

**COURSE DATA****Data Subject**

Code	44606
Name	Advanced organic chemistry
Cycle	Master's degree
ECTS Credits	5.0
Academic year	2018 - 2019

Study (s)

Degree	Center	Acad. year	Period
2218 - M.U. en Química	Faculty of Chemistry	1	First term

Subject-matter

Degree	Subject-matter	Character
2218 - M.U. en Química	1 - Advanced chemistry	Obligatory

Coordination

Name	Department
GAVIÑA COSTERO, PABLO	325 - Organic Chemistry

SUMMARY

The subject Advanced Organic Chemistry has been designed to supplement the knowledge acquired by the student in the area of organic chemistry during the degree studies. The objectives to be achieved can be summarized in the following points:

- Know the kinetic and thermodynamic aspects of organic reactions.
- Study the usual methods used to establish reasonable reaction mechanisms.
- Deepen knowledge of the stereochemical characteristics of organic molecules and reactions.
- Recognize the interactions that are weaker than covalent interactions that are essential in molecular recognition processes.
- Study the different types of catalysis that can be used in organic reactions.

Know the reactions taking place under thermal or photochemical activation, as well as the processes that involve uncharged species.



PREVIOUS KNOWLEDGE

Relationship to other subjects of the same degree

There are no specified enrollment restrictions with other subjects of the curriculum.

Other requirements

No enrolment restrictions with other subjects in the curriculum have been specified. Extensive knowledge in the field of organic chemistry is required, especially as regards synthesis, mechanisms and structure.

OUTCOMES

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- Students should apply acquired knowledge to solve problems in unfamiliar contexts within their field of study, including multidisciplinary scenarios.
- Students should be able to integrate knowledge and address the complexity of making informed judgments based on incomplete or limited information, including reflections on the social and ethical responsibilities associated with the application of their knowledge and judgments.
- Students should communicate conclusions and underlying knowledge clearly and unambiguously to both specialized and non-specialized audiences.
- Be able to solve complex chemistry problems, whether in the academic, research or industrial application areas at a specialization or masters-level.
- Promote, in academic and professional contexts in the field of economic policy, ... technological, social or cultural progress within a society based on knowledge and respect for: a) fundamental rights and equal opportunities between men and women, b) the principles of equal opportunities and universal accessibility for people with disabilities and c) the values of a culture of peace and of democratic values.
- Be able to design, perform, analyse and interpret experiences and complex data in the environment of chemistry at a specialization level.
- Acquire advanced knowledge to assess the importance of chemistry in health, the environment, new materials and energy.

LEARNING OUTCOMES

On successful completion of the course students should be able to:

Obtain and interpret relevant kinetic data on chemical reactions, based on proposed mechanisms.



Describe and identify the topics related to the stereochemistry of organic molecules and the stereoselectivity of organic reactions.

Describe and explain in detail the physicochemical aspects of organic reactions.

Undertake further study of reaction mechanisms and the function of the catalysts, and differentiate homogeneous catalysis and heterogeneous catalysis in organic reactions.

Correlate the molecular and supramolecular structure of organic materials with their physical and/or chemical properties.

Study thermal or photochemical activation processes and processes involving uncharged species as reactive intermediates.

DESCRIPTION OF CONTENTS

1. Study of reaction mechanisms in organic chemistry

Thermodynamic and kinetic aspects that define a chemical process. Tools to determine the reaction mechanisms: identification of reaction products; determination of intermediates; crossover experiments; isotopic labeling; stereochemical studies; effects of solvent on the reaction rate. Kinetic studies for determining mechanisms: rate equations. Kinetic theories: Arrhenius equation and collision theory; transition state theory and Eyring equation. Microreversibility principle. Kinetic and thermodynamic control: Curtin-Hammett principle. Nature of the transition state: Hammond postulate. Primary and secondary kinetic isotopic effects.

2. Stereochemistry, stereoselectivity and stereoelectronic effects

Symmetry of molecules: symmetry elements and symmetry operations (axes, planes, centers and axes of rotation-reflection). Concept of chirality: chiral molecules. Chirogenic elements or generators of chirality. Stereogenic center: nomenclature of configuration, absolute and relative configuration, molecules with several stereogenic centers, conformation and chirality. Stereogenic axis: conditions of chirality in molecules with stereogenic axes, R_a/S_a descriptors, cumulenes, spiranes, alkylidene-cycloalkanes, catenanes, ortho-ortho'-tetrasubstituted biphenyls, atropisomers. Stereogenic plane: R_p/R_s descriptors, cyclooctenes, cyclophanes, metallocenes. Helicity as a chirogenic element. Topicity: heterotopic, homotopic, enantiotopic or diastereotopic groups. Prostereogenicity and prochirality. Nomenclature of ligands and prochiral and/or prostereogenic faces: stereodescriptors pro-R/pro-S, Re/Si, pro-E/pro-Z. Origin of reactivity in homotopic, enantiotopic and diastereotopic groups against achiral and chiral reagents.

Stereoelectronic effects: relation to electronic interaction, basic aspects of the interaction between orbitals. Effects on conformation: anomeric effect, gauche effect, effect on sp² centers. Effects on reactivity: effects through links, effects through space, Baldwin's rules. Reactivity control by stereoelectronic effects: substitution reactions on saturated carbon, reactions of addition to bonds, elimination reactions, rearrangement and fragmentation reactions.

