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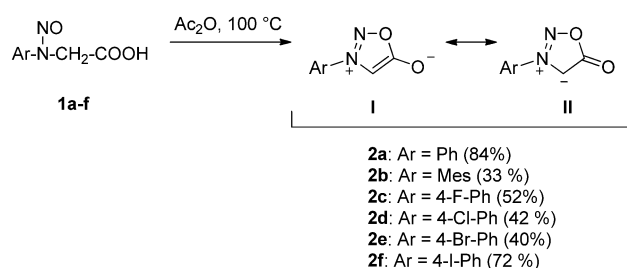
Sydnone anions and abnormal N-heterocyclic carbenes of O-ethylsydrones. Characterizations, calculations and catalyses†

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Deprotonated sydrones, which can be represented as anionic N-heterocyclic carbenes, were prepared as Li adducts and compared with deprotonated O-ethylsydrones (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 sydrones are probably the most prominent. Sydrones (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.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 sydrones 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 sydrones as well as on O-ethylsydrones (5-ethoxy-1,2,3-oxadiazolium salts) and deprotonated species derived thereof.

We prepared a series of sydrones **2a–f** by cyclization of N-nitroso amino acids **1a–f** with acetic anhydride (Scheme 1). Among eight



Scheme 1

dipolar resonance forms of sydrones, **I** is the most common. The best single representation which reflects the properties of sydrones, 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 sydrones are no aromatics.

In contrast to other mesoionic compounds such as nitron **3**⁹ and imidazolium-4-aminide **4**¹⁰ no hints on tautomeric equilibria between sydrones 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** [$\Delta E = +191 \text{ kJ mol}^{-1}$] (Scheme 2). Except for few photochromic sydrones,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 sydrones for further functionalizations at C4,^{3,7} caused a decomposition of the sydrones **2a–f**, when we tried to isolate the deprotonated species. Fortunately, deprotonation by cyanomethylolithium, 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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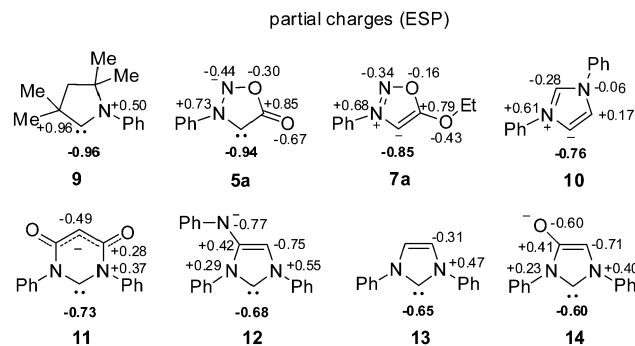
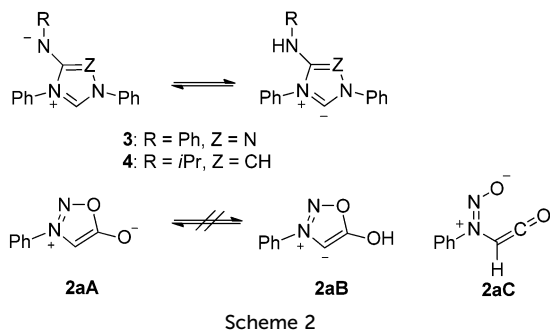


Fig. 1 Calculated partial charges of the title compounds and selected NHCs.

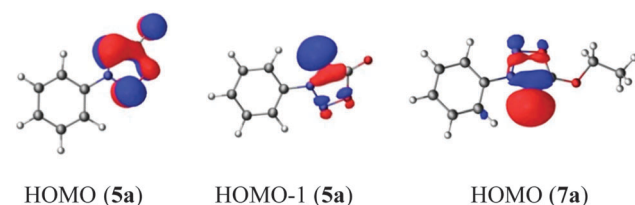
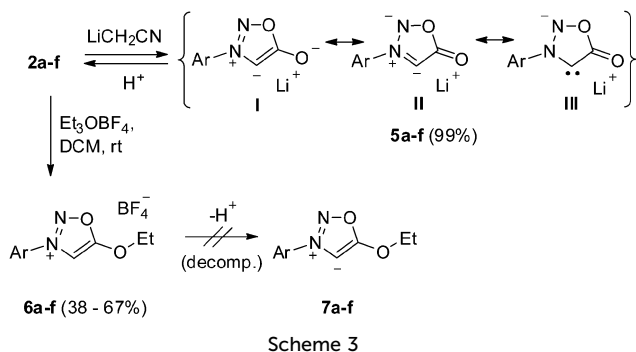


Fig. 2 Calculated highest occupied molecular orbitals.

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 sydrones **2a-f** occurred, which were recovered quantitatively in all cases. Ethylation of the sydrones **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*-ethylsydrones are slightly more aromatic than the corresponding sydrones. The isolation of the abnormal N-heterocyclic carbenes (aNHC) **7a-f**, however, failed, as all attempts to deprotonate the *O*-ethylsydrones resulted in decomposition products.

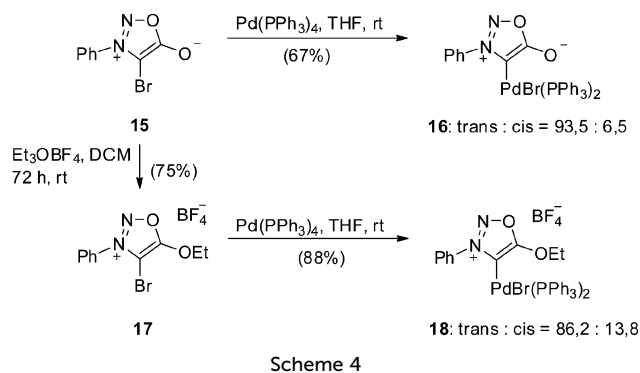
Sydnone anions can be represented by several resonance forms, among those representations as anionic abnormal NHCs **I** and **II**, and the anionic NHC **III**. Do sydnone anions bear more than a formal relationship to N-heterocyclic carbenes? As a matter of fact, the calculated bond lengths of C4–C5 (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 $\text{C}_{\text{sp}^2}\text{--O}$ and $\text{O--C}_{\text{sp}^3}$ 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 **9**¹³ on the one hand, and the aNHC **10**¹⁴ on the other (Fig. 1). As a comparison, we also calculated the phenyl derivatives of carbene **11**¹⁵ derived from a cross-conjugated mesomeric betaine, the anionic NHCs **12**¹⁶ and **14**¹⁷ derived from the mesoionic compounds imidazolium-4-aminide and

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



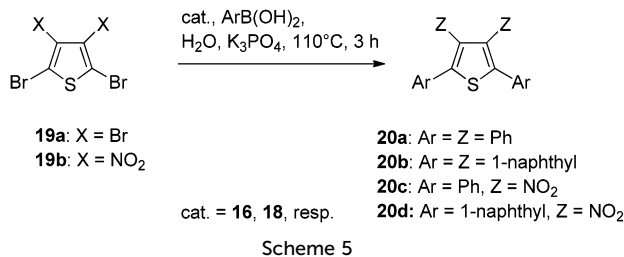


Table 1 Catalysts and yields

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 Isolated 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 pernaphtylation 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 cross-coupling 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(PPh₃)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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