

Structure, Reactivity and Mechanism in Organic Chemistry

1. GENERAL

SCHOOL	NATURAL SCIENCES		
ACADEMIC UNIT	CHEMISTRY		
LEVEL OF STUDIES	UNDERGRADUATE		
COURSE CODE	XO 101	SEMESTER	1 st
COURSE TITLE	STRUCTURE, REACTIVITY AND MECHANISM IN ORGANIC CHEMISTRY		
INDEPENDENT TEACHING ACTIVITIES <i>if credits are awarded for separate components of the course, e.g. lectures, laboratory exercises, etc. If the credits are awarded for the whole of the course, give the weekly teaching hours and the total credits</i>	TEACHING HOURS PER WEEK	ECTS CREDITS	
<i>Lectures</i>	3	5	
<i>Seminars</i>	1		
<i>Laboratory work</i>	0		
<i>Add rows if necessary. The organisation of teaching and the teaching methods used are described in detail at (d).</i>			
COURSE TYPE <i>general background, special background, specialised general knowledge, skills development</i>	Field of Science (Organic Chemistry)		
PREREQUISITE COURSES:	There are not prerequisite courses because this course is the first one of a series of Organic Chemistry undergraduate courses		
LANGUAGE OF INSTRUCTION and EXAMINATIONS:	Greek. The course can be, however, taught in English in case foreign students attend the course.		
IS THE COURSE OFFERED TO ERASMUS STUDENTS	YES		
COURSE WEBSITE (URL)	http://www.soclab.chem.upatras.gr (→ Education → Teaching material → Structure, Reactivity and Mechanism in Organic Chemistry)		

2. LEARNING OUTCOMES

<p>Learning outcomes</p> <p><i>The course learning outcomes, specific knowledge, skills and competences of an appropriate level, which the students will acquire with the successful completion of the course are described.</i></p> <p>Consult Appendix A</p> <ul style="list-style-type: none"> • Description of the level of learning outcomes for each qualifications cycle, according to the Qualifications Framework of the European Higher Education Area • Descriptors for Levels 6, 7 & 8 of the European Qualifications Framework for Lifelong Learning and Appendix B • Guidelines for writing Learning Outcomes
<p>By the end of this course the student will be able to:</p> <p><i>Structure of organic compounds</i></p> <p>Describe the bonds involved in organic compounds with C-C or C-heteroatom single or multiple and conjugated bonds and their influence on the geometry and the reactivity of the system.</p> <p><i>Nomenclature of the main classes of organic compounds</i></p> <p>Know the correct names (prefixes and suffixes) of the common functional groups. Given a structure or a condensed formula, use the IUPAC nomenclature to name correctly alkanes with a linear or branched chain, monocyclic alkanes, benzene, naphthalene, simple aromatic compounds and their simple substituted</p>

derivatives. Given an IUPAC name for any of the above-mentioned compounds, to draw correctly their structure.

Use the priority rules to determine the configuration, to identify and name correctly isomers of compounds with double bonds or rings having the E or the Z configuration or isomers [or isolated stereogenic (chiral) centers] having the R or the S absolute configuration.

Stereochemistry

Recognize a stereogenic (chiral) center in a molecular structure. Identify and distinguish between identical molecules, enantiomers and diastereomers from their structural representations. Recognize a meso-compound from its structure. With or without the use of molecular models, represent the three-dimensional structure of a molecule using «wedge bonds» or the conventions of the Newman and Fischer projections. Describe methods for the analysis of racemic mixtures. Recognize the stereochemical congestion between neighbouring groups in bonds or across rings. Correlate the dynamic energy with the dihedral angle during rotation around bonds and account for the selection of a favourable conformation. Correlate *cis* and *trans* substituents in cyclohexane rings with their axial or equatorial arrangement. Use the known stereochemistry of a reaction to predict the outcome of reactions on saturated centers, double bonds and cyclohexane rings. Use the products of a reaction to identify stereochemical pathways of reactions.

Reactions and Mechanisms

Classify a given chemical transformation as addition, elimination, substitution, condensation, rearrangement, solvolysis, oxidation, reduction as well as subject to base or acid catalysis. Use the principle of the functional group to predict the chemical behaviour of a given molecule. Indicate the polarization caused by the electronegativity of atoms in a given molecule and use it to predict the direction of heterolysis, the basic or acidic properties, and the electrophilic or nucleophilic properties or positions of electrophilic or nucleophilic attack.

