

Chemistry of Iminium Salts and Related Compounds

The papers in this issue of *Zeitschrift für Naturforschung B – Chemical Sciences* are related to scientific contributions to the 9th Conference on Iminium Salts (ImSaT-9) which took place in Bartholomä/Ostalbkreis (Germany) on September 7–10, 2009.

Traditionally, compounds containing a C=N bond form the general basis of this conference series, but iminium salts and imines certainly show up most frequently in the oral and poster presentations. As the contributions to this issue show, the terms “iminium salts” and “imines” should not be understood as limited to the definition set by the nomenclature rules. For example, iminium character is not only found in the “true” iminium salts, but also in amidium, guanidinium, imidazolium and related salts, to some extent also in enamino-carbonyl compounds.

The orthoester amides dimethylformamide dimethylacetal and *tert*-butyloxy-bis(dimethylamino)methane (Bredereck's reagent) are useful for the introduction of a dimethylaminomethylene group adjacent to a carbonyl function. *B. Stanovnik* and coworkers (Ljubljana) applied this transformation to the condensation product obtained from malononitrile and a dialkyl acetone-1,3-dicarboxylate, for which they established the constitution of an alkyl (3-cyano-6-alkoxy-2-oxo-1,2-dihydropyridin-4-yl)acetate, thereby correcting an earlier structural assignment found in the literature. *J. Svete* and coworkers (Ljubljana) made use of Bredereck's reagent in a six-step synthesis of a series of 4-(arylamino)methylidene-substituted (S)-*N*-Boc-pyroglytamic acid derivatives, which can be considered as conformationally constrained heterocyclic analogs of the dipeptide Δ - β -Ala-AlaOH.

P. Pale and coworkers (Strasbourg) give an overview of their work on metal-exchanged zeolites as green catalysts for several organic reactions. The solid catalysts can easily be recovered by filtration and can be reused several times without significant changes of effectiveness. A copper(I)-exchanged zeolite performed well in catalyzing the 1,3-dipolar cycloaddition of organoazides and terminal alkynes, and also the synthesis of propargylamines by a Mannich-type addition of alkynes to iminium ions produced *in situ* from aldehydes and amines. This three-component reaction was found to have a wide scope and could be run without an additional organic solvent.

The reaction of bis(arylamino)-substituted pyrido[1,2-*a*]pyrazines with substituted 1,4-naphthoquinones was used by *R. Beckert* and his coworkers (Jena) to prepare a series of highly substituted 2-azaanthraquinones. The latter compounds are strong chromophores, and due to their polyfunctionality they can also act as novel multifunctional ligands.

Four contributions are devoted to guanidines and guanidinium salts. *S. Herres-Pawlis* and coworkers (Paderborn) have synthesized and structurally characterized several new copper(I) and copper(II) complexes with *N*-peralkylated bis-guanidine ligands. First results concerning the catalytic performance of these complexes for the atom transfer radical polymerization of styrene are reported. *W. Kantlehner* (Aalen, Stuttgart), *H. Hartmann* (Merseburg) and *J. C. Ivanow* (Sofia) and their coworkers have synthesized a large number of peralkylated guanidines and guanidinium salts, mainly with the intention to furnish new ionic liquids. For future applications, the availability of a large collection of guanidinium-based ionic liquids with different physicochemical properties is desirable, which can be fine-tuned by variations of the alkyl chain length and of the anion as well as by additional functionality in the cation. For applications as reaction media, the polarity of ionic liquids is one of the relevant parameters. *G. Maas* (Ulm), *M. Bogdanov* (Sofia, Aalen) and their coworkers have therefore determined polarity data for a large number of hexaalkylguanidinium salts with different anions on the $E_T(30)$ scale using Reichardt's dye. In another contribution, *W. Kantlehner* and coworkers describe the synthesis and the solid-state structures of dicationic pentasubstituted guanidinium salts, *N*-(ω -dimethylammonio)alkyl-*N',N',N'',N''*-tetramethylguanidinium chloride tetraphenylborate, for which intra- and intermolecular N-H...Cl hydrogen bonds contribute to the molecular and crystal structure.

Imidazolium salts are in the focus of two papers. *D. Kunz* (Tübingen) and coworkers present reactivity studies on the uronium salts derived from dipyrido-[1,2-*c*;2',1'-*e*]imidazol-2-ones. Borohydride reduction provides an access to the dipyridoimidazolium salts, with *in situ* formation of the nucleophilic carbene as a side reaction under certain conditions. *H. Schottenberger* and coworkers (Innsbruck) describe the synthesis of new 1,3-di(benzyloxy)imidazolium salts which are converted into the imidazole-2-thione, -2-selone, and 2-bromoimidazolium salt *via* the nucleophilic heterocyclic carbene intermediate. Also described are the formation of silver(I), gold(I), and rhodium(I) complexes with these carbene ligands as well as the solid-state structures of the complexes.

D. Kaufmann (Clausthal) and coworkers show how 2-nitro-perchlorobutadiene can be converted into a great variety of other compounds with a C_4 or C_3 core by stepwise reaction with heteronucleophiles. These compounds feature an unusual accumulation and combination of functional groups, among them imines, amidines and nitroenamines.

V. Jäger (Stuttgart) gives an account of his research group's occupation with 2-oxazolinium salts. Through reactions with a wide range of nucleophiles, α -deprotonation and reductive cleavage of the nitrogen-oxygen bond, this particular category of iminium salts give access to several classes of multiply functionalized

compounds, including aminoalcohols, aminopolyols, 1,2-diamines, and amino acid derivatives.

The papers in this issue demonstrate once more that the chemistry of iminium salts and imines is a multifaceted area of organic chemistry. Reactivity, versatility in synthesis, and physicochemical properties represent only a few keywords characterizing the importance of these functional groups. My thanks go to all the scientists who by their contributions have documented the ongoing interest in the chemistry of iminium salts and related compounds.

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