UČNI NAČRT PREDMETA / COURSE SYLLABUS	
Predmet:	ŠTUDIJ MEHANIZMOV TRANSFORMACIJ ORGANSKIH SPOJIN
Course Title:	STUDY ON MECHANISMS OF ORGANIC TRANSFORMATIONS

Študijski program in stopnja Study Programme and Level	Študijska smer Study Field	Letnik Academic Year	Semester Semester
DR Kemijske znanosti, 3. stopnja	**/**	**1.**	**1. in 2.**
Doctoral programme in Chemical Sciences, 3rd Cycle	**/**	**1st**	**1st and 2nd**

Vrsta predmeta / Course Type: izbirni/Elective

Univerzitetna koda predmeta / University Course Code: KZ310

Predavanja Lectures	Seminar Seminar	Vaje Tutorial	Klinične vaje Work	Druge oblike študija	Samost. delo Individual Work	ECTS
30	**30**	**/**	**/**	**30**	**60**	**5**

Nosilec predmeta / Lecturer: izr. prof. dr. Janez Cerkovnik /Dr. Janez Cerkovnik, Associate Professor

Jeziki / Languages:

Predavanja / Lectures:	**slovenski / Slovenian**
Vaje / Tutorial:	**slovenski / Slovenian**

Pogoji za vključitev v delo oz. za opravljanje študijskih obveznosti:	Prerequisites:
Študent oz. kandidat mora imeti predmet opredeljen kot študijsko obveznost.	The course has to be assigned to the student.

Vsebina:	Content (Syllabus outline):
Študent s soglasjem mentorja med spodaj navedenimi temami v izbere tiste, ki so najtesneje povezane z njegovim raziskovalnim delom. Nosilec predmeta in vodja študija poskrbita, da obseg študentovega dela ustreza 5 KT. Če je izvajalcev več, izvajanje koordinira nosilec. - *Pregled metod študija mehanizmov organskih reakcij.* Nekinetične metode: identifikacija produktov, reaktivni intermediati, kemijske in fizikalne metode (spektroskopske metode: NMR, ESR, UV/VIS, IR) detekcije in karakterizacije intermediatov, izotopsko zaznamovanje, stereokemija in mehanizem.	From the topics listed below the student selects (in agreement with the supervisor) those that are mostly related to his research work. The course coordinator, who is in charge of the course, and the leader of the study take care that the student's workload corresponds to 5 credits. If more persons are taking the study programme, the whole process is coordinated by course coordinator. - *Survey of methods for studying organic reaction mechanisms.* Non-kinetic methods: identification of products, reactive intermediates, chemical and physical methods (spectroscopic methods: NMR, ESR, UV/VIS, IR)

Kinetične metode: kinetični principi reakcij v raztopini, prehodno stanje, aktivacijski parametri in njihova interpretacija, Hammondov postulat, princip reaktivnost-selektivnost, kinetični izotopski efekti, korelacija strukture in reaktivnosti, linearno prosto energijske zveze in prehodno stanje. Empirične korelacije učinka topil na hitrost reakcij.
- *Študij mehanizmov oksidacij s posebnim poudarkom na oksidacijah s peroksidi in ozonom.* Sinteza, fizikalne lastnosti in reaktivnost najpomembnejših razredov peroksidov, t.j. organskih derivatov vodikovega peroksida (HOOH). Mehanizem prenosa kisika pri nekataliziranih in kataliziranih reakcijah oksidacije različnih organskih substratov s peroksidi. Oksidacije organskih substratov s singletnim (1O2) in tripletnim (3O2) kisikom in ozonom. Peroksidi v bioloških sistemih. Kemija vodikovega trioksida (HOOOH) ter njegovih organskih in organokovinskih hidrotrioksidnih (ROOOH) derivatov.
- *Organska fotokemija.* Nastanek in obnašanje vzbujenih stanj molekul je pomembno za razumevanje fotokemičnih reakcij. Te informacije lahko dobimo iz študija kinetike fotofizikalnih in kemičnih procesov in jih lahko uporabimo pri načrtovanju struktur molekul, ki bodo vodile do želenih končnih produktov fotokemičnih procesov. a) Fotofizikalni procesi: absorpcija fotona, singletna in tripletna stanja. Emisija fotona (fluorescenca, fosforescenca, kemiluminiscenca). Izbirna pravila za prehode (medsistemsko križanje, interna konverzija) Franck-Condonovo načelo. b) Eksperimentalne tehnike: "time resolved" spektroskopija, omogoča opazovanje kratkoživih vzbujenih stanj in reakcijskih intermediatov, na nano- in femtosekundni skali. Merjenje kvantnega izkoristka emisijskih pojavov in fotokemičnih procesov. Razlikovanje med vrstami vzbujenih stanj s specifičnimi inhibitorji. c) Fotokemični procesi: Značilni kromoforji in njihova reaktivnost. Uporaba fotokemičnih procesov v organski sintezi.