Distinguish between a transition state (activation complex) and a reactive intermediate. Under defined reactions conditions, recognize reagents as electrophiles or nucleophiles. Given the starting materials (substrates), reagents and reaction conditions, suggest the outcome of a reaction and given or not the products, suggest a possible mechanism for the progress of the reaction with the use of "curved arrows" to show the electron movements. Explain the different stability of the reactive intermediates involved and the influence of this stability in the reaction progress.

Nucleophilic displacement

Given the reactants (a) identify the nucleophilic and electrophilic center, and the leaving group, (b) decide (if possible) whether S_N1 or S_N2 reaction will be followed, (c) predict the structure of the products, (d) suggest how changes in the reaction conditions or the reactants would affect the outcome of the reaction, (e) decide whether or not the reaction will take place, and (f) comment on the relative S_N reaction rates. Suggest the best reagents and reaction conditions to carry out a given transformation. Use curved arrows and diagrams of reaction progress to show the mechanism of S_N1 and S_N2 reactions.

Elimination

Given the substrate, the reagent and the reaction condition, (a) predict the structure of the product(s), indicating the stereochemistry wherever this is necessary, (b) predict which elimination product will be the main wherever more than one may be formed, (c) predict whether substitution or elimination will be the main reaction (d) explain how the conformation and the configuration of a substrate can affect the outcome of an elimination reaction. Use curved arrows and diagrams of reaction progress to show the mechanism of E1 and E2 reactions.

Addition

Given the reactants (a) predict the structure of the product, indicating its stereochemistry and (b) predict which adduct will be the main product, whenever more than one can be formed. Explain why the selection of a reagent can determine the orientation of addition. Specify the reagents and the conditions required for the formation of a given product in an addition reaction.

General Competences

Taking into consideration the general competences that the degree-holder must acquire (as these appear in the Diploma Supplement and appear below), at which of the following does the course aim?

Search for, analysis and synthesis of data and information, with the use of the necessary technology

Project planning and management

Adapting to new situations

Respect for difference and multiculturalism

Respect for the natural environment

<i>Decision-making</i>	<i>Showing social, professional and ethical responsibility and sensitivity to gender issues</i>
<i>Working independently</i>	
<i>Team work</i>	<i>Criticism and self-criticism</i>
<i>Working in an international environment</i>	<i>Production of free, creative and inductive thinking</i>
<i>Working in an interdisciplinary environment</i>	<i>Others</i>
<i>Production of new research ideas</i>	

By the end of this course the student will, furthermore, have develop the following skills (general abilities):

1. Ability to exhibit knowledge and understanding of the essential facts, concepts, theories and application which are related to Organic Chemistry.
2. Ability to apply this knowledge and understanding to the solution of problems related to Organic Chemistry of non-familiar nature.
3. Ability to adopt and apply methodology to the solution of non-familiar problems.
4. Study skills needed for continuing professional development.
5. Ability to interact with others in chemical or of interdisciplinary nature problems.

Generally, by the end of this course the student will, furthermore, have develop the following general abilities (from the list above):

Searching, analysis and synthesis of facts and information, as well as using the necessary technologies

