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Sydnone 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 aryl couplings of thiophenes.

Of all the 228 theoretically predicted mesoionic compounds¹ sydnones are probably the most prominent. Sydnones (1,2,3oxadiazolium-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.² They are not only known as versatile 1,3-dipoles in [2+3]-cycloadditions but also as biologically active compounds.³ So far the chemistry of sydnones has not been associated with the chemistry and applications of 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 betaines⁶ 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 carbonyl 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)⁸ value of 2a (-6.8) 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 3⁹ and imidazolium-4-aminide 4¹⁰ no hints on tautomeric 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** [$\Delta E = +191$ kJ mol⁻¹] (Scheme 2). Except for few photochromic sydnones,¹¹ valence isomers such as 2aC are not detectable.

A base screening employing LiOtBu, NaOtBu, KOtBu, KH, LiAlH₄ and *n*BuLi 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 *n*BuLi and anhydrous MeCN, resulted in the formation of the sydnone anions 5a-f in quantitative yields

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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_{sp}^{2} -O and O- C_{sp}^{3} 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 CAAC 9¹³ on the one hand, and the aNHC 10¹⁴ on the other (Fig. 1). As a comparison, we also calculated the phenyl derivatives of carbene 1115 derived from a cross-conjugated mesomeric betaine, the anionic NHCs 12¹⁶ and 14¹⁷ derived from the mesoionic compounds imidazolium-4-aminide and





Fig. 2 Calculated highest occupied molecular orbitals.

imidazolium-4-olate, respectively, and the NHC imidazole-2vlidene 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-Nphenylsydnone 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





Scheme 5

Table 1 Catalysts and yields	able 1	Catalysts a	nd yields
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Entry	Starting material	Product	Catalyst	Yield ^a (%)
1	19a	20a	16	55
2	19a	20a	18	74
3	19a	20b	16	53
4	19a	20b	18	60
5	19b	20c	16	91
6	19b	20c	18	85
7	19b	20d	16	80
8	19b	20d	18	79
^a Isolate	d yields.			

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.²⁰ The pernaphthylation of 19a to the hitherto undescribed 2,3,4,5-tetra(naphthalen-1-yl)thiophene 20b gave 53% and 60% yield, respectively, when the complexes 16 and 18 were employed (entries 3 and 4). The 2,5-bisarylation of 2,5-dibromo-3,4-dinitrothiophene 19b with phenylboronic acid gave 3,4-dinitro-2,5-diphenylthiophene 20c in excellent yields under catalysis of 16 and 18, respectively (entries 5 and 6). Compound 20c has been prepared before in 37% yield by crosscoupling using Pd(PPh₃)₄, K₂CO₃ in MeOH and toluene over a period of 8 h at reflux temperature.²¹ An alternative procedure uses 1,2-dimethoxyethane as solvent to give 80%, however, after a reaction time of 13 h at reflux temperature.²² Whereas the cross-coupling to 2,5-di(naphthalen-1-yl)-3,4-dinitrothiophene **20d**, which is a new compound, under $Pd(PPh_3)_4$ catalysis proceeded in only 40% yield, catalysis by 16 or 18 gave very good yields (entries 7 and 8).

Sydnone anions share typical features with N-heterocyclic carbenes, and their deprotonated *O*-ethyl derivatives, 5-ethoxy-1,3,4-oxadiazol-4-ylidenes, belong to the class of abnormal NHCs. Either species form stable Pd complexes which are efficient catalysts in Suzuki–Miyaura cross-coupling reactions.

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