

## Part III Exam Questions Reports 2018/19

### Paper 1

**Q.1.** Most of the students performed well in identifying the correct monomer(s) involved in the polymers shown as well as the majority of the polymerisation conditions. They were also able to calculate the polymer percent conversion ( $\rho$ ) and identify polymerisation growth mechanisms. However, they struggled when asked to suggest alternative methods to polymerise MMA into PMMA, which unfortunately was directly out of the course notes. Clearly students have been taught to memorise reactions of starting materials to products and some mechanism, but do not pay attention to the importance of reaction conditions.  
18 scripts, average 12.9

**Q.2.** The first part of the question, which is very closely related to problems covered in the lectures and in the supervision work was not answered well by the majority of candidates. Most could remember the form of the expression for the energy of the allowed spin states but forgot the method used to obtain it. Most candidates did a decent job of extracting data from the graph and using it in further manipulations. There were some problems characterising the nature of the Jahn-Teller distortion, but the candidates who did this correctly then produced good descriptions of the sigma kinetic superexchange pathway and were able to discuss the effect of ligand bulk.  
26 scripts, average 13.1

**Q.3.** Part (a) was bookwork and most answers recognised this and made a reasonable attempt at reproducing the biosynthetic pathway and mechanisms given in the notes. Only one answer seemed to have no recall of the biosynthesis that had been described and got low marks. The most common mistake was that a number of answers forgot that the biosynthesis proceeds via the penicillin (with the 5-membered sulphur-containing ring that is then ring expanded) and went straight for the 6-membered ring.

Part (b) was new to them and the standard of answers was much more variable. In (i) many failed to specify that the KS domain catalyses two steps – transfer of the upstream acyl group onto the active site cysteine and then the decarboxylative condensation with Malonyl-S-ACP. In (ii) many did not come up with a reasonable mechanism that allowed the beta-C atom of the cysteinyl residue be a nucleophile to attack the upstream thioester. Overall a good question. The marks came out just right with a good spread.  
23 scripts, average 13.0

**Q.4.** This question was moderately well answered. In part (a) people generally got the idea of rotating the crystal being important, but defining why this needed to be done (i.e. diffraction conditions need to be satisfied, so reciprocal lattice point and Ewald sphere must be coincident) was poorly described. Part (b) was very well answered with marks lost from poor description of powder assumption (crystals in all orientations) or formation of DS cones. Part (c) – the mathematical calculation was well done with most realising there were two phases in the EDX and handling this well. Putting in back in context and considering the

diffraction data was were almost all students lost marks. Many were stumped by the lack of a wavelength to get lattice parameter – which they were expected to estimate from their compositions and the lattice parameters given. Similarly, only two students were able to calculate the concentrations of the phases (and only one related it to intensities). Many failed to note simply that the two phases at 300C also appear to be fcc, and that the difference in LP causes the peaks to split and that this is apparent at high  $2\theta$ , but not low  $2\theta$ .

18 scripts, average 13.6

**Q. 5.** (a,b,c), The energy landscapes part of this question was not done particularly well. It is basically a simple exercise in probability, which tripped up a couple of the candidates. The last part, commenting on the range of the potential, also produced a spread of marks, including a couple of essentially correct answers.

(d,e,f) (soft matter). This question was overall done well. There were some inaccurate answers to part (e), which requires some care in the definition of the accessible volume and how it depends on the distance between the colloids. For part (f), most answers gave the correct ranking but the question specifies that a clear justification is required in order to obtain all 3 marks.

6 scripts, average 11.5

**Q 6.** (a) This question proved to be reasonably testing, particularly in terms of the accurate manipulation of 2D and 3D representations of stereochemistry, leading to clear divisions between a very good answer (correctly assigned stereocentres and convincing Ireland-Claisen mechanistic rationalisation), a satisfactory answer (half correct) and answers where the stereochemistry was completely wrong but the overall mechanism was roughly OK. Therefore, it produced a good spread of marks as anticipated.

