

Organic Chemistry

Research and teaching staff:

Christina Moberg	professor
Peter Somfai	professor
Torbjörn Norin	professor emeritus
Björn Åkermark	professor emeritus
Peter Baeckström	Ph D
Jan Bergman	Ph D (professor, KI)
Anna-Karin Borg-Karlson	Ph D (associate professor) professor 2, NTNU, Norway
Styrbjörn Byström	Ph D (associate professor)
Jonas Hellberg	Ph D (associate professor)
Ulla Jacobsson	Ph D (associate professor)
Christian Linde	Ph D
Mats Svensson	Ph D
Sture Strömberg	Ph D
Rikard Unelius	Ph D (associate professor)
Krister Zetterberg	Ph D (associate professor)

Administrative and technical staff:

Henry Challis	lab. technician
Jan Olov Lindström	lab. technician
Ingvar Larsson	secretary
Lena Skowron	secretary

Organic chemistry is a fundamental science dealing with the synthesis and reactions of organic compounds, the investigation of their properties and the relationships between their molecular structures, interactions and functions. The role of organic compounds and reactions in industrial processes is well recognized and numerous applications exist. The teaching and research activities of our section are therefore rather broad and some applied aspects are also part of the programme.

Asymmetric catalysis, organic synthesis, natural product chemistry, bioorganic chemistry, and ecological chemistry are the principal research areas. The research is mainly of fundamental nature but there are also research projects of applied character carried out in collaboration with industry. The research may be summarized in brief as follows:

- The function and use of transition metal catalysts in organic synthesis.
- New selective synthetic methods using organometallic reagents.
- Synthesis of complex organic compounds of biological, pharmaceutical or technical interest.
- The use of enzymes in organic synthesis – scopes and limitations.
- Natural product chemistry including studies of biologically active compounds of natural origin.
- Ecological chemistry – analysis of biologically active compounds in insect/insect and insect/plant relationships.
- Molecular recognition and interactions – studies on structure/activity relationships using experimental methods and molecular modelling.
- Synthesis and properties of specialty chemicals such as electro- and magnetoactive organic materials, surfactants, and colloids.
- Computational chemistry.

ADVANCED UNDERGRADUATE TEACHING

- Organic chemistry I, (3B 1510, fortsättningskurs, 10 credits)
- Organic chemistry I, for B.Sc. students in chemistry (6D 2941, 4 credits)
- Organic chemistry II, for B.Sc. students in chemistry (6D 2943, 4 credits)
- Diploma work (3B 1005 and 1015)

Members from Organic Chemistry have also participated in the teaching of three compulsory undergraduate courses for the chemical engineering students (School of Chemistry, Chemical Engineering and Biotechnology and KTH College of Engineering) as well as a course in general chemistry for the School of Civil Engineering.

Staff members of Organic Chemistry have taken active part in the development of Master and PhD programmes in Organic Chemistry in developing countries (Moçambique and Sri Lanka). These development actions have been sponsored by SIDA/SAREC.

GRADUATE SCHOOL

Registered and active graduate students

45 (incl. visiting and external students)

Dissertations 6 PhD (tekn dr)

2 Tekn lic

Graduate courses

The following courses have been given:

- On-line literature search, optional course for graduate students in chemistry and chemical engineering (2 credits)
- Research frontiers in organic chemistry (3 credits)
The course is continuously going on with literature seminars once a week and research seminars (see below)
- Methodology in research (compulsory graduate course for all students in chemistry and chemical engineering, 3 credits)
- Organic stereochemistry (4 credits)
- Stereochemistry for chemical engineers (1 credit)
- Preparative separation methods for organic chemists (2 credits)
- New trends in organic chemistry (2 credits)
- Spectroscopic methods in organic chemistry (3 credits)
- Chemical engineering for chemists (1 credit)

Graduate research work

The registered graduate students are carrying out their PhD-work as members of research groups of the organic chemistry division (24) or as external students performing their research work at an industrial laboratory, research institute or the University College of Mid Sweden (Mithögskolan).

RESEARCH SEMINARS

Research seminars have been given by 10 visiting scientists from various parts of the world. The seminar activities also include presentations of current research work by members of the organic chemistry division and presentations of diploma work carried out by undergraduate students.

Professor Gregory C. Fu from Department of Chemistry at MIT in Boston has been invited as the second speaker in the special seminar series in the honor of late professor Holger Erdtman. He gave the lecture "Asymmetric catalysis with 'planar-chiral' heterocycles." Part of his visit was also devoted to discussions with our graduate students.

