

Part II 2012

Examiners' Comments

Q 2

This question was only answered by two candidates despite being similar in form to questions from recent years. Parts (a) and (b) on bond valence sums were well answered, as was part (e) on organothorium chemistry. In parts (c) and (d) neither candidate was able to make the link between the d^2 electronic configuration of Os^{6+} and the *trans* dioxo structure, or reproduce the MO diagram for π bonding in this fragment.

Q3

There were **69** answers to this question and the mean mark was **15.9**

No change in the published marking scheme

There were 20 first class answers but only 3 or so that were excellent (the others contained chemical errors).

There were only 4 very poor answers but this was clearly due to candidates running out of time.

(a)

(1) Well answered with answers showing a good understanding of regio-specific enolates and controlling alkene geometry via Wittig or alkyne chemistry. Good to see most answers using a formal retro-synthesis even though not asked for.

(2) Very poorly answered with very few answers spotting the reconnection and Baeyer-Villiger – very surprising given the target is very similar to a lecture problem. This part of the question was marked extremely generously.

(b)

Target molecule (3). Very well answered with very good retro-synthetic analysis. Answers demonstrated a good understanding of the A2 Core course with appropriate use of cuprates, control of RCHO alkylation and hard/soft carbanions.

Target molecule (4). Generally well answered with good retrosynthetic analysis. Approached via 1,5-dicarbonyl chemistry or late stage alkylation of the 6-membered lactone constructed using Baeyer-Villiger. Most answers displayed good understanding of Core chemistry.

Q4

There were **29** answers to this question and the mean mark was **16.7**.

No change in the published marking scheme

Generally well answered with a slightly higher average than Q3. Less popular than Q3 – this is very surprising since it was thought all four target molecules had fairly straightforward retrosyntheses. There were 11 first class answers but only 2 of these were outstanding. There were only 2 very poor answers but once again this would appear to be due to lack of time spent on this section.

(a)

(1) Well answered with good explanation of the *cis-endo* Diels-Alder. Good use of Wittig chemistry and control of aldol condensations.

(2) Good answers for this part with good use of Diels-Alder chemistry and the Mannich reaction.

(b)

Target molecule 3. Generally well answered. Good retro-synthesis via epoxide opening with enolates.

Target molecule 4. Very well answered. Very good retrosynthetic analysis leading to good synthetic schemes – good use of enolate alkylation and reductive amination.

Qu. 5: 18 answers, average 14.3

This was not a popular question, no doubt because part (a) looked unfamiliar. Some people spotted what (a) was about and gained high marks with minimal effort. Part (b) was straightforward for most.

(a) (i) The weaker sets of lines are simply rotational transitions within higher vibrational levels (the clue is the high temperature and the modest vibrational frequency). There was all sorts of nonsense written about P and R branches, centrifugal distortion and so on.

(ii) As the spacing is $2B$, it is easy to work out that the lowest frequency strong line is from $J = 15$

(iii) If candidates had not cracked (i) then this part is not possible. However, many people used a splitting to determine a bond length, and some credit was given for this. The number of errors arising from muddling up units was truly depressing. $B_e = 11.0435$ GHz, $R_e = 176.7$ pm.

(b) Was pretty straightforward, and all that was needed was to identify correctly the values of M_J and then evaluate the formula. This was generally well done, and people were able to deduce the expression for the splitting (although in some cases it appeared to have been reverse engineered from the given answer).

(iii) Again it was truly depressing that so many people got into a muddle with the units, which are clearly specified for each quantity. Splitting is $4.11 \times 10^{-6} \text{ cm}^{-1}$; rather small.

Qu 6: 68 answers, average 16.6

This was far more popular than Qu. 5, perhaps because it looked more familiar.

(a) Was bookwork, but too many people spent too long on this when a short answer would have been sufficient. Very few people had anything sensible to say about the condition that the lines in a sequence are closely spaced (simply that the vibrational frequencies of the upper and lower states are similar). Lots of people rambled on at length about Frank-Condon factors, which are utterly irrelevant here.

(b) The MO diagram was generally produced satisfactorily, although the labeling left something to be desired. Most people got the B state $(3\sigma_g)^1(1\pi_g)^1$, but the C state was more tricky $(2\sigma_u)^1(2\pi_g)^1$. For full credit an explanation of how the configuration gave rise to the state was required.

