

Project description for the general public:

Since a long time, carbenes are recognized as a group of reactive intermediates, which are known to display highly electrophilic properties (e.g. the most popular dichlorocarbene $[:\text{CCl}_2]$). In general, carbenes of that type can't be isolated and therefore, generated in situ are immediately reacted with the appropriate substrates possessing such structural elements as multiple bonds $\text{C}=\text{C}$ or $\text{C}=\text{X}$ ($\text{X} = \text{N}, \text{O}, \text{S}$) or, alternatively, some heteroatoms with the free valence electron pairs (alcohols, thiols, amines).

Much later nucleophilic carbenes were also discovered and their characteristic structural feature is the location of the carbenic center, with only six valence electrons (two-valent C-atom) between two surrounding heteroatoms e.g. O- or N-atoms, as is the case in dimetoxycarbene $[:\text{C}(\text{OMe})_2]$ abbreviated as DMC.

In the early 1990's Arduengo made a breakthrough discovery which consisted in the successful preparation of nucleophilic carbenes with the carbenic center located at the C(2) atom of the imidazole ring. In addition, two bulky adamantan-2-yl substituents were attached to nitrogen atoms N(1) and N(3). These representatives could be isolated and stored under ambient conditions, without further transformation (e.g. without the typical for carbenes dimerization) for a longer time. Initially, they have been considered as rare organic compounds, admittedly interesting from academic point of view, but without practical significance for further usage in organic synthesis. The following years have shown, however, that these carbenes, named as NHCs (Nucleophilic Heterocyclic Carbenes) exhibit new, remarkable catalytic properties. Besides imidazolylidenes analogous nucleophilic carbenes were obtained starting from corresponding 1,3-thiazole, 1,2,4-thiadiazole as well as 1,2,4-triazole derivatives. The rapid development of the chemistry of NHCs led to the introduction to the current organic synthesis, apart from achiral also chiral, enantiomerically pure models, which proved to be efficient catalysts in diverse asymmetric reactions. At the moment, a growing interest in the NHCs chemistry is well documented by enormous increase of the number of publications in leading chemistry journals.

Authors propose the development of a new class of nucleophilic carbenes, characterized by the presence of the alkoxy substituent bonded to the N(3) atom of the imidazole ring. They were referred to the acronym NOHC (Nucleophilic-oxo-Heterocyclic Carbenes) and for their preparation, stable, chiral and achiral 2-unsubstituted imidazole N-oxides, prepared according to well elaborated procedures, will be used as starting materials. Preliminary computational work has shown that NOHCs should exhibit enhanced nucleophilicity, which may have an important impact on the modification of their catalytic reactivity and therefore opens new horizons for their exploration.