PRESENTATIONS OF RESEARCH AND TEACHING ACTIVITIES

An important task of the division of organic chemistry is to inform various groups of the society about the research and teaching activities and to transfer knowledge to industry and society. The division has been actively engaged in several arrangements for these purposes. Thus members of our division have been engaged in the "Berzelius days", organized by the Swedish Chemical Society, for high school students (380 students and 120 teachers from all parts of Sweden). The organic chemistry division is also engaged in a summer school for high school students.

The transfer of knowledge to industry is mainly performed via research projects sponsored by NUTEK. Our industry partners continuously receive information from the research groups and take part in project meetings.

RESEARCH

The research is carried out on different but more or less interrelated research projects. Organic synthesis and natural product chemistry are the principal lines.

An important area of the research is the development of selective methods for synthesis of organic compounds of biological, pharmacological, physical or chemical interest. The research also deals with reaction mechanisms as well as the stereochemistry and dynamics of those organic molecules. Molecular modelling is an important tool in these research activities.

Another general line of research, which is becoming an important topic, is studies of molecular recognition and interactions in relation to catalysis,

Graduate students:

Fredrik Andersson
 Fredrik Allared
 Oscar Belda
 Jan Blid
 Ulf Bremberg
 Emma Dahlstedt
 Helen Edlund
 Carina Eriksson
 Hans Frykman
 Jenny Fältd
 Kristina Hallman
 Björn Hedman
 Jan Holmbäck
 Dan Isaksson
 Staffan Karlsson
 Fredrik von Kieseritzky
 Daniel Koch
 Fredrik Lake
 Abraham Langlet
 Michael Larsson
 Marica Lindmark
 Charlotta Lindquist
 Mona Lindström
 Rong Liu
 Raimondas Mozuraitis
 Ba-Vu Nguyen
 Christina Jönsson
 Kristina Neimert Andersson
 Berit Olofsson
 Felisberto Pagula
 Monika Persson
 Peter Piispanen
 Fredrik Rahm
 Per Renström
 Erik Risberg
 Didier Rotticci
 Ellen Santangelo
 Åsa Sjöholm
 Olof Smitt
 Robert Stranne
 Carina Svensson
 Anh Tran

Visiting scientists (>1 month visit):

Darshika Akiyasena	Sri Lanka
Maria Fusto	Italy
Patrick Kelly	US
Uttam Khamrai	India
Sacha Legrand	France
Ilme Liblikas	Estonia
Serguei Lutsenko	Kazakhstan
Patrice Marchand	France
Colin Ray	Great Britain
Heimo Schmitt	Germany
Jean-Luc Vasse	France
Roel Wijnmans	Netherlands
Annie Yart	France

enzyme/substrate and receptor interactions as well as surface phenomena, such as adsorption and self-assembly (supramolecular chemistry). Research in this interdisciplinary area is carried out in collaboration with theoretical chemists, biochemists, biologists, molecular biologists and physical chemists. Molecular modelling is an important tool in these research activities.

Current research topics can be summarized under the following headings:

- New selective synthetic methods using organometallic reagents.
- The function and use of catalysts (organic, organometallic, bio-organic) in organic synthesis.
- Synthesis of complex organic compounds of biological, pharmaceutical or technical interest.
- Natural product chemistry including studies of biologically active compounds of natural origin.
- Molecular interactions and studies on structure/activity relationships, molecular modelling.
- The use of enzymes in organic synthesis, scopes and limitations.
- Specialty chemicals and products including electro- and magnetoactive organic materials, reagents, surfactants, and colloids – syntheses and properties.
- Analysis of biologically active compounds in insect – plant relationships, especially enantiomeric separation.

RESEARCH PUBLICATIONS AND PARTICIPATION IN SCIENTIFIC MEETINGS

Apart from official reports to various research councils and short articles in Swedish journals and newspapers, 20 scientific papers have been published in international journals during 2000. In addition 6 PhD-theses and 2 Lic-theses have been produced. The publications are listed in the appendix.

Staff members and graduate students of the division of organic chemistry have participated in a number of international scientific meetings in different parts of the world (invited lectures, short communications and poster presentations).

SHORT PRESENTATIONS OF THE RESEARCH GROUPS

Terpenoid synthesis and separation techniques

Peter Baeckström

Synthesis.

