Part II Examinations 2013

Q3

There were **46** answers to this question and the mean mark was **16.96**

No change in the published marking scheme

There were 17 first class answers with 10 of these scoring 20 or above.

There was only 1 very poor answer but this was clearly due to candidate running out of time.

(a)(i) Very well answered with the majority of answers offering explanation for the reagents or conditions that were suggested (Kinetic enolate, cuprate, Lindlar catalyst or unstabilised ylid and reductive amination). Good to see most answers using a formal retro-synthesis even though not asked for.

(ii) Well answered with almost everyone using the Diels-Alder and standard Wittig chemistry. Some errors with the Diels-Alder stereochemistry and final imide formation.

(b)**Target molecule 1**. Poor retro-synthesis caused problems with many answers jumping in with the pinacol rearrangement rather than ⊟u̶n̶s̶a̶turated carbonyl followed by reconnection. Nevertheless majority of answers identified the 5,5-spiro system as coming from the pinacol rearrangement.

Target molecule 2. Reasonably well answered but with a wide spread of marks. Common error was using an enamine in the Diels-Alder reaction and missing the endo selectivity in the same reaction.

Q4

There were **40** answers to this question and the mean mark was **17.03**.

No change in the published marking scheme

There were 17 first class answers with 8 scripts scoring 20 or above – these were excellent answers. There were no very poor answers to this question.

(a)

(i) Well answered with good control of the two double bond geometries.
(ii) Good answers for this part with good use of Diels-Alder chemistry.

(b)**Target molecule 1**. Generally well answered. Good retro-synthesis via Beckmann rearrangement.

Target molecule 2. Generally well answered with good use of umpolung reactivity.

Qu. 5

(a)(i) Poorly answered; most people did not see the point that a change in dipole was required for IR activity, and a change in polarizibility was needed for Raman activity.
(ii) Fine

(b)(i) Answering this required careful attention to detail about which were the upper and lower levels, and quite a lot of people made errors as a result. Hardly anyone specified the J values associated with their expressions for the O and S branch lines.
(ii) People often drew diagrams which were inconsistent with their answers to (i), indicating that they were relying on (often faulty) recall
(iii) Most people got that the Q branch lines would be spread out, but getting the direction right was more tricky.
(c) Was plainly too easy, with many people achieving full marks for this part.

Qu. 6

In retrospect quite a bit easier that Qu. 5, but chosen by far fewer people
(a)(i) Fine
(ii) Generally OK, but people were careless about the level from with D_0 values came, and the correct use of ' or ''
(iii) Caused quite a bit of confusion; as ever, a clear diagram sorts it out.
(b)(i) Poor description of the Deslandres table
(ii) Too many people made mistakes in the algebra of this trivial derivation
(iii) Fine
(iv) Generally fine, although a significant people got in a muddle due to their incorrect answer to (ii)

Q10

There were four attempts of this question this year. The quality of answers ranged from the very good (22/25) to the weak (2/25).

The first part was in general not satisfactory, with only one candidate mentioning the separability of the Schrodinger equation. The factorized form of the wave function was generally given, along with appropriate quantum numbers. It proved problematic to show that the 2s orbital was an eigenfunction of the Hamiltonian provided, with only one candidate coming close. In general, the candidates knew what was required, but the difficulty of differentiating twice proved conclusive in all cases.
The form of the RDF was correctly sketched, and one candidate correctly wrote down the functional form of the p orbital. The effect of increasing Z was noted correctly by two candidates.

Qu. 11

There were three answers, none of which was a serious attempt. Very disappointing for what was a straightforward question.

Q13

Twenty six students attempted question 13. As expected, parts (a) and (b) were straightforward and generally well answered. Some students had difficulties in giving examples of TM complexes undergoing an associative and dissociative mechanism or to indicate the charge/oxidation state of the examples of their choice. Parts (c) and (d) were significantly more difficult and caused problems. The intramolecular ET from the reduced Ru to the Co(III) centre causing aquation of the labile Co(II) ion was only recognised by the very good students. The role of light, water and Et_3N in part (d) was correctly answered by multiple students, but most struggled with the mechanism such as photo-

induced electron transfer from the Ru to the Co ion. An average mark of 16.38 was awarded (top mark was 24 out of 25).

