

## Chemistry of Iminium Salts and Related Compounds

The articles in this themed issue of *Zeitschrift für Naturforschung B – Chemical Sciences* relate to oral and poster contributions presented at the 10<sup>th</sup> Conference on Iminium Salts (ImSaT-10), which took place in Bartholomä/Ostalbkreis (Germany) on September 12–15, 2011.

Iminium, formamidinium, and pyridinium salts are in the focus of four papers. *H. Hartmann* and *J. Schönewerk* (Dresden) report that the reaction of *N,N*-diarylformamides with oxalyl chloride does not provide the expected chloroformamidinium chloride, as in the case of *N,N*-dialkylformamides, but the isomeric non-ionic (dichloromethyl)diarylamines. *W. Kantlehner* and coworkers (Stuttgart/Aalen) give an account of their studies on the reaction of *N, N, N', N'*-tetramethyl-chloroformamidinium chloride with sodium, potassium, magnesium, zinc/copper couple, and low-valent titanium. In the course of synthetic efforts toward the formylation of functionalized thiophenes, *D. Kaufmann* and coworkers (Clausthal) made the unexpected observation that 2-chloro- and 2,5-dichlorothiophenes bearing additional electron-donating substituents under Vilsmeier-Haack conditions undergo a regioselective *ipso*-formylation with displacement of a chloro substituent. *E.-U. Würthwein* and coworkers (Münster) have found that the deprotonation of 1-allyl-2-iminopyridinium salts with a strong base triggers an electrocyclic 1,5-cyclization to give imidazo[1,2-*a*]pyridines after air oxidation. Quantum chemical calculations were performed to elucidate the mechanistic details of the cyclization reaction.

Four papers deal with guanidines and guanidinium salts. *W. Kantlehner* and coworkers (Stuttgart/Aalen) have examined potential synthetic routes to 2-formyl-1,1,3,3-tetramethylguanidine. While this compound can be prepared from tris(dimethylamino)-ethoxy-methane and formamide, reactions of 1,1,3,3-tetramethylguanidine with common formylating reagents, such as DMF dimethylacetal, generate the isomeric 1,1-dimethyl-3-dimethylaminomethylene urea. In a research program on cationic lactide polymerization, *S. Herres-Pawlis* and her coworkers (Dortmund/München) have prepared and structurally characterized Zn(II) complexes with new guanidine-quinoline ligands. The complexes formed from zinc triflate show high activity in the polymerization of *rac*-lactide. Hexaalkylguanidinium-based ionic liquids were investigated as reaction media for transition metal-catalyzed carbenoid reactions of diazoesters by *G. Maas* and coworkers (Ulm). Among other aspects, the concept for catalyst immobilization in the ionic liquid was investigated for rhodium- and ruthenium-catalyzed styrene cyclopropanation and intramolecular N–H insertion. *V. Jäger* and colleagues (Stuttgart) present the synthesis of new chiral ionic liquids, among which are those with the

formally  $C_3$ -symmetric  $N, N', N''$ -tris(1-phenylethyl)guanidinium cation, and discuss their structures in solution and in the solid state.

Some chemistry of azolium salts is addressed in two articles. *A. Schmidt* and coworkers (Clausthal) compare two types of heterocyclic mesomeric betaines, pyrazolium-3-carboxylates and pyrazolium-4-carboxylates as precursors for nucleophilic heterocyclic carbenes. A carbene could be generated only from the former pyrazole betaine, and a pyrazol-3-ylidene palladium complex derived therefrom could be isolated and structurally characterized. *H. Schottenberger* and *G. Laus* (Innsbruck) have studied bromination reactions of 1-hydroxyimidazole, 3-hydroxyimidazolium-1-oxide and its 2-methyl derivative. The obtained mono-, dibromo- and tribromoimidazole derivatives should be useful for further derivatization, for example catalytic C,C coupling and heterofunctionalization.

*R. Beckert* and associates (Jena) report on an unexpected oxidative cyclization cascade of 2,3-diarylamino-quinoxalines giving rise to hexacyclic bis-benzimidazo[1,2- $\alpha$ :2',1'- $c$ ]quinoxalines. These compounds show a strong blue fluorescence in solution and have a potential as ligands in transition metal complexes.

Functionalized enamines appear as synthetic building blocks in two papers. *H. Kunz* and *E. Klegraf* (Mainz) have achieved the stereoselective synthesis of 3-substituted and 3,4-disubstituted piperidine and piperidin-2-ones. The key step in their synthesis, which starts from 2-pyridone, is the reaction of electrophiles with amide enolates derived from an *N*-galactosyl-piperidin-2-one. *W. Kantlehner* and coworkers (Stuttgart/Aalen) present an improved procedure for the preparation of trimethoxyacetonitrile, which was then used for the  $\alpha$ -trimethoxymethylation of nitriles, ethyl acetate, and methylketones. The resulting  $\alpha$ -imino/enamino ortho-carboxylic acid esters could be cyclized to form substituted pyridinium salts and a pyridine-2-orthocarboxylic acid trimethylester.

In summary, the contributions to this issue demonstrate once more the versatility of the chemistry of imines and iminium salts of various kinds. Interesting structural and mechanistic aspects as well as the broad scope of synthetic applications nourish the continuous attractivity of this specific branch of organic chemistry.

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Member of the Editorial Board