(b) Must recognise the alcohol/amine is a better nucleophile than the vinyl silane, and so attacks the activated aldehyde first. The rather surprising stereochemistry of the second product was explained well by many candidates, noting that the C-Si bond has to be orientated to stabilise the beta-cation and so induce steric crowding around the ring

34 scripts, average 12.9

**Q.7.**

2 scripts average 19.0

**Q.8.** (a) Straightforward book work on thermally stimulated depolarisation current technique for measuring activation energy barriers for ionic diffusion. The majority of the candidates correctly described appearance of the peak feature in depolarisation current temperature response. However, a few candidates wrote nothing about linear regime for heating. (b) The question of describing the radioactive tracers was answered correctly by most of the students. Some of them provided detailed descriptions on experiments and their advantages and disadvantages compared with other alternatives for measuring diffusion coefficients of species of interest. (c,i) Only a small fraction of students made a mistake on the Schottky-defect reaction and the concentration of the defect. (c,ii) This question of the number density of defects were answered correctly by most of the students. (c,iii) The first question of calculating the mobility of the vacancies were unfortunately

omitted by some of the students, although many of them calculated the ionic conductivity correctly.

16 scripts, average 11.7

**Q.9.** The question was split into two halves representing both parts of the course taught by R. Less and A.E.H. Wheatley. Part (a) called for a description and comparison of bonding in a structurally-related compounds. A large proportion were able to recall the electron-deficient bonding model of  $(AlCp^*)_4$  covered in lectures. Although not explicitly covered, many were also able to relate the structures of other clusters using Wade's Rules, the 18-electron rules and electron-precise bonding. Only one student recognised that the silicon cluster has a similar molecular orbital arrangement as Al, but with an extra four bonding electrons. Not many answers discussed metal-ligand bonding even though it was asked in the question and fewer still recognised that Ni had additional backbonding from filled d-orbitals to the  $Cp^*$  ligand. In part (b) all candidates were aware of aggregation states of lithiated amide A, but many thought it was a trimer rather than dimer. For the imide B, a ladder structure was a popular answer and relatively few were able to correctly assign lithiated structure C as a tetramer although more could identify intramolecular coordination of NMe<sub>2</sub>. Even if the correct structural motifs were not given, credit was awarded for knowing that THF would not affect chelated structures. For part (c) most could explain monomer-oligomer equilibria but not many could actually use the values of molecular weight given to show the ligand decoordinating the monomer.

32 scripts, average 13.1

**Q.10.** Answers to this question varied in quality from 10/20 through to 18/20 (one outlier with 2/20) so there was a good spread from which average mark was generated. The question was so well answered, however, that relatively small differences in quality of the answer were used to differentiate between candidates. Paper 1 questions are generally designed to be a little less challenging but this was perhaps set at a less challenging level than was required.

(a) Generally very good answers to this part. Those who talked about sulphur co-ordinating the BuLi and showed clearly that the aldehyde is not generated until the addition of water at the work up stage got the most credit in part (i). In part (ii), greatest credit went to those who had got the mechanism for oxidation of the pyridine N correct, recognised that  $Cl^-$  would then generate the  $CN^-$  required for attack onto the activated pyridine ring (by attack onto the Si) and gave the correct final break down mechanism to provide the product. (8/20)

(b) (i) Answers to this part were a little more varied and most students used the DMF dimethylacetal in the correct way. Those who then provided the most sensible pathway to product, which began with the deprotonation between the two carbonyl groups, were given most credit for this part. (6/20)

(ii) Some students used piperidine in the same way as they used methoxide in part (i) but protonated piperidine has a pK<sub>a</sub> of around 11 and this is not the most likely pathway; perhaps better is the formation of an enamine on the conjugated carbonyl group first. As much credit was awarded as possible for all reasonable variations on the mechanism. (6/20).

Scripts: 42, Average: 13.8.

**Q.11** (a) Typically most candidates got the basic idea. The main differentiation came with those who spotted that the Houk model should be applied to rationalise conformation. In the context of the Houk model azide is small due to its linearity, which some students did pick up on. Suitable credit was given for rationalising the stereochemical scrambling in the rearranging step which is key to the process.

(b) This question was mostly well answered. Some students tried to include hydrozirconation even though the question specified only one catalyst was to be used and several even tried to attempt this without Pd. There were several orders of events followed, and appropriate credit was given for plausible combinations. Many students tried to do the hydrostannylation without a catalyst, but this process requires Pd – of all the reactants the Sn-H bond is weakest and would likely therefore undergo oxidative addition first.

39 scripts, average 13.0

**Q.12**

28 scripts, average 13.1

**Q.13.** This question was answered reasonably well by most candidates and only a couple of particularly low-scoring attempts. The majority of candidates scored highly on parts (a) and (b) which were relatively similar to supervision questions and/or past exam questions. Part (c) proved a little trickier, as some candidates seem not to have properly interpreted the described structure; those who got the structure correct were able to correctly answer this part of the question. Part (d) was similarly varied in terms of answers, although here the discriminating factor was generally whether the candidates had properly counted all of the dangling bonds implied by the given structure. Overall, not a bad set of scripts for a question that did require a certain amount of structural visualisation.

