Tetrahedron 70 (2014) 8672–8680

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

N-Heterocyclic carbenes from ylides of indolyl-imidazolium, azaindolyl-imidazolium, and indolyl-triazolium salts, and their borane adducts

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ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form 9 September 2014
Accepted 12 September 2014
Available online 17 September 2014

Keywords:
Mesomeric betaine
Mesoionic compound
Borane adducts
Carbenes
Indole

ABSTRACT

Indol-2-yl-imidazolium salts were deprotonated at N1 of the indole ring to give ylides. Their tautomeric *N*-heterocyclic carbenes (NHCs) were trapped by sulfur to give imidazole-2-thiones. Treatment of the ylides with triethylborane resulted in the formation of zwitterionic borane adducts. An analogous sequence of reactions was performed with 8-azaindol-2-yl-imidazolium salts, which served as precursor to prepare first representatives of a new heterocyclic ring system on reaction of their NHC-tautomers with triethylborane. Similarly, an indol-2-yl-1,2,4-triazolium salt was examined with respect to ylide–NHC tautomerism and trapping reactions. A nucleophilic ring transformation of indol-3-amine with a 1,3,4-oxadiazolium salt gave an indol-3-yl-triazolium salt, which was converted into a triazolethione by trapping of the tautomeric *N*-heterocyclic carbene of its ylide.

1. Introduction

The term ylide is used for compounds in which a carbanion is directly attached to a heteroatom bearing a positive charge, as exemplified by the general formula **I**. Subclasses of *N*-ylides are ammonium-ylides (**II**), cycloammonium-ylides (**III**), immonium-ylides (**IV**), cycloimmonium-ylides (**V**), nitrile-ylides (**VI**), and diazonium-ylides (**VII**) (Fig. 1).[1]

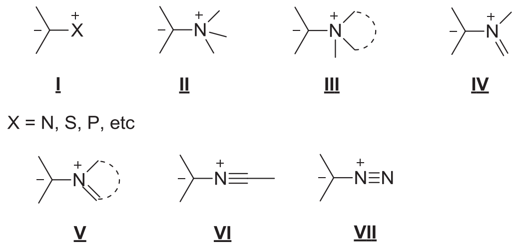

Fig. 1. Types of *N*-ylides.

When cycloimmonium-ylides **V** are composed of (hetero)aromatic partial structures, which delocalize the positive and the negative charge, they can be regarded as members of one of four distinct classes of heterocyclic mesomeric betaines.[2–4] They are usually represented by 1,2-dipolar resonance structures and play important roles in heterocyclic synthesis, as they usually are versatile 1,3-dipoles in [2+3]-cycloadditions.[1–4]

Ylides also allow for the generation of radicals as well as *N*-heterocyclic carbenes (Fig. 2). Calculations showed that the biradical form of the azomethine ylide of 1,1-dichloro-*N*-methylenemethanamine is more stable than the zwitterionic form.[5] Indeed, Merrifield resins, which are functionalized with 4,4′-bipyridiniums are photochromic materials as they form ylides, which undergo reversible electron transfers to α- and π-radicals by disproportionations.[6] Under these conditions, biradicals were not detected. We found recently that imidazolium-ylides are able to tautomerize to *N*-heterocyclic carbenes and that deprotonation of these ylides result in unstable anionic *N*-heterocyclic carbenes.[7,8]

Some relationships between the classes of mesomeric betaines (MB) and *N*-heterocyclic carbenes (NHC) are as follows. Heteroaromatic cycloimmonium ylides are related to conjugated heterocyclic mesomeric betaines (CMB), which can be set apart from cross-conjugated (CCMB) and pseudo-cross-conjugated