Transformations in terpene chemistry *e.g.* photooxidations with simultaneous oxidation and reduction, allylic rearrangements and isoprenoid chain elongation. During year 2000 Felisberto Pagula from Moçambique has been engaged in this type of work.

Separation techniques.

Developing efficient methods for liquid adsorption chromatography has been a longstanding investigation to enable efficient separations of large amounts of synthetic mixtures or extracts of natural products. The task was originally undertaken with the slogan “Minimum Effort Liquid Chromatography.”

By studying the effect of different types of gradient elution, and emphasizing column length (amount of adsorbent) as a crucial parameter, solvent, adsorbent and time consumption have been drastically reduced compared to conventional methods. A program that will minimize time or cost for a given separation has been written in MS Excel. The isolation of azadirachtin from seeds of *Azadirachta indica*, the most potent naturally occurring insecticide known at present, has been used as a model for group separation of

compounds by combined extraction and chromatography in columns loaded with seeds mixed with silica. The results of this project clearly indicates that percolation with solvents or Soxhlet extraction can be bypassed for relatively dry plant material.

Our methodology, has been presented at numerous workshops on separation techniques. Most of these, sponsored by SIDA-SAREC, IFS and IPICS, have been held in developing countries. During 1999 two workshops were held, one in Sri Lanka and the second in Botswana. Further, three students from developing countries, two from Sri Lanka (sponsored by IPICS) and one from Nigeria (sponsored by the Swedish Institute), have been accepted for training and participating in further developing the techniques.

During year 2000 the methodology of combined extraction and group separation was extended to the isolation of glycosides directly from the wet pulp of the palmyra fruit. This work was conducted in cooperation with Darshika Akiyasena from Sri Lanka, sponsored by IPICS, Uppsala University.

During the fall semester of year 2000 a course in methods for optimizing preparative chromatography using silica gel was given for the PhD students at KTH.

Ecological chemistry

Anna-Karin Borg-Karlson, Torbjörn Norin and Rikard Unelius

The research is focused on the structural determination and biological activity of insect and host – plant related compounds, *e.g.* separation, identification and synthesis of chemical signals released by living organisms. The biological significance of the compounds, that constitute the signals, is evaluated in close collaboration with biologists. By combining experience in analytic and synthetic organic chemistry as well as in entomology, ethology, biochemistry, microbiology and polymer technology we can reach one of the main goals: to replace the use of insecticides with environmentally friendly ecochemicals (green chemicals) for monitoring and control of insect pests.

Part of the research is organised in the inter-disciplinary program, “Pheromones and Kairomones for Control of Pest Insects,” financed by MISTRA (Foundation for Strategic Environmental Research, Stockholm, Sweden). Other parts of our research is financed by two EC-projects with the participation of forest entomologists, physiologists and ecologists from China, France, Spain, Portugal, Finland and Sweden. Visiting scientists from the Baltic region are engaged in these projects. They are financed by the Swedish Institute within the program “Ecological chemistry and the control of insect pests”.

Host-plant related compounds and their biological activity

Pine and spruce. Terpenes are important as signalling compounds in insect – plant interactions. We are studying the composition of volatile terpenes of host trees to be able to correlate insect attraction to healthy as well as stressed pine trees from China and Europe. These studies will allow us to predict factors affecting the susceptibility and resistance in conifers. We are also analysing, by 2D-GC and GC/LC-MS techniques, the dynamics of the fungi-induced chemical defence in infested trees. The expression of monoterpene synthases in different tissues of the trees can be estimated by correlating the relative amounts of monoterpenes to each other.

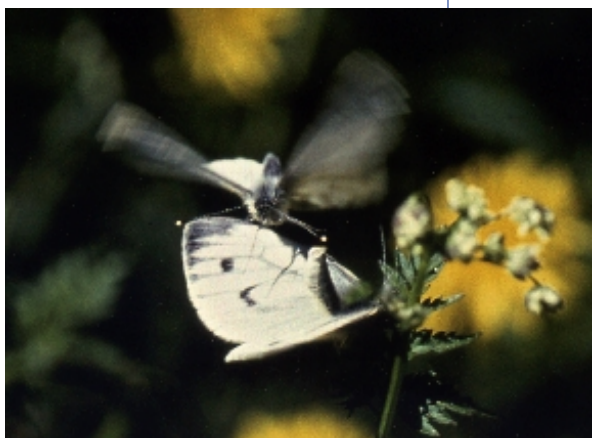
Butterfly plant-derived pheromones. A new class of aromatic insect pheromones has been identified by using SPME (Solid Phase Micro Extraction).