(c) (i) Was very easy to do, but hard to explain.

(ii) This was an absolutely standard piece of work which people made a great meal out of and got in a muddle. A simple diagram helps you to work out what to subtract from what, and what the difference is equal to. $\omega = 2035$ and $\omega_x = 17 \text{ cm}^{-1}$.

(iii) People got in even more of a muddle with this. Again, a simple diagram sorts it out. $\omega = 1734$ and $\omega_x = 14.5 \text{ cm}^{-1}$

Q9

Scripts = 3, Average grade = 16.7/25 (67 %)

This question was difficult and this was indicated by only three people attempting the question. The difficulty was mainly due to the tricky integration in part (c). Part (a) was standard and correctly understood. Part (b) was correctly answered using a mathematical proof. Interestingly, no candidate realized that the result could be shown rapidly by symmetry. Part (c) no one achieved the correct numerical result but the correct integration was generally attempted. Part (d) the answers lacked depth but the general idea was understood. No one took the result to the limits.

Q10

Scripts = 9, Average grade = 18.9/25 (75.6 %)

This question was a very standard question and proved to be a little too easy as evidenced by the average mark. This indicates that the course had a strong cohort this year – previous years struggled with questions of similar difficulty. Parts (a-d) were answered near perfectly and marks were only lost for poor definitions. However, part (e) was answered very poorly especially in the derivation of the total angular quantum number (L).

Qu. 11: 8 answers, average 21.0

This question was very well answered, with two candidates scoring 25/25. Those who chose to answer this question clearly knew what they were doing and applied the correct methods with confidence and directness.

Q13

Question 13 was only attempted by one student and the response was of a poor standard. The discussion of parts (a, i) was insufficient and derivation of the Eigen-Wilkins rate law was not attempted. The student responded part (a, ii) well, but did not attempt (a, iii). A fast outer sphere electron transfer was recognized in Part (b), but a possible inner-sphere mechanism was not discussed. Part (c) was not attempted. The final mark was 7 out of 25 points.

Q14

Scripts: 44 Average mark: 15.95/25

Overall parts a) and b) well answered, with a great deal of variation in part c).

- (a) Most students showed the relevant part of the mechanism and classified it correctly using Baldwin's Rules. Some then said that poor orbital overlap was the root cause of the 5-membered ring forming more slowly but full marks could only be awarded if students also attempted to show this using a diagram (lots of leeway in what exactly was a good diagram here). (6/25)
- (b) As with part a), this was mainly well done and most people could correctly identify the starting materials with the correct double bond geometry for the diene. There was then variation in the answers to the rest and for full credit to be awarded, candidates needed to be clear about what exactly secondary orbital overlap was, supply a good three dimensional representation of the reaction process and clearly show why the regioselectivity was this way round. (7/25)
- (c) (i) Answers to this part varied the most, with only the smaller proportion of candidates getting the right answer. Credit was also given for alternative mechanisms for the first

reaction, with a sliding scale for the marking, depending on how outlandish the mechanisms ended up. Krapcho decarboxylation and ester hydrolysis had less credit attached to them and were generally done more correctly by more candidates. (8/25)

(ii) Good answers to this: if the first mechanism in part (i) was not right but the explanation given fitted well with their initial idea, full credit could be awarded for this part. (2/25)

(iii) Students either got it or did not in the main but for woolly answers, one mark was usually awarded. (2/25)

Q15

The question was, on the whole, answered competently, with NMR data assigned rationally and used to propose reasonable conformational and stereochemical assignments.

- a) Most candidates were able to successfully assign the NMR data to a flat structure, although a common error was misassignment of the two sets of methylene protons (possible on the basis of 2J coupling)
- b) Stereochemical / conformational assignment of the cyclic portion was reasonably well derived, most candidates identifying the trans ring fusion. The acyclic portions were less well handled, which differentiated the higher scores from the rest.
- c) Straightforward question, well answered
- d) Most candidates understood the heteronuclear HMBC NMR experiment and able to use the information to identify the correct product. A number of candidates failed to recognise the 3J limit for $^1\text{H} / ^{13}\text{C}$ coupling however.