21 scripts, average 12.0

**Q.14.** Overall this question was answered well. The highest mark was 18/20 and the lowest mark was 8/20. The low mark was as a result of some sections of the question not being answered. Part A and Part B were answered well and the mechanism of CYP mediated oxidation was answered well.

26 scripts, average 13.6

**Q.15.**

4 scripts, average 13.5

**Q.16.** Most students understood that (a) was a Suzuki coupling; the few who did not struggled to obtain many points in subsequent parts, although points were given for plausible structures involving chemically implausible starting materials. Likewise many got the correct structure in (b) and gave plausible characterisation methods. (c) stumped only a few. (d) appeared hardest, as planned, and very few got the reversible uptake concept correct. Near-full marks were nonetheless given for several plausible and coherent answers. 12 scripts, average 14.25.

**Q.17.** Overall well answered. Some very good discussions of thermodynamic stability v. kinetic pathways for nucleation. Especially with comparison to nuclei which may be generated in solution depending on the nature of the solvent, supersaturation etc. The final

part (d) was straightforward but I would like to have seen more justification that the two polymorphs were monotropically related since no thermal data other than melting points were given to counter any possibility of a phase transformation.

21 scripts, average 13.0

**Q.18.** Overall, this was answered close to the average: (i) was fine; (ii) was in general poorly done with students ignoring the major clue in the spectral data - 3 distinct methyl groups

(iii) mixed, I was fairly generous in this part. Most got the rough idea with no one really getting it all right

22 scripts, average 12.7

## Paper 2

**Q.19.** Most students understood the polymerisation mechanism involved in the ring-opening polymerisation of norbornene and could identify how a second monomer was added to prepare a diblock copolymer. However, only a few students were able to think beyond the taught material to elucidate how backbiting impacts the polymerisation of a low ring strain monomer such as COT.

12 scripts, average 14.4

**Q.20:** In general there was a lack of identification of sec-BuLi which is disappointing for candidates at the Part III level. The students clearly understood the different parts of a controlled polymerisation, namely initiation, propagation and termination and could readily give a mechanism for the controlled polymerisation of styrene. Most students could offer a good guess at the  $^1\text{H}$  NMR of polystyrene from a specific initiator.

12 scripts, average 17.5

**Q.21.** This question differed from that set on this material in recent years in requiring some description of experimental techniques. There were some very good answers to these parts, but many candidates forgot to discuss the underlying processes e.g. how the creation and destruction of domains is responsible for the differences in field-cooled and zero-field-cooled magnetization measurements. Most candidates were then able to recognise the canted antiferromagnetism and metamagnetism in the various graphs.

22 scripts, average 16.6

**Q.22.** Most candidates demonstrated good recall of the spinel structure and the mechanism of double exchange. A minority of candidates struggled to work out the quantity of Mn(III) versus Mn(IV) and almost no-one saw that the number of possible double exchange pathways depended on the amount of Mn(III) present. No candidate realised that high spin Mn(III) must have a very strong Jahn-Teller distortion and that this would make double exchange less favourable than it is in magnetite. The question should have included the oxygen atoms in the formula given for the MnFe perovskite but all students assumed them and there was no evidence that anyone was disadvantaged.

There were some good descriptions for why the coupling between Ir(VI) is so strong. Most candidates correctly identified the nature of the Ir-Ir and Ir-Ni couplings and were able to

derive a picture of one layer in the magnetic ground state. No candidate attempted to draw an adjacent layer which would have shown a more frustrated tetrahedral structure.

12 scripts, average 16.0

**Q.23** The parts of this question that were bookwork were well done – formation of the pyrrolidine ring in (a) and (b)(i). Linking the two rings in (a) was done badly by all but two or three. (b)(ii) was fairly variable – everyone saw that the linear precursor is geranylgeranyl PP and had a plausible folding of the chain but many of the reactions for making C-C bonds were implausible. It would be worth emphasising to future years that the terpene cyclase enzyme usually does all the cyclisations via carbocation intermediates (and does not use NADPH, ATP, Fe=O etc). Part (b)(iii) was done right by at least half the students.

