Mesomeric betaine – N-heterocyclic carbene interconversions of 1,2,4-triazolium-phenolates. Sulfur, selenium, and borane adduct formation†

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The conjugated mesomeric betaines 2-(1-phenyl-4H-1,2,4-triazolium-4-yl)phenolates are masked N-heterocyclic carbenes of 1,2,4-triazole which can be trapped as thiones and selenones. Reaction with triethylborane and triphenylborane resulted in the formation of the first hetarenium-phenolates (1,2,4-triazolium-phenolates) which are in equilibrium with their tautomeric carbenes. Reaction with triethylborane and triphenylborane resulted in the formation of the first hetarenium-phenolates (1,2,4-triazolium-phenolates) which are in equilibrium with their tautomeric carbenes. Two of them were not recognized until 2013.3 As summarized in the first review articles,2 the types of conjugation of mesomeric betaines also determine their transformations into N-heterocyclic carbenes. Thus, some pseudo-cross-conjugated mesomeric betaines (PCMB) are widely applied as stable precursors of normal N-heterocyclic carbenes (nNHC).2 Scheme 1 shows the PCMB imidazolium-2-carboxylate 1, which gives 2 upon decarboxylation.4 Other suitable PCMBs for the generation of nNHCs are pyrazolium-3-carboxylates,5 indazolium-3-carboxylates6 and pyridinium-2-carboxylates.7 N-heterocyclic carbenes as well as anions derived thereof can also be generated from conjugated mesomeric betaines (CMB), as exemplified by 3–7. Thus, nitron 38 and imidazolium-4-aminide 49 are in tautomeric equilibrium with their corresponding NHCs. The anionic N-heterocyclic carbenes 510 and 611 are deprotonated sydnones and sydnonimines, respectively, whereas the carbene 7 was generated from an ylide.12 By contrast, carbene 813 is a deprotonated cross-conjugated mesomeric betaine (CCMB).

In continuation of our research interests (polycations,14 mesomeric betaines,5,6,12 synthesis and catalysis with NHCs15) we report here on the first hetarenium-phenolates (1,2,4-triazolium-phenolates) which are in equilibrium with their tautomeric carbenes. They form the first representatives of a new ring system upon treatment with boranes.

We started the preparation of the title compounds from 2-aminophenol 9a and its 4-methyl derivate 9b which induced a nucleophilic ring transformation of 3-phenyl-1,3,4-oxadiazolium salt 10 to give the salts 11a,b in reasonable yields, respectively (Scheme 2). The OH group can be detected at δ = 11.22 ppm (11a) and 10.95 ppm (11b) in DMSO-d6. Potassium hydroxide in methanol (method A) converted the salts 11a,b at rt into the 2-(1,2,4-triazolium)phenolates 12a,b the tautomers A of which are members of the class of conjugated heterocyclic mesomeric betaines (CMB). Upon formation of betaine, the resonance frequency of the OH groups of 11a,b disappears while the signals of 3-H of the triazolium at δ = 11.27/11.25 ppm broaden considerably. The largest shift differences are observable for the phenolate protons which shift by Δδ = 0.15–0.25 ppm to a higher field. The betaine tautomers 12a,b(A) proved to be stable
in polar protic solvents such as methanol ($E_N^T = 0.762$). In aprotic, less polar solvents such as DMSO ($E_N^T = 0.444$) or THF ($E_N^T = 0.207$), however, decomposition occurs. The carbene tautomers $12a,b(B)$ can be trapped as triazolethiones $13a,c$ by reaction with sulfur in toluene in 50% and 60% yield, respectively (method D). The carbene tautomers were also trapped starting from the salts $11a,b$ in a one-step reaction (methods B and C): deprotonation of $11a,b$ with potassium 2-methylbutan-2-olate in the presence of sulfur and selenium, respectively, gave the triazolethiones $13a,c$ and triazoleselenones $13b,d$ in acceptable to good yields.

Suitable single crystals of the salt $11b$ were obtained by slow evaporation of a concentrated solution in ethanol (Fig. 1). The phenol substituent is twisted by 56.24(19)$^\circ$ ($C5–N4–C6–C7$) from the plane of the triazolium ring, whereas the phenyl ring and the triazolium ring form an almost planar system in the crystal (see ESI†).

Suitable single crystals of the corresponding betaine $12b$ were obtained by slow evaporation of a concentrated solution in EtOH–EtOAc. The betaine, which adopts tautomer $12b(A)$ in the crystal, is stabilized by water of crystallization (Fig. 2). One hydrogen bond is formed from $3-H_{triazole}$ (CH-5, crystallographic numbering) to the oxygen atom of water (H · · · O–O–H · · · O: 203 pm/172$^\circ$), another from the phenolate oxygen atom (O18) to the hydrogen atoms of two water molecules (H · · · O–O–H · · · O: 188(2) pm/177(3)$^\circ$; 192(2) pm/163(3)$^\circ$). In contrast to the corresponding salt $11b$, the phenol substituent is twisted only slightly by $7.4(3)^\circ$ ($C3–N4–C12–C17$) from the plane of the triazolium ring. Upon deprotonation, the C–O bond of the phenol shortens by approximately 6 pm (see ESI†).

Borane adducts of N-heterocyclic carbenes have attracted considerable attention in the last few years.16 The betaine-carbene tautomers $12a,b$ reacted with triphenylborane and tris(pentafluorophenyl)borane in dioxane at rt to form the triazolium phenoxytriphenylborates $14a–d$, respectively (Scheme 3). Triethylborane and triphenylborane converted $12a,b$ at elevated temperatures into first representatives of the new heterocyclic ring system benzo[1,2,4-triazolo[3,4-c][1,4,2]oxazaborininium-4-ide $15a–d$ which are formal trapping products of an anionic N-heterocyclic carbene possessing a phenolate moiety. Correspondingly, the phenylborates $15b,d$ are also available in excellent yields starting from $14b,d$ upon heating. The $^{11}B$ NMR resonance frequencies of $14b,d$ shift from $–6.56$ and $–6.57$ ppm, respectively, to $–0.08$ and $–0.80$ ppm upon ring closure to $15b,d$.

Suitable single crystals of $14c$ were obtained by slow evaporation of a concentrated solution in DMSO. The bond length between the phenolate oxygen and the boron atom (O19–B20) was determined to be 150.30(19) pm. The phenyl rings are twisted by $120.8(3)^\circ$ ($C5–N1–C6–C7$) and $148.59(15)^\circ$ ($C5–N4–C12–C17$) $[–35.7(2)^\circ$ ($C5–N4–C12–C13$)] from the plane of the triazolium ring (Fig. 3).

Finally, suitable single crystals of the new ring system $15a$ were obtained by slow evaporation of a concentrated solution in ethanol...
The B–C carbene bond is longer [165.2(2) pm] than in indoles, trapping products of anionic imidazole-2-ylidenes, the 162.7(2) pm [160.3(2) pm and 161.8(2) pm]. In imidazodiazaborolophenolate-1,2,4-triazolium-3-ylidenes are quite rare. One literature-known example is the trapping (Fig. 4). In the elemental cell two molecules are connected.

Fig. 3 Molecular drawing of triazolium phenoxypentaphenylborate 14c (displacement parameters are drawn at the 50% probability level).

Fig. 4 Molecular drawing of the new heterocyclic ring system 15a (displacement parameters are drawn at the 50% probability level).

In triazolium phenolates represent an additional class of mesomeric betaines which are in equilibrium with their N-heterocyclic carbenes. This equilibrium gives the access to new borane-containing heterocyclic ring systems which are formed upon trapping with boranes.

Notes and references