1st 25

II:1 16

II:2 22

III 5

U 2

Q16

Chemical Biology

Mechanism of ATP citrate lyase

(a) Generally well done.

(i) Most recognised phosphoenzyme intermediate

(ii) Most understood but were not very precise in their answers about exchange and reversibility

(iii) ProS well identified. Oxygen transfer generally understood but few commented on equivalence of oxygens.

(iv) Most considered the incubation with 3 almost incidental and did not use it in other than a confirmatory way.

(b) Most got inversion plus inversion, few recognised need to use S as a label as well as oxygen 17 and oxygen 18.

Q17

Set and Marked by DRS

Answers = 43

Average mark = 15.70

SD = 3.95

Min mark = 1

Max mark = 22

The question was very well answered. Part (a) asked for the FAD mechanism of monoamine oxidase, and there were many very detailed answers. Less than half could state that FAD was covalently linked to the enzyme as indicated by the X. Part (b) was more variable in answers, but almost all came to a covalently inhibited enzyme. Part (c) involved the TPP catalysed decarboxylation mechanism and was well attempted by the majority, with few bad answers.

Q20

Question 20 was answered by 4 students.

The question was either answered very well (over 20 out of 25) or very poorly (3.75). Average score: 18.75

The first two parts of the question should have been no problem for someone who had read and understood the lecture notes. Part c) was closely related to an exercise. Part d) was also based on the lecture notes, but a different part of the syllabus. And finally, part e required the students to combine these two parts. The student who scored low lacked basic knowledge and was therefore unable the "straight recall" parts.

One of the good students did well on parts a)-d) but went astray on part e).

Q21

Question 21 was answered by 10 students who, again, did very well (7) or rather poorly (3). Average score: 19.05

Parts a) and b) should have been no problem for students who had read the lecture notes (even less if they had done revisions). Part c) was trivial if the student realised that it required the same

approach (and, but for the notation, yielded the same answer) as part b). Most students got this right. In case where the student got part b) wrong but part c) identical to b), I gave 50% for part c). Part d) required some simple algebraic manipulations. However, if the students got parts b) and c) wrong, d) would fail. Hence, d) could act as a check if the answers to b) and c) were correct - but those who went astray on parts b) and c) did not pick this up. Part e) required one sentence stating that identical sites adsorb equally strongly (or something equivalent). On the whole, this question was answered well, but sometimes not very clearly.

Q 22

SECTION G

This question presented the candidate with an unfamiliar Hamiltonian to the course, consisting of an electron spin in a time-dependent magnetic field. Despite this, the question attempted to guide the student through a series of steps which were entirely analogous to the electron in a time-dependent electric field which was expounded in the notes and lectures. However, this unfamiliarity almost certainly led to only four students attempting the question, and in marking, allowances were made for the new setting of the problem. Another consequence of this was often an overcomplicating of the questions asked. For instance, when asked about transition probabilities, two students attempted to integrate out the frequency dependence of the amplitudes unnecessarily. A slightly low mean mark of 12.75 out of 25 was obtained, although it must be noted that since only four answers were obtained, this is of limited significance.

Q27

Matching sets of NMR data with structures in part (a) was generally done well. More detail could have been put into the explanations of the correspondence between the two. In (b), the significance of R_1 as relating to (H_2) and $(H)_2$ ligands was explained well, but an explanation of how to obtain a R_1 value was not always given. Part (c) proved difficult because many candidates neglected to consider how the chemical shifts of ethyne might change when the molecule becomes a ligand. The paramagnetic neighbouring group effect of the ethyne was generally explained well. Part (d) was done particularly well, but the HOMO was usually not identified so that discussion of ΔE was not as focussed as it might have been.

Q28

27 candidates answered this question and there was a very wide spread of marks from 7 to 23 out of 25. The average was 16.1. The best scripts showed a very high level of understanding of the course material and could also apply this knowledge and correctly interpret data given in the question. In addition, the best answers showed a considerable level of thinking around a problem and use of

general chemical knowledge. Although no candidate correctly answered part (d), many candidates came up with some original ideas and were therefore awarded marks. The poor scripts were in general very patchy and in many cases were incomplete or showed a complete lack of understanding of some basic material (relating directly to a problem they did in the supervisions).