Q14

There were 50 answers to this question.

Mean mark = 14.4

Min. mark = 6

Max. mark = 21

SD = 3.37

Some changes made to the published mark scheme

This was a popular question and there was a very wide spread of marks. There were several very low scores that skewed the average mark, despite a fair degree of leniency in places and extensive re-marking. The question was certainly sufficiently discriminating.

Part a) was very well answered, part b) was well answered on the whole and there was a great deal of variation in c), with c (ii) evidently especially challenging.

(a) Very similar to material from the lectures and supervision problems. Most students could draw mechanisms for the formation of both products. Full marks awarded for comments regarding 'good' and 'bad' orbital overlap and for attempting to show this using annotated diagrams (lots of leeway in what exactly was a good diagram here). Classification using Baldwin's Rules leading to the correct conclusion as to which the major product only allocated a maximum of 3 marks if not diagrams used. (5/25)

(b) A lot of variety in the quality of 3D representations of the two molecules. Most students could draw the first one well, but had problems with the second. Most suggested a 1 step mechanism – partial credit was given for this, but for full marks a 2 step mechanism was needed (the two reaction planes are askew to each other), with a discussion of the relevant orbital interactions (many just talked about anti-periplanar relationships for which partial credit was given). Several very low scores, unable to tackle the requirement for 3D drawings and thus get on with the question properly. (8/25)

(c) (i) This was pretty much book work, and very similar to a supervision problem from the notes. Therefore, strange to see so much variation in the level of understanding shown in answers. Most students recognized the fact that a rhodium carbenoid is generated, that can be treated as a free carbene in terms of reactivity. Accepted singlet and triple carbene mechanisms as notes said that carbenoids 'generally' react as singlet. For full credit, needed curly arrows and some discussion as to how the carbene behaves, e.g. relevant orbital interactions in the singlet cases). Partial credit given for just assuming a free carbene was generated and reacts. (4/25)

(ii) This proved to be very challenging; answers to this part varied the most, with only a very small proportion of candidates scoring highly. A minority of students spotted the correct reaction sequence (electrocyclic ring closure followed by Diels Alder cycloaddition). Some truly odd mechanisms. Those who did follow the correct two-step reaction sequence generally scored well. Woodward-Hoffmann rules were generally applied correctly. Very few students were able to rationalise the stereochemistry of the product. Tried to be as lenient as possible with marking, some credit given for alternative mechanisms (if not too outlandish) and correct WH analysis and other comments even if incorrect mechanistic pathway followed. (8/25)

Q15

61 answers. This question was generally well done. In part (b), the large majority of the candidates were able to assign the protons correctly, indicating their ability to process chemical shift and coupling constant data. For part (c), most of the candidates correctly assigned the stereochemistry. Surprisingly, many candidates struggled with part (a), with some merely guessing at the number of possible stereoisomers. A sizeable proportion of the answers to part (d) were on the abstract side of 3D drawing.

Q16/17??

The first part of the question asked about an enzyme mechanism.

It tested:

(i) assignment of R or S – done well

(ii) inference about use of a single enzyme base – generally noted

(iii) question about what a lack of isotope incorporation told you. Some got this partly right. None mentioned issues.

The second part looked at the changes in reactivity caused by replacing the first amino acid (proline) with an alanine.

This enzyme catalysed a different reaction, that went though a Shiff base mechanism- generally well answered. They were presented with mass spec data that pointed towards modification of the terminal amino group on Ala. Only a few saw this. Many used the amide nitrogen of the glutamine as the base, showing a very poor appreciation of its reactivity.

Final part comparing roles of amino acids and also change or reaction , neither particularly well done.

Q18

4

40 answers, mean mark 16.1

This was a generally straightforward question. While many candidates made a reasonable effort, and there were some very good answers, there was also a significant number of disappointing answers.

