

ICHO Training: Experiences and Insights

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ABSTRACT

The International Chemistry Olympiad (ICHO) is an annual competition for high school students from around the world. Specialized training is necessary for these students as one third of the test materials¹ are beyond the ordinary high school curriculum. I had the opportunity to be involved in training the Singapore squad from 2004 – 2007 and in the process, I came out with some strategies, particularly in organic chemistry. In this paper, I will discuss some of these, with a focus on the types of interesting problems created to stimulate students' thinking and a story-telling approach to the teaching of pericyclic reactions.

Keywords

International chemistry olympiad, organic chemistry, story-telling approach, pericyclic reactions

INTRODUCTION

The International Chemistry Olympiad (ICHO) is an annual competition for high school students from around the world. Figure 1 below illustrates how the National University of Singapore (and hence Singapore) selects/prepares students to take part.

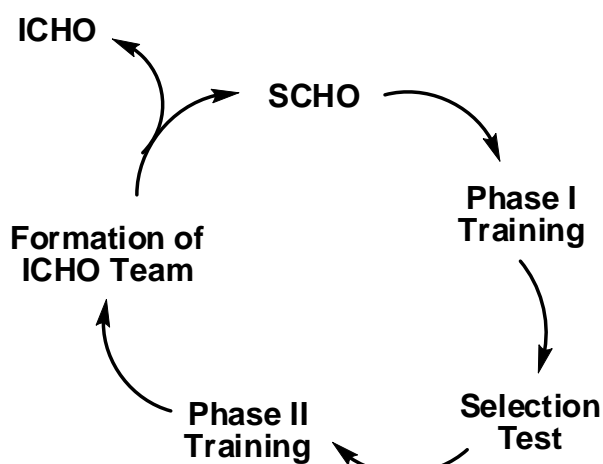


Figure 1: Flow chart of how Team Singapore is being selected.

The Singapore Chemistry Olympiad (SCHO) is usually held at the end of November or early December. It consists of a theory round and a practical round and the top 25 to 30 local candidates are invited for Phase I Training. This takes place from January to April of the following year and the students are trained by teachers from the different Junior Colleges (JCs)². They then take a selection test and the top six undergo Phase II training. This is conducted by NUS and the mentors are usually professors or senior students.

The training of students for ICHO is of utmost importance because they usually go on to pursue a degree related to the chemical sciences. Eventually they will become leading researchers whose research may one day benefit mankind. It is thus imperative to inculcate a passion for learning in them and to train them to think critically. This is by no means a simple task and in this paper, I want to share some of the strategies/approaches that I have used or developed.

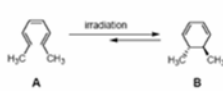
STRATEGIES

- Using past ICHO questions as a platform to introduce the more advanced topics.

A number of ICHO questions introduce students to more advanced topics in chemistry (most of which are beyond what they will cover in the ICHO syllabus). However, students are still able to answer them by context inference. While going through such questions with the students, it is worthwhile teaching them these advanced concepts briefly in order to stretch their thinking. From my experience, students tend to appreciate this way of teaching as they are taught to understand why certain reactions happen instead of merely accepting the facts as they are. Students reaching Phase II Training are definitely not satisfied with just inferring the answer from the context; they are hungry for knowledge and yearn to know more. Presenting them with these foundations, it springboards them and propels them to read further. Figure 2 illustrates one such question.

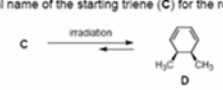
Problem 14: Photochemical Ring Closure and Opening

1,3,5-Hexatriene is known to undergo light-induced cyclization to give 1,3-cyclohexadiene. The photochemical reaction is reversible and stereospecific. Thus, irradiation of (2E,4Z,6E)-octatriene (A) with UV-light gives cyclohexadiene (B). The choice of the wavelength of light depends on the absorption maximum of the compound to be irradiated, and the absorption maximum is related to the number of conjugated double bonds in a chain.



