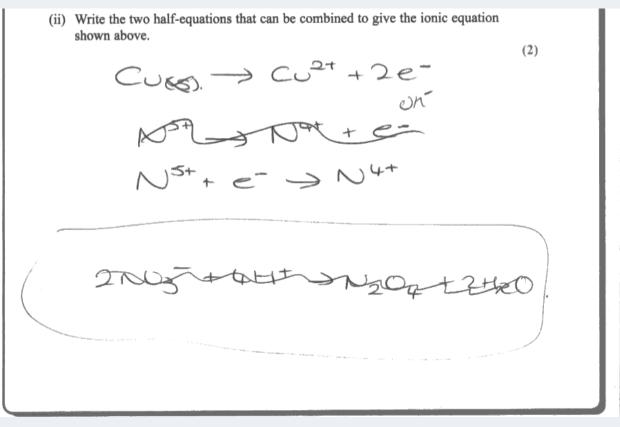
Question 21(a) (i)

This question was generally answered well with correct values for the changes in oxidation state for copper and nitrogen. Errors occurred occasionally with the values for nitrogen.

Question 21(a) (ii)

The half equations for oxidation of copper by nitrate ions were usually well known. Common errors, almost all of them in the reduction of nitrate, included starting with N⁵⁺ rather than the nitrate ion; and either omitting electrons or showing the wrong number of them.

This shows incorrect use of oxidation states to answer the question.





The nitrate ion is the species reduced; the N^{5+} ion does not exist and should not be shown.

Question 21(a) (iii)

Many candidates knew that the conditions were not standard so gained one mark, but failed to mention exactly why. Vague comments such as 'solutions not 1 mol dm⁻³ ' were common, but a specific reference to concentrated nitric acid was required for the mark.

(iii) Explain why the standard electrode potentials for the two ionic has that you have written give an incorrect value for E _{cell} for this reac described above.	
	(2)
this reaction does not occur according t	to Standard.
conclutions the munim amount of cons	elentration
used for runic acid not 1.0 mol	dm3.80-
the Ecell would be aftered from the	E'cell value.
district the second sec	



This clip shows specific reference to the concentrated nitric acid and so scores full marks.

(iii) Explain why the standard electrode potentials for the two ionic half-equations that you have written give an incorrect value for E_{cell} for this reaction as described above.

(2)

Standard electrode potentials is measured at standard conditions, as the molarity of NO₃ or Cu²⁺ may not be IM, therefore it is not at standard condition and would enterprise an it incorrect value for Eccu if we see the standard electrode potentials for calculation.

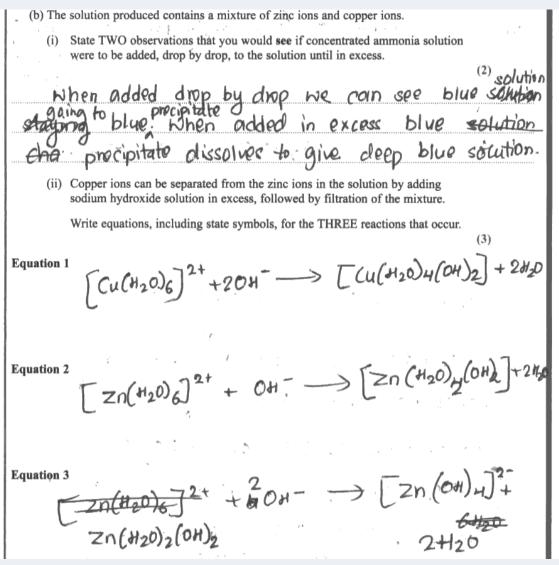


This answer is vague on the second marking point and does not identify the non-standard condition sufficiently precisely.

