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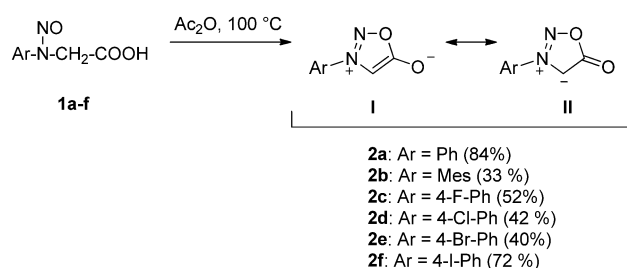
# Sydnone anions and abnormal N-heterocyclic carbenes of O-ethylsydnones. Characterizations, calculations and catalyses†

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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<sup>1</sup> 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.<sup>2</sup> They are not only known as versatile 1,3-dipoles in [2+3]-cycloadditions but also as biologically active compounds.<sup>3</sup> 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  $\sigma$ -donor capacity in catalytically active metal complexes.<sup>4</sup> 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.<sup>5</sup> In continuation of our interest in N-heterocyclic carbenes and mesomeric betaines<sup>6</sup> 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



Scheme 1

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**.<sup>7</sup> Resonance form **II** is in agreement with carbonyl stretching frequencies of **2a–f** between 1728 cm<sup>-1</sup> and 1736 cm<sup>-1</sup>. 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)<sup>8</sup> 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 **3**<sup>9</sup> and imidazolium-4-aminide **4**<sup>10</sup> 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<sup>-1</sup>] (Scheme 2). Except for few photochromic sydnones,<sup>11</sup> valence isomers such as **2aC** are not detectable.

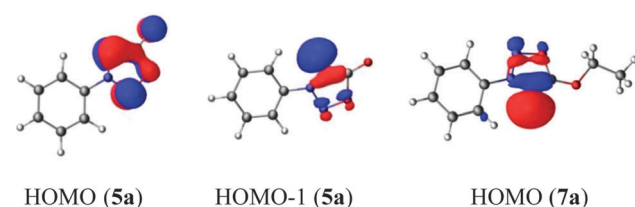
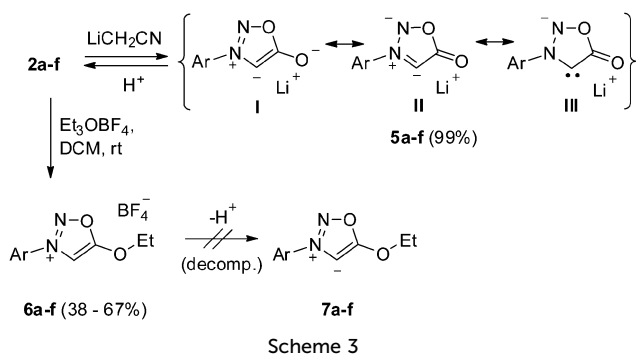
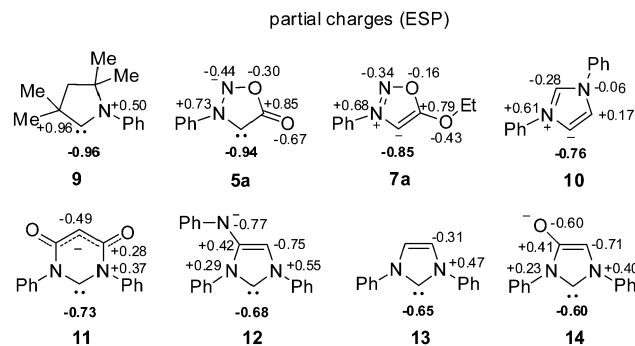
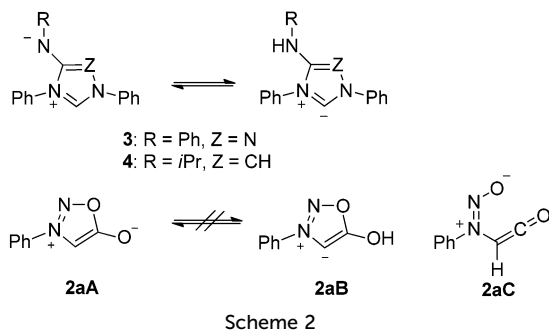
A base screening employing LiOtBu, NaOtBu, KOtBu, KH, LiAlH<sub>4</sub> and *n*BuLi in a variety of solvents, respectively, which have been used earlier to deprotonate sydnones for further functionalizations at C4,<sup>3,7</sup> caused a decomposition of the sydnones **2a–f**, when we tried to isolate 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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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.