20 answers, average 16.6

**Q. 24.** In part (a) almost all answers could see how the two precursors need to be joined together to make the product. One subtlety was that after ring opening and enol-keto tautomerisation and hydrolysis and decarboxylation of the MeO<sub>2</sub>C ester, there would be two prochiral CH<sub>2</sub>CHO side-chains. The stereochemistry of the prochiral centre tells one which side-chain forms which part of ajmaline but hardly anyone considered the stereochemistry and a lot got the two side-chains the wrong way round. A lot of answers decided to have C-3 of the indole attack the free –CHO as the first step. However this is not only getting the side-chains the wrong way round but also it spoils the mechanisms for other necessary steps such as the Pictet-Spengler reaction and the decarboxylation. So in fact this attack needs to be almost the last step.

In part (b) everyone decided this was a polyketide pathway. No-one spotted that this was a biosynthetic pathway given in the notes but they did generally see that either an oxidative cleavage or a rearrangement (e.g. pinacol rearrangement) would be needed and there were quite a lot of different but plausible solutions to the problem which got due credit. A few suggested two polyketide chains combine to form polivione and were marked down for this. 14 answers, average 16.9

**Q.25.** In general, this question was very well answered. Marks were mainly lost on the explanation parts of the question (a) and (e). In part (a) people often failed to identify terms in their expansions, lost Fourier transforms or convolutions. In part (e) although an envelope was alluded to, people often did not show how it would arise (i.e. from integral), or reference how the decay in features at high  $|S|$  will result in the loss of low-d features in the image. For the problem steps the main error was a lack of justification as to which turning points were being used (and why  $\pi/2$  is the first solution) and the definition of the conditions of the Scherzer focus and interpretable limits of the microscope.

16 scripts, average 17.4

**Q.26.** This question was not as well answered as the previous one. In part (a) people demonstrated the systematic absence, but not the intensity patterning for (hkl) i.e. a 2-fold rotation in the diffraction pattern. In (b) people often failed to describe the physical effects underlying each of the factors (e.g. Polarisation, Lorentz and Extinction). Part (c) generally well done, but a couple of people could not identify the unit cell of NaCl. Part (d) – identification of the primitive structure was well done – but explaining it was not (i.e. that K

and Cl have similar scattering lengths and so will 'look' the same, and hence the use of neutron diffraction necessary to see the elements as different).

15 scripts, average 16.5

**Q.27.** The answers to this question varied somewhat in quality; none were poor, and none were excellent. Only one candidate actually tried to integrate the steepest-descent equations, and did not do so accurately. However, there were some reasonable contour sketches. Overall, the intended separation into easy, medium, and harder parts worked quite well.

4 scripts, average 17.0

**Q.28.** M4 (soft matter). Most answers to this question were good. However, there were a few pitfalls. Many students gave vague answers to part (a). In particular, one might expect attractive forces to be present -- under what circumstances are these negligible? A good answer to part (c,iii) needs some care since the numerical factors in the formula for  $v_{cell}$  and the value of  $V_0$  would both be different for a b.c.c. lattice, but only the value of  $V_0$  affects the pressure. Answers to (e) often contained a lot of information but the logic was not always clear. The dominant effect in (f) is likely to be the surface tension between the phases, which appears when computing the rate by classical nucleation theory.

4 scripts, average 14.8

**Q.29.** This question was generally well done, although the first bit of part (c) proved testing for almost all in the suggestion of suitable reagents for the required transformation. In part (a), many candidates failed to translate the Burgi-Dunitz trajectory from an acyclic to a cyclic system. In part (b), most candidates were able to outline a rationalisation of the selectivity in the Diels-Alder reaction, however, the 3D representations presented were often on the abstract side. Overall, this question served to test the manipulation of organic structures in 3D, mechanistic reasoning and stereochemical aspects.

31 scripts, average 16.7.

**Q.30.** (a) Generally done well; dipolar cycloaddition may be better than ionic formation of five-ring; many people had the initial delocalised anion attacking the imine rather than the softer conjugated ester, which makes it hard to see the overall process.

(b) Provided a role for magnesium was found, various reasonable routes were given credit. Mg might form a silyl Grignard with TMSCl, or else add electrons to the ynone.

(c) The role of ArI was ignored by many candidates, but other creative ways to use the oxidant were suggested.

(d) The benzyne-like mechanism was spotted by many candidates. Alternative internal salts are much less likely, but were given appropriate credit. Endo/Exo selectivity was considered in some answers.