**3. Supramolecular chemistry. Noncovalent interactions and molecular recognition**

Definition and development of supramolecular chemistry. Host-guest relationship. Chelate and macrocycle effects. Pre-organization and complementarity. Thermodynamic and kinetic selectivity. Nature of supramolecular interactions: ion-dipole, dipole-dipole, hydrogen bond, π -cation, stacking interactions, hydrophobic interactions, Van der Waals interactions. Complex supramolecular architectures: clamp molecules, self-assembly via hydrogen bonds, molecular switches.

4. Catalytic processes

General principles of catalysis: catalytic reaction, homogeneous and heterogeneous catalysts. Interaction of the catalyst with the substrate and with the transition state; reaction coordinate diagrams; analysis of a thermodynamic cycle; union and proximity effects. Catalysis by Brønsted acids and bases: specific and general acid catalysis, specific and general basic catalysis. Electrophilic catalysis: electrostatic interactions, catalysis by metal ions. Nucleophilic catalysis: Baylis-Hillman reaction, electrophilic substitution in carboxylic acid derivatives catalyzed with pyridine derivatives. Covalent catalysis: organocatalysis, enamine-iminium activation. Tension and distortion. Phase transfer catalysis (PTC): mechanism of PTC, quaternary phosphonium and ammonium salts, practical applications of PTC, alkylation reactions. Enzymatic catalysis: Michaelis-Menten equation.

5. Unsaturated systems processes with thermal or photochemical activation. Processes with uncharged reaction intermediates

Thermal reactions of conjugated unsaturated systems. The Diels-Alder reaction: synthetic interest. Mechanism. Stereoselectivity and regioselectivity. Effects of Lewis acids on Diels-Alder reactions. $[3 + 2]$ cycloaddition reactions: synthesis of heterocyclic compounds. Mechanisms of $[3 + 2]$ cycloaddition reactions. Electrocyclic reactions of conjugated unsaturated systems. Sigmatropic reactions: migration of C-C and H-C single bonds. Cope and Claisen reactions. Tautomerization processes. General principles of photochemistry. Photochemistry of unsaturated systems: cis/trans isomerization of alkenes. $[2 + 2]$ cycloaddition photochemically activated reactions. Photochemistry of the carbonyl group. Cycloaddition reactions of carbonyl compounds with alkenes: Paterno-Büchi reaction. Uncharged reaction intermediates. Free radicals: structure, stability and generation methods. Stable and persistent free radicals. Reactions of free radicals: substitution, addition, oxidation and reduction. Intramolecular reactions. Carbenes: structure, generation and reactivity. Reactions of carbenes. Nitrenes: structure, generation and reactivity. Reactions of nitrenes.

**WORKLOAD**

ACTIVITY	Hours	% To be attended
Theory classes	35,00	100
Tutorials	5,00	100
Seminars	5,00	100
Computer classroom practice	5,00	100
Development of individual work	15,00	0
Study and independent work	30,00	0
Readings supplementary material	10,00	0
Preparation of evaluation activities	20,00	0
TOTAL	125,00	

TEACHING METHODOLOGY

Theoretical classes: participatory lecture.

Supervised practical activities in class (problem-based lessons)

Participatory workshops.

Virtual Classroom: virtual space where students can find all information considered appropriate for the development of different subjects, theories, problems, etc.

EVALUATION

First examination sitting:

Oral and/or written tests (examinations) based on specific learning outcomes and objectives, covering both theory and practice. Tests will account for 80% of the final mark. To pass the course a minimum score of 4.5 (out of 10) in this section is required.

Continuous assessment of coursework carried out by the student through participatory attendance, assignments, problem solving, etc. This section will contribute 20% of the overall mark.

Second examination sitting:



In the second examination sitting the mark will be that obtained in the exam.

REFERENCES

Basic

- Felix A. Carroll Perspectives on Structure and Mechanism in Organic Chemistry, 2nd Edition, John Wiley & Sons, 2010
- Francis. A. Carey, Richard J. Sundberg Advanced Organic Chemistry. Part A: Structure and Mechanisms, 5th Edition, Springer, 2007
- Ángel Manuel Montaña Pedrero Química Orgánica Estructural. Volumen II, Estereoquímica y propiedades moleculares. 2a edició. Editorial Pearson, Madrid, 2012
- A. J. Kirby Stereoelectronic Effects. Oxford Chemistry Primers, núm. 36. Oxford University Press, New York, 1996
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- J. W. Steed, J. L. Atwood Supramolecular Chemistry. John Wiley & Sons, 2009
- E. V Anslyn, D. A. Dougherty Modern Physical Organic Chemistry, University Science Books, Sausalito, California, 2005
- P. D. Beer, P. A. Gale, D. K. Smith Supramolecular Chemistry. Oxford University Press, 1999
- Mc.QUARRIE, D. A. Statistical Mechanics, University Science Books, Sausalito, 2000
- J. Clayden, N. Greeves, S. Warren Organic Chemistry, 2nd Edition, Oxford University Press, 2012