Question 21(b)

- (i) Most candidates gave a good account in b(i) of what is seen when ammonia is added to an aqueous mixture of zinc and copper ions. A few treated the two substances independently and suggested you would simultaneously see a colourless and a deep blue solution.
- (ii) Most candidates made things very hard for themselves in b(ii), by starting with hexaqua copper(II) or zinc(II) ions and then getting tangled up with equation balancing problems. The majority favoured the unnecessarily complex [Cu(H2O)4(OH)2] for copper(II) hydroxide, whereas Cu(OH)2 is perfectly sound and carries no difficulties with it. Many candidates forgot the need for state symbols and gave none. Only those appropriate to the metal-containing product were required.

In part (iii), most candidates did not notice, or did not realise the implication of, the reactions of zinc compounds which the question wanted. Large numbers of answers started from the hexaaquazinc(II) ion, which is not what was asked. Others stated that zinc metal is amphoteric, which is certainly untrue. However, many salvaged one mark from this question with a good understanding of what is meant by ligand exchange although some confused this with deprotonation.



*(iii) Give examples of amphoteric behaviour and ligand exchange, by reference to the reactions of zinc compounds.

Zn (OH)₂ is amphoteric as it can react with both acid and bases.

Zn(OH) (Ha) +20H - (Zn(OH)) (2+2Ha)

 $Zn(OH)_{2}(H_{2}O)_{2} + 2OH^{-} \rightarrow \left[Zn(OH)_{4}\right]^{2} + 2H_{2}O$ $Zn(OH)_{2}(H_{2}O)_{2} + OH^{-}2H^{+} \rightarrow \left[Zn(H_{2}O)_{3}\right]^{2+}$ It can also undergo ligard exchange when excess ammonia is added. $Zn(H_{2}O)_{2}(OH_{3})_{3} + 4NH_{3} \rightleftharpoons \left[Zn(NH_{0})_{2}\right]$



This clip gives a good account of the observations in (i), and is excellent on the amphoteric nature of zinc hydroxide in (iii). The formulae would perhaps have been better without the two water molecules.

The equations in (ii) are rather complicated and could have been simplified by using Cu2+ and Cu(OH)2, for example. There are no states; and the second is unbalanced. The result is 1/3.



Questions need to be read very carefully, so that the requirement for state symbols is met. In general, the simplest equation that will answer the question should be used.

Question 21(c)

- (i) Perhaps half the candidates were able to give the correct equation for reaction of thiosulfate ions with iodine. For the others, there was much confusion between thiosulphate, sulfate, persulfate and sundry other sulfur-containing ions.
- (ii) There was widespread success with the calculation of the composition of Admiralty Brass, even from numerous candidates who got the equation in part (i) wrong. In these cases, credit was given irrespective of the answer in (i); however, if candidates did use an erroneous equation in (i), then as much credit as possible was given consequentially in (ii). Inevitably, some ignored the injunction to 3 s.f. for the final answer.

The layout of calculations has improved greatly in recent years with candidates much more prepared to show what their thought processes are. Not everyone is in this happy position, however, and there are still answers where a lack of units or of linking words makes the whole process very difficult to follow.

(iii) Many candidates failed to gain the first mark by stating that some of the thiosulfate would be needed to fill the jet and, therefore, the titre would be too high. That is the significance of 'Explain...' in the question. Examiners need to know why the candidate thinks it is too high. Most gained the second mark for commenting on the consequential effect on the calculated percentage of copper.

Question 22(a) (i)

The mechanism for the nitration of benzene was widely understood and clearly written by many. The errors that occur are predictable and were duly seen. The arrow from the benzene ring should come from the delocalised ring and go to the nitrogen of the nitronium ion and not to the oxygen. The loss of the proton from the intermediate must show an arrow from the C-H bond and not from the hydrogen atom, this arrow going to the interior of the ring. The delocalisation was often shown sloppily - it must not embrace the sp3 hybridised carbon, nor must it simply be a decorative addition going over maybe only a quarter of the hexagon.

Candidates need to think of the mechanism as a representation of a dynamic process, and therefore have a picture in their mind of moving molecules and electron pairs.

(i) Give the mechanism for the nitration of **benzene**, including the equation for the reaction that produces the electrophile.