Premises:

Modern research and teaching laboratories and offices in relatively new and reconstructed buildings.

Equipment:

Advanced spectroscopic (NMR, MS, GC-MS, IR and UV) and chromatographic (GC, LC and HPLC) instruments and equipment for distillation. Equipment for research work under inert atmosphere. Computer facilities and advanced equipment for molecular modelling.



By ^{13}C labelling experiments, we have shown that aromatic amino acids are precursors for the “antiaphrodisiac” compound transferred to the female by the male during copulation, and then emitted by mated females.

Figure 1. The male butterfly, *Pieris napi*, approaches a mated female showing the typical signalling posture.

Pine weevil. Antifeedant compounds derived from conifers are identified, synthesised and their biological effect has been evaluated using behavioural tests. The work has been performed in collaboration with forest entomologists at the Swedish University of Agriculture (SLU, Uppsala). Three patent applications have been filed on this topic. The compounds will hopefully replace the presently used insecticide permethrin, which will become an important step towards sustainable forestry.

Biologically active host – plant constituents in moths

The use of host – plant compounds in combination with pheromones is a promising tool for the control of the codling moth *Cydia pomonella*, the major pest on apple. The research is focused on isolation, characterisation, and synthesis of host – plant compounds. Similar research is also carried out on the economically important polyphagous moths *Helicoverpa armigera* and *Heliothis virescens* (in collaboration with a research group in Trondheim). An important technique for determining biological activity of plant constituents is to measure the electrophysiological responses of antennal odour receptor neurons. The sesquiterpene germacrene D, *E,E*- α -farnesene, and a large number of aliphatic “apple” and “pear” esters are evaluated by EAG (ElectroAntennoGraphy), in wind tunnel bioassays and in field tests using males and females of *C. pomonella*. By using a chiral column in combination to single cell recordings, the selectivity to the germacrene D enantiomers has been determined in *H. armigera* and *H. virescens*. In cooperation with the neurobiologists at the Freie Universität in Berlin, the reception of host-plant compounds has been tested in insects. The location and pattern of the neuronal activity in the brain is measured and found to be characteristic for each odour.

Bioremediation

Cooperation with groups at KTH and Stockholm University, working with environmentally related topics, has been established. Microbial degradation of diesel, aliphatic hydrocarbons, polyaromatic hydrocarbons and phenols as well as constituents in bitumen and related materials and trapping of chlorinated organic solvents are studied mainly by GC-MS. The new concept, with repeated sampling during the degradation process using SPME, is found to be effective.

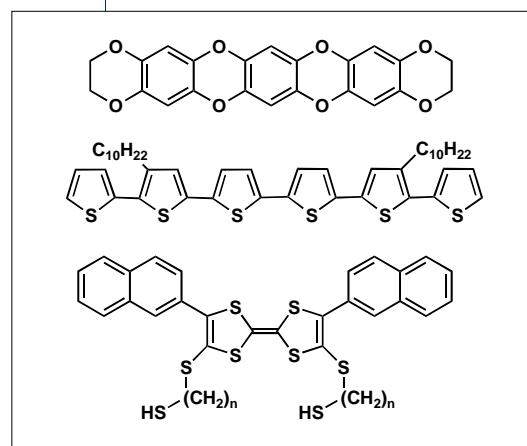
Synthesis and properties of electroactive organic materials

Jonas Hellberg

Organic compounds as electrical conductors are a relatively new phenomenon. Cation radical salts of electron-rich aromatic donors belong to a class of compounds where metallic conductivity and even superconductivity can be found. Our group is studying the synthesis and properties of these fascinating materials. Most systems are based on a tetrathiafulvalene, thiophene,

or dibenzodioxine core; examples of structures synthesized are shown in Figure 2. Our group is also engaged in the modification of these systems to self-assembly and Langmuir-Blodgett amphiphiles, for use in thin-film applications for molecular electronics, *e.g.* amorphous organic transistors. We are also studying the effect of chalcogenation substitution on the light-emitting diode (LED) properties of polythiophenes.

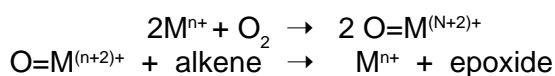
Figure 2. Examples of electron-rich aromatic donors.