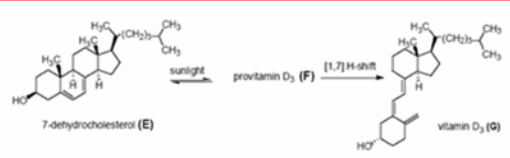
A $\xrightarrow{\text{irradiation}}$ B

14-1 What is the chemical name of the starting triene (C) for the related reaction shown below?



C $\xrightarrow{\text{irradiation}}$ D

A similar reaction mechanism is involved in the synthesis of biologically active molecules. For example, in the presence of sunlight, 7-dehydrocholesterol (E) undergoes an electrocyclic ring opening reaction to give provitamin D₃ (F), which can be further transformed through a [1,7]-hydrogen shift to yield vitamin D₃ (G).



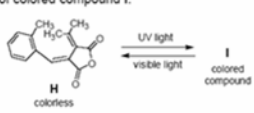
7-dehydrocholesterol (E) $\xrightarrow{\text{sunlight}}$ provitamin D₃ (F) $\xrightarrow{[1,7]\text{H-shift}}$ vitamin D₃ (G)

14-2 Of the two compounds 7-dehydrocholesterol (E) and vitamin D₃ (G), which would you expect to absorb light with the higher energy? (E or G)

14-3 What is the chemical structure of F?

This principle has been elaborated to develop photochromic materials. For example, irradiation of colorless compound H with UV light gives colored compound I. The color change is reversed upon exposure to visible light.

14-4 Give the structure of colored compound I.



H $\xrightarrow{\text{UV light}}$ I (colored compound) $\xrightarrow{\text{visible light}}$ H

Figure 2: Problem 14 extracted from the preparatory questions of ICHO 2005³.

This question deals with electrocyclization and sigmatropic rearrangement, two types of pericyclic reactions. Scrutinizing the question carefully, students are not required to know pericyclic reactions to answer it. Questions are guided with similar examples; students are just required to predict the product/s by inferring from the examples given. When I go through this question with students, I briefly introduce the concept of pericyclic reactions to

them from the frontier orbital perspective. This is supplemented with the transition state aromaticity model and the correlation diagram, provided they are able to catch the former approach. This way of introducing pericyclic reactions will be further illustrated in the final section.

Students are receptive to this method and they go on to read about them further on their own during their free time. Following that, I show them research papers utilizing pericyclic reactions. The beauty of organic chemistry is better appreciated when they are able to understand this intriguing class of reactions in some detail.

Organometallic chemistry, a branch of chemistry that utilizes knowledge from both organic and inorganic chemistry (particularly transition metal chemistry), is an area that remains relatively unexplored in most high school curriculum. Figure 3 below shows one of the very few questions devoted to it in ICHO.

Problem 12: Metal Carbonyl Compounds

Carbon monoxide, as a two electron donor ligand, coordinates to transition metals to form metal carbonyl compounds. For example, iron forms the pentacarbonyl metal complex, $\text{Fe}(\text{CO})_5$. Nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$, has been used for the purification of Ni metal in the Mond process. Electron counts of these metal carbonyl complexes show that they obey the 18-electron rule. Cobalt and manganese react with CO to form dinuclear complexes $\text{Co}_2(\text{CO})_8$ and $\text{Mn}_2(\text{CO})_{10}$, respectively. (Electronic configuration of Mn is $[\text{Ar}][3d^5]4s^2$) A metal-metal bond between the metal centers is considered essential in order for the compounds to obey the 18 electron rule. The cyclopentadienyl anion C_5H_5^- has also been widely used as a η^5 -ligand. For example, ferrocene (C_5H_5)₂Fe, a classical compound, obeys the 18 electron rule.