This example shows a good dynamic understanding of the mechanism. Arrows are used clearly. The removal of a proton by a hydrogensulfate ion is not a marking requirement, but does show that the candidate understands what is going on and is very much worth including.

(i) Give the mechanism for the nitration of **benzene**, including the equation for the reaction that produces the electrophile.

 $HNO_{3} + H_{2}SO_{4} \xrightarrow{SSQ} H_{2}NO_{3}^{-} + HSO_{4}^{-}$ $H_{2}NO_{3}^{-} \xrightarrow{H_{2}SO_{4}} NO_{2}^{+} + H_{2}O$ Relectrophile $HNO_{2} + NO_{2}^{+} \xrightarrow{HSO_{4}^{-}} O NO_{2}$ $HNO_{2} + HSO_{4}^{-} \xrightarrow{HSO_{4}^{-}} O NO_{2}$ $HSO_{4} \xrightarrow{HSO_{4}^{-}} O NO_{2}$



This clip encapsulates a number of common errors. In the first equation the charge is wrong on the first ion meaning that the second does not balance. Attack of the ring on the nitronium ion is shown going to the oxygen atom rather than the nitrogen atom. The remainder of the mechanism is shown correctly.



Arrows need to be drawn with accuracy. They represent what electrons are actually doing during a reaction.

Question 22(a) (ii)

The activating effect of the lone electron pair on the oxygen of the hydroxyl group on phenol was often known. A few candidates mentioned hydroxide instead of hydroxyl and a few did not mention the oxygen lone pair.

Question 22(a) (iii)-(iv)

- (iii) Most candidates knew the reagents needed to reduce a nitro group to an amino group. Concentrated hydrochloric acid was needed. Several involved sodium hydroxide as well; if this was added after the tin and concentrated hydrochloric acid then it was ignored, but if the candidate gave the impression that all were added together then a mark was lost. Other reducing mixtures such as zinc and acid, or lithium aluminium hydride, were sometimes suggested; these either do not work at all or give different products so do not gain credit.
- (iv) Virtually all candidates gave a suitable reagent for the ethanoylation of the amino group in aminophenol.

Question 22(b)

Good accounts of steam distillation were very rare indeed. Some candidates passed steam over the mixture, others used it to heat the mixture but failed to make clear that the steam is passed into it rather than used as a steam bath. Many candidates confused it with fractional distillation.

*(b) In the nitration of phenol, step 1, two compounds are produced.

2-nitrophenol

4-nitrophenol

These compounds can be separated by steam distillation, since 2-nitrophenol is volatile in steam but 4-nitrophenol is not.

Describe briefly the technique of steam distillation and give ONE advantage of steam distillation over normal distillation.

This is the usage of steem to carry the guscow compound know from the other compound. This In this case, it wars 4-nitrophenol behind. Steam distillation and doesn't decompose substances that normal distillation



This example does not make clear how the steam is used, but it does give one advantage of the method.

*(b) In the nitration of phenol, step 1, two compounds are produced.

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Describe briefly the technique of steam distillation and give ONE advantage of steam distillation over normal distillation.

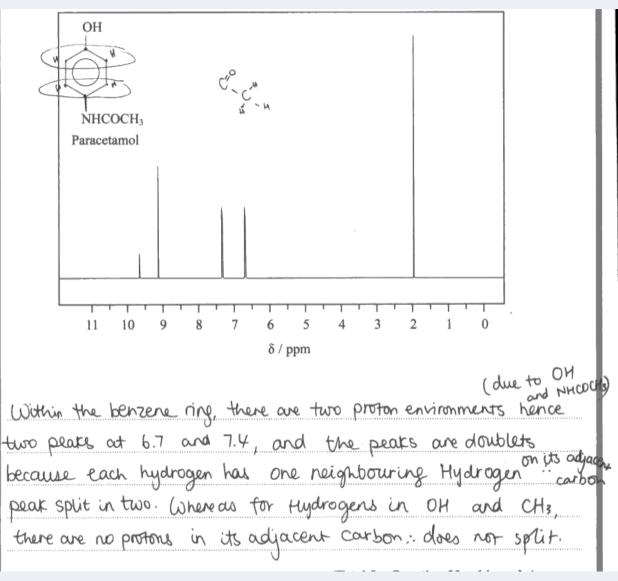
The mixture containing the 2 comparates
is breated an added to water and boiled to
water boiling point). At 100°C the water will got
to evaporate off teching 2 nino pherol with it, and there to re
leaving behind 4-ninopherol. This is better than no mall
distillation because the phenols don't reachture boiling points.