Most problems arose in part (b), which involved a fairly standard manipulation of steady state expressions. Quite a few candidates could not see that the reaction $O(^1D)+N2O$ constitutes a negligible sink for odd oxygen and so got themselves into unnecessary complexity. Most disturbing was the high proportion (nearly a fifth) who used the given value for ground state [O] rather than calculating the concentration of $O(^1D)$.

Q19

20 answers, mean mark 16.4

The three parts of the question were answered quite differently.

The 1st part asking about the effects of NOx on tropospheric chemistry was generally very well answered.

The 2nd part of the questions was a mixture of tropospheric and stratospheric chemistry and it was clear that a number of students did not revise the stratospheric part of the lecture and therefore could only poorly or not at all answer the stratospheric part of the question.

The 3rd part of the question was answered less well. The link between particle size and composition was clearly the most challenging part of the entire question and was answered correctly only by a few students.

Q25

This question was answered rather well. With one exception, all students gave the correct answer to parts a and b. Also part ci went fairly well.
Points were lost mainly due to computation errors. Another error made more than once was forgetting to square the matrix element of the perturbation hamiltonian. Part cii was attempted by half of the students who got it mostly right although only a couple were aware that it should reproduce the perturbation result of ci. In all I get the impression that this question was a bit too easy, or at least in the orginal marking scheme. The marking scheme was therefore adjusted from 50% for a+b and 50% for c to 40% vs 60%. Even then there was an usual high fraction of
24 out of 25 marks.

Q29

Twelve students answered question 29. The question consisted of two parts – basics of dynamic electrochemistry in part (a) and an inorganic example in part (b). The quality of the answers was generally good and an average mark of 16.58 was awarded (top mark was 24 out of 25). The reversibility criteria were well discussed by most students and sketching a reversible and irreversible

CV was no major obstacle (although only a small number labeled the axis of the CVs!). Many students had problems giving examples of transition metal complexes, which feature a reversible or irreversible CV despite several examples in the lecture notes and supervisions. The description of the role of the electrolyte in (a,ii) and recognition of non-Faradaic currents in (a,iii) also caused problems to several students. Example (b) was also well answered by several students and the best students recognized the catalytic isomerization.

Q30

15 candidates attempted this question and the marks varied between 11 and 20 out of 25. Some parts of the question were book work and these were generally done well as expected. Other parts of the question were much more challenging and required the candidates to think. The answers were mixed. The best students performed very well, clearly understanding the course material and also aspects of mechanistic organic and physical chemistry. Some candidates did not come up with the correct answer but had plausible mechanisms and ideas (given the information in the question). These answers were marked generously. In other cases, the candidate clearly misunderstood the question, the course material or both! The average mark is 16.1. It was decided this was sufficiently close to the guideline value and the scripts were not remarked.

Q31

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The three sections tested different aspects of the 6 lectures I
give on metalloproteins. Parts a) and b) are simple recall of concepts
with specific examples required. They were not done as well as I
expected but all answers used the same approach. The best answers used
diagrams (thermodynamic cycles) rather than text. Part c) revealed
that 12 of the students cannot read a question. It was an enzyme mechanism
of a type they had not seen before, but given the  basic principles
taught, was actually one of the simpler mechanisms they have
encountered. Only two students read the question properly and
essentially provided a perfect answer. The rest chose to ignore the
seen before and hence got the sequence of events wrong. A couple of
weak answers involved fantasy iron carbon bonds, which can only be the result
of exam pressure.
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Q36
5 Sub Parts

There were 29 Scripts - average 16.4 out of 26. There was a reasonable distribution and the students performed well on material that was taken directly from the course.

When asked to extrapolate from the course material, however, only a few students stood out and were able to provide any sort of creative answer.

Q37

7 Sub Parts
1st Sub Part - required student to identify a 'Diels-Alder' reaction, followed by a step growth polymerisation.

Finally the students needed to recall the structure of lactic acid as well as lactide, both of which were highlighted several times in the lecture and the lecture notes. The students performed miserably on this question with the average being 11.5.