The reaction of $\text{W}(\text{CO})_6$ with sodium cyclopentadienide NaC_5H_5 yields an air sensitive compound **A**. Oxidation of **A** with FeSO_4 yields compound **B**. Compound **A** can also be prepared from the reaction of **B** with Na/Hg , a strong reducing agent. In the 1600-2300 cm^{-1} region of the IR spectrum, **A** shows absorption bands at 1744 and 1894 cm^{-1} and **B** absorption bands at 1904, and 2010 cm^{-1} . Compound **A** is a strong nucleophile and a good starting material for the synthesis of organometallic compounds containing metal-carbon σ -bonds. The reaction of **A** with propargyl bromide ($\text{HC}\equiv\text{CCH}_2\text{Br}$) gives compound **C** containing a metal-carbon σ -bond. At room temperature compound **C** undergoes a transformation to yield compound **D**. The same chemical composition was found for compounds **C** and **D**. The chemical shifts (δ) of the CH_2 and CH resonances and coupling constants J_{CH} of propargyl bromide, **C** and **D** in the respective ^1H NMR spectra are listed in the following table.

^1H NMR	$\text{HC}\equiv\text{CCH}_2\text{Br}$	C	D
δ (CH_2)	3.86	1.90	4.16
δ (CH)	2.51	1.99	5.49
J_{CH} (Hz)	2.7	2.8	6.7

12-1 Explain the differences in the IR spectra of **A** and **B**.

12-2 Draw chemical structures for **A**, **B**, **C** and **D**.

12-3 The transformation of **C** to **D** involves a migration of the metal on the propargyl ligand. If $\text{DC}\equiv\text{CCH}_2\text{Br}$ is used for the synthesis of **C**, draw the structures of **C** and **D**.

Figure 3: Problem 12 extracted from the preparatory questions of ICHO 2005³.

The beauty of this question is that students do not require much knowledge of organometallic chemistry to solve it. In addition, it serves as a platform through which many wonderful concepts can be discussed. Examples include NMR, how the IR frequency of the CO bond is being affected by the degree of back bonding, usage and limitations of the 18 electrons rule etc.

- **Theme based worksheets.**

During Phase II Training, I designed a couple of theme based worksheets for students to do as homework. These usually consist of comprehension of a simple research paper followed by some stimulating questions. An example is illustrated in Figure 4 below.

ICHO Organic Chemistry Training 2006 – Exercise 1	
<p>This exercise is about literature appreciation and understanding. Please refer to the attached paper on "Spiroacetal Biosynthesis ..." by Brett D. Schwartz et. al. <i>Org. Lett.</i> 2005, 6, 1173.) and answer the following questions.</p> <p>Question 1</p> <p>One fine day, Charlie was reading the above paper to Grandpa Joe, Grandma Josephine, Grandpa George & Grandma Georgina. 4 of them made the following statement at the end of the day:</p> <p>Grandpa Joe: Great work. Finally the exact pathway leading to (5) has been elucidated.</p> <p>Grandma Josephine: Yes, and little did I realized that nature is able to selectively synthesized and used nine-carbon units from carbohydrates.</p> <p>Grandpa George: How do chemists know which intermediates leads to (5) in this paper?</p> <p>Grandma Georgina: That's simple. They did labeling studies using ^2H and GCMS. (11) & (18) were found to be the intermediate leading to (5)</p> <p>Grandpa Joe: And the beauty is that nature is able to produce (5) in a stereoselective manner.</p> <p>Comment on their statements.</p>	<p>Question 2</p> <p>Refer to page 1174 second last line "...the spiroacetal 5 retained all four deuterium atoms ..." What does this tells you about the mechanism of the pathway leading to (5)?</p> <p>Question 3</p> <p>Using curve arrows, illustrate the mechanism of (13) to (5).</p> <p>Question 4</p> <p>An isomer of (5) has the following structure (A) and it has 3 conformations in equilibrium as follow:</p> <div style="text-align: center;"> </div> <p>Which is the most stable form? Briefly explain why.</p>

Figure 4: A theme based worksheet based on a research paper.