13 scripts, average 16.2

**Q.31.** (a) The easiest way to show that the inequality  $RHS \leq LHS$  holds is to rewrite it in the form  $RHS - LHS \leq 0$ , and subsequently apply the approximation stated in the hint.

Difficulties occurred mostly when trying to simplify the RHS and LHS independently.

(b) The proof requires inserting the canonical distribution functions for  $p$  and  $q$  into the result given in part a), and then simplifying. Other approaches that did not rely on this inequality were, however, accepted.

(c) Some candidates experienced difficulties in identifying a suitable perturbation  $W$  for their example system. The prototypical choice would be the ideal-gas Hamiltonian as  $H_0$ , with the perturbation  $W$  capturing Lennard-Jones interactions between the gas particles.

(d) This part required reproducing basic facts about MC simulations, in particular the Metropolis acceptance criterion and trial moves (such as random particle displacements). Loss of points was largely due to not addressing all aspects of the question (e.g., the averaging procedure) or misstating the acceptance rule.

(e) The key step here is to express the average  $\langle H_1 - H_0 \rangle$  in terms of the radial distribution function (as practised in the problem sets). This leads to two statements that are mutually contradictory.

2 scripts, average 10.5

**Q.32.** 0 scripts

**Q.33.** (a) Most of the students correctly answered this question. (b,i) More than 2/3 of the students correctly answered this question with the correct defect reaction, but the last of them were confused with the type of defects, thereby giving a wrong answer on the defect reaction. (b,ii) This question was answered correctly by most of them. (b,iii) About half of the students gave wrong answers for the oxidation reaction and equilibrium constant. (b,iv) The answer for this question is straightforward if they remember the formula for calculating electronic conductivity. Most of the students applied the formula correctly to this question, but many of them obtained numerically wrong results. (b,v) Only a few students reached the correct conclusion, because of the wrong numerical values obtained for either (b,iv) or (b,ii).

10 answers, Mean: 15.4

**Q.34.** General comment: I presume that mainly strong students attempted this question. That is why the mean mark is slightly above the target one, 16.75

(a) Straightforward book work. One mark has been lost by practically all the candidates for not explaining the meaning of factor 2 in the denominator of the formula for diffusion constant. (b,i) This part was straightforward, but two candidates calculated the mean displacement instead of mean-squared. (b,ii) Practically all candidates gave the derivation by using from the start  $p \pm 1/2$  rather than derive the general formula and then set  $p \pm 1/2$  which is useful in (b,iii). No mark reductions were given for this. (b,iii) In some of the answers to this part of the question, there was some misunderstanding in defining diffusion coefficient in case of action of external field. Otherwise, the question was answered mainly correctly. (b,iv) A straightforward estimate for diffusion coefficient was done well by all the candidates.

Answers 8, Mean: 18.625

**Q.35.** In part (a) candidates generally gave a very good account of bonding in heavier alkene derivatives. Given they struggled with the later parts of the question, slightly more credit was awarded for part (a) in final marking to compensate for this. Part (b) similarly attracted strong answers although not all recognised the higher stability of the Pb(II) oxidation state

in comparison to Si and Sn. I expected students to struggle to explain the unusual geometry of C in comparison to linear A but most coped admirably, many identifying sp hybridisation at the central M atoms and donor-acceptor interactions with adjacent MR<sub>2</sub> groups. Very few, however were able to predict the cyclic decomposition product. Part (d) was where candidates struggled the most. A good number could recognise the presence of Pb-Mn pi-bonding in E and sigma-donors reducing this, as in G but not many were aware of the competing pi-donor ligand in F. There were hardly any attempts to construct MO diagrams showing pi-bonding in E or identifying isolobal Mn fragments.

11 scripts, average 16.1 (17.3 if the discounted mark of 5 is not included)

**Q.36.** The answers to part (a) showed most candidates had understood the main principles from lectures and had revised the material well, correctly identifying B, C and D, but the quality of explanation of the mechanism varied quite considerably. The majority could correctly identify the reaction steps although not all followed these stages all the way to the final product. Nearly all were aware of the need for coordinatively unsaturated 16e Zn species. The representation of the transition state and the important interactions was, however, relatively poor. Part (b) was generally well answered though not everyone could describe the correct coordination environment at Li. Part (c) the students found most challenging. A large proportion could identify the highly symmetric F and associated NMR data but far fewer could recognise the isomer F' even though it simply resulted from interchange of two metal centres. Many highly complex structures were proposed. Some credit was awarded if these were consistent with the NMR data.