Adaptation to new situations

Decision making

Autonomous (Independent) work

Exercise of criticism and self-criticism

Promotion of free, creative and inductive thinking

3. SYLLABUS

<p>1. Organic Chemistry - Organic compounds</p> <ul style="list-style-type: none"> • What is Organic Chemistry • Sources of organic compounds • Properties of organic compounds and their significance in living organisms • Organic compounds and Chemical Industry <p>2. Nomenclature of main homologous series of organic compounds</p> <ul style="list-style-type: none"> • Homologous series – Functional groups • Rules for naming open-chain and cyclic organic compounds and applications • Naming of organic compounds with many functional groups – Priorities of main functional groups • Nomenclature of aromatic compounds • Common or trivial names of very common organic compounds (simple alkenes, alkynes, alcohols, aldehydes and ketones, carboxylic acids and derivatives thereof, and aromatic and heterocyclic compounds) <p>3. Bonds in Organic Chemistry</p> <ul style="list-style-type: none"> • Ionic and covalent bonds • Periodic Table and the Octet Rule • Examples of electronic octets with transfer (ionic bonds) and with sharing (covalent bonds) electrons • Ποσοτικοποίηση της ικανότητας των στοιχείων να δίνουν ή να αποδέχονται ηλεκτρόνια -Δυναμικό Ιονισμού και Ηλεκτρονική Συγγένεια • Polar covalent bonds - Dipole moment - Inductive effect • Electron repulsion and shape of molecules
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- Lewis structures - Rules - Applications
- Kekulé structures
- Resonance structures
- Conventions for drawing organic compounds - Condensed Kekulé structures
- The Quantum-Mechanical description of atoms - Atomic orbitals (s, p, d) - Electron configurations of atoms - Pauli's Principle - Hund's Rule- Aufbau Principle - Configurations of closed cell or closed layer (configurations of electron duet and octet)
- Bond types
- Localized chemical bond - covalent bond
- Molecular orbitals in diatomic molecules (bonding and antibonding orbitals)
- Molecular orbitals in multi-atom molecules - hybrid orbitals - hybridization (sp, sp² and sp³ hybrid orbitals)
- The molecular structure (lengths, angles and strengths of bonds) of methane, ethane, propane, H₂O, NH₃, methanol, methanamine, ethylene and acetylene
- The relationship of number of bonds and bond length and strength
- The relationship of hybridization of C atom and bond length, angle and strength
- C-C bonds in small rings (three-membered - cyclopropane)
- Multiple bonds C-Heteroatom (Double bonds C=O and C=N and triple bond C≡N)
- Delocalized chemical bonds - Resonance effect - Canonical structures (forms) - Resonance hybrid - Conjugated systems - Hyperconjugation effect
- The bonds in the allylic system, 1,3-butadiene and 1,3,5-hexatriene, benzene, and the heteroaromatic systems (pyridine, pyrrole, thiophene and furan) with the Method of Molecular Orbitals
- Electronic effects (Inductive, Resonance) - Methodology for drawing resonance - Stereochemical effect
- Bonds weaker than covalent - van der Waals forces [dipole-dipole, induced or temporary dipole - induced or temporary dipole (London forces)] - Hydrogen bond

4. Structure of Organic Compounds-Stereochemistry

- Stereochemistry - Isomerism - Isomers - Constitutional isomers - Regioisomers - Double bond equivalents - Stereogenic (chiral) centre - Chiral molecule
- Configuration - Stereoisomers - Stereoisomerism - Geometrical isomerism - Optical isomerism - Nomenclature system Cahn-Ingold-Prelog (C-I-P) - Geometrical isomerism (E- and Z-geometrical isomers) and examples of alkene nomenclature - Absolute configuration - Enantiomers - Diastereomers - Meso isomers - Achiral compounds - Examples of determining isomers - Molecular models - Skeletal models - Space-filling models - ball and stick models - Examples of molecular models - Determination of configuration on the basis of C-I-P rules (*R*- and *S*-configuration) - Methodology for determining configurations and examples - Optical isomerism and optical activity - Specific rotation - Optical purity - Enantiomeric excess (ee) - Representation of stereoisomers - Stereochemical structures - Fischer projections - zig-zag structures - Sawhorse representations - Newman projections - Interconversions of the different structural types - Molecules with one stereogenic centre - Enantiomerically pure compounds - Racemic mixtures (racemates) - Racemization - Analysis of racemates - Molecules with more than one stereogeniccentres - Enantiomers - Relative configuration - Diastereomers (*erythro*-, *threo*-, *syn*-, *anti*-) - Epimers - Meso structures - Molecular asymmetry (allenes, spiranes) - Molecules with heteroatom stereogeniccentres (chiral amines and phosphines and chiral sulfoxides) - Walden inversion
- Conformation - Conformers (or rotamers) - Conformational effects - Conformations of open-chain molecules (ethane, propane, butane) - Eclipsed conformation - Staggered conformation - Torsional angle - Torsional strain - Diagrams depicting dynamic energy variation with torsional angle - Stereochemical congestion - Stereochemical strain - Stereochemical hindrance - Conformation analysis - *syn-periplanar* and *anti-periplanar* conformations - *gauche* conformation - Conformations of cyclic compounds (cyclopropane, cyclobutane, cyclopentane, cyclohexane) - Angle strain - Torsional strain (or σ-bond opposition strain) - Total ring strain - Puckered conformation - Small, common-medium and large rings - Envelope conformation - Half-chair conformation - Chair conformation - Boat conformation - Twisted-boat

conformation - Ring inversion - Transannular strain - Axial and equatorial bonds/substituents - 1,3-Diaxial interactions - Methodology for drawing chair conformations and axial and equatorial bonds - Chiral compounds found in Nature - Natural sources - Chiral pool - α -Amino acids - Alkaloids - Hydroxy acids - Terpenes - Carbohydrates - Asymmetric synthesis - General diagram of stereochemical relationships in organic compounds