In general, part (a) which was book work was answered well, particularly the first part which was purely descriptive. The last part of this question was incorrectly answered by many candidates who thought the two transitions related to cold and thermal unfolding. However, a number of candidates got the correct answer. This part of the question was just awarded 1-2 marks. Part (b) which was based on a supervision question, was either answered very well or completely incorrectly, and demonstrated the candidates understanding of the example given. If candidates had answered part (b) well then they usually gave good answers to part (c) and vice versa. Not a single candidate got part (d) completely correct (although one candidate came very close) which required them to think beyond examples provided in the lectures or supervisions. Some incorrect but plausible answers were given which were awarded marks. This question was extremely good at distinguishing how much the candidates understood. Part (e) was a little more straightforward and all candidates received some marks.

N.B. I marked the scripts twice (once in blue ballpoint putting ticks and crosses and comments in the margins without awarding marks, and then again in black ink once I had got a good feel for how well the question had been answered).

Q31

Set and Marked by DRS

Answers = 67

Average mark = 16.12

SD = 3.31

Min mark = 9

Max mark = 22

The question was well answered by most. Part (a) proved a simple mechanistic answer for many, but diagrams often left something to be desired. Part (b) was similar to the previous question in stereoselectivity, but mechanistically proved to be more challenging. Some proposed a carbene mechanism by alpha-elimination, and some thought the diester was a source of Br⁺. Part (c) was unproblematic with most answers giving the correct stereochemistry. Few commented on the reversible formation of the iodonium ion. Part (d) confused some, with the majority of answers suggesting a 1,2-migration, rather than the more simple, and more likely, stepwise process. Part (e) was the most challenging, with many giving up, but some perfect answers.

Q36

The question tested the derivations and some of the working knowledge of the Hartree-Fock and MP2 methods. It also tested how these methods could be expected to perform in a simple case and how they fit in to the general area of quantum chemistry. The answers were of a very high standard.

Q37

The question tested the knowledge of Kohn-Sham DFT. Knowledge of each of the terms. Including being able to evaluate them for a given density/orbital. Also it tested the knowledge that the Kohn-Sham equation is a minimum and also the practical knowledge of functionals beyond that given in the question. The question was answered very well.

Q38

10 scripts

Overall the question was reasonably well-answered with a good spread of marks. I was satisfied that the question was sufficiently discriminating. Parts a) and b) i, ii were fine for most candidates. The AZT part of part a) was addressed better than Ciprofloxacin with several responses failing to note the importance of topoisomerases for Ciprofolxacin activity. Responses to part b) iii) were rather variable and this proved to be a discriminating question. For part b) iv) no answers actually suggested a base-flip mechanism, however, there were a number of thoughtful responses that suggested a 'DNA distortion' mechanism to help accessibility.

Q 39

Most people made a good or very good attempt to this question. Section a (i) was mostly answered well, except that very few mentioned the non-aqueous (acetonitrile) conditions. In (ii) only a few remembered that there are three reaction types that are initiated by ammonia treatment (base deprotection, cyanoethyl removal and linkage cleavage). Mechanism drawing was mostly correct, except that no one realized that there are two possible cleavage mechanisms for the succinate linkage (direct attack at the ester carbonyl group as well as an internal cyclization mechanism involving the amide). Most people got the types of interactions possible between Hoechst and DNA in section b and all knew that this was minor groove binding. Very few mentioned the narrowing of the minor groove as the drug binds. Only a few got the correct hydrogen bonding sites on the A and T bases. Most people worked out that the drug binds to A:T rich DNA sequences. Several made good attempts at section c and were able to work out that introduction of an NH group in the ring might lead to improved interaction with G, but several put the N on the outer instead of the inner curved surface.

Qu. 40: 30 answers, average 15.1

I was a bit disappointed with the answers for what I felt was a straightforward question with lots of hints. A few people saw what was going on, but many were floundering.

(a) Was book work, but the instruction was to use words and not simply reproduce the calculation (those who did got little credit). Generally people seem to have understood how INEPT works.