Catalytic oxygenation reactions

Christian Linde

The development of an efficient catalytic system for aerobic oxygenation reactions remains a great challenge in chemistry of today. Several biological systems, *e.g.* cytochrome P-450, are able to convert hydrocarbons to alcohols by using dioxygen as the terminal oxidant. These systems generally require a sacrificial reductant to deliver the electrons and protons needed to complete the catalytic cycle. Single-oxygen transfer agents, *e.g.* iodosobenzene, peracids, peroxides, N-oxides and hypochlorite are therefore used by chemists in order to avoid the need for stoichiometric amounts of co-reductant. However, these oxidants are either expensive or produce stoichiometric amounts of the reduced form of the oxidant as a byproduct. The generation of active single-oxygen transfer species directly from dioxygen which could transfer both oxygens to *e.g.* an alkene would therefore be desirable especially for industrial applications.



Our research is focused upon the study and development of ruthenium complexes for catalytic aerobic oxygenation reactions. There are some properties of ruthenium that makes it a promising candidate for this purpose. There are several oxidation states on ruthenium, which are reversibly accessible. Stable oxo-ruthenium species are known, $[\text{Ru}^{\text{VI}}(\text{O})_2]$ and $\text{Ru}^{\text{IV}}\text{O}$, which do transfer oxygen to *e.g.* alkenes. Indeed, there are also a few examples of ruthenium catalyzed oxygenation reactions where dioxygen is used as the oxygen source without the aid of a coreductant. These systems all work catalytically but reaction rates are extremely slow and product selectivity is often poor. We are using both experimental and theoretical methods in collaboration with Dr. Mats Svensson, KTH, in order to investigate these systems and to design new complexes that are able to catalyze the reaction with increased efficiency. An additional goal is to develop stereoselective catalysts for these reactions.

Transition metal catalysis in selective organic synthesis

Christina Moberg

Access to synthetic methods allowing the preparation of chiral compounds is highly important as such compounds are needed for a variety of applications, including the production of pharmaceuticals, flavors, fragrances, food additives *etc.* By the use of chiral transition metal catalysts, large amounts of chiral compounds can be prepared using a small amount of the metal compound. Asymmetric metal catalysis is therefore a strongly expanding area within the field of organic chemistry.

Our research deals with the investigation of transition metal-catalyzed processes and the study of metal complexes and their interaction with or-

ganic molecules. It involves the areas of catalysis, organometallic chemistry, coordination chemistry and host guest chemistry. The general aim of our studies is to develop new chemo-, regio- and stereoselective (particularly enantioselective) processes for application in organic synthesis. The work involves the design and preparation of new ligands for use in stereoselective processes. In the design of the new ligands and metal complexes, particular attention is devoted to the steric, electronic and symmetry properties of the compounds.

One type reaction that has been studied by our group is the palladium- and molybdenum-catalyzed substitution of allylic acetates and carbonates. The reaction is synthetically highly versatile as it allows the formation of carbon – carbon as well as carbon - heteroatom bonds with high regio- and stereoselectivity. For the molybdenum-catalyzed process a new catalyst, yielding the product with higher stereoselectivity than previously published catalysts, has been prepared. The reactions, where this catalyst as well as some catalysts containing palladium are used, have been shown to be accelerated by microwave irradiation, which allows complete reaction within a few minutes without loss of selectivity, see Figure 3.

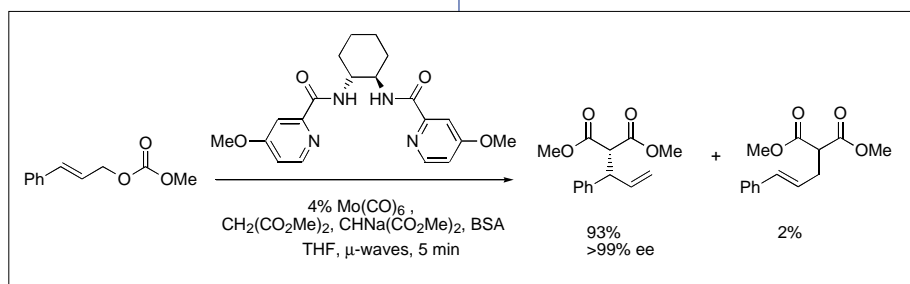


Figure 3. Microwave-mediated enantioselective molybdenum-catalyzed allylic alkylation.