- **“Effective Learning – Journal Club Discussion”.**

“Effective Learning” is a way of learning among my peers that I developed during my undergraduate studies in NUS. It is based on the Greek word *Koinonia* (κοινωνία), which describes the profound experience gained when a group of like-minded individuals gather to share ideas and to provide mutual care, concern and motivation. The idea of *Koinonia* is summarized in the paragraph⁴ below:

“*Koinonia* symbolizes our vision for a truly cohesive and committed learning community. It represents the desired outcome of proceedings to be conducted within our discussions. To achieve *Koinonia*, we must go around the three bases of a triangle. The first triangle is information sharing – where we share our ideas and knowledge with one another. The second is affirmation giving – where we provide moral support and respond positively to differing ideas and views. The third is inspiration getting – where we inspire one another in order to attain greater academic excellence. With *Koinonia*, we will continue to cherish our shared legacy and inspire each other to march confidently towards our destiny with a common vision.”

The vision of *Koinonia* is introduced to the students and they are encouraged to help one another throughout the training. They are then be presented with a number of interesting research papers and asked to discuss among themselves the key concepts involved. They are required to look up those they do not understand in textbooks, learn and teach them to the rest of their peers. This is a form of learning by discovery, a term coined by Jean Piaget. It was believed that such an approach towards learning allows students to retain the concepts that they learnt well and to apply them in future context. This approach also trains students in their critical thinking, an important aspect in education that cannot be overemphasized⁵. Two interesting research papers are shown in Figure 5 below.

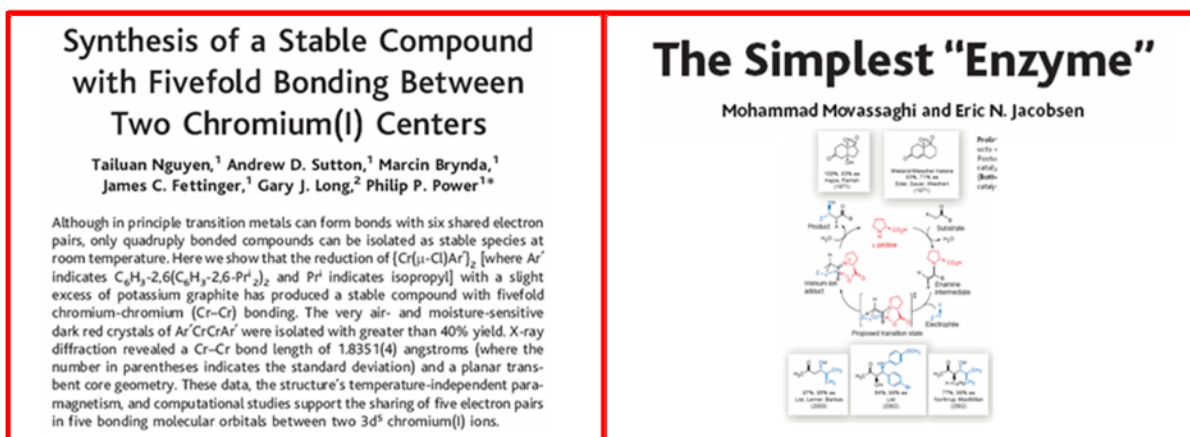


Figure 5: Interesting research papers^{6,7}.

These articles were chosen for their impact and the simplicity of their style of writing. JC students learn about triple bond in their curriculum; those who go one step further will read about the quadruple bonds in inorganic complexes. Students at this stage will wonder whether a quintuple bond is possible. The first science article will excite them and impress upon them that indeed, the sky is the limit. In the course of their studies, students will learn about using metals as a catalyst when performing reactions. What about small organic molecules? Can they serve as a catalyst as well? The second science article helps briefly illustrate the concept of the emerging field of organocatalysis. I believe that exposing students to this contemporary research allows them to think beyond the textbook and to think about what they want to do or become in the future. After all, it is interesting things like this that sparked the passion of numerous scientists in days of yore.

ORGANIC CHEMISTRY PROBLEMS FOR SCHO 2006

Three questions I developed for SCHO 2006 are attached in the appendix section. These represent a good mix – inference, comprehension and straightforwardness.