(b) (i) Was straightforward and well done

(ii) Few people had anything sensible to say. The key point is that after the start of B there are no S spin pulses to cause transfer (the 180 does not cause transfer).

(iii) Most people did not read the question carefully and so introduced offset modulation during one of the periods (it is refocused, as it says). Quite a few people, however, forgot to put in the coupling evolution for the final \square period, leading to a lot of muddle.

(iv) Most people knew that a difference experiment was needed, but there was muddle over which pulse to invert.

(v) A few people spotted that DEPT is longer, so relaxation losses will be more significant.

Qu. 41: 33 answers, average 16.5

Generally much better answers than Qu. 40

(a) Straightforward bookwork, but a disappointing lack of clear diagrams and too many words

(b) (i) Everybody got this

(ii) A common mistake here was to forget that the β pulse had to be applied to both spins. If you fail to do this you can't really get the required expression.

(iii) The same error reoccurred.

(iv) Most people know how to do this, but there was sloppiness in working out the modulation in t_1 (you need to use the trig. identities). Only the best candidates spotted that there were two equal contributions to the diagonal peak multiplet which resulted in cancellation and hence only two of the four components of the multiplet are in fact present.

Q42

Many candidates drew an MO diagram appropriate for B_4Cl_4 , i.e. a molecule with a one electron donor substituent, rather than for the two electron donor carbene. In the second part very few candidates recognized that a B-only two electron π system was possible.

Q43

Mostly well answered although some candidates couldn't see that B_4H_8 had to be isoelectronic with C_4H_4 .

Q44

Far too many candidates tried to use Wade's rules to answer this very straightforward question.

Q 45

Most candidates had the right idea but answers could have been more complete.

Q46

Most candidates could see that large Δ would favour square geometry and that ligand bulk would favour tetrahedral. Many candidates failed to recognize that Cl is a π donor ligand and that PEt_3 is a π acceptor, erroneously assigning geometry based on ligand bulk. Many candidates were convinced, presumably by the influence of our teaching in organometallic chemistry, that all d^8 complexes must be square.

Q47

Control of alkene geometry via Wittig and Alkyne reduction. Very well answered. Mean = 4.2

Q48

Well answered, with most of the answers selecting the appropriate reagents for F/C acylation and ozonolysis to unmask the RCHO. Mean = 3.4

Q49

Well answered and good understanding of the disconnections. Mean = 3.6

Q50

Very poorly answered with 15 scripts scoring zero (no attempt to answer the question). Simple Baeyer-Villiger and similar to past Tripos questions. Maybe the B/V was difficult to spot due to the time pressure? Mean = 2.6

Q51

Well answered and displaying a good understanding of Reconnection strategy, enolate alkylation and Beckmann rearrangement. Mean = 3.5

Qu. 52

Was way too easy. A large number of candidates scored 100%

Qu. 53

The only real challenge of this was making sure that you did not get muddled up in converting units. It's surprising that by the end of three years some people seem unable to work out the relationship between wavelength, wavenumber and frequency. Several people lost marks due using the reduced mass of I_2 .

Qu. 54

This is an extremely straightforward question, but people lost marks by not reading it carefully and hence not answering the question.

Qu. 55

On the whole well answered, but a lot of people forgot that a Q branch transition has a vibrational component. Several people reproduced the complex diagram from the notes showing overlapping PQR branches, but did nothing else: it's incredible that people would bother to memorize such things.

Q60

Question 60 was very popular and 53 students answered the question. Part (a) was generally well answered. Typical problems were wrong assignments of the spin states of the complexes, which led to wrong description of the kinetic rates of the complexes. The faster electron transfer rate in (b) was recognized by most students as inner-sphere electron transfer, but the electronic explanation was often missing or wrong. The average mark of this question was 6.4 and eleven students were given the full marks (10).

Q61

There was great disparity between the quality of answers for the two halves of the question.

The first part, involving structural determination of a simple 6-carbon molecule was on the whole well answered, with most candidates readily identifying symmetry and functional groups, and able to combine this to derive the correct answer. A significant number identified a regioisomer which was distinguishable on the basis of chemical shift and 2J values.