In one project chiral ligands with rotational symmetry, in particular with C₂ and C₃ symmetry, are studied in catalytic applications. Furthermore, chiral ligands containing additional groups capable of supramolecular interactions with the reacting substrates are prepared and investigated in catalytic processes. To allow recovery and use of the often expensive ligands and metal catalysts, methods for grafting the catalysts on polymeric supports are being developed.

Within the framework of an SSF programme (the Swedish Foundation of Strategic Research) on nanochemistry, a collaboration with the instrumentation laboratory at the Department of Signals, Sensors and Systems, KTH, was initiated. One aim of the project is to develop microdevices for catalytic reactions. Such devices are useful *et cetera* for combinatorial chemistry. So far, chiral metal complexes have been bound to silica chips. The chips are presently tested for catalytic applications.

Biocatalysis and natural product chemistry

Torbjörn Norin

Studies of enzyme properties and of enzyme/substrate and enzyme/solvent interactions are current research topics, which are carried out in close collaboration with theoretical chemists of our department as well as with biochemists of the Department of Biotechnology. Methods for asymmetric synthesis and in particular the use of enzymes for this purpose are important goals of our program. Simulation models (molecular modelling) and a computational approach have been developed for prediction of selectivity and for enzyme modification by protein engineering. Focus has been on the detailed catalytic mechanism and dynamics of hydrolytic enzymes such as lipases and esterases. The geometries of the transition states of the hydrolytic reactions have been calculated. Water assisted catalysis and the role of

water in these systems have been studied (Figure 4 and 5). The docking modes of substrates of secondary alcohols have been calculated and provide good models for the prediction of enantioselectivity [for references see F. Hæffner and T. Norin, *Chem. Pharm. Bull.* **1999**, *47*, 591]. Site-directed mutagenesis has been applied to improve the enantioselectivity of a lipase catalyzed reaction (*Candida antactica* lipase B).

Figure 4. Part of the active site of *Rhizomucor miehei* lipase showing the water channel ending at the carbonyl carbon of the acyl enzyme intermediate.

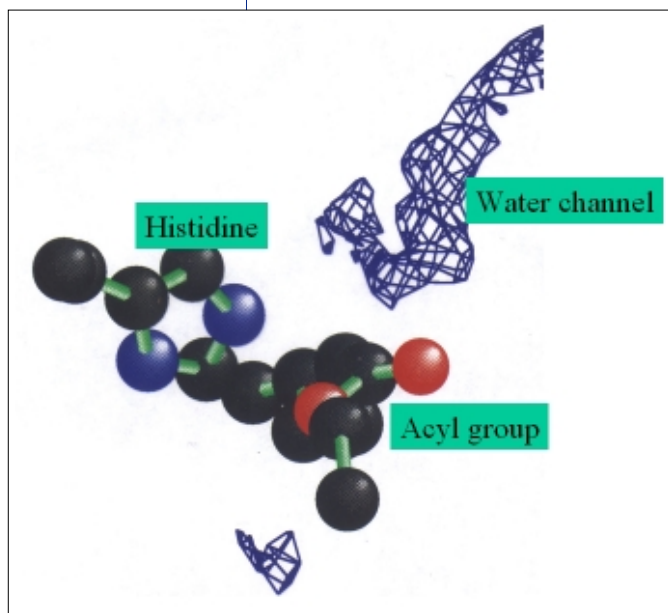
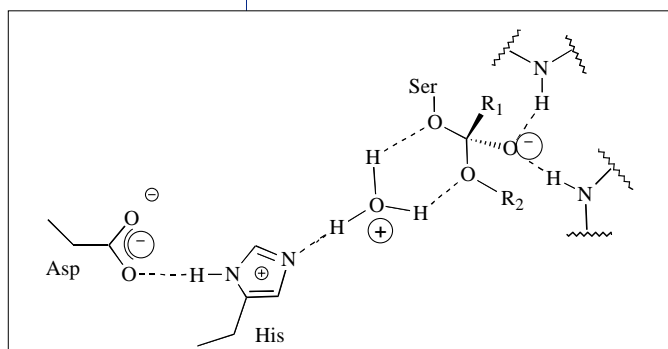


Figure 5. A hypothetical 6-membered ring transition state of a water assisted enzyme catalyzed ester hydrolysis reaction.