Question 1 requires the student to infer from a concept (Felkin-Ahn Model) that they have not been taught. This is illustrated with some details in the question and students are then asked to predict the product of a given reaction. Half of those who managed to answer the question completely, got it wrong because they simply put the phenyl group, the methyl group and H atom into R^L , R^M and R^S respectively of the model provided. Their mistake was: they failed to realize that by doing so, the stereochemical configuration of the chiral center was inverted. The examiner is thus able to infer how much the students understood from the given information and were able to apply it to slightly modified unknown situations.

Question 2 is my favourite and it took me quite a while to write it. It requires the students to comprehend the article, assimilate the content and assess the written conversation critically. This is by no means an easy task and it was set out to identify the top few students. Question 3 is the kind of direct question that most schools expect. However, it is in fact more difficult than question 2. This achieves some sort of a balance; an easier article complemented with more difficult questions while a harder article is tested more in-depth.

The feedback I received from the schools was that they did not expect a style of question similar to question 2. Most JCs prepared their students for the reactions and mechanisms, but

did little to link them up. My feeling is that it is better to train students to look at the big picture and examine the fundamental concepts, rather than learning reactions in isolation.

A STORY-TELLING APPROACH TOWARDS PERICYCLIC REACTION

The three methods for analyzing pericyclic reactions^{8,9,10} are summarized in Figure 6 below.

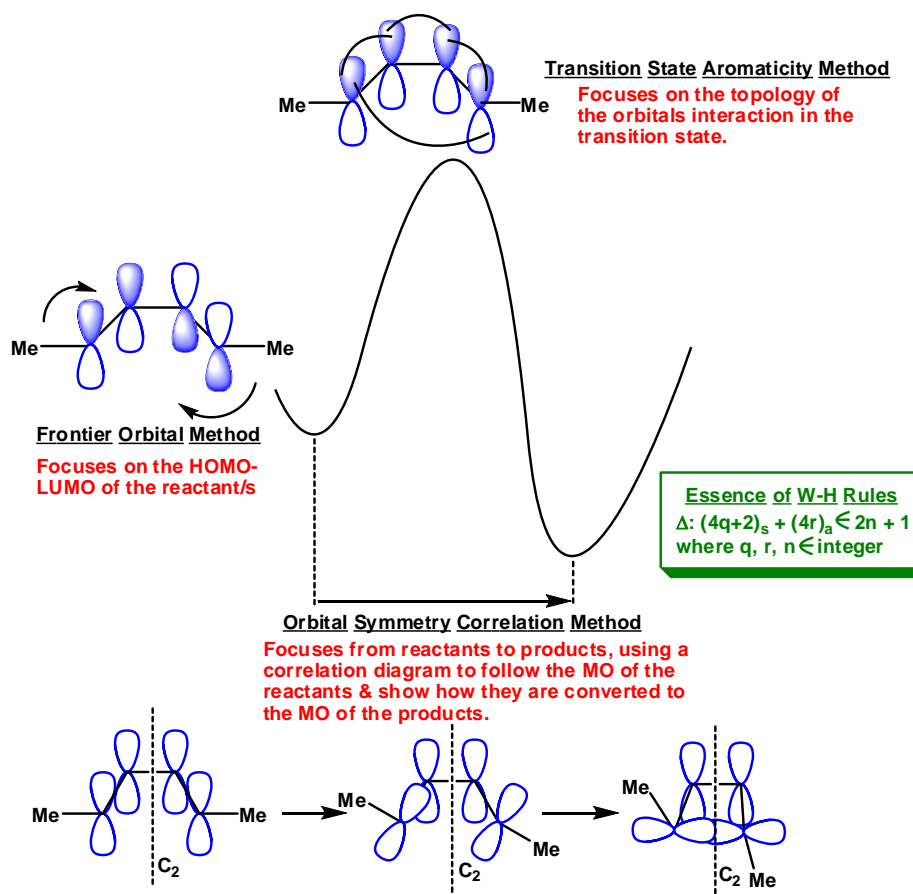


Figure 6: Summarizing the 3 methods to analyze pericyclic reactions (in this case, electrocyclicization).