The second part, requiring a mechanism for fragmentation / aromatisation was very poorly answered, with only a single candidate providing a complete, correct answer. Following a central theme of the course, candidates were expected to consider appropriate orbital overlap in their proposed mechanism; nearly all answers involved an elimination pathway that could not be considered feasible on this basis. A feasible mechanism would invoke a Favorskii-like 2π electrocyclic ring opening event followed by elimination / aromatisation; this type of process had been well covered in the lectures / supervisions.

Q62

Biological catalysis

Mechanism of aldolase

Generally well done and marks centred around 6-7/10.

(a) Almost all mentioned imine. Some knew cyanoborohydride was selective, some inferred lysine, very few thought about order of binding.

(b) Mechanism very similar to lecture. Quite a few mentioned imine v ketone comparison. Some mentioned stereospecificity on enzyme (but only in passing).

(c) Non-enzymic reaction. Most discussed other products based on aldol reactivity. Relatively few compared reactivity of aldehyde. Many saw loss of stereochemistry but no-one gave a great answer.

Q64

Question 64 was answered by 14 students.

Four students had no problem with this question, three were utterly unable to answer it. The rest was in between. Average score: 6.27 out of 10.

The question could be answered if the first few pages of the lecture notes (definition of the classical partition function and expression for the average energy) had been studied, and certainly if the exercises had been understood.

The total failure of three students to write anything meaningful makes one wonder why they chose to answer this question in the first place.

Q65

This question presented the candidate with an application of nearly-degenerate perturbation theory to an anharmonic perturbation which coupled two normal modes in carbon dioxide. This example was explicitly worked through in a lecture, and questions on the use of ladder operators needed for its solution were given in supervision questions. From 16 solutions received, the distribution of marks was substantially bi-modal, with almost all candidates achieving a 1st, or failing the question, I presume dependent on the candidates' familiarity with ladder operators. The mean mark was 64.4%. A small catch in the question was the fact that one of the normal modes was a linear combination of two degenerate modes, and this was used to differentiate at the very top of the marks. This pitfall meant that only one student achieved full marks, although one other student spotted this.

Q67

Question 67 was attempted by 22 students. Most students had a good understanding in the physical principles of cyclic voltammetry, but major problems arose in the interpretation of the underlying chemical processes. Many students did not recognize the Ru^{III}/Ru^{II} redox couple and several assigned reversible waves to ligand-based radicals. Only one student recognized that waves a and b correspond to the same species formed by a non-redox process (from complex A) and a redox-induced solvolysis (B).

Q72

A standard evaluation of Slater determinant matrix element important to the whole area of quantum chemistry. Generally answered very well.

Qu. 74: 30 answers, average 3.6

The answers were, with two exceptions, universally awful. Many people not know what the steady-state NOE experiment was, and many confused it with the transient experiment. A correct analysis of the latter gained a small amount of credit. Those answering this question must have known that they had little idea how to do it, so given so much choice on the paper why choose this question?

Q75

Scripts = 9, Average grade = 3.7/5 (73 %)

Some very good answers. I was expecting the pyridine part of the question to confuse more people. Points were mainly lost by poor definitions of the Coulomb and resonance integrals.

Q76

Scripts = 9, Average grade = 3.8/5 (77 %)

Well answered question. Clarification often needed for the order in which to apply Hund's rules. Various mistakes on the term symbols because of easy mistakes.

Q77

Scripts = 9, Average grade = 3.2/5 (64 %)

Most people understood that the orbital was a pz but did not follow through to defining it as 3pz. Hence the diagram of the orbital was often of the 2pz orbital. Some poor definitions of nodes and nodal planes.

Q78

Scripts = 9, Average grade = 2.7/5 (53 %)

Poorly answered question. Mathematical definitions of the Coulomb and resonance integral were often slovenly. Nobody appreciated that 2s and 2px orbitals have incorrect symmetry and hence there is no overlap.

Qu. 79

Was well done

Qu. 80

Quite well done, but several people could not count the number of valence electrons in V^{2+}

Qu. 81

Was quite well done, but the sketches of where the C_3 axis was in the *fac* isomer were almost all dreadful.

Qu. 82

Nobody understood that the p_x orbitals can be broken down into *three groups* which do not interconvert under the operations of the group. As a result, nobody could complete the question. Some credit was given for identifying the IRs.