Chemistry of Iminium Salts and Related Compounds

This issue collects 15 papers which relate to lectures presented at the 7th Conference on Iminium Salts (ImSaT-7) which was held September 6–8, 2005, in Bartholomä/Ostalbkreis (Germany). Iminium salts and their neutral relatives, the imines, are frequently encountered in the large area of organic chemistry, be it as reagents, as intermediates in multiple-step syntheses, or as functional groups in target molecules of interest in different fields, such as natural product chemistry, material science, and bioactive compounds. The contributions to this issue are like spotlights on the different areas where imines and iminium salts play a role.

The account by P. Maienfisch (Basel/Switzerland) on the synthesis and activity of the successful insecticide thiamethoxam not only presents an important biologically active compound with the pharmacophoric nitroguanidine function, but also documents once more the synthetic usefulness of the classical Mannich reaction which involves a reactive methyleniminium intermediate. The Mannich reaction and Mannich bases also played a role in the preparation and transformation of pyrido[2,3-d]pyrimidines (D. Heber, Kiel). The imine function is present in various 4-amino-5-imino-4H-imidazoles which were characterized inter alia by cyclovoltammetry and could be converted into deeply colored tetraazaborapentalenes (R. Beckert, Jena).

Iminium chemistry is the basis of an important formylation reaction of aromatic and heteroaromatic ring systems. Classical Vilsmeier and Vilsmeier-Haack-Arnold methodology was used to prepare hetarene-carbaldehydes which were transformed subsequently into analogues of the alysinospin alkaloids and the β-carboline–thiohydantoin ring system (B. Stanovnik and J. Svete, Ljubljana/Slovenia) or into tetracyclic derivatives of dibenzofuran, dibenzothiophene and dibenzoselenophene (G. Kirsch, Metz/France). On the other hand, W. Kantlehner and coworkers (Stuttgart and Aalen) have probed the novel reagent combination tris(2-chloromethyl)amine/Lewis acid for the formylation of benzene and substituted benzenes. S. Laschat and coworkers (Stuttgart) have looked at the transformation of N-acylated tyrosine and m-tyrosine into 1,3-oxazoles under Bischler-Napieralski conditions and report that bulky acyl groups have an adverse effect on the yield, suggesting that chloroiminium rather than nitrilium ions are involved in the cyclization. Short-lived iminium ions also appear in the mechanistic scenario of some other transformations, e.g., in the two-carbon ring expansion of cyclic enamines with dimethyl acetylenedicarboxylate and subsequent thermal isomerization of the products (G. Maas, Ulm). DMF-dimethylacetal, hexamethylguanidinium salts and various amidium salts have been employed to functionally modify certain pyranosides, introducing in particular push-pull dienyl or
dimethylaminomethylene substituents as well as fused pyrazole and pyrimidine rings (K. Peseke, Rostock).

Sometimes, the iminium function comes along in disguise. This is the case when the iminium moiety is part of a heteroaromatic ring system or another conjugated \( \pi \)-system. Examples are 4,6-diamino-1,3,2-dioxaboronium salts and related compounds which are mentioned in the review on monocyclic and spirocyclic boronium compounds (H. Hartmann, Dresden), bis- and tris(4-dimethylaminopyridinio)pyrimidines (A. Schmidt, Clausthal), and 2-di-alkylamino-1,2-thiazolium salts (B. Schulze, Leipzig). Undeniably, nitrones represent another type of iminium derivatives. One paper describes the synthesis of novel functionalized five-membered cyclic nitrones by bromocyclization of unsaturated oximes (V. Jäger, Stuttgart), another one shows how a small library of 1,3-aminoalcohols can be prepared from a 3-oxopiperazine-based cyclic nitrone using solid-support techniques (K. Rück-Braun, Berlin).

Evening lectures in conferences often serve the purpose to widen the horizon of the participants beyond the specific theme of the conference. This was certainly true for the lecture of A. R. Katritzky (Gainesville/Florida) who summarized the results of a 15-year effort to implement QSPR (Quantitative Structure-Property Relationships) techniques for the prediction of a range of physical and other properties from chemical structure. The review by A. R. Katritzky, D. A. Dobchev (Tartu/Estonia) and M. Karelson (Tallinn/Estonia) illustrates the applicability and power of QSPR techniques for the prediction of very diverse properties of chemical compounds ranging from physical and chemical to biological and technological properties.

Gerhard Maas
Member of the Editorial Board