32 scripts, average 17.1

**Q.37.** Generally, this question was done very well but marks varied enough to tell between the students who attempted it. Marks varied between 11/25 and 22/25 (one outlier with 1/25). (a) Some students were economical with their answers to this question: most students got much of this right with the distinguishing feature of all parts being the level of detail covered. (9/25) (b) Some candidates really went into a lot of detail for every part of this question and others were rather more reserved. It was relatively straightforward to distinguish between them, depending on the level of detail provided. For example, in part (i), in order to receive 2 marks, two reasons needed to be provided as to how quinolone G inhibits COMT. As long as the reasoning in part (iv) matched with the response, credit was given. (7/25). (c) (i) Answers to this were variable and as much credit as possible was awarded, even when students had taken a more unusual pathway to get to the product. (4/25) (ii) More students got through to the product in part (ii) of the question but again, answers varied enough to allow candidates to be relatively well distinguished from one another. (5/25)

Scripts: 33, Average: 16.3 (16.8 if the script which scored 1 is discounted)

**Q.38.** There were 18 answers to the question and so this was obviously perceived harder than the other Medicinal Chemistry question. Nevertheless, all candidates scored reasonably well on parts which they attempted.

(a) The S<sub>N</sub>Ar reaction was identified by all candidates. Many candidates then recalled the Dimroth rearrangement from the lecture notes either by name or knowing that it involved a ring fragmentation. However, it was disappointing as to how few candidates were able to correctly show the mechanism for this. Many proposed highly unlikely intermediates.

(b) The addition of an organolithium into a nitrile is a reaction taught in Part 1(a). So, it was surprising how many candidates missed this and chose to attack the benzene ring or do an ortho lithiation. I suspect this was because the reagent was BuLi and they assumed its behaviour without thinking, even though the formula of the product was given and required incorporation of a butyl group. Those who did initially attack the nitrile were then able to complete the Fischer Indole synthesis.

(c) Many candidates described the basic factors here. The better answers included specific relation to Lipinski's rules, for example having counted the number of H-bond donors and acceptors on the molecule and compared these to the rules. Many candidates have a very poor knowledge of how polar molecules are. This molecule would clearly be incredibly polar, yet many suggested it would fail Lipinski for having a LogP > 5, i.e. non-polar! Also, not enough candidates discussed obvious sites for metabolism on this molecule, which would clearly be vulnerable to this.

(d) The hardest part. Most candidates spotted that this would occur via cycloadditions, although there was a split over which step students attempted to do first. Although some students correctly showed the loss of nitrogen to give an intermediate for a 1,3-dipolar cycloaddition as the second step, many tried to do the second reaction before losing nitrogen gas, meaning the pericyclic reaction they drew was not one of the standard reactions. The question implied that the research group targeting the compound in this question were doing so to understand the natural product in part (c). Hence, they would be targeting a model compound with the same stereochemistry and so this was a rationalisation of stereochemistry question rather than a prediction. Many students missed this and gave products with very different stereochemistry. Many correctly converted groups syn in the starting material to syn in the product, however having regard for the tethers between rings favouring cis-fused rings and the endo rule were not done well.

(e) This question was overall attempted rather well by those that did it. However, several students left this part blank (which may be due to time pressure). The main issues arose from adding the two nitrogen substituents to the benzene ring. This was correctly done with one nitration and one  $S_NAr$ . Errors were made when electrophilic aromatic substitution was implied as the mechanism by which the ring-nitrogen bond was made (where there was no generation of any electrophile) or  $S_NAr$  with a poor nitrogen nucleophile.

18 Answers, Average 16.6, Std Dev 4.0, Max 23, Min 8

### Paper 3

**Q.39** (a) Generally well attempted and many saw the intramolecular olefination of the ester, highest marks given for detailed explanation of the processes involved.

(b) A number of students saw the combination of a Nicholas reaction and Pauson-Khand, enabled by Cobalt complexation. Highest marks for well explained and rationalised PK mechanism.

(c) Whilst most saw the alkyne carbopalladation there were a variety of mechanistic approaches for the final reaction at the ortho position of the electron rich arene. This provided a nice insight into the creativity when seeing a challenging transformation and appropriate credit was given for reasonable answers.

(d) A range of answers for this question, the best identifying the inner sphere and outer sphere delivery of the nucleophile and showing the key intermediacy of pi allyl palladium

complexes. Some students suggested the alcohol may direct the Pd in a syn addition, and appropriate credit was given for this.

