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

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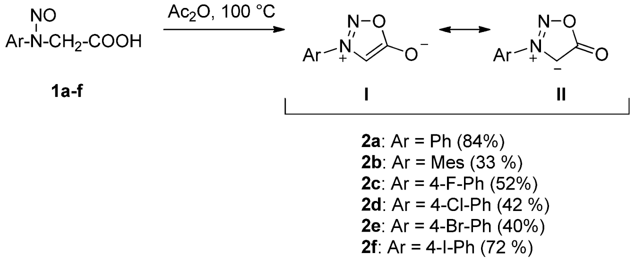
Deprotonated sydnones, which can be represented as anionic N-heterocyclic carbenes, were prepared as Li adducts and compared with deprotonated *O*-ethylsydnones (5-ethoxy-1,2,3-oxadiazol-4-ylidenes) which belong to the class of abnormal NHCs. The Pd complexes of the sydnone anions (X-ray analysis) as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

Of all the 228 theoretically predicted mesoionic 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.[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 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 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.



2a: Ar = Ph (84%)
2b: Ar = Mes (33 %)
2c: Ar = 4-F-Ph (52%)
2d: Ar = 4-Cl-Ph (42 %)
2e: Ar = 4-Br-Ph (40%)
2f: Ar = 4-I-Ph (72 %)

Scheme 1

In contrast to other mesoionic compounds such as nitron **3**[9] and imidazolium-4-aminide **4**[10] 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** [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 LiO*t*Bu, NaO*t*Bu, KO*t*Bu, KH, LiAlH$_4$ 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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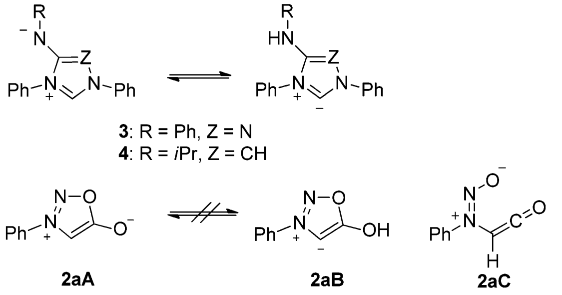
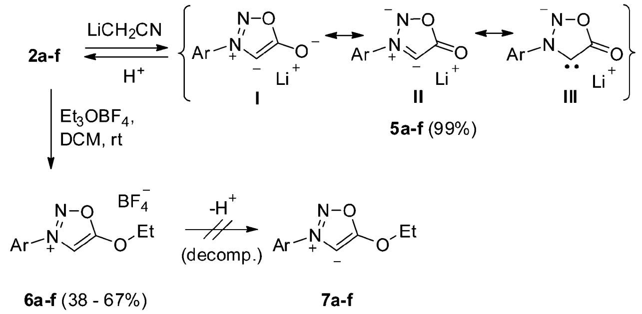


Scheme 2



Scheme 3

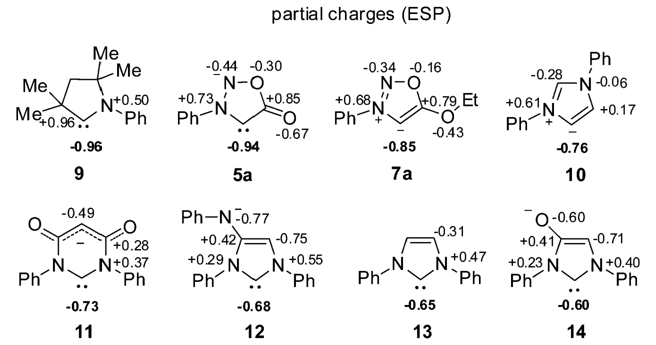


Fig. 1 Calculated partial charges of the title compounds and selected NHCs.

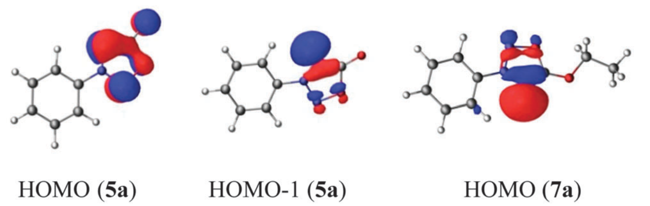

HOMO (**5a**) HOMO-1 (**5a**) HOMO (**7a**)

Fig. 2 Calculated highest occupied molecular orbitals.

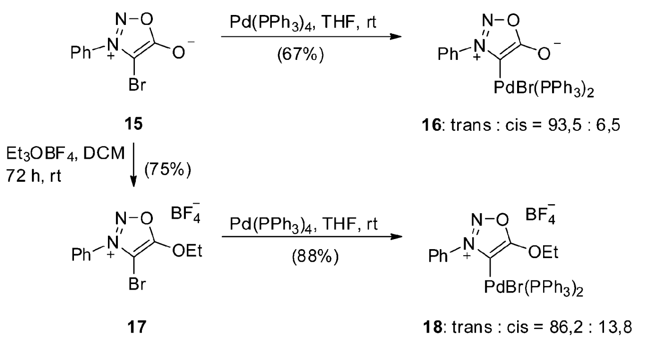
as colorless, moisture-sensitive compounds which proved to be stable under an inert atmosphere for several weeks (Scheme 3). On exposure to water or protic solvents, reprotonation of **5a–f** to the sydnones **2a–f** occurred, which were recovered quantitatively in all cases. Ethylation of the sydnones **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 **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 ylides[18] 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).

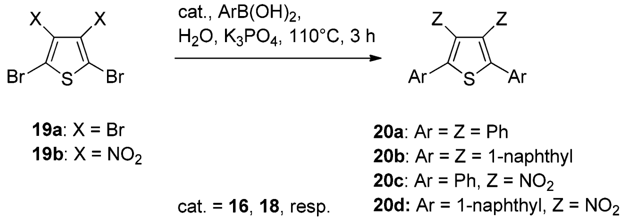
As expected the HOMO of the aNHC **7a** is mainly a σ-type molecular orbital as shown.

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



Scheme 4



Scheme 5

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 $Pd(PPh_3)_4/K_3PO_4$ (tol, H_2O, 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 cross-coupling using $Pd(PPh_3)_4$, K_2CO_3 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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