

CH3E9-15 Advanced Organic Chemistry and Laboratory

20/21

Department

Chemistry

Level

Undergraduate Level 3

Module leader

Paul Wilson

Credit value

15

Module duration

6 weeks

Assessment

33% coursework, 67% exam

Study location

University of Warwick main campus, Coventry

Description

Introductory description

n/a.

[Module web page](#)

Module aims

The objective of this module is to provide the students with the information they need to be able to determine the products from complex pericyclic reactions, intramolecular cyclisation processes, rearrangement reactions of reactive intermediates, and reactions creating new stereogenic centres by either substrate, reagent, or catalyst control.

By the end of the module students will be able to predict the products arising from reactions. Be familiar with the empirical rules and models related to concerted, cyclisation, rearrangement, and stereoselective reactions. Student should be able to use their knowledge to devise syntheses of complex molecules.

This module also builds on Year 1 and Year 2 modules in which skills in organic chemistry laboratory practice are developed (5 CATS). Here, more advanced aspects are encountered and particular emphasis is placed on experimental design. Since, the students have (in some cases

indirect) access to research-quality analytical equipment, evaluation and interpretation of original data is highlighted. The chemical systems and molecules that will be characterised will be generally of a known nature however in some cases novel and unknown systems and molecules will be studied. Safety aspects of laboratory work will also take a step closer to the research context since some of the associated hazards will vary considerably between one student's work and the next

Outline syllabus

This is an indicative module outline only to give an indication of the sort of topics that may be covered. Actual sessions held may differ.

Pericyclic reactions including photochemistry.

Cycloadditions (including 1,3-dipolar cycloadditions), electrocyclisations and sigmatropic rearrangements. Frontier orbital theory will be used to explain the stereochemical observations made in pericyclic reactions.

Polar rearrangements

Carbocation induced alkyl and hydride shifts, Wagner-Meerwein, Pinacol, Tiffeneau-Demyanov, hydride shifts, cyclisations. Nucleophilic rearrangements to carbon involving carbanions, Favorskii.

Radicals

Cyclisations, ring-openings, 1,5-H translocations.

Carbenes

Structure, reactivity and generation. Insertion reactions, cyclopropanation, metathesis

Rearrangement reactions to electron deficient nitrogen and oxygen.

Nitrenes. Baeyer-Villiger

Reactions of chiral compounds (3 Lectures DJF)

Nucleophilic Addition to alpha-stereogenic carbonyl compounds: non-polar-Felkin model, polar Felkin model, chelation model. Addition to beta-stereogenic carbonyl compounds. Electrophilic addition to chiral alkene containing compounds: Houk-type model for control of reaction stereochemistry, including steric, and chelation factors, including the reaction of chiral allyl silanes.

Synthesis of enantiomerically enriched compounds (2 Lectures DJF)

Evans Auxiliary: alkylation, aldols, conjugate additions, Diels Alder reaction.

Chiral reagents: terpene-borane reductions, hydroboration, allylation.

Asymmetric catalysis (reagent control) (5 Lectures MW)

Sharpless Asymmetric Epoxidation (AE) and dihydroxylation (AD)

Additions to carbonyls, reductions (Noyori). Menthol synthesis.

Enolate chemistry : alkylations aldol

Modern chiral Bronstead acid catalysis

Pd catalysed allylation

includes simple catalyst based kinetic resolution

and catalyst based DKR e.g. Noyori Hydrogenation of beta-ketoesters

Laboratory component:

Organic Laboratory (5 CATS); This features a multi-stage preparation and characterisation of a target molecule assigned at random. Students are required to plan and execute the synthesis of the required target using guidance provided in the laboratory manual.