This clip adds water to the mixture and boils it, which is an acceptable method, and shows that the wanted material comes off with the steam; it also gives enough detail of the advantage, so read as a whole is worth 3/3.

Question 22(c)

Generally, the understanding of the nmr spectrum and spin-spin coupling was very poor. Candidates did not clearly state which protons were coupled; they seldom referred to hydrogen on adjacent carbon atoms. Instead, there was much talk of 'environments' which did not build into a picture of the coupling pattern. Very few candidates scored both marks, sometimes because they only addressed half of the question and mentioned only the doublets, or only the singlets.





This example addresses both points clearly.

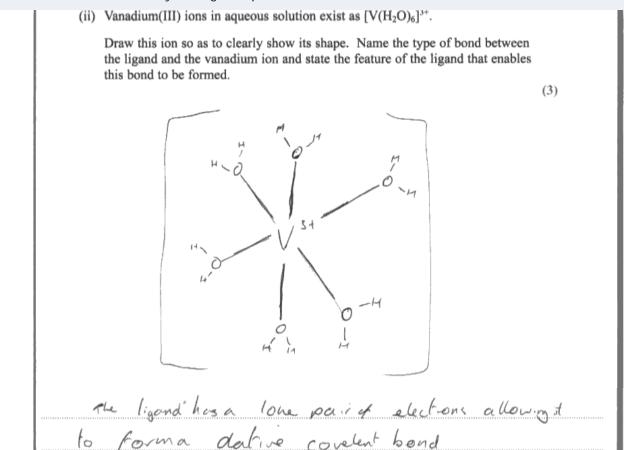
Question 23(a) (i)

Question 23 was easily the best-answered extended question in the paper. Even candidates who were otherwise rather weak on other sections of the paper, were able to score well, scores above 8/10 being common.

(i) The majority of answers concerning properties of vanadium compounds were correct. Those that lost credit did so either by referring to the metal, or to partially-filled d-orbitals in the metal ions. This is not a property of a compound.

Question 23(a) (ii)

Most candidates scored well on this question on complex ions. Most were able to give convincing 3-D drawings of $[V(H_2O)_\delta]^{3+}$ and say correct things about the bonding. However, there is not enough attention paid to the conventions of 3-D representations and in particular the meaning of the different style of wedges. If these had been interpreted rigorously, some of the octahedral ions would have had a very strange shape indeed.





The 3-D structure of the ion is not evident from this drawing so does not score.

Draw this ion so as to clearly show its shape. Name the type of bond between the ligand and the vanadium ion and state the feature of the ligand that enables this bond to be formed.

(3)

OH2

H2011111 OH2

OH2

OH2

Feature Covalent bond.

to allow formation of bond.

- lone poir of electron.



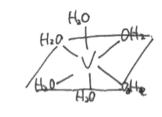
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This clip shows a good 3-D drawing with proper use of wedges, together with a very clear answer to the rest of the question.

(11) Vanadium(III) ions in aqueous solution exist as [V(H₂O)₆].

Draw this ion so as to clearly show its shape. Name the type of bond between the ligand and the vanadium ion and state the feature of the ligand that enables this bond to be formed.

(3)



transition metal in a oxidation som state of the or higher it will be covalent bond,



This clip shows a perfectly good way of showing a 3-D ion without using wedges, though the remainder of the question does not score.



Candidates need to practise drawing these ions until the skill has been learnt. The exam is too late to do this.

Question 23(b) (i)

This answer, requiring data to be found from the Data Booklet, was invariably correct.