for detection and characterization of intermediates, isotopic labelling, stereochemistry and mechanism. Kinetc methods: kinetic principles of reactions in a solution, transition state, activation parameters and their interprettion, Hammond's postulate, reactivity-selectivity principle, kinetic isotope effect, structure-reactivity correlation, linear free energy relationships and transition state. Empiric correlation between solvent effect and reaction rate.
- *Organic reaction mechanism studies with emphasis on oxidations with peroxides and ozone.* Synthesis, physical properties, and reactivity of important organic peroxides. Mechanism of oxygen transfer in (non)catalyzed oxidations of organic molecules with peroxides. Oxidations with singlet (1O2) and triplet (3O2) oxygen and ozone. Peroxides in biological systems. Chemistry of hydrogen trioxide (HOOOH) and its organic and organometallic hydrotrioxide (ROOOH) derivatives.
- *Organic photochemistry.* Formation and behaviour of molecules in excited state is important for understanding of photochemical reactions. These informations can be obtained from kinetcs of photophysical and photochemical processes and can be applied in designing of molecular structures leading to the desired final product of photochemical processes. a) Photophysical processes: photon absorption, singlet and triplet states. Photon emission (fluorescence, phosphorescence, chemiluminiscence). Selection rules for transitions (intersystem crossing, internal conversion) Franck-Condon principle. b) Experimental techniques: "time resolved" spectroscopy, enables monitoring of short-term excited states and intermediates on nano- in femtosecond scale. Determination of quantum yield of emission phenomena and photochemical processes. Discrimination between different types of excited states with specific inhibitors. c) Photochemical processes: typical chromophores and their reactivity. The use of photochemical processes in organic synthesis.

- *Kemija radikalov.* a) Struktura in reaktivnost radikalov. Uporaba eksperimentalnih tehnik za študij reaktivnosti: kinetične in "time resolved" spektroskopske metode (laserska bliskovna fotoliza na nanosekundni skali idr.) elektronska spinska resonanca. Elektronski efekti pri radikalskih reakcijah. Uporaba računskih metod (DFT) za študij energetike radikalskih reakcij. b) Uporaba radikalskih procesov v organski sintezi. Kemija stananov in sorodnih hidridov, redoks procesi idr. Kataliza z obratom polarnosti. Kemija ozračja.	- *The chemistry of radicals.* a) Structure and reactivity of radicals. Experimental techniques in reactivity studies, kinetic and "time resolved" spectroscopic methods (lasers flash photolysis on nanosecond scale, etc.) electron spin resonance. Electronic effects in radical reactions. Computational methods (DFT) radical reaction energy studies. b) The use of radical processes in organic synthesis. The chemistry of stananes and related hydrides, redox processes, etc. Catalysis with “Umpolung”. Chemistry of the atmosphere.

Temeljna literatura in viri / Readings:

- M. B. Smith, J. A. March, *Advanced Organic Chemistry: Reactions, Mechanism, and Structure*, 6th ed., Wiley, New York, 2007.
- H. Maskill, *The Investigation of Organic Reactions and Their Mechanisms*, Blackwell Publishing, Oxford, 2006.
- T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd ed., Plenum, New York, 1987.
- R. A. Moss, M. S. Platz, M. Jones, Jr. *Reactive Intermediate Chemistry*, Wiley-Interscience, New York, 2004.
- N. J. Turro in soavtorji, *Modern Molecular Photochemistry of Organic Molecules*, University Science Books, 2010.
- A. Gilbert, J. Baggott, *Essentials of Molecular Photochemistry*, Blackwell Scientific Publications, 1991.
- S. Z. Zard, *Radical Reaction in Organic Synthesis*, Oxford University Press, 2003
- J. Fossey in soavtorji, *Free Radicals in OrganicChemistry*, Wiley, 1995

Cilji in kompetence:	**Objectives and Competences:**
Poglobljeno poznavanje izbranih področij organske kemije. Kandidat se seznani z modernimi metodami organske kemije, kar ga usposobi za samostojno reševanje problemov iz tega področja dejavnosti.	Advancement of knowledge on selected topics and methods of organic chemistry, which is a basis for student ability to solve practical problems in organic chemistry.