Learning outcomes

By the end of the module, students should be able to:

- Understand how carbenes and nitrenes can be used in organic synthesis
- Understand and apply Baldwin's rules for intramolecular cyclisation reactions.
- Develop ability to formulate potential routes to compounds using their knowledge of reactive intermediates and their reactions.
- Understand how cation and anion rearrangements occur and can be used in organic synthesis
- Understand how radical rearrangements and cyclisations can be used in organic synthesis
- Understand how reactions can form different stereoisomers of products
- Building on Year 2 modules, be able to draw simple transition-states in 3 dimensions
- Successfully predict simple aldol stereochemistry based on metals and enolate geometry
- Use facial steric arguments to predict stereochemical outcome
- Use stereoelectronic arguments (e.g. Houk's rule) to predict stereochemical outcome
- Understand basics of chiral resolution via diastereoisomer formation
- Identify useful amino acids and know how they can be turned into chiral auxiliaries and templates.
- Explain and predict the stereochemical outcome of Evans alkylations, aldols, conjugate additions and cycloadditions
- Explain and predict the stereochemical outcome of chiral reagent controlled reactions such as terpene / borane mediated reductions and additions.
- Understand and apply empirical rules and models related to stereoelectronically-controlled reactions of organic molecules.
- Understand and apply selection rules for pericyclic reactions and intramolecular cyclisations, and understand their theoretical basis.
- Understand the frontier orbital approach to pericyclic reactions and use this to predict the outcome of reactions.

Indicative reading list

Much of the material for this module is taken from compulsory organic chemistry text by Clayden et al.; "Organic Chemistry" by Clayden, Greeves, Warren and Wothers, Oxford 2001.

The following books will also be compulsory

"Reactive Intermediates" C. J. Moody and G. H. Whitham, Oxford University Press, 2001.

"Polar Rearrangements" L. M. Harwood, Oxford University Press, 1992.

"Pericyclic reactions" I. Fleming, OUP 1998, Primer

"Organic Synthesis – Strategy and Control" Wyatt and Warren, Wiley, 2007

The following texts may be consulted for further information on the contents of the module:

Review on Woodward-Hoffmann rules: R. B. Woodward and R. Hoffmann in *Angew. Chem., Int Ed. Engl.*, 1969, 8, 781.

"Organic Reactions and Orbital Symmetry", T. L. Gilchrist and R. Storr, Cambridge Academic Press, 1979.

Subject specific skills

Problem solving

Critical thinking
Independence and initiative

Transferable skills

Problem solving
Critical thinking
Independence and initiative

Study

Study time

| Type | Required |
|-------------------|-----------------------------|
| Lectures | 20 sessions of 1 hour (13%) |
| Practical classes | 5 sessions of 6 hours (20%) |
| Private study | 100 hours (67%) |
| Total | 150 hours |

Private study description

N/A

Costs

No further costs have been identified for this module.

Assessment

You do not need to pass all assessment components to pass the module.

Students can register for this module without taking any assessment.

Assessment group D1

| | Weighting | Study time |
|--------------------|-----------|------------|
| Laboratory Report | 33% | |
| Online Examination | 67% | |
| 1.5 hour exam | | |

Feedback on assessment

Cohort level examination feedback provided via Moodle. Written feedback on laboratory report from assessor.

[Past exam papers for CH3E9](#)

Availability

Pre-requisites

To take this module, you must have passed:

- All of
 - [CH161-30 Introduction to Organic Chemistry](#)
 - [CH270-15 Selective Organic Synthesis](#)
 - [CH271-15 Mechanistic and Biological Chemistry](#)

Post-requisite modules

If you pass this module, you can take:

- CH408-15 Advanced Medicinal and Biological Chemistry
- CH402-15 Synthetic Chemistry I (Organic)
- CH401-60 Research Project & Methodology

Courses

This module is Core for:

- UCHA-4 Undergraduate Chemistry (with Intercolated Year) Variants
 - Year 4 of F101 Chemistry (with Intercolated Year)
 - Year 4 of F122 Chemistry with Medicinal Chemistry (with Intercolated Year)
- UCHA-3 Undergraduate Chemistry 3 Year Variants
 - Year 3 of F100 Chemistry
 - Year 3 of F100 Chemistry
 - Year 3 of F121 Chemistry with Medicinal Chemistry
- Year 3 of UCHA-F110 Undergraduate Master of Chemistry (with Industrial Placement)
- Year 4 of UCHA-F107 Undergraduate Master of Chemistry (with Intercolated Year)
- UCHA-4M Undergraduate Master of Chemistry Variants
 - Year 3 of F100 Chemistry
 - Year 3 of F105 Chemistry
 - Year 3 of F125 MChem Chemistry with Medicinal Chemistry
- Year 4 of UCHA-F127 Undergraduate Master of Chemistry with Medicinal Chemistry(with Intercolated Year)