Question 23(b) (ii)-(iii)

- (ii) Disproportionation was well-explained in the majority of cases, which is pleasing.
- (iii) Many candidates gave correct answers to this part, though some inevitably got the sign of the potential reversed. There was a minority that obtained some magnitude other than 0.66V; these could still score one mark for a correct interpretation of the sign. Candidates must be explicit that a negative potential means that the reaction is not feasible, for example.

 Use your data booklet (page 15) to find the standard electrode (reduction) potential for the reduction of vanadium(IV), VO²⁺, to vanadium(III), V³⁺. 	
	(1)
+0-34	
*(ii) Explain the term disproportionation.	- 1
	(2)
When an element in as bevotion in oxidized and at the	*
Some time reduced	
(iii) Use your answer to (b)(i), and the data below, to calculate E_{cell}^{\oplus} for the forms of vanadium(V) and vanadium(III) from vanadium(IV) in acidic solution. S if the reaction is feasible under standard conditions and justify your answer. Vo ³⁺ + 2 A + e ⁻ \Rightarrow V 3 + \Rightarrow V 0, 3 5 VO ₂ ⁺ (aq) + 2H ⁺ (aq) + e ⁻ \Rightarrow VO ²⁺ (aq) + H ₂ O(1) E^{\oplus} = + 1.00 V	
+100 +(+0.35) = b & = b 100.35	
the bevetion in fearible under Standard condition	
become it gives a positive E°CUL V	



This example shows a (surprisingly large) positive value for the potential, but it is explicitly linked to feasibility in the second statement so scores the second mark.

(iii) Use your answer to (b)(i), and the data below, to calculate E_{cell}^{Θ} for the formation of vanadium(V) and vanadium(III) from vanadium(IV) in acidic solution. State if the reaction is feasible under standard conditions and justify your answer.

VO₂⁺(aq) + 2H⁺(aq) + e⁻ = VO²⁺(aq) + H₂O(I) E^{Θ} = + 1.00 V

Equation (1)

(ii) Use your answer to (b)(i) and the data below, to calculate E_{cell}^{Θ} for the formation of vanadium(V) and vanadium(III) from vanadium(IV) in acidic solution. State if the reaction is feasible under standard conditions and justify your answer.

VO₂⁺(aq) + 2H⁺(aq) + e⁻ = VO²⁺(aq) + H₂O(I) E^{Θ} = + 1.00 V

Equation (2)

Equation (3)



Here is an example of a very good clear answer to the question.



Candidates must be explicit when asked to justify their answers and not leave examiners to second-guess what they mean.

Question 24(a)

Question 24 assessed a wide variety of organic chemistry and gave candidates of whatever level, an opportunity to show what they could do.

Many candidates knew which carbon atom on carvone is chiral. Some of those that didn't write out the full structure still came to the right answer that way. Candidates who have trouble visualising skeletal formulae could consider this option since there's space to accommodate this approach. Others guessed wrongly with almost all the incorrect possibilities having been chosen.

Question 24(b)

The basis for a good answer to this question is the recognition that paracetamol isn't chiral. Candidates who started from this usually made sensible comments about the lack of need to separate enantiomers with the accompanying loss of material. If the initial point was not made directly, or not made at all, candidates often floundered in a morass of words which might or might not make some valid points. This part highlighted the necessity for a candidate to think an answer through completely before writing anything. In this way a crisp, relevant answer that does not repeat the question – and incidentally, is unlikely to go out of clip – is a more likely prospect.

(b) Explain why the synthesis of paracetamol is more efficient than the synthesis of a single enantiomer such as (-)-carvone.

(3)

There is no need to separate the a enantioners

made to get (-)-carvore alone. There is no chiral indecules in paracetamol. There is no chiral indecules in paracetamol. There are not any enantioners to separate so you keep 100% of the yield produced. In (-)-carvore, you lose 50% if not more of the yield as a racenic mixture is thely to have been some of son which produces indestree enantioner.