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http://dx.doi.org/10.1016/j.tet.2014.09.035
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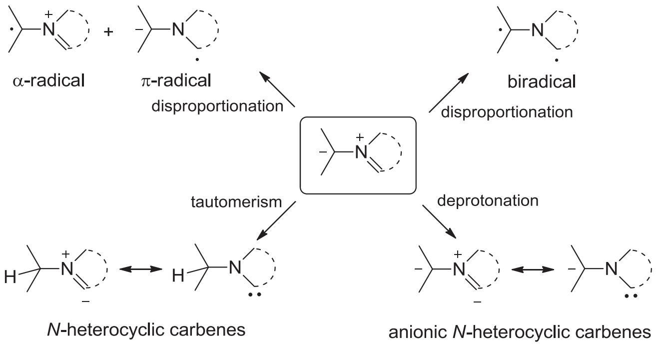


Fig. 2. Interconversion of *N*-ylides into radicals and *N*-heterocyclic carbenes.

mesomeric betaines (PCCMB).[2] Interconversions of suited representatives of these four classes of mesomeric betaines into *N*-heterocyclic carbenes have been reviewed.[9] As example, the reagent nitron **1** exists as mesoionic compound **1A** and as tautomeric *N*-heterocyclic carbene **1B**[10] (Fig. 3). Pseudo-cross-conjugated imidazolium-2-, pyrazolium-3-, and indazolium-3-carboxylates are versatile starting materials for the generation of imidazol-2-ylidenes,[11–16] pyrazol-3-ylidenes,[17–19] and indazol-3-ylidenes,[20–22] respectively (e.g., **2**→**3**). The mesoionic compound imidazolium-4-olate **4**, a conjugated mesomeric betaine (CMB), was deprotonated to the anionic *N*-heterocyclic carbene **5**.[23,24] The diaminocarbene moiety of **5** is bridged by an enolate, and an *active* position of the highest occupied molecular orbital (HOMO$_{\text{enolate}}$) is involved. The cross-conjugated mesomeric betaine (CCMB) 6-oxo-1,3-pyrimidinium-4-olate **6** was deprotonated to the anionic carbene **7**.[25] In anion **7** the diaminocarbene moiety is bridged through *inactive* positions of the HOMO$_{\text{acrylaldehyd-3-olate}}$ of the anionic fragment in accordance to the definition of cross-conjugation in mesomeric betaines.[2,26,27] These inactive positions, however, result in two π-electronically relatively independent partial structures.

In continuation of our interest in mesomeric betaines,[3,4,28] zwitterionic molecules,[29] organic polycations,[30] as well as *N*-heterocyclic carbenes in heterocycle synthesis[17] and catalysis,[31] we report here on recent examples of ylide–carbene interconversions. We prepared indol- as well as azaindol-2-yl-imidazolium salts and new triazolium-substituted indoles and converted them into ylides, which are tautomers of *N*-heterocyclic carbenes. We also report on trapping reactions of these carbenes. We continued this project with the non-alternant anionic partial structure shown in Fig. 4. The indolid anion allows for the construction of conjugated systems by joining the iminium moiety to the 2- as well as to the 3-position, which are both active positions in the HOMO$_{\text{indolid}}$ (Fig. 4). Therefore, both isomers belong to the class of conjugated mesomeric betaines, when hetarenium rings are attached.