I have tried to remark this question taking several hours to approach an average mark closer to 16.5. However it was impossible to increase the average, because so many of the scores came from 0% on each of the sub parts to the question. Moreover, a few students answered the question extremely well and there was no way to apparently increase the marks from students with scores below 10, while at the same time keeping the top mark within a 25 point scale.

Q40

23 scripts

(a) (i) This was answered reasonably well by all.

(ii) Most responses correctly picked up on the activated species for both molecules. Very few commented on the geometrical requirement for the Bergman Rearrangement and how this was brought about for the enediyne (**A**).

(iii) This was the best-answered part of the whole question with very good mechanisms and many scripts gaining full (or almost full marks). The error in the question (missing methylene group), which was pointed out by the invigilator to all candidates, was not an issue for any of the scripts.

(b) This was the part of the question for which there was the greatest spread of marks between scripts. It proved to be the most challenging question and there were a small number of high scoring answers. Most answers recognised that Fe(II)•EDTA was somewhat analogous to the Fe entity in Bleomycin (which was in the lectures). Where marks were lost, was in providing sufficient detail on adapting the molecule to recognise specific DNA sequences.

Q41

(a) (i) Generally reasonable answers, though many failed to label 5' and 3' end of tRNA, correctly locate variable region or identify the loops.

(ii) A range of answers of variable depth mostly focusing on the role of the tRNA in aminoacylation and mRNA recognition. A few scripts addressed the tRNAs interactions with the ribosome or other translation factors.

(iii) This was the part of the question led to a spread of marks, with some candidates struggling with the relationship between conservation and function.

(b) i) I was generally pleased with the answers here, and the basic approach was grasped by most candidates.

ii) Most candidates noted the difference between the molecules, many identified hydrogen bonding, but few made a note of steric differences.

iii) The overall similarity of hydrogen boding was noted but the steric differences were rarely commented on.

iv) Generally well answered

v) Some very good answers to this, proposing a range of plausible experimental routes to adapting SELEX-type experiments to discovering aptamers that differentiate the two molecules.

Qu 42

In retrospect perhaps not quite challenging enough.

(a) Generally well done, but most people decided that rather than assuming that they offset way refocused by the spin echo they would show this explicitly: this was not necessary.
(b) Again generally well done with most people utilising the fact that the coupling simply evolves for 2 $\Box$.
(c) Assuming that the results to (a) and (b) were correct, most people spotted this part.
(d) Generally OK, but rather too many people forgot that at the start of the sequence there would be only z-magnetization.
(e) Generally OK, but not that many people mentioned the range of long-range couplings as being a problem.

Qu 43

(a) Well done, but the diagrams were not always clearly drawn
(b) (i) Well done; (ii) very few people spotted that the in-phase term is just the same as the one arising in (a) and so no further calculation was necessary; (iii)/(iv) the calculation was well done, but the interpretation caused more difficulties – the main point is that the cross peak is now in phase in $\Box$ hence there is less cancellation; (v) sensible suggestions, but few mentioned problem with a range of couplings.
(c) Not many people spotted that the additional spin echo would result in cross-peaks which were in-phase in both dimensions.

Q49
Well answered: with majority of answers using alternatives to the RCHO enolate. Mean = 3.16

Q50
Generally well answered, with most of the answers showing good recall of kinetic alkylation and the Mannich reaction. Mean = 3.43

Q51
Well-answered and good understanding of the disconnections. Mean = 3.29

Q52

Well answered. Good understanding of basic Grignard chemistry, reductive amination and Diels-Alder reaction. Mean = 3.45

Q53

Well answered and good understanding of SN1 type alkylation of enolates, Baeyer-Villiger oxidation and simple Wittig chemistry. Mean = 3.57

Qu 54

Many people got in a muddle computing the rotational constant for the isotopic species and also a common error way to confuse the spacings of the lines in the spectrum of one species with the spacing between the species.

Qu 55

Apart from some elementary trigonometric errors, generally well done.

Qu 56

A few people did not spot that only the Xe—F stretches were asked for, but apart from this the question was well done. The degenerate E_u mode caused a few difficulties.