This candidate states clearly that paracetamol is not chiral, and then goes on to make two sensible further points.

(4)

Question 24(c)

The tests for C=O and C=C were widely and well understood, the majority of candidates scoring full marks on this question. For those that didn't it was usually that they were answering a different question relating to the reactions of aldehydes rather than ketones using Fehling's solution or Tollens' reagent.

(c) Carvone contains two types of functional group. For each of these, give a suitable chemical test to show its presence, and state what you would see in each case.

(4)

For (=(all branine water - the branine water decolourises for (=0 all a few drops of 2,4-dintrophenylhydrazine - a yellow-orange precipitate forms



This extract gives a crisp answer to the question - easy to understand and easy to mark.

(c) Carvone contains two types of functional group. For each of these, give a suitable chemical test to show its presence, and state what you would see in each case.

Test for the \$\$ C=0 group with \$\simes\$ bradys reagent it will turn from orange to green if present.

Test for a cortanyl group with fehlings solution.



This clip shows the two most common errors. Firstly, there is no mention of the precipitate from treatment with 2,4-DNP - and the colour change is wrong.

Secondly, Fehling's solution is erroneosly chosen as the reagent for testing for a ketone.



Candidates must be careful to answer the question set. There is nothing here that asks for a comparison of aldehyde and ketone reactions, unlike many questions from past papers.

Question 24(d)

- 24(i) There were many good answers to this question. For those that scored less well, a common error was failing to distinguish between hydrogen atoms and hydrogen molecules when calculating the amount of hydrogen used. If the first two points were correct it was common to find reduction of one of the double bonds and the C=O bond in the carvone molecule.
- (ii) The differences in the infra-red spectra of carvone and limonene were generally well-understood. The common error was to quote the value for the C=O absorption for an aldehyde rather than that for a ketone.
 - (d) Carvone can be reduced in a variety of ways.
 - (i) On reduction with hydrogen, in the presence of a platinum catalyst, 4.5 g of carvone reacted with 1.44 dm³ of hydrogen. Use these data to deduce the skeletal formula of the reduction product.

[Molar mass of carvone is 150 g mol⁻¹; molar volume of hydrogen at the temperature and pressure of the experiment is 24 dm³ mol⁻¹.]

(3)

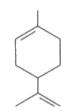
Working

Amount of hydrogen reacted =
$$\frac{4.5}{150}$$

Amount of hydrogen reacted = $\frac{1.44}{1.50}$

Hence skeletal formula of reduction product.

(ii) Reduction of carvone, using hydrazine in potassium hydroxide solution, gives limonene.



How would you show from a comparison of the infra-red spectra of carvone and of limonene that this reduction had occurred? You should quote appropriate data, from the data booklet, to support your answer.

(2)

The	IR	spectr	้นพ	of carv	ONE	will	hove	z a	peak	ał	1700	- 1680	Em -1
- hich		1						spectrum					
				an an Andrea (An an	**********								1



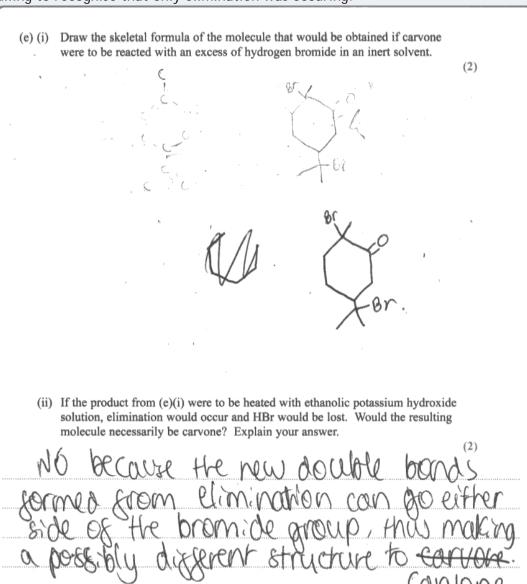
This question is well-answered but should have indicated that the amount of hydrogen molecules is being calculated initially. This point is saved by the correct structure being given.