27 scripts, average 17.0

**Q.40.** (a) Generally most students realised that the boron is a chiral Lewis acid and so variation came in the way the TS was constructed. Many candidates realised there was an attractive pi-pi interaction between the electron deficient boron-complexed carbonyl and the electron rich naphthalene ring.

(b) Chiral iminium catalysis was apparent to all candidates. What differentiated were considerations of exo and endo TS and also making sure that the correct sequence of cycloadditions was followed. Some students did not correctly depict the most stable iminium conformation which would lead to the wrong enantiomer of product. A number also used the trans isomer of the starting material, which would lead to the wrong diastereomer.

(c) Generally well attempted. Mainly what differentiated answers was clarity of explanation and drawing of the key TS. There were many errors made when translating stereochemistry in 3D diagrams post-Claisen into 2D drawings, which was a bit disappointing at this stage.

(d) A good number of students saw the reduction, SAE, SAD sequence that would give rise rapidly to the desired product. Appropriate credit was given to other plausible alternatives.

27 scripts, average 16.7

**Q.41.** 20 scripts, average 16.6

**Q.42.** 16 scripts, average 16.9

**Q.43.** This question was tackled rather well by the majority of candidates, with no scores below 10. Part (a) was essentially bookwork, and answered pretty uniformly. Part (b) was a little patchier, but nearly all candidates made some sensible comments about surface sensitivity, albeit few hit all the relevant points. Part (c) was also answered adequately by most; some candidates suggested explanations for the data that were not in line with the model solution, but nevertheless plausible within the information provided, and so received decent marks here. Most candidates successfully answered part (d), with just a few failing to realise that averaging the binding energy for the Shockley state would not simply average the Fermi wavenumbers of that state. Finally, the particularly testing part (e) elicited a range of responses, some of which were plausible and received decent marks, but only one hit the nail entirely on the head. In summary, candidates reliably succeeded on the more standard sections of this question, while performance on the more challenging sections provided appropriate discrimination.

21 scripts average 16.9

**Q.44.** This question was answered by rather fewer candidates than the others for this course, but those who did tackle it did pretty well, with no particularly low scores. It may be that the unfamiliar system discussed put some candidates off, although the work required was not all that difficult underneath the veneer of novelty. Part (a) required the calculation of effective masses for a set of parabolic bands, and most candidates knew how to set about this. Unfortunately, there were several errors in unit conversion – some essentially trivial, and others more subtle – so that only a small number got close to full marks on this section.

In contrast, parts (b) and (c) were completed perfectly by nearly all candidates. Results for part (d) were more varied, with only a few candidates correctly deducing that the shape of the bands close to the point of intersection would be conical, and that the system hinted at was therefore graphene; some candidates did mention graphene (or graphite) but without clarity as to how the electronic structure might be related to the case at hand. Finally, part (e) was generally quite well answered by most candidates, although not all paid full attention to the fact that techniques were sought that could distinguish between different spin states. Overall, those who were able to look past the unfamiliarity of the subject matter found some parts of this question quite straightforward, but there was still enough difficulty to provide discrimination between candidates.

15 scripts, average 17.2

**Q.45.** Overall this question was answered well. There was a small error in part b(iii) where the CN group was missing in the scheme (molecule 5). This did not have an effect on the outcome of the question and equal marks were awarded for this part of the question where the GE was calculated with or without the CN present. In (b) LE and GE values were calculated well. The comments on these varied where some students went into significant detail and others used one-word description. Part c of the question proved the most challenging, however in the majority of cases this was answered well.

23 scripts, average 17.0. Max. 22, Min 13

**Q.46.** The question consisted of 5 parts that assessed student's knowledge on the inverse electron-demand Diels-Alder reaction (iEDDA). In general, all students were able to clearly highlight the differences between the "normal" and "inverse electron-demand" reactions, as well as the factors that contribute to accelerated iEDDA reactions. Also, they were able to draw mechanisms of iEDDA based decaging of a cytotoxic from an antibody-drug conjugate and to highlight the key features of an antibody to be used in a chemically-induced drug release mechanism from an antibody-drug conjugate. The level of the responses was in accordance with the enthusiasm the students had on the topic during the lectures.

