How to pass successfully the first year exam?

1) Introduction

The first year exam is an important event in your PhD, as it signifies your definitive acceptance at the doctoral school. The goal is to evaluate your potential for research, and control that you have understood the basics of organic chemistry. The importance of revising regularly your basics and understanding them deeply cannot be enough emphasized. To illustrate that, I would like to cite two chemists, which have been hiring for years for the agrochemicals industry:

"*I am always surprised to see how members of leading group in the fields with strong recommendations and publications record will disappoint us during interview when coming to simple basic knowledge and understanding of organic chemistry*"
Dr. Andrew Plant, Syngenta Crop Science

"*When we give a problem during an interview to a candidate, we don't care so much about the solution. What interests us is how the candidate approach the problems based on his fundamental understanding of chemical reactivity*"
Dr. Mark Ford, Bayer Crop Science.

Below you will find a few helpful indications how to pass your first year exam, and continue progressing afterwards.

2) Form of the exam

The exam consists in three parts:

- **The written report**: The report has to be given to the jury one week before the exam. Please ask each jury member if they wish to have a printout. I will help you to bring your report to high quality standards (see group guidelines on this topic, you can use your 6-months report as basis). To let enough time for improvement and correction, it is important to plan to have a complete version of the report **two weeks** before the exam.
- **The oral presentation and exam**: The oral presentation should take **around 20 min**, it will be followed by up to 45 min of questions on the project and general organic chemistry. A training session can be organized during group meeting. It is the responsibility of the candidate to organize the exam in collaboration with the doctoral school: Please contact Ms. Odegaard as soon as the schedule has been fixed.
- **The administrative requirements of the doctoral school**: This is mostly having four validated credits for lectures.

3) What will be evaluated at the exam/How to pass?

3.1) Efficiency and dedication in the research laboratory

Often, students do not realize that this is the most important part of the evaluation. The core of the PhD is the research work. More than the results themselves, it is your motivation to obtain them, and the progress you make on the way that are really important. If you have made a good job during the year, the most important part is already done!

3.2) Specific knowledge on your project.

It is particularly important to be able to explain well all what you have in the oral presentation or in the report, as this will be the first source of questions during the exam. Check carefully each reaction you present and be sure you understand its mechanism and can classify and compare it with other known reactions. Read also carefully all the publications you cite in your report and presentation. It is also important to know your competitors in the field and to highlight the novelty of your project compared to them.

3.3) General theoretical knowledge in organic chemistry.

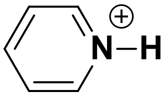
After the first year of PhD, you are not yet expected to be a perfect expert in the field. However, it is important to have a good understanding of the basics of organic chemistry. The jury will be especially expecting a good knowledge in the following points:
1) **Important calibrating values** in organic chemistry (you need to have a few fix points to deduce all the rest!). See list in annex I.
2) **Relative electronegativity** and **size** of the elements and the polarization effect on sigma and pi bonds.
3) How to draw **resonance structures** and the difference between resonance and equilibrium.
4) A **clean arrow pushing**, following point 2), to show the movement of electrons.
5) The knowledge on the **orbital structure** in organic chemistry (s, p, and hybridation of atoms)
6) A **certain number of reactions**, including a few name reactions with a good knowledge of their mechanisms. Usually, remembering the name of reactions is not the most important. However, a few reactions have become so classical that you just need to know them. See annex II.

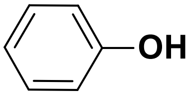
In general, an EPFL PhD student will be expected to be able to teach any of the organic chemistry lectures at EPFL. You should read and now well the contents of these lectures. Key Lectures are Fonctions and Reactions Organiques I-II, Synthèse asymétrique et Rétrosynthèse, Structure and Reactivity and Total Synthesis of Natural Products. You should go shortly through the content of these lectures before the exam.

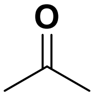
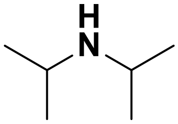
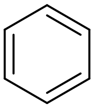
Annex I: Calibrating Values to Remember in Organic Chemistry

Calibrating PKa value**s:**

CF_3SO_3H	HCl	H_2SO_4	H_3O^+	CF_3CO_2H
-14	**-8**	**-3**	**-1.7**	**0**

H_3PO_4	CH_3CO_2H		$H_2PO_4^-$
2	**4.7**	**5**	**7**

NH_4^+		HCO_3^-	$H\overset{\oplus}{N}Et_3$	HPO_4^-	H_2O	EtOH
9	**10**	**10**	**11**	**12**	**15.7**	**16**

	CH_3CN	$H-\equiv-H$	H_2			CH_4
20	**25**	**25**	**36**	**36**	**43**	**50**

Approximate strength of C-H bond: 100 Kcal/mol

Approximate strength of C-C bond: 80 Kcal/mol

Approximate strength of hydrogen bonding: 10 Kcal/mol

Relation equilibrium-energy: 10:1 = 1.4 Kcal/mol at RT

Ambient Energy at RT: 21 Kcal/mol

A value of methyl: 1.7 Kcal/mol

Approximate C-C bond length: 1.5 Angstrom (150 pm).

Annex II: Important reactions to know well

The reactions below represent the core of the knowledge in organic chemistry. During all you career, you will be expected to know them and be able to explain their mechanism. It is always a good idea to refresh these reactions before an exam or an interview.

- Substitution Reactions: SN1, SN2
- Elimination Reactions: E1, E2, E1cb
- Cyclic Elimination Reaction: Chugaev and Selene oxide
- Addition Reactions and the Markovnikov rule
- Addition reactions on carbonyls, Grignard Reaction
- Esterification
- Aldol Reaction and condensation, Claisen condensation
- Amide bond formation, including carboxyl acid activation
- Imine formation and reductive amination, Mannich reaction
- Oxidation of alcohols and reduction of carbonyls: LAH, $NaBH_4$, Jones oxidation, Swern oxidation
- Michael addition
- Wittig and Horner-Wadsworth-Emmons olefination
- Electrophilic and nucleophilic aromatic substitution. Including Friedel-Crafts.
- Birch reduction
- Diels-Alder reaction
- Ozonolysis and azide alkyne cycloaddition.
- Sigmatropic rearrangements, Cope, Claisen
- Electrocyclic reactions, Nazarov
- Hydroboration of olefins
- Epoxidation of olefins with MCPBA
- Dihydroxylation of Olefins
- Sharpless Epoxidation and Dihydroxylation
- Felkin-Anh and Chelate models for addition to carbonyls
- Evans auxiliary and aldol
- Mukaiyama aldol
- Allylation reactions of carbonyl compounds
- Hydrogenation of olefins and carbonyls and Lindlar reduction
- Rearrangements from carbenes and nitrenes. Curtius and Wolff rearrangements
- Cross-coupling reactions: Suzuki, Stille, Sonogashira, Heck, Kumada-Corriu, Negishi, Buchwald-Hartwig
- Olefin metathesis
- Dithiane Umpolung