Great care needs to be taken with hydrogen and other diatomic gases. It must always be clear whether atoms or molecules are being discussed.

Question 24(e)

- (i) Many candidates saw that two moles of HBr had to be added across two C=C bonds and they successfully drew the product structure. The orientation of the addition next to the methyl group did not matter, but that across the exocyclic double bond was expected to be correct for the second mark. Some candidates got into difficulties with the number of carbon atoms on the sidechain and lost one in their formula for the addition product.
- (ii) The identity of the possible elimination products from the dibromo compound in e(i) was not always clearly described. Many candidates would have been much better off drawing a structure of one of the products; instead they attempted to describe loss of hydrogen from either side of the bromine-bearing carbon which had they done this clearly would also have worked perfectly well. The impression given is that few candidates think on paper in structural questions so get themselves into difficulties. There is plenty of space in questions of this type which can be used to work out the answer. Some thought that the reaction would be a substitution of Br by OH, failing to recognise that only elimination was occuring.





This clip shows correct addition of the two moles of HBr, but part (ii) does not make the possible loss of hydrogen from either side of the bromine-bearing carbon quite explicit enough.

(e) (i) Draw the skeletal formula of the molecule that would be obtained if carvone were to be reacted with an excess of hydrogen bromide in an inert solvent.

(2)

(ii) If the product from (e)(i) were to be heated with ethanolic potassium hydroxide solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.

(2)

No because substitution may occur and the module by have an off group which may replace the 'Br? This would result in a eligibility module with an alceled group.



This clip shows addition of bromine correctly, but it isn't the reagent that was asked. Part (ii) fails to answer the question about elimination.

Question 24(f) (i)

This question, on mechanism related to stereochemistry, was done well by a significant number of candidates. Problems arose if they started from a non-chiral starting material in the case of SN1 or SN2, or from a symmetrical ketone if nucleophilic addition was chosen. As with other mechanisms, candidates should remember that the arrows represent dynamic interactions so should have in their mind what the electrons have to do to achieve the desired end. Those candidates who scored poorly did so because they had not understood what the conventions used in representing mechanisms mean for the real substances in the test-tube. A significant number started from molecules that were not chiral (substitution) or from symmetrical ketones (addition).

(f) *(i) Give the mechanism of one nucleophilic reaction of your choice, which either gives rise to a racemic mixture or results in the inversion of the chirality of the starting material. Explain what your mechanism predicts about the stereochemistry of the product.

$$H_{3}C \stackrel{f}{\underset{C}{\longleftarrow}} \stackrel{\wedge}{\longrightarrow} H \stackrel{(5)}{\longrightarrow} H \stackrel{(5)}{\longrightarrow}$$

The mechanism shows that there will be 2 optical isomers in the product mischne, there will be an equal amount of beth sports a resultinguina recense mischne as the most nucleophile can attack from above or helow the plane, as the reactant in planar the sections



This example shows a clear mechanism with the planar nature of the reactant explicitly stated and the reason for racemisation clearly explained.

(f) *(i) Give the mechanism of one nucleophilic reaction of your choice, which either gives rise to a racemic mixture or results in the inversion of the chirality of the starting material. Explain what your mechanism predicts about the stereochemistry of the product.

(5)

$$H_3C$$
 H_3C
 H_3C

This is a SN2 reaction where only there is one step in the reaction



This is a good example of a substitution reaction, showing the lack of a chiral starting material as well as a common error where the charge on the intermediate is absent. There is no explanation of the effect on the stereochemistry of the product.

Question 24(f) (ii)

Most candidates knew that heterogeneous catalysts are easily separated from the products. A few candidates clearly thought that 'catalysts do not need to be separated from the products' is an equivalent statement which, unfortunately, it is not.

Grade boundaries

Grade	Max. Mark	A*	Α	В	С	D	E	N	U
Raw boundary mark	90	73	66	59	53	47	41	35	0
Uniform boundary mark	120	108	96	84	72	60	48	36	0

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