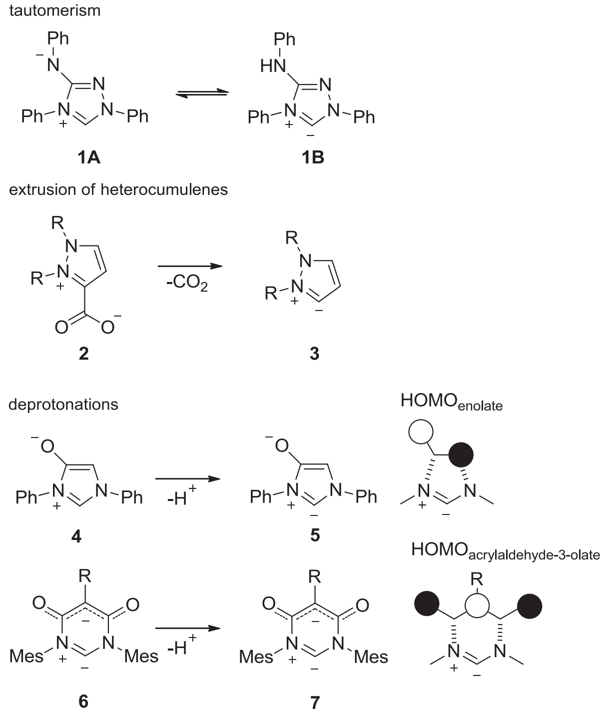


Fig. 3. Some relationships between mesomeric betaines and *N*-heterocyclic carbenes.

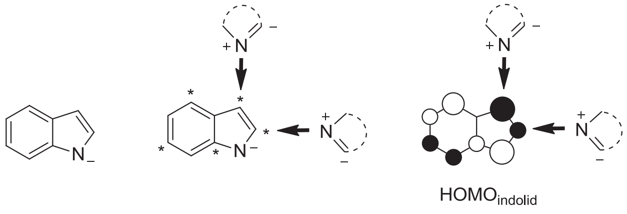
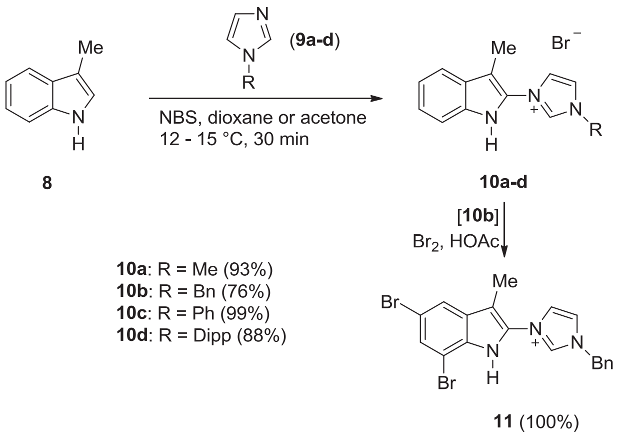


Fig. 4. Attachment of hetarenium rings or *N*-heterocyclic carbenes (NHCs) derived thereof to the 2- as well as 3-position of indolid results in conjugated mesomeric betaines and conjugated anionic NHCs, respectively.

2. Results and discussion

3-Methylindole **8** was treated with the imidazoles **9a–d** in acetone (**9a**,**d**) or dioxane (**9b**,**c**) according to a modified literature procedure[32] (Scheme 1). After cooling to 12–15 °C, *N*-bromosuccinimide was added portionwise within 5 min. The colorless to yellowish salts **10a–d** precipitated within 30 min. Characteristic chemical shifts are as follows: The NH signal appears between 12.06 and 12.19 ppm in DMSO-d_6; the $^1J_{\text{NH}}$ coupling is approximately −95 Hz, and proved to be independent on the substitution pattern. The resonance frequency of C-3 of indole can be detected at approximately 105 ppm in all derivatives. We performed a model reaction with respect to electrophilic heteroaromatic substitutions and found that **10b** reacts smoothly with bromine in excess acetic acid to the dibromo derivative **11** in quantitative yield.



Scheme 1. Synthesis of indol-2-yl imidazolium salts.

^{1}H NMR investigations of the salt **10a** at different temperatures in the presence of DABCO show a spontaneous H/D exchange of the NH proton to **10a**-d_1 at room temperature (Scheme 2). The signal of 2-H of the imidazolium ring broadens at approximately 60 °C and disappears at 120 °C due to deuterium exchange to **10a**-d_2. The deprotonated species of **10a**, i.e., the ylide **12a** or its tautomeric *N*-heterocyclic carbene **12′a** is detectable by electrospray ionization mass spectrometry (ESIMS) as prominent peak between 0 and