The three ways of analyzing pericyclic reactions are complementary to one another and give the same results; the focuses are different, however. The students are first introduced to pericyclic reactions via the more familiar frontier orbital approach as this is a concept that is the easiest to be digested and understood among the three methods. The focus of this approach, which is on the starting materials, is stressed to the students. Following that, the transition state aromaticity model is introduced to impress upon the students that the transition state of the reaction can also be used to predict the course of the reaction (the complementary nature of the two methods must be emphasized). Hückel and Möbius aromaticity is introduced, and this is usually the fun part as students begin to learn another aspect of aromaticity and at the same time, experience the sophistication of pericyclic reactions. Building up on these two approaches, the orbital symmetry correlation method is introduced to show how the analysis can be done by looking at the whole course of reaction, from the reactants to the products.

This is called a “story telling approach” because the three analytical methods are presented in the form of a story. The first story is from the reactant perspective; the second from the transition state perspective and the third looks at the whole reaction course. In the end, upon linking them up, they are presented with a short equation, which represents the essence of the Woodward-Hoffmann rule.

This pedagogy of introducing pericyclic reactions (“story telling approach”) was used in the Phase II Training (2005 – 2007) and also in a pericyclic reaction workshop that I helped the NUS Chemical Sciences Society to conduct in early 2007. It was well received by the ICHO team. They commented that it allowed them to see the big picture and link up the nitty-gritty details. Having said that, however, some students in the workshop found it hard to absorb, probably due to a rather steep learning curve (cognitive disequilibrium results) as some of them had yet to complete sophomore organic chemistry. Therefore, this method is recommended for post-sophomore or junior organic courses, i.e. it should be beneficial to students who have already reached a certain command in organic chemistry.

CONCLUSION

The rigorous training for the team in preparation for ICHO cannot be overemphasized. In this short summary paper, I have shared some of the strategies that I used for the past three years; some of the interesting questions that I prepared for SCHO 2006 were briefly touched on and it ended with a short mention of the story telling approach in the teaching of pericyclic reactions. Further refinements and improvements are ongoing and it is my hope that this sharing will help the readers to come out with better strategies in future ICHO trainings.

ACKNOWLEDGMENTS

I would like to express my gratitude to my NUS Honours year supervisor, Prof. Lai Yee Hing for his teaching and guidance. In addition, special thanks go to Dr. Karen Mak for inviting me to join the SCHO 2006 committee, thereby giving me the opportunity to learn more through setting and marking the test. I would also like to thank all teachers from ACJC, HCJC, NJC and YJC for their comments. Finally, my thanks go to my friends for their support, particularly to Ms. Ng Su Ling, Ms. Suzana Sou and Mr. Edward Long for taking time to vet and criticize this manuscript.

REFERENCES

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[http://www.icho.hu/Files/IChOsyllabus\(2004\).pdf](http://www.icho.hu/Files/IChOsyllabus(2004).pdf) . (retrieved: November 15, 2007)

²Junior Colleges refer to institutions in Singapore where students study for 2 years in preparation for their GCE “A” level exams.

³ICHO 2005 Preparatory Questions.

⁴Effective Learning Newsletter 01/03.

⁵D. F. Halpern. (1993). *Journal of General Education*. 42, 238; D. F. Halpern. (1995). *Thought and Knowledge: An Introduction to Critical Thinking 3rd Edition*. Lawrence Erlbaum.

⁶T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power. (2005). *Science*, 310, 844.

⁷M. Movassaghi and E. N. Jacobsen. (2002). *Science*, 298, 1904.

⁸R. B. Woodward et. Al. (1965). *J. Am. Chem. Soc.*, 87, 395; K. Fukui. (1971). *Acc. Chem. Res.*, 4, 57.

⁹R. Hoffmann et. Al. (1965). *J. Am. Chem. Soc.*, 87, 2046; R. Hoffmann et. Al. (1968). *Acc. Chem. Res.*, 1, 17.