Development of new methodology in organic synthesis

Peter Somfai

The focus of our research efforts is efficiency in organic synthesis and various aspects of this can be readily identified. For example, the yield of a given reaction, its environmental friendliness and cost efficiency, if it can be converted into a catalytic process or, alternatively, into an asymmetric one are all important issues that have to be considered when choosing a suitable reaction for affecting a desired transformation. We are mainly interested in developing new methodology in organic synthesis with the intention of applying the chemistry for the total synthesis of natural products. Presently, we are interested in finding new routes to scalemic vinylaziridines and study their selective ring expansions, develop a regio- and stereoselective synthesis of *vic*-amino alcohols, and investigating the intramolecular cyclization of cationic aminyl radicals. These projects are summarized below.

1. Ring-expansion in vinylaziridines

Vinylaziridines are useful intermediates in organic synthesis. We have recently developed a novel entry to *N*-H vinylaziridines and shown that these substrates can be selectively ring expanded to the corresponding 6- and 7-membered heterocycles, respectively, in good yield and excellent selectivity (Figure 6). We are currently investigating the scope and limitations of these transformations, and we are also applying them as key steps in the synthesis of alkaloids.

2. Stereodivergent synthesis of *vic*-amino alcohols

1,2-Amino alcohols represent a structural subunit common to several biologically active compounds as

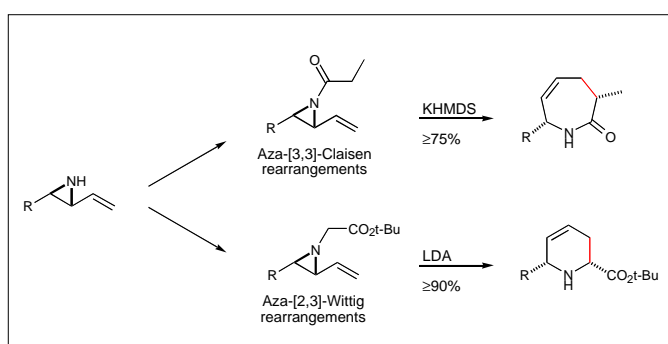


Figure 6. Ring-expansion in vinylaziridines.

well as to auxiliaries and ligands for asymmetric synthesis. Although large efforts in developing efficient routes leading to *vic*-amino alcohols have been made, no general route towards all eight possible isomers (regioisomers included) has been presented. The development of such a route would be ideal for obtaining structure – activity relationships for pharmacologically active derivatives incorporating this structural motif and for optimizing the performance of chiral ligands containing this substructure.

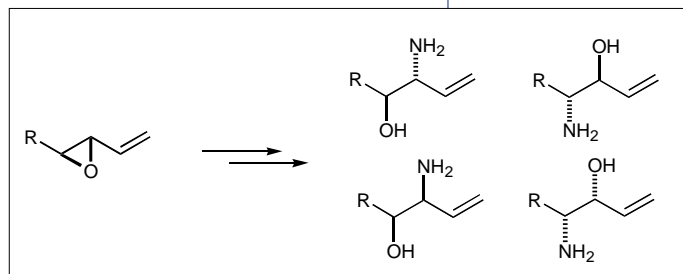


Figure 7. Synthesis of *vic*-amino alcohols from a vinyl epoxide.

We are developing a general and stereodivergent route to all possible isomers of *vic*-amino alcohols starting from vinyl epoxides, that can be readily synthesized (Figure 7). The chosen synthesis route leads to four isomers of the *vic*-amino alcohol, the remaining four isomers can be obtained by starting with the enantiomeric vinyl epoxide.

3. Intramolecular cyclization of cationic aminyl radicals

N-Chloroalkenylamines can be cyclized into the corresponding pyrrolidines under acidic, photochemical or metal-catalyzed conditions (Figure 8). We are investigating the inherent diastereoselectivity of this reaction with the aim of developing an enantioselective version.

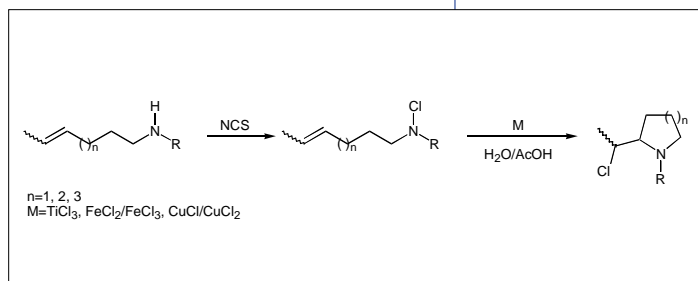


Figure 8. Metal-catalyzed cyclization of *N*-chloroalkenylamines.