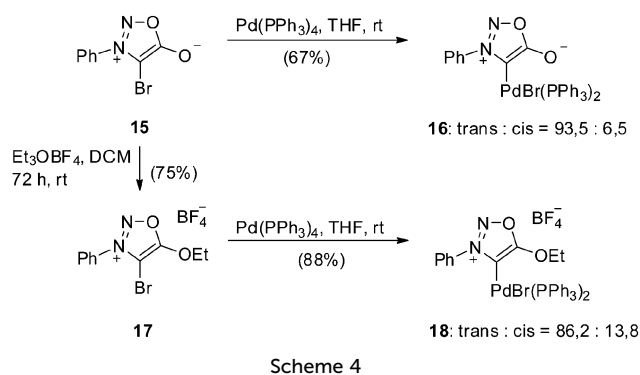
Sydnone anions can be represented by several resonance forms, among those representations as anionic abnormal NHCs I and II, and the anionic NHC III. Do sydnone anions bear more than a formal relationship to N-heterocyclic carbenes? As a matter of fact, the calculated bond lengths of C4–C5 (1.451 Å), 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,<sup>12</sup> 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<sup>13</sup> on the one hand, and the aNHC 10<sup>14</sup> on the other (Fig. 1). As a comparison, we also calculated the phenyl derivatives of carbene 11<sup>15</sup> derived from a cross-conjugated mesomeric betaine, the anionic NHCs 12<sup>16</sup> and 14<sup>17</sup> 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<sup>18</sup> the calculated HOMO of 5a is a  $\pi$ -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  $\sigma$ -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).<sup>19</sup> We were able to perform a single crystal X-ray analysis of *trans*-16 (ESI<sup>†</sup>). 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



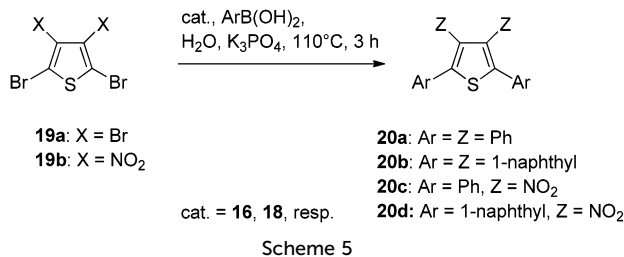


Table 1 Catalysts and yields

Entry	Starting material	Product	Catalyst	Yield <sup>a</sup> (%)
1	<b>19a</b>	<b>20a</b>	<b>16</b>	55
2	<b>19a</b>	<b>20a</b>	<b>18</b>	74
3	<b>19a</b>	<b>20b</b>	<b>16</b>	53
4	<b>19a</b>	<b>20b</b>	<b>18</b>	60
5	<b>19b</b>	<b>20c</b>	<b>16</b>	91
6	<b>19b</b>	<b>20c</b>	<b>18</b>	85
7	<b>19b</b>	<b>20d</b>	<b>16</b>	80
8	<b>19b</b>	<b>20d</b>	<b>18</b>	79

<sup>a</sup> 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<sub>3</sub>)<sub>4</sub>/K<sub>3</sub>PO<sub>4</sub> (tol, H<sub>2</sub>O, 12 h, 90 °C) which gave 37% yield of **20a**.<sup>20</sup> 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(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub> in MeOH and toluene over a period of 8 h at reflux temperature.<sup>21</sup> An alternative procedure uses 1,2-dimethoxyethane as solvent to give 80%, however, after a reaction time of 13 h at reflux temperature.<sup>22</sup> Whereas the cross-coupling to 2,5-di(naphthalen-1-yl)-3,4-dinitrothiophene **20d**, which is a new compound, under Pd(PPh<sub>3</sub>)<sub>4</sub> 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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