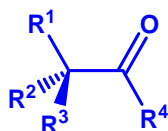
¹⁰M. J. S. Dewar .(1971). *Angew. Chem. Int. Ed. Engl.*, 10, 761; H. E. Zimmerman. (1966). *J. A. Chem. Soc.*, 88, 1564.

APPENDIX

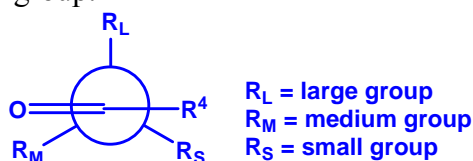
Shown below are three of the questions that I set for SCHO 2006. The first question is an example of a question that requires the students to make use of the additional information given (something that they would most probably not have learnt) to answer the question. Questions 2 and 3 are examples of “literature appreciation” questions. The journal articles are sent to all the JCs and the questions will be given on the day of the test. During SCHO 2006, students are required to do either question 2 or 3; both are set in different style.

Question 1

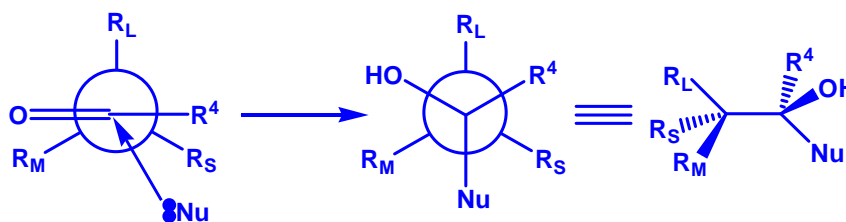
Felkin-Ahn model is being used to predict the stereochemical outcome of the nucleophilic addition of a nucleophile onto a carbonyl compound. The structure below shows a compound having a carbonyl group next to a chiral center.



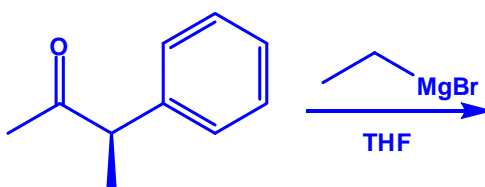
We normally classify the 3 groups using large, medium and small, depending on their size. After that, we arrange the resultant into the Newman project below, with the large group “orthogonal” to the carbonyl group.



The nucleophile will approach the molecule at an angle of 109° from the least hindered site as follow.



Using the above information, predict the major product from the below reaction.



Question 2

Please read the attached article “One-pot organocatalytic Domino Michael-Aldol and Intramolecular S_N2 Reactions. Asymmetric Synthesis of Highly Functionalized Epoxycyclohexanone Derivatives” by Mauro Marigo et. al. *J. Am. Chem. Soc.* **2006**, 128, 5475 – 5479.

While they are hiking along the MacLehose trail at Sai Kung East Country Park, Tom and Jerry decide to discuss about the above mentioned article as it is related to their research interest. Their conversations are as follow:

Tom: I am wondering why the author chooses epoxycyclohexanone as the target to be synthesized.

Jerry: Well, one of the reasons is that it exhibits antifungal property. Another reason I can think of is that such compound serves as useful starting materials in organic synthesis.

*Tom: Sounds fine to me. The reaction steps are beautiful, with compound **7a** being used to protect the carbonyl group of compound **1** at the strategic instant.*

Jerry: Yeah; however, the drawback is that the nature of R^1 affects the reaction significantly. In general, electron withdrawing groups give a much higher yield than electron donating groups.

(a) Comment on the above conversation.

Jerry: The article talked about “one-pot” reaction and strategy that is based on “atom economic principle”. Why are such reaction/ strategy appealing?

Tom: Hmm...

(b) Can you help Tom?

*Tom: Referring to scheme 2, how does compounds **7a** and **1** leads to the first intermediate?*

Jerry: Hmm, I am not so sure.

(c) Please help Jerry by illustrating the mechanism of the reaction.

