

Chemistry of Iminium Salts, Imines, and Related Compounds

Most of the papers in this themed issue of *Zeitschrift für Naturforschung B – Chemical Sciences* originate from oral contributions or poster presentations, which were given at the 11th Conference on Iminium Salts held at Goslar (Germany) on September 22–25, 2013. Over more than twenty years now, the biennial conference series has brought together synthetically oriented chemists working in one way or another with iminium salts, imines, enamino(n)es and related compounds.

Preformed or *in-situ* formed iminium salts are popular reagents for the introduction of a formyl group at electron-rich aromatics and other electron-donating reaction centers. *H. Hartmann* and coworkers (Dresden), however, present a case where the Vilsmeier reagent ($[(\text{Me}_2\text{N})_2\text{C}=\text{CHCl}]^+ \text{Cl}^-$) does not induce the formylation of a 2-hydroxynaphthalene ring system but converts the hydroxy group into a leaving group, thus preparing the naphthalene moiety for a cyclization reaction to obtain fluorescent polycyclic azolo[1,2,4]triazinium salts. *G. Kirsch* and coworkers (Metz/France) have used the Vilsmeier-Haack-Arnold reaction to convert 2-alkylidene-malononitriles into 2-chloro-3-cyanopyridines which were subsequently transformed into (1,2,3-triazol-1-yl)-thieno[2,3-*b*]pyridines.

The so-called Bredereck-Simchen reagent (*tert*-butyloxy-bis(dimethylamino)methane) is an aminal ester, which is known to formylate primary amines and even weakly acidic methylene compounds. *Kantlehner* and coworkers (Aalen, Stuttgart) report now the one-step formation of 1,3-dimethylthymine from this reagent and *N*-methylpropionamide, a result that is both unexpected and not yet well understood mechanistically. Another two papers from the same research group deal with the optimized laboratory synthesis on a 1–2.5 molar scale of three powerful formylating reagents: tris(dichloromethylamine), *N,N,N',N'*-tetraformylhydrazine, and tris(diformylamino)methane.

Iminium salt intermediates are involved in Ugi four-component reactions which have been applied by *T. J. J. Müller* and coworkers (Düsseldorf) in a modular approach to phenothiazine-aromatic hydrocarbon couples separated by an α -acetyl-amino-carboxamide backbone. The electronic properties, including the photo-induced electron-transfer, of these compounds were studied by cyclovoltammetry, spectroscopy and quantum-chemical calculations.

The reactivity of acetylenic iminium salts is in the focus of two papers. *B. Stanovnik* and colleagues (Ljubljana/Slovenia) present a metal-free access to 2,4,5-trisubstituted pyridines and pyridine-*N*-oxides, starting with a [2 + 2] cycloaddition of acetylenic iminium salts and various enamino(n)es that were generated *in situ* from methyl ketones and dimethylformamide dimethyl acetal. *G. Maas* and coworkers (Ulm) were able to isolate dicationic 1 : 1 adducts from the conjugate addition of isoquinoline at propyne iminium salts, and dicationic 1*bH*-pyrido[2,1-*a*]-isoquinoline-1,3-diyl-bis(methyleniminium) salts resulting from a pseudo three-component reaction.

Guanidines and guanidinium moieties can be found in two papers. *D. Kunz* and coworkers (Tübingen) have prepared a dipyrifidofulvalene from a twofold pyridoannulated guanidinium salt. Their target compound appears to have the highest ylide character known so far among diamino-fulvenes and -fulvalenes, according to a crystal structure determination and DFT calculations. *Herres-Pawlis* and coworkers (München, Dortmund) describe two new copper(II) halide complexes with an *o*-phenylene-bridged bis(tetramethyl)guanidine as a ligand and the application of this ligand for the CuBr-catalyzed atom transfer radical polymerization of styrene.

An iminium moiety can also be recognized as a part of various nitrogen-containing heteroaromatic cations. *A. Schmidt* and coworkers (Clausthal) have synthesized indol-2-yl- and indol-3-yl-pyridinium salts and have converted them into ylides, which are members of the class of heterocyclic mesomeric betaines. Theoretical calculations have provided information on the bond structure and frontier orbitals of these ylides. *R. Wilhelm* and coworkers (Paderborn) have found that imidazol(in)ium 2-dithiocarboxylate betaines can be used for the colorimetric detection of Hg^{2+} and Ag^+ ions. A 1,3-thiazolium ring is part of the molecular structure of thiamine pyrophosphate (vitamin B₁), a co-enzyme involved in many enzymatic processes in all kinds of living matter. In an informative essay, *N. Müller* (Wallhausen) writes about the relevance of thiamine pyrophosphate for wine-making, looking in particular at thiamine-dependent enzymatic reactions of microorganisms (yeasts and lactic acid bacteria) and their influence on the wine aroma. (Conference participants had the pleasure

to get a better understanding of this by practical examples.)

Azomethine imines are useful 1,3-dipolar building blocks for the synthesis of diazoles by [3+2] cycloaddition reactions. *J. Svete, B. Stanovnik* and their coworkers (Ljubljana/Slovenia) now report that semicyclic azomethine imines derived from 3-pyrazolidinones undergo the cycloaddition with electron-poor terminal alkynes under exceptionally mild conditions, regioselectively, stereoselectively, and in good yield, when the reaction is catalyzed with copper(I) iodide and Hünig's base.

In two papers, compounds with a reactive imine moiety serve as starting materials. *R. Beckert* and colleagues (Jena) have combined oxalic amidines and bis(imidoyl) chlorides to construct 2,5-bis(arylamino)-3,6-bis(arylimino)-3,6-dihydropyrazines which were further converted into hexaaza-pentacenes. The latter compounds show strong fluorescence with high quan-

tum yields and very small Stokes shifts. In a project to develop a new convergent synthesis of the natural product class of lamellarin alkaloids and structurally related compounds, *T. Opatz* and coworkers (Mainz) have tried to achieve a cyclocondensation of 1-benzyl-3,4-dihydroisoquinolines and cyclic/acyclic α -halogen ketones; in one case, a chromeno[2',3':4,5]pyrrolo[2,1-*a*]isoquinoline could be obtained. So far unknown ring-contracted structural analogs of the lamellarin skeleton could be prepared by a palladium-catalyzed cyclocarbonylation reaction.

The sixteen articles in this issue of the journal illustrate again the importance of iminium salts, imines, and related compounds, for example in synthetic organic, bioorganic and coordination chemistry and beyond.

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Member of the Editorial Board