5. Reactivity in Organic Chemistry (Reactions - Mechanisms)

- Thermodynamics of organic reactions - Free Energy Gibbs (G) - Enthalpy (H) - Entropy (S) - The equation $\Delta G = \Delta H - T\Delta S$ - Exergonic/Endergonic reaction - Exothermic/Endothermic reaction - Bond formation enthalpies (bond strengths) - Calculation of the ΔH of reactions - Thermodynamically/Entropically favoured/unfavoured reaction - Chemical equilibrium - Equilibrium (chemical) constant (K) - The relation between ΔG and K - The LeChatellier principle
- Kinetics of organic reactions - Reaction rates - Reaction mechanism - Rate constant k - Reaction coordinate - Activation energy - Activation complex or Transition state - Energy barrier - Single- and multi-step reactions - Reaction intermediate - The rate-limiting step - Arrhenius equation - kinetic/thermodynamic stability - Reactions with competing steps - Kinetic versus thermodynamic control Κινητικός - Product from kinetic/thermodynamic control - Overcoming energy barriers - Reaction solvent
- Reaction mechanism - Chemical reactivity - Lewis Acids/Bases - The concept of Filicity - Types of electrophiles/nucleophiles in organic reactions - Polarizability effects - Theory of hard and soft acids and bases - The convention of curved arrows - Classes of reaction mechanisms - Polar mechanisms - Free radical mechanisms - Concerted mechanisms - Metal-mediated mechanisms ((ligand coupling reactions) - The principle of microscopic reversibility - Reaction selectivity - Chemoselective reaction/chemoselectivity - Protection/deprotection of functional groups - Regioselective reaction/regioselectivity - Diastereoselective reaction/diastereoselectivity - Enantioselective reaction/enantioselectivity - Types of solvents (polar/non-polar/, protic/aprotic)
- Redox reactions - Oxidation number - Oxidation state - When an organic reaction is oxidation/reduction - Which organic reactions are not redox reactions

6. Acidity-Basicity

- Lowry and Brønsted theory of acids and bases - Conjugate base/conjugate acid - Chemical equilibrium constant K_a and pK_a - Logarithmic scale of acidity
- Organic acidity - Organic acids - Table of pK_a values for common functional groups - Table of pK_a values for common protonated functional groups - Acidity of carboxylic acids - Acidity of alcohols and phenols - Acidity of aliphatic and aromatic amines - Acidity of carbonyl compounds - Acidity of hydrocarbon - Organic basicity - Solvation effects
- Organic bases - Strong bases (organolithium compounds, amide and alkoxide anions) - Aliphatic and aromatic amines as bases - Basicity of amides - Amidines and guanidines as bases - Basicity of heterocyclic compounds of nitrogen (pyrrole, pyridine, piperidine)

7. Reactive intermediates in Organic Chemistry

- Tri- and tetravalent reactive intermediates with central C atom - Carbocations - Carbanions - Free radicals - Carbenes
- Carbocations: Structure, factors stabilizing carbocations, generation and reactions, rearrangements
- Carbanions: Structure, carbanions from hydrocarbons, factors stabilizing carbanions, carbanions with covalent character (organometallic compounds)
- Free radicals: Structure, factors stabilizing free radicals, generation and reactions
- Carbenes: Structure, stability, generation, reactions

8. General mechanisms of organic reactions with simple examples

General mechanisms with simple examples for the following classes of organic reactions:

- Nucleophilic substitution on a saturated C atom (S_N2 and S_N1)

