



UNIVERSITÀ  
DEGLI STUDI DI MILANO-BICOCCA

## SYLLABUS DEL CORSO

### Chimica Organica Superiore

2223-1-F5401Q019

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#### Aims

Detailed discussion of the main reaction mechanisms of organic molecules. Advanced reactivity of aromatic and heteroaromatic systems. Cyclization reactions.

#### Knowledge and understanding skills developed

At the end of the course the student knows

- The main theoretical / practical tools to address the mechanistic study of reactions in organic chemistry
- The subdivision of reactions in organic chemistry through the study of the main mechanistic families
- The application of the concepts learned in the course in an advanced laboratory of organic chemistry.

#### Knowledge and understanding skills applied

- At the end of the course the student has the tools in order to study the organic reactions from a mechanistic point of view, in order to obtain selective regio and stereo reactions
- At the end of the course the student is able to choose the best reaction conditions to optimize the regio and stereo selection of a reaction
- At the end of the course the student is able to work in an advanced organic chemistry laboratory.

## Autonomy of judgment

At the end of the course the student is able to evaluate which is the best mechanistic model to develop the study of an organic reaction

## Communication skills

- Knowing how to describe the organic reaction mechanism using the correct terminology
- Knowing how to describe in a laboratory notebook an organic reaction carried out in the laboratory using the correct terminology

## Ability to learn

- Apply the knowledge learned during the course to correctly interpret any organic chemistry article

## Contents

Elements of electronic structure of organic materials. Frontier molecular orbitals (FMO) and the Klopman-Salem equation. Mechanisms: thermodynamics and kinetics, thermodynamic and kinetic control of product composition, acidity and basicity, electrophilicity and nucleophilicity, free-energy relationships, Hammond's postulate, general and specific catalysis). Reactions: nucleophilic substitution, addition, elimination, oxidation and reduction. Reactive species: nucleophiles and electrophiles, carbanions, radicals, addition to carbonyl group. Aromaticity. Aromatic substitution. Pericyclic reactions. Molecular rearrangements.

The lab module is addressed to provide the student with the safety and behavior aspects for conducting correctly an organic chemistry experiment. The experiments carried out in the laboratory are intended to exploit the basic technical operations in organic chemistry to synthesise some organic compounds using multi-step synthetic protocols

## Detailed program

Basic mechanistic concept: kinetic versus thermodynamic, Hammond's postulate, Curtin-Hammett principle, microscopic reversible principle.

Linear correlation structure-reactivity: Hammett equation

Primary kinetic isotopic effect

Acid and bases: Acids stronger than  $\text{H}_3\text{O}^+$ , nucleophilic scale: Swain-Scott and Ritchie equations.

Acid catalysis: general and specific catalysis

Nucleophilic substitution: the limiting cases  $\text{S}_{\text{N}}1$  e  $\text{S}_{\text{N}}2$ , borderline mechanism, nucleophilicity and solvent effect, leaving group effect, rearrangements of carbocation

Polar addition and Elimination reactions, additions of hydrogen halides to alkenes, acid-catalyzed hydration, addition of halogens, electrophilic addition involving metal ions, the  $\text{E}1$ ,  $\text{E}2$ ,  $\text{E1}_{\text{cb}}$ , mechanism, stereochemistry of  $\text{E}2$  reactions.

Reactions of carbonyl compounds; hydration and addition of alcohols to aldehydes and ketons, addition of carbon nucleophiles to carbonyl groups, ester hydrolysis, amide hydrolysis

Aromaticity: the concept of aromaticity, the annulenes, Homoaromaticity, fused-ring system, heterocyclic rings.

Aromatic Substitution: Electrophilic Aromatic Substitution, Structure-Reactivity Relationship, reactivity of polycyclic and heteroaromatic compounds. Specific substitution mechanism

Pericyclic Reaction: electrocyclic reaction, sigmatropic rearrangements, cycloaddition reaction,

In the laboratory will be presented the safety rules and behavior to be followed in an organic chemistry laboratory, the main techniques of analysis and purification of organic substances (crystallization, distillation, chromatographic techniques, selective extraction with solvents) and how to handle organic chemistry reactions for the synthesis of molecules obtained as a result of multistep synthesis.

## **Prerequisites**

Knowledge of Organic and Physical chemistry at bachelor level

## **Teaching form**

Oral lessons

## **Textbook and teaching resource**

F. A. Carey, R.J. Sundberg "*Advanced Organic Chemistry*", Ed. Plenum Press, New York

Elementi di Chimica Organica Fisica Giorgio Molteni Aracne Editrice 2009

## **Semester**

1 semester

## **Assessment method**

Oral examination aimed at verifying adequate knowledge of: a) the chemical physical basis of mechanisms in organic chemistry b) the main general mechanisms of reaction in organic chemistry c) the capability to plan the synthetic access to simple organic multifunctional molecules.

For the laboratory part, the activity carried out will be evaluated as well as the compilation of the laboratory

notebook. Furthermore, two tests relating to the skills acquired to be done during the course on the e-learning platform will complete the evaluation of the laboratory course.

### **Office hours**

upon request, generally 8:30-18:00

### **Sustainable Development Goals**

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