Abstract

The evaluation of the potential of N-heterocyclic carbenes (NHC) towards the Umpolung of alkyl halides is described. Imidazolin-2-ylidenes were reacted with alkyl halides in the presence of base. This led to the formation of ene-1,1-diamines, whose structure and properties were characterized. The ene-1,1-diamines exhibit a strongly polarized exocyclic double bond. Therefore the polarization of the previously electrophilic α -carbon in the alkyl halide has been converted into a nucleophilic donor position. The strength of its nucleophilicity is dependent on further substituents. Trapping reactions with alkyl halides resulted in 2-substituted imidazolium salts, which could be deprotonated to form ene-1,1-diamines with tetrasubstituted exocyclic double bonds. Given that such compounds were not too sterically crowded, they were subjected to subsequent alkylation. The resulting salts underwent base-mediated elimination of NHC. Thereby an olefin was formed. The sequence of multiple alkylations and deprotonations and final elimination was employed for the development of a new carbene-mediated olefin synthesis. 2-Vinyl-substituted ene-1,1-diamines, synthesized from imidazolin-2-ylidenes with allylic halides, were evaluated with regard to their capability to act as synthetic equivalents for allyl anions in [3+2]-cycloadditions. The mechanism of the reaction of epibromohydrin with an imidazolin-2-ylidene forming a 2-keto-substituted ene-1,1-diamine was investigated.