- Elimination reactions (E2 and E1)
- Addition reactions on C-C multiple bonds

4. TEACHING and LEARNING METHODS - EVALUATION

<p style="text-align: center;">DELIVERY <i>Face-to-face, Distance learning, etc.</i></p>	Lectures and seminars face to face															
<p style="text-align: center;">USE OF INFORMATION AND COMMUNICATIONS TECHNOLOGY <i>Use of ICT in teaching, laboratory education, communication with students</i></p>	<p>Use of Information and Communication Technologies (ICTs) (PowerPoint) in Lectures. Course lectures and exemplary solved problems for every chapter, in the form of ppt files, are uploaded in the internet (http://www.soclab.chem.upatras.gr), from where they can be freely downloaded using a password which is provided to the students at the beginning of the course.</p> <p>Seminars. Problems are solved in an exemplary way summarizing before the theory behind each problem.</p> <p>Communication with the students is established either through mail or through the webpage of the Chemistry Department.</p>															
<p style="text-align: center;">TEACHING METHODS <i>The manner and methods of teaching are described in detail.</i></p> <p><i>Lectures, seminars, laboratory practice, fieldwork, study and analysis of bibliography, tutorials, placements, clinical practice, art workshop, interactive teaching, educational visits, project, essay writing, artistic creativity, etc.</i></p> <p><i>The student's study hours for each learning activity are given as well as the hours of non-directed study according to the principles of the ECTS</i></p>	<table border="1" style="width: 100%; text-align: center;"> <thead> <tr> <th style="text-align: left;"><i>Activity</i></th> <th style="text-align: left;"><i>Semester workload</i></th> </tr> </thead> <tbody> <tr> <td>Lectures (3 contact hours per week x 13 weeks)</td> <td>39</td> </tr> <tr> <td>Seminars (1 contact hour per week x 9 weeks) - solving of representative problems</td> <td>9</td> </tr> <tr> <td>Half-term evaluations (2, one in the middle and the other at the end of the semester, 2 contact hours each)</td> <td>4</td> </tr> <tr> <td>Final written examination (3 contact hours)</td> <td>3</td> </tr> <tr> <td>Private study time of the student and preparation for the half-term evaluations and final examination</td> <td>70</td> </tr> <tr> <td>Course total</td> <td>125</td> </tr> </tbody> </table>	<i>Activity</i>	<i>Semester workload</i>	Lectures (3 contact hours per week x 13 weeks)	39	Seminars (1 contact hour per week x 9 weeks) - solving of representative problems	9	Half-term evaluations (2, one in the middle and the other at the end of the semester, 2 contact hours each)	4	Final written examination (3 contact hours)	3	Private study time of the student and preparation for the half-term evaluations and final examination	70	Course total	125	
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<p style="text-align: center;">STUDENT PERFORMANCE EVALUATION <i>Description of the evaluation procedure</i></p> <p><i>Language of evaluation, methods of evaluation, summative or conclusive, multiple choice questionnaires, short-answer questions, open-ended questions, problem solving, written work, essay/report, oral examination, public presentation, laboratory work, clinical examination of patient, art interpretation, other</i></p> <p><i>Specifically-defined evaluation criteria are given, and if and where they are accessible to students.</i></p>	<ol style="list-style-type: none"> 1. Optionally, preparation of two home-works involving the solution of a series of organic chemistry problems by groups of two students. 10% of the mean mark of the two home-works will be added to the final mark only when in both home-works the minimum grade 5 has been obtained and in the final exam paper the students secure at least the grade 4. This option will be valid (a) ONLY when the incoming number of students were reduced drastically and (b) for ERASMUS student. 2. Optionally, half-term written examinations, the first one in week 7 of the semester and the second in week 14 (immediately after the end of the semester). 20% of the mean mark X for these two exams will be added to the final mark only when $3,5 < X < 5$ and in the final exam the student secures at least the grade 4. It is prerequisite that the students should at least obtain the grade 4 in the first half-term examination in order to be allowed to participate in the second one. 3. Written examination after the end of the semester - final mark, unless the student participated in home-works and/or half-term examinations. In the latter case, the percentage(s) of the marks described above are added). Minimum passing grade: 5. 4. The home-works, the half-term examinations and the final written examination take place in the Greek language and for 															

	<p>the foreign students (for example, ERASMUS students) in the English language.</p> <p>5. All above described assessment activities of the progress of students concern solving problems which combine concepts and theories taught. Each problem is associated with a certain mark so that the total number of marks is equal to 10.</p>
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5. ATTACHED BIBLIOGRAPHY

<ol style="list-style-type: none">1. J. McMurry, "Organic Chemistry", Translation to Greek: A. Varvoglis, M. Orfanopoulos, I Smonou, et al, University of Crete Publications, 2012.2. L. G. Wade, Jr., "Organic Chemistry", Translation to Greek: D. Komiotis, et al, A. Tziola and Sons Publications, 2010.3. J. Clayden, N. Greeves, S. Warren, "Organic Chemistry", Vols I and II, Translation to Greek: G. Kokotos et al, Utopia Publications, 2017.4. P. Sykes, "Guidbook to Mechanisms in Organic Chemistry", Translation to Greek: D. Gakis, Pneumatikos Publications, 1994.5. D.E. Levy, "Arrow pushing in Organic Chemistry: an easy approach to understanding reaction mechanisms", Wiley-Interscience, 2011.
