

**CHIM3430 Chimie organique avancée**

[22.5h] 2.5 crédits

Enseignant(s): Istvan Marko (coord.)
Langue d'enseignement : français
Niveau : Troisième cycle

Objectifs (en termes de compétences)

Enseignement de troisième cycle à périodicité bisannuelle visant à approfondir les connaissances des étudiants en chimie organique. L'enseignement traitera de stratégies récentes pour l'obtention de cibles particulières et de méthodologies générales assurant le contrôle de la sélectivité (chémo-, régo-, stéréo- et énantiosélectivité) en synthèse

Objet de l'activité (principaux thèmes à aborder)

Le contenu de cet enseignement diffèrera d'année en année ; il abordera notamment les aspects suivants :- les nouveaux réactifs, les nouvelles réactions et les nouvelles stratégies en synthèse totale ;- l'utilisation des métaux de transition en synthèse organique ;- les développements récents en chimie radicalaire, en photochimie et en chimie hétérocyclique ;- la synthèse asymétrique ;- la chimie supramoléculaire ;- la chimie organique des dérivés du bore, du silicium et du phosphore.

Résumé : Contenu et Méthodes

Enseignants : Prof. Dr. Norbert KRAUSE (11,5 h)

Yoshinori YAMAMOTO (11 h)

1ère partie: Prof. Dr. Norbert KRAUSE

Contenu du cours :

Copper- and Rhodium-Catalyzed Enantioselective 1,4-Additions to Substituted Enones

Tetrasubstituted Allenes in Ligand Synthesis

Stereoselective Synthesis of α -Allenic Isocarbacyclin Derivatives

Synthesis of New Macrocyclic Allenes

Transition Metal-Promoted Synthesis of Functionalized and Unfunctionalized Pyridylallenes

Oxidation of Allenic Zirconium Enolates : Efficient Access to Functionalized α -Hydroxyallenes

Allenes Synthesis with Functionalized Grignard Reagents

Diastereoselective Synthesis of α -Hydroxyallenes with Functionalized Grignard Reagents

Diastereoselective Gold-Catalyzed Cyclization of α -Hydroxyallenes : Precursors in Natural Product Synthesis

Gold-Catalyzed Cycloisomerization of Aryl-Substituted α -Hydroxyallenes : Synthesis of Goniathalesdiol

Gold-Catalysis in Organic Synthesis : Mechanism of the Cycloisomerization of α -Hydroxyallenes to 2,5-Dihydrofurans.

2ème partie: Yoshinori YAMAMOTO

Contenu du cours :

(1) Total Synthesis of Gambierol and Brevetoxin B

Marine polycyclic ethers have attracted much attention of synthetic chemist due to their structural novelty and potent biological activities. Recently, we have developed a new method for the convergent synthesis of polycyclic ether frameworks via the intramolecular allylation of α -acetoxy ethers followed by ring-closing metathesis. The methodology was successfully applied to the total synthesis of gambierol and brevetoxin B. DFT computations for understanding the stereochemistry of a key cyclization step leading to Brevetoxin B has been carried out. Details of the studies will be discussed.

(2) "Coinage Metals" in Organic Synthesis. p -Electrophilic Lewis Acids Catalyzed New Organic Transformation

A typical role of Lewis acids to enhance the reactivity and selectivity is the formation of a complex with lone pairs (s -electrons). However, some Lewis acids form a complex with p -electrons preferably. We found that the AuX_3 -catalyzed intermolecular [4+2] benzannulation between enynal units 1 and alkynes gave the naphthyl ketones 2 in high yields, and a similar [4+2] cycloaddition between 1 and alkenes took place in the presence of $Cu(OTf)_2$ catalyst to give the 1,2-dihydronaphthalene derivatives 3 in good to high yields (Scheme 1). Application of this type of reactions to the synthesis of polycyclic natural products, such as (+)-ochromycinone and (+)-rubiginone B2, will be discussed.

(3) Palladium-Catalyzed C-N Bond Formation

Hydroamination, the formal addition of N-H bond across a C-C unsaturated bond, is a highly desirable and atom-economical process for the preparation of amine derivatives. It is known that hydroamination of alkenes and alkynes can be catalyzed by (1) organolanthanides, (2) alkalimetals, (3) early (Ti and Zr) and (4) late (Pd, Rh, Ru, Ir and Ni) transition metals, and (5) heterogeneous systems. Depending on the catalytic system, either an activation of the C-C multiple bond or the N-H bond takes place; the former activation occurs in the case of (4) and the latter type takes place in the case of (1)-(3). The other important knowledge for the hydroamination is that (a) the intermolecular hydroamination is more difficult to proceed than the intramolecular version and (b) the hydroamination of alkynes is easier to proceed than that of alkenes.

We found that the hydroamination of alkynes proceeds in the presence of combined catalyst of palladium and benzoic acids, and also this type of hydroamination proceeds in a catalytic asymmetric manner using Renorphos. Related reactions, such as hydrocarbonylation and hydroalchoxylation, will be discussed.

Autres crédits de l'activité dans les programmes

SC3DA/C

Diplôme d'études approfondies en sciences (Chimie)

(2.5 crédits)