Predvideni študijski rezultati:	**Intended Learning Outcomes:**
<u>Znanje in razumevanje</u> Študent pozna osnovne reakcijske mehanizme v organski kemiji in vplive reakcijskih parametrov na potek reakcij ter metode določanja mehanizmov. Pozna osnovne mehanizme oksidacij, s poudarkom na reakcijah reaktivnih kisikovih zvrsti. Razume pojem vzbujenih stanj, njihovih življenjskih dob in reaktivnosti ter načine	<u>Knowledge and Comprehension</u> Knowledge of basic reaction mechanisms on organic chemistry. Influence of reaction parameters on the reaction course and methods of determining mechanisms. Basic mechanisms of oxidations with reactive oxygen species. Basic knowledge of excited states, their reactivity and lifetimes. Determination of the

določanja in lastnost vzbujenih stanj in reakcijskih intermediatov. Pozna uporabo nekaterih reprezentativnih fotokemičnih pretvorb. Pozna lastnosti, načine tvorbe in reaktivnost radikalov ter metode za opazovanje. Uporaba računskih metod za študij strukture radikalov in drugih reakcijskih intermediatov.	properties of excited states and reaction intermediates. Application of representative photochemical transformations. Properties, formation and reactivity of radicals; methods of observation. Computational methods for studying of the structure of radicals and other reaction intermediates.
Uporaba Glede na primer študija zna izbrati primerne metode in predvidi rezultate pri uporabi posameznih metod in jih zna interpretirati. Zna uporabiti oksidacije z reaktivnimi kisikovimi zvrstmi v organski sintezi. Zna načrtovati in izpeljati fotokemične in radikalske procese v organski sintezi.	Application The ability to choose the appropriate research methods according to the study subject. Prediction and interpretation of the results obtained by methods applied. Application of oxidations by reactive oxygen species in organic synthesis. Planning and implementation of photochemical and radical processes in organic synthesis.
Refleksija Študent bo znal ovrednotiti dobljene rezultate študija reakcijskih mehanizmov in njihove interpretacije na izbranem področju. Z uporabo znanj, dobljenih pri tem predmetu bo znal voditi raziskave.	Analysis The ability to evaluate and interpret the results of the study of reaction mechanisms and in the selected field. Application of knowledge to conduct the research.
Prenosljive spretnosti Dostopanje do literaturnih virov -Zbiranje, interpretacija in kritično vrednotenje podatkov -Identifikacija in reševanje problemov	Skill-transference Ability Ability to find and select literature sources. Collection, interpretation and critical evaluation of data. Identification and solving of problems.

Metode poučevanja in učenja:	**Learning and Teaching Methods:**
Predavanja in seminarji.	Lectures, seminars.

Načini ocenjevanja:	Delež (v %) / Weight (in %)	**Assessment:**
Ustni izpit	100 %	oral examination

Reference nosilca / Lecturer's references:

- CERKOVNIK, Janez, TUTTLE, Tell, KRAKA, Elfi, LENDERO KRAJNC, Nika, PLESNIČAR, Božo, CREMER, Dieter. The ozonation of silanes and germanes: an experimental and theoretical investigation. J. Am. Chem. Soc., 2006, 128, 4090-4100.
- KOVAČIČ, Saša, KOLLER, Jože, CERKOVNIK, Janez, TUTTLE, Tell, PLESNIČAR, Božo. Dihydrogen trioxide clusters, (HOOOH)n (n = 2-4), and the hydrogen-bonded complexes of HOOOH with acetone and dimethyl ether: implications for the decomposition of HOOOH. J. Phys. Chem. A, 2008, 112, 8129-8135.
- BERGANT, Ana, CERKOVNIK, Janez, PLESNIČAR, Božo, TUTTLE, Tell. An efficient methyltrioxo-rhenium(VII)-catalyzed transformation of hydrotrioxides (ROOOH) into dihydrogen trioxide (HOOOH). J. Am. Chem. Soc., 2008, 130, 14086-14087.

- CERKOVNIK, Janez, PLESNIČAR, Božo, KOLLER, Jože, TUTTLE, Tell. Hydrotrioxides rather than cyclic tetraoxides (tetraoxolanes) as the primary reaction intermediates in the low-temperature ozonation of aldehydes. The case of benzaldehyde. J. Org. Chem., 2009, 74, 96-101.
- TUTTLE, Tell, CERKOVNIK, Janez, KOLLER, Jože, PLESNIČAR, Božo. The search for protonated dihydrogen trioxide (HOOOH): insights from theory and experiment. J. Phys. Chem. A, 2010, 114, 8003-8008.
- CERKOVNIK, Janez, PLESNIČAR, Božo. Recent advances in the chemistry of hydrogen trioxide (HOOOH). Chem. Rev., 2013, 113, 7930-7951.
- STRLE, Gregor, CERKOVNIK, Janez. A simple and efficient preparation of high-purity hydrogen trioxide (HOOOH). Angew. Chem. Int. Ed. 2015, 54, 9917-9920.