Qu 57

Despite clearly asking for the band head in the P branch, quite a few people reproduced a proof of the R branch band head which appeared to have been committed to memory (why on earth would you learn such a thing?). There were numerous algebraic errors, and even if people got the right expression they did not always interpret it correctly.

Q63

This question was, on the whole, very poorly answered (65 scripts, mean mark of 2.9). Only a handful of candidates spotted the 1,3-dipolar cycloaddition (a reaction that does appear in the notes on a couple of occasions) – perhaps this was due to time pressure? Those that did tended to score highly. A large number of candidates could not draw a reasonable mechanism involving nucleophilic attack onto the carbonyl leading to the iminium-type species (precursor to nitrone). Many did not read the question properly and gave structures that did not contain fused rings. Even with a very generous marking scheme, the average mark was very low.

Q65

40 answers, mean mark 7.5

On average the question was very well answered.

The question was probably a bit short, likely due to last minute changes: In discussion with Stuart Clarke I decided to slightly shorten the answer scheme as the last part of the question was slightly

misunderstanding. In hindsight it might have been better to alter the question and not simply delete the last part.

Q71

27 candidates attempted this question which tested their basic knowledge and understanding of protein fluorescence and its change on protein unfolding. There was a very wide range of marks from 3 to 10. The best scripts (and there were quite a few) showed both an excellent knowledge and understanding of protein structure and the basic physical principles underpinning fluorescence. The answers were not only correct but also provided good detail. In contrast, those scripts which scored very low, showed a very weak knowledge and a remarkable lack of understanding of even the most basic principles of fluorescence. This was disappointing. The question worked well at distinguishing between the most able and the weakest students. The average is 6.5 in line with guidelines.

Q76

The answers to this question were disappointing. Candidates could have got 9 marks purely by understanding the course work on the interactions of molecules in the minor groove and of intercalators. The best mark was only 7.5 and the worst 0.5. The average mark across all 31 candidates was 4.4.

a) Although practically everyone realised that this molecule would bind in the minor groove (for 0.5 marks) extremely few got the other half mark that the molecule would bind in A-T rich regions but with alignment to a G base. Some were able to show hydrogen bonding to bases but very few knew to where on the bases. A number obtained a mark for p-pi interactions of O4' to the imidazole ring. Many got that there were hydrophobic (VDW) interactions (for half a mark) but only some said this was with sugar regions in the floor of the groove. Only a couple obtained the bonus mark that further p-pi interactions were possible between molecules if two were to interact in the groove. There were potentially 6 marks on offer here and only one person got the maximum but then failed to answer part b.

b) A very disappointing set of marks here. Almost all got that the molecule would intercalate between base pairs and most mentioned pi-pi interactions. But very few said that the intercalation would be above a G base and very few mentioned unwinding of the helix. Some said that the phenyl and ethyl substituents would protrude into the minor groove. Nobody at all mentioned that the long axis of the ethidium would be parallel to the long axis of a neighbouring base pair (this was a hard point to get, but I would have expected 2 or 3 correct answers here). A very large number of people wrote about electrostatic interactions of the positively charged atom with phosphates, which is entirely wrong.

Altogether I was disappointed with the standard of answers. I would have expected a median closer to 6.5 rather than the 4.4 obtained.

Qu77

In retrospect perhaps not quite challenging enough. Just about everybody got the basic idea, but fewer were able to quite put their finger on the final part.

Q78
generally good, candidates confident in huckel approximations

Q79
generally well done, box filling and values for angular momentum correct. some problems identifying L=6 label

Q80
not all candidates gave all appropriate wave functions, reasons for antisymmetrized product wave function generally not given, meaning of alpha, beta nomenclature missing, association of antisymmetric product with vanishing wave function for triplet 1s2 configuration mentioned by the higher scoring candidates.

Q81
problems defining px correctly, physical interpretation of eigenvalue also largely missing.

Q82

It was very depressing that so many people did not know the shapes if these simple molecules.

Q83

Generally well done.

Q84

Most answers did not seem to know what a SO was.

Q85

Generally OK