20 scripts, average 17.3

**Q.47.** Parts (a)-(d) were well answered by both candidates (book work). In part (e), candidates lost marks by not explaining how the phase shifts control the scattering amplitudes. Part (f) was more challenging, with both candidates struggling with the algebra/time available, although both were on top of the conceptual basis of the question. Part (g) was not well answered and would have required the candidates to think for themselves about the behaviour of scattering wave functions at scattering resonances.

2 scripts, average 18.5

**Q.48.** 3 scripts, average 18.3

**Q.49.** Most got the structure in part (a) correct, although some key details were missing in some answers. Most also understood the essential role of hydrophobic effects in (b), although hydrogen-bonding was (incorrectly) cited as a driving force in water by several. (c) Likewise was grasped well by most, although very few cited the loss in conformational freedom in the larger ketones as a reason for the diminishing binding constants. (d) posed more of a challenge to many, with difficulty in justifying why C and D behaved differently.

For (e) many understood the entropic reasons why binding was disfavoured, but very few noted the adoption of gauche conformations as an enthalpic factor limiting binding strength. For (f) many got the broad idea right, although quite a few thought that ketone F might deprotonate at pH 12, which is unreasonable.

11 scripts, average 15.9.

**Q.50.** Only six answered this one. Everyone got the mechanism (a) right or very nearly right. (b) was also generally answered correctly, excepting two who thought that smaller molecules were entropically favoured somehow, an error which propagated into subsequent parts. About half got the prismatic structure of 3 correct, and more still correctly got 4. Almost no one answered (d) correctly - that product 4 would be quite insoluble with these Ar groups, and its precipitation would drive the reaction forward - but much partial credit was given for plausible answers. Those who had the structure of 3 wrong had trouble with (e), but again partial credit was given where possible. About half of answers got (f) correct, understanding the role of entropy of activation in closing the rings of 6 vs. 7.

6 answers, average 16.5.

**Q.51.** Generally high marks for this question. The description of cocrystals and synthons was good although this was familiar ground from the lectures. Most discussed the template mechanism well although in part (c) I would like to have seen more discussion why if miscible in forming a solid solution they are not isostructural re Cl/Me and the role of the Br in their own individual crystals. Few specifically drew attention to the need for the intramolecular distance within the template needling to match the required intermolecular distance for the reacting molecules. The CSP part was covered in the lectures but this was a chance to bring the overall picture together and on the whole was well done.

21 scripts, average 17.4

**Q.52.** A very disappointing number of answers, made even more strange by the fact that those who did try this question usually gave excellent discussions of the possible mechanisms etc. operating. The X-ray analysis was straightforward but answers were sometimes a little weak on factors that might influence the balance between kinetic and thermodynamic stability and surprisingly few commented on the need to study the patterns as a function of grinding time to establish whether the amount of liquid present was affecting the time-dependence of the process and thereby hiding possible intermediate crystal phases.

7 scripts, average 18.4

**Q.53.** Mostly ok, but the major comment on this is that clearly students do not know the mechanism of the Birch reduction! Also some 'creative' answers to the Diels Alder part.

18 scripts, average 16.4

**Q.54.** Similar level as the other long question. A number came unstuck when asked to work out a synthesis of a key intermediate and there were some interesting answers in the role of mCPBA, but also a number got this right. If I remember rightly one person got full marks on this part.

10 scripts, average 16.3

## Paper IDP1

**Q.1.** Generally well answered. Some candidates talked about general factors controlling the radiative importance of a gas rather than focussing specifically on the properties of methane. A small number of attempts used mass mixing ratios rather than volume mixing ratios. The discussion in part (g) needed to focus on the likely difference in chemical regime in then tropics vs SE USA (ie NO<sub>x</sub>-poor vs NO<sub>x</sub> rich); some, instead, focussed on likely differences in OH in the two regions.

29 answers, average 16.5

**Q.2.** Overall students did well, except for question b(ii) and c(ii). For b(ii) students lost marks if the graph axes weren't labelled, and only a few students provided a correct answer to the question asking about the increase in the mass of solute and its effects on the critical radius and critical saturation ratio, which required reading beyond lecture material so not surprising that only a few students achieved full marks here. As for question c(ii) only about ½ the students answered correctly. Question d(ii) about ½ the students achieved full marks here, others failed to realise that both direct and indirect radiative effects on climate ought to be discussed here for an excellent answer.

13 answers, average 17.4

**Q.3.** Many very good answers. The numerical parts of the questions were usually answered very well. The answers to the descriptive parts were more varied. Some were very well written while some were jumbled and confused or lacked any elaboration.

34 answers, average 17.6