*Tom: Gosh! Did the article made a mistake? Shouldn't compound **2** attacks to the top of the first intermediate since there is favourable hydrogen bonding present in the top face? Hmm, I am wondering about the reaction mechanism of this reaction; seems complicated to me.*

(d) What do you think?

Jerry: Well, I am not too sure about that since I haven't been touching organic chemistry for 2 years. However, one thing I know for sure. That is, AcONa is a stronger base than K_2CO_3 .

Tom: Fair enough. But how does compound 3 leads to compound 4?

Jerry: That's easy. AcONa deprotonates compound 3 at the α position bonded to the chlorine atom first. Following that, the nucleophilic α position then attacks the aldehyde via electrophilic addition.

(e) Comment on the above conversation.

Tom: From scheme 3, it shows that 4d(I) is more stable than 4d(II). To me, it doesn't make a difference.

(f) What do you think?

Tom: Oh yah, another beautiful thing about this article is that it doesn't matter what type of solvent we used for the reaction.

Jerry: Hmm, I doubt so. From theory, polar solvent should work the best. For example, MeCN should give the best yield and ee.

(g) What do you think?

Tom: There is something I am not clear about. If you take a look at Table 3, you will realize that there are 4 possible products, depending on the base and solvent system that you use. I am just curious how compounds 5a, 6 and 8 are obtained.

Jerry: All you have to do is to sit down and sketch out the mechanism using curve arrows!

(h) Can you help Tom by illustrating mechanisms leading to compounds 5a, 6 and 8?

Tom: Hmm ok but I'll leave that till later. Before we take a rest, I will like to check with you on the last part of the article under "Product Elaboration". What does the first statement of the first paragraph of the last page mean? How does the presence of ester functionality aids as a "superb handle"? In addition, why is product 11m obtained in the diastereoisomeric form as shown in figure 1? (in another words, how is it more stable than the rest of its diastereoisomers?)

Jerry: Hmm this question requires some thinking...

(I) Can you help Jerry so that they can go and take their well deserve break?

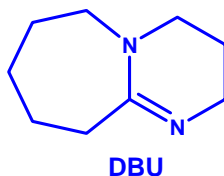
Off they proceed to their well deserved break.

Note: All parts are worth 4 points except for part (h) and part (I), which are worth 6 points each.

Question 3

Please read the attached article “A Short Enantioselective Pathway for the Synthesis of the Anti-Influenza Neuramidase Inhibitor Oseltamivir from 1,3-Butadiene and Acrylic Acid” by Ying-Yeung Yeung et. al. *J. Am. Chem. Soc.* **2006**, 128, 6310 – 6311.

- (a) Give 2 disadvantages of the industrial method of production Tamiflu.
- (b) Illustrate the mechanism of the reaction of 1,3-Butadiene with Acrylic Acid leading to compound **3**. What is the role of compound **2**?
- (c) Illustrate the mechanism of the reaction of compound **4** leading to compound **5**.
- (d) Draw the **most stable** conformation of compound **5**.
- (e) Why is there a need for compound **5** to be transformed into compound **6**?
- (f) The structure of DBU is given below. What is the role of DBU in the transformation of compound **6** into compound **7**?



- (g) Illustrate the mechanism of compound **8** leading to compound **9**. (clue: 2 things happened also simultaneously)
- (h) Intuitively, illustrate the mechanism of compound **7** leading to compound **8**. (clue: treat AIBN as a radical source)
- (I) Illustrate the mechanism of compound **9** leading to compound **10**. Explain (*using electronic factor*) the stereochemistry of the 2 new chiral centers generated (i.e. why are they “trans” to one another instead of “cis”). Give the name of this mechanism.
- (J) Do you think the stereochemistry of the newly generated chiral centers of compound **12** can be explained using the same reasoning given for (f)? Why?

Note: All parts are worth 4 points except for part (g), which is worth 6 points. The total no. of points for this Q will therefore be 42 points. The 2 extra points are served as bonus points.