Theoretical studies of organometallic reactions

Mats Svensson

Computational based chemistry is a fast growing research field both in the academic world and in the industry. The speed of modern workstations together with the development of more efficient methods and algorithms have made computer-based chemical research an interesting complement to experimental chemistry. As a confirmation, the 1998 Nobel prize in chemistry was awarded to two quantum chemists, John Pople and Walter Kohn. Our main interests concern the chemistry involving transition metals as catalysts. This is a field particularly well-suited for a theoretical study since many of the intermediates are hard to isolate under normal experimental conditions.

We are working in close collaboration with experimental groups in our department and at other universities. The goal is an increased understanding of the electronic and steric effects governing the reaction profiles of organometallic reactions. Projects presently under study are:

- *Epoxidation of alkenes catalyzed by manganese-salen complexes.* This is an in house collaboration in the organic chemistry group at KTH, Dr. Christian Linde, together with professor Björn Åkermark, Stockholm University, and assoc. professor Per-Ola Norrby at the Royal Danish School of Pharmacy. The theoretical part of this project is aiming for an understanding of the mechanism governing the isomerization and the selectivity of this important epoxidation reaction. The reaction is a two-state reaction in which the spin changes from triplet to quintet. The timing of the spin-flip is believed to be important for the amount of cis-trans isomerization (see Figure 9).

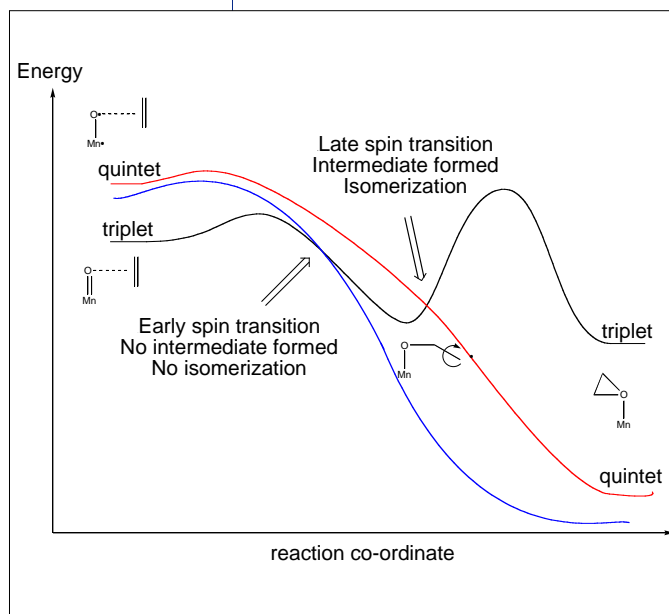


Figure 9. The potential energy profile for the Mn(salen) catalyzed epoxidation of alkenes.

- *Late transition metal complexes as catalysts for olefin polymerization.* The initial steps, the π -complexation and migratory insertion of the olefin into the metal-alkyl bond is studied in detail in order to understand the influences of the substituent on the olefin and the role of the metal. This is a very promising reaction for the development of new polymers; a collaboration between Dr. Krister Zetterberg and Dr. Staffan Strömberg.
- *Regiocontrol in the Heck reaction.* A combined theoretical and experimental study of ligand and substrate effects on the regioselectivity in the Heck reaction using the biphosphine ligands dppe and dppp; a collaboration with professor Björn Åkermark and Henrik von Schenck.
- *Nitrogen fixation by nitrogenases.* We have studied the fixation of nitrogen, step by step using Fe_2 and Fe_4 models for the active site in the nitrogenase. This projects is a collaboration with professor Per Siegbahn and Joakim Westerberg, Stockholm University, and professor Robert Crabtree, Yale University.

Transition-metal catalysis and olefin polymerization

Krister Zetterberg

In its simplicity, the straightforward association of an alkene to a σ -alkyl transition metal and the following migratory insertion (M.I.) represent a part in common for some, in all respects, very productive organic reactions catalyzed by transition metals.

Actually, this short sequence can summarize the process of strategic scale transition metal-catalyzed polymerization of alkenes. Despite the importance of this process and the vast research caused by it, there still remains an uncomfortably large number of chemical questions to be settled. These important questions are to be answered by research in the field of fundamental organometallic chemistry.

Our research is especially devoted to the chain-building step, the migratory insertion. The experimental studies are combined with *ab initio* calculations, the latter in cooperation with Mats Svensson at our division.

Our efforts will concentrate on calculations combined with experimental work.