Chemistry of Iminium Salts and Related Compounds

This issue collects 13 papers relating to lectures presented at the 8th Conference on Iminium Salts (ImSaT-8), which took place in Bartholomä/Ostalbkreis (Germany) on September 11–13, 2007. Generally speaking, the common theme of this conference was the chemistry of compounds containing a C=N structural unit. Iminium salts and imines are definitely the major classes of compounds to be mentioned here. It must not be forgotten, however, that iminium and imine moieties are often found embedded in more complex functional groups. For example, the iminium group can be recognized in cationic five- and six-membered N-heteroaromatic compounds, in amidium and amidinium moieties, as well as in several 1,3-dipoles such as azomethine imines, azomethine ylides, and nitrones. The papers presented here visit all of these compound classes, providing new examples for the use of iminium salts and related compounds as substrates and reagents, and also for their occurrence as reactive intermediates.

The issue starts with two short reviews. H. Walter describes, from the point of view of an industrial research chemist, the syntheses and structure-activity relationships of pyrrole carboxamides which have attracted interest as potential agrochemical fungicides with Complex II inhibition properties. M. Małosza summarizes the efforts to prepare pyridines and quinolines with perfluoroalkyl side-chains by oxidative nucleophilic substitution of hydrogen at acceptor-substituted pyridinium and quinolinium rings.

J. Svete and colleagues have studied regio- and stereoselectivity of the microwave-assisted 1,3-dipolar cycloaddition of certain chiral pyrazolidin-1-ium-2-ides (which are semicyclic azomethine imines) with ethyl propiolate. Maas and coworker have investigated the behavior of acetylenic iminium salts toward another type of dipoles, 1,3-oxazolium-5-olates (münchnones). The latter react either as 1,3-dipoles of the azomethine ylide type or by nucleophilic conjugate addition with the iminium-activated alkynes.

Some papers report on transformations using iminium chemistry. Kantlehner, Ivanov, and colleagues show that aryl formates can be prepared by O-formylation of hydroxyarenes with triformaldehyde, which are formed conveniently in situ from sodium diformamide and methanesulfonyl chloride. In another paper, Kantlehner and colleagues introduce the novel reagent bis(diformylamino)methane which in combination with aluminum chloride constitutes a good alternative to the Gattermann-Koch and the Olah methods for the formylation of aromatic compounds. Stanovnik and coworkers describe the two-step synthesis of 1,4-dihydropyridazin-4-ones from dimethyl acetonedicarboxylate, including a dimethylaminomethylation using DMF dimethylacetal.
Heterocycles are also the subjects of three other contributions. Beckert and colleagues report that amino/imino-substituted 1,3,4-selenadiazines and 1,3,4-thiadiazines undergo ring contraction reactions when treated with aqueous acetic acid. These reactions, which include amidinium intermediates, constitute useful methods for the preparation of carboxamide-substituted 1,3,4-thiadiazoles, 1,3,4-selenadiazoles and 5-selenoxo-1,2,4-triazoles. Schulze and coworkers have found that in N-aryl-4,5-diphenyl-1,2-thiazolium salts, the N-aryl moiety can be exchanged by another one through reaction with a more basic ring-substituted aniline derivative. Kunz and coworker present the stereoselective synthesis of the quinolizidine alkaloid (-)-lasubine II; the synthesis includes a highly diastereoselective imino-Diels-Alder reaction. C=N containing functional groups in the form of ketimines (asymmetric α-alkoxyallylation) and nitron (addition of a Grignard reagent) have been employed by Jäger and coworker for the synthesis of phenylisothretonine derivatives that are of interest as taxol side-chain analogues.

Heterocyclic compounds with iminium character were the targets of two studies. Schmidt and coworker have prepared polymer-supported pyridinium-enolates which are active in reversible photocatalytic electron-transfer reactions. Schottenberger and colleagues have synthesized an impressive number of new 1-alkoxy-3-alkyl-imidazolium salts. While some of these organic salts are solids and have been characterized by their solid-state structures, others are of interest as novel room-temperature ionic liquids.

The contributions to this issue are good examples of the general usefulness of imines and iminium salts, and they illustrate once more that novel applications of these compound classes, either based on their physico-chemical properties or on their transformations in chemical synthesis, await to be detected now and in the future.

Gerhard Maas
Member of the Editorial Board