



News & Views in Organic Chemistry

Editor:

Matteo Zanda

(matteo.zanda@polimi.it)

Catalytic Coupling of Haloolefins with Anilides (*J. Am. Chem. Soc.* 2005, 127, 4156-4157).

The functionalization of traditionally unreactive C-H bonds is a topic of intense current interest. Unfortunately, C-C bond forming reactions arising from C-H bond activation are less common despite the wider availability, lower price, and environmental advantages of the starting hydrocarbons compared to functionalized compounds. As a consequence, the development of efficient methods that lead to C-C bond formation is of special value.

An important goal for polymer chemists is to copolymerize nonpolar olefins with polar monomers. However, a persistent problem that has prevented researchers from using vinyl chloride and other monomers that contain leaving groups in transition-metal catalyzed polymerizations is β -heteroatom elimination. An attempt to turn this problem into something productive led to the development of a new catalytic cycle. In fact, Prof. Olafs Daugulis and postdoctoral fellow Vladimir G. Zaitsev, at the Department of Chemistry, University of Houston, Texas, recently described a novel, important catalytic coupling of haloolefins with anilides.

"Postdoc Vladimir Zaitsev was able to show that the concept is viable not only on paper but also in the lab." Said Prof. Daugulis when contacted by LOC. "An interesting feature of this catalytic cycle is that the Pd oxidation state does not change during the



Prof. O. Daugulis

reaction, setting it apart from the usual catalytic processes with the Pd(0)-Pd(II) catalytic couple. This should lead to increased functional group tolerance. Only alkenes that contain electron-withdrawing groups react with anilides, but we are trying to extend the concept to simple arenes containing no directing groups. In the latter case, we have preliminary results showing that simple haloolefins are also reactive."

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Room Temperature Ionic Liquids from 20 Natural Amino Acids (*J. Am. Chem. Soc.* 2005, 127, 2398-2399).

Ionic liquids, salts having melting point around room temperature, collect many interests from scientists in various fields such as chemistry, electrochemistry, and even biochemistry.

Prof. Hiroyuki Ohno and coworkers Dr. Masahiro Yoshizawa, and Mr.



Prof. H. Ohno

Kenta Fukumoto at Tokyo University of Agriculture & Technology have synthesized ionic liquids from natural amino acids. After coupling with 1-ethyl-3-methylimidazolium (**emim**) cation, all 20 different amino acids formed ionic liquids. "We have been synthesizing

more than one hundred unique ionic liquids from different ions." said Prof. Ohno. The idea of using amino acids as functional anions was presented by Mr. Fukumoto in 2001.

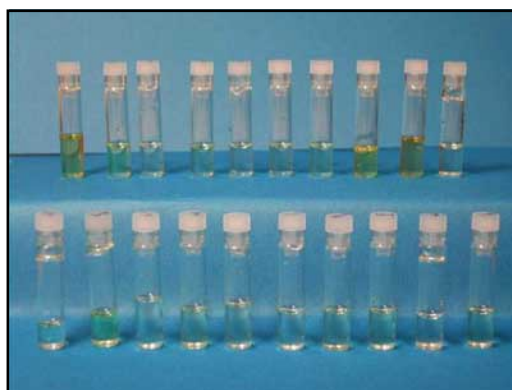
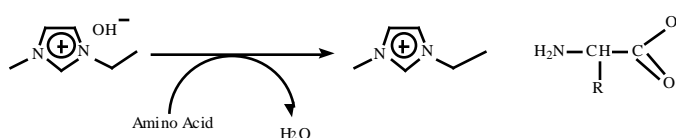
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"There were a few troublesome matters to be accomplished including purification process." said Mr. Fukumoto. "A few years later, we were surprised by the liquids composed of [**emim**] and [glycine] first prepared in our laboratory," they said.



K. Fukumoto

Amino acid ionic liquids exhibit potential to tune the physico-chemical properties of ionic liquids, because properties such as glass transition temperature, ionic conductivity and miscibility with organic molecules are dramatically changed by the side groups. "Since there is little information on the effects of anion structures on the properties, this paper should also be quite valuable to design novel ionic liquids." continued Prof. Ohno. "Amino acid ionic liquids are recognized as molten salts composed of natural ions, expecting less toxic and widely applicable for bio-related research fields. We are preparing new ionic liquids composed of both natural cation and anion such as [choline] [glycine]. Recently, these amino acid ionic liquids were found to have high polarity, suggesting some applications as polar and non-volatile solvents."



All these ionic liquids were prepared from natural amino acids.

“They are polar ionic liquids higher than any other ionic liquids ever synthesized,” concluded Mr. Fukumoto. “There are lots of potential applications surrounding these amino acid ionic liquids!”

An Acid-Stable *Tert*-Butyldiarylsilyl (TBDAS) Linker for Solid-Phase Organic Synthesis (*Org. Lett.* **2005**, *7*, 1777–1780).

Linkers for attaching substrates to solid supports play a key role in solid-phase organic synthesis and combinatorial chemistry. The ideal linker should withstand a wide variety of reaction conditions used to process the attached



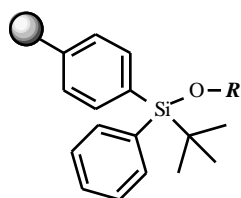
Prof. D.S. Tan, PhD.

Prof. Derek S. Tan, Dr. Christine M. DiBlasi, and Dr. Daniel E. Macks at the Memorial Sloan–Kettering Cancer Center, New York, have developed a new, robust *tert*-butyldiarylsilyl (TBDAS) linker for solid-phase organic synthesis.

“Our research program focuses on the diversity-oriented synthesis of libraries that are based on privileged structural motifs from natural products” said Prof. Tan, contacted by LOC. “For several of these syntheses, we required a linker for solid phase synthesis that would withstand strong protic and Lewis acids. Silyl ether linkers



C.M. DiBlasi, PhD.



TBDAS linker

appeared particularly attractive because they can be cleaved by mild, chemoselective fluoridolysis. However,

investigation of several previously reported silyl linkers revealed that they were not stable under the acidic conditions we required. Noting that the commonly-used TBDPS protecting group is generally stable under such conditions, we designed the TBDAS linker analogously, with linkage to the solid support through one of the aromatic rings. As hoped, this linker proved to be quite robust under a variety of acidic, and also basic reaction conditions.” Prof.



D.E. Macks, PhD.

Tan’s group demonstrated that products can be cleaved using TBAF or TAS-F and that the residual salts can be removed easily by passage of the cleavage product through a short plug of reverse phase over normal phase silica gel. Prof. Tan concluded, “Importantly, we have found that because of the closely aligned reactivity profiles of the TBDPS protecting group and our TBDAS linker, solution phase model studies can be translated to solid phase synthesis quite readily.”