Sydnones anions and abnormal N-heterocyclic carbenes of O-ethylsydnones. Characterizations, calculations and catalyses†

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Deprotonated sydnones, which can be represented as anionic N-heterocyclic carbenes, were prepared as Li adducts and compared with deprotonated O-ethylsydnones (5-ethoxy-1,2,3-oxadiazol-4-ylidenes) which belong to the class of abnormal NHCs. The Pd complexes of the sydnone anions (X-ray analysis) as well as of the O-ethylsydnone carbenes proved to be efficient catalysts in arylic couplings of thiophenes.

Of all the 228 theoretically predicted mesoionic compounds 1 sydnones are probably the most prominent. Sydnones (1,2,3-oxadiazolium-5-olates) are 5-membered representatives of the class of conjugated mesomeric betaines (CMB) which is one of four distinct categories of this class of compounds. 3 They are not only known as versatile 1,3-dipoles in [2+3]-cycloadditions but also as interconversions of mesomeric betaines into N-heterocyclic carbenes which have developed rapidly during the last two decades. Numerous structural variations of N-heterocyclic carbenes have been described, most of them aiming at enhancing the electron density at the carbene center and thus influencing the σ-donor capacity in catalytically active metal complexes. 4 Recently mesomeric betaines including mesoionic compounds, however, have also come into the focus of carbene research. First results of interconversions of mesomeric betaines into N-heterocyclic carbenes and vice versa are summarized in recent review articles. 5 In continuation of our interest in N-heterocyclic carbenes and mesomeric betaines 6 we report here on sydnones as well as on O-ethylsydnones (5-ethoxy-1,2,3-oxadiazolium salts) and deprotonated species derived thereof.

We prepared a series of sydnones 2a–f by cyclization of N-nitroso amino acids 1a–f with acetic anhydride (Scheme 1). Among eight dipolar resonance forms of sydnones, I is the most common. The best single representation which reflects the properties of sydnones, however, appears to be II. 7 Resonance form II is in agreement with carbynyl stretching frequencies of 2a–f between 1728 cm−1 and 1736 cm−1. Bond length (1.197 Å), calculated from IR spectra of 2a, and bond order (1.99) correspond to an exocyclic C=O double bond which can also be seen in a single crystal X-ray analysis of 2b (ESI†).

We calculated the NICS(1) value of 2a which is between the cyclopentadienyl anion (−12.3) and cyclopentane (−2) (DFT LACVP*/B3LYP). In summary these values confirm that sydnones are no aromatics.

In contrast to other mesoionic compounds such as nitron 30 and imidazolium-4-aminide 31 no hints on tautomerism equilibria between sydnones and their N-heterocyclic carbenes can be found in the spectra. DFT calculations revealed that the mesoionic form 2aA is considerably more stable than its tautomer 2aB [ΔE = +191 kJ mol−1] (Scheme 2). Except for few photochromic sydnones, 11 valence isomers such as 2aC are not detectable.

A base screening employing LiO₂Bu, NaO₂Bu, KO₂Bu, KH, LiAIH₄ and nBuLi in a variety of solvents, respectively, which have been used earlier to deprotonate sydnones for further functionalizations at C₄, 3,7 caused a decomposition of the sydnones 2a–f, when we tried to isolate the deprotonated species. Fortunately, deprotonation by cyanomethyllithium, freshly prepared from nBuLi and anhydrous MeCN, resulted in the formation of the sydnone anions 5a–f in quantitative yields.

† Electronic supplementary information (ESI) available: Crystallographic data of 2b and trans-16. CCDC 987516 and 987969. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc05461j
as colorless, moisture-sensitive compounds which proved to be stable under an inert atmosphere for several weeks (Scheme 3). On exposure to water or protic solvents, reprotonation of 5a–f to the sydnones 2a–f occurred, which were recovered quantitatively in all cases. Ethylation of the sydnones 2a–f by triethyloxonium tetrafluoroborate gave the 5-ethoxy-1,2,3-oxadiazolium salts 6a–f which are stable under an inert atmosphere up to approximately 60 °C. As the calculated NICS(1) value of 6a is −8.9 these O-ethylsydnones are slightly more aromatic than the corresponding sydnones. The isolation of the abnormal N-heterocyclic carbenes (aNHC) 7a–f, however, failed, as all attempts to deprotonate the O-ethylsydnones resulted in decomposition products.

Sydnone anions can be represented by several resonance forms, among those representations as anionic abnormal NHCs I and II, and the anionic NHC III. Do sydnone anions bear more than a formal relationship to N-heterocyclic carbenes? As a matter of fact, the calculated bond lengths of C4–C5 (1.451 Å), C5=O (1.227 Å), and N3–C4 (1.353 Å) are best represented by resonance form II. As calculated by us and found IR-spectroscopically,12 the lithium cation is located between C4 and the exocyclic oxygen of 5a. By contrast, the aNHC 7a is best represented as shown, as the calculated C4–C5 bond (1.390 Å) is shortened in comparison to 5a, whereas the C5–O and O–Et bonds are essentially C sp2–O and O–C sp3 single bonds (1.325 and 1.445 Å, resp.). The ESP partial charges of C4 of the sydnone anion 5a as well as of the aNHC 7a adopt values between the CAAC13 on the one hand, and the aNHC 14 derived from the mesoionic compounds imidazolium-4-olate, respectively, and the NHC imidazole-2-ylidene 13. Similar to N-heterocyclic carbenes derived from ylides18 the calculated HOMO of 5a is a π-orbital with a large coefficient on C4, whereas the HOMO – 1 is perpendicular to the HOMO and contains the lone pair of electrons at C4 (Fig. 2). As expected the HOMO of the aNHC 7a is mainly a σ-type molecular orbital as shown.

Palladium complexes to stabilize the aNHC 7a and to study catalytic activities were prepared as follows. 4-Bromo-N-phenylsydnone 15 formed the palladium complex 16 of the sydnone anion 5a as a mixture of trans and cis isomers (Scheme 4).19 We were able to perform a single crystal X-ray analysis of trans-16 (ESI†). Ethylation of the bromosydnone 15 under exclusion of moisture resulted in the formation of the new 4-bromo-1,2,3-oxadiazolium salt 17 in good yields, which served as starting material for the preparation of the Pd complex 18 of the aNHC 7a.

The Pd complexes 16 and 18 of the sydnone anion 5a as well as the aNHC 7a proved to be efficient catalysts in Suzuki–Miyaura
cross-coupling reactions (Scheme 5). Thus, the perphenylation of tetrabromothiophene 19a to 20a proceeds in considerably higher yields and in shorter periods of time under the conditions shown (Table 1, entries 1 and 2) in comparison to the catalyst system Pd(PPh3)4/K3PO4 (tol, H2O, 12 h, 90 °C) which gave 37% yield of 20a. The pernaphthylation of 19a to the hitherto undescribed 2,3,4,5-tetra(naphthalen-1-yl)thiophene 19b was performed in only 40% yield, catalysis by Pd(PPh3)4, K2CO3 in MeOH and toluene over a reaction time of 13 h at reflux temperature. Whereas the use of 1,2-dimethoxyethane as solvent to give 80%, however, after 4 h of reaction time, 22 whereas the cross-coupling to 2,3-di(naphthalen-1-yl)-3,4-dinitrothiophene 20d, which is a new compound, under Pd(PPh3)4 catalysis proceeded in only 40% yield, catalysis by 16 or 18 gave very good yields (entries 7 and 8).

Table 1 Catalysts and yields

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* Isolated yields.

Notes and references