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Mesomeric Betaine – N-Heterocyclic Carbene Interconversions of 1,2,4-Triazolium-phenolates. Sulfur, Selenium, and Borane Adduct Formations

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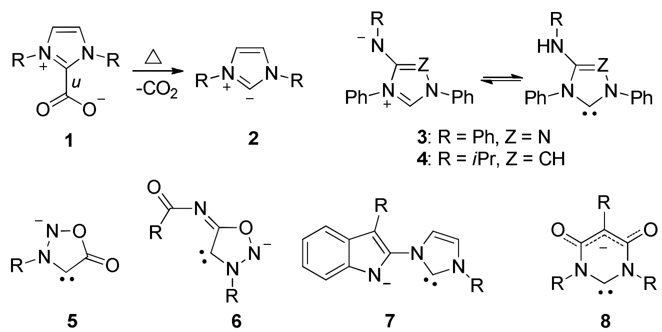
The conjugated mesomeric betaines 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolates are masked N-heterocyclic carbenes of 1,2,4-triazole which can be trapped as thiones and selenones. Reaction with triethylborane and triphenylborane resulted in the formation of first representatives of a new zwitterionic heterocyclic ring system, benzo[*e*]1,2,4-triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ide, as formal trapping product of an anionic N-heterocyclic carbene.

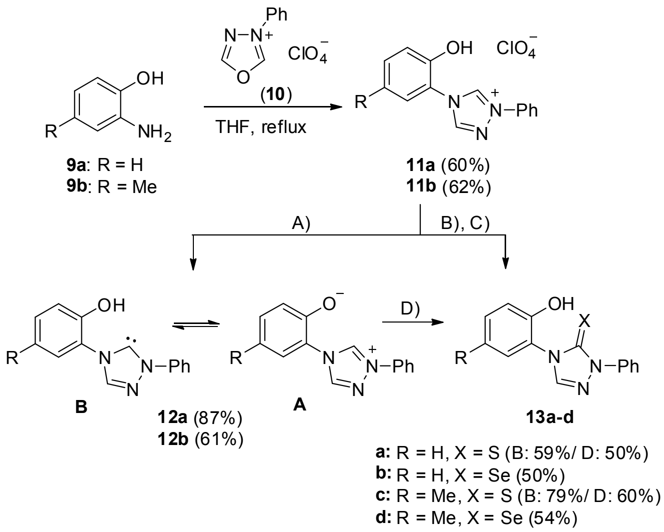
Recently, mesomeric betaines (MB) have come into the focus of N-heterocyclic carbene (NHC) research as it was recognized that mesomeric betaines not only comprise versatile starting materials for the preparation of a broad variety of NHCs, but also stimulate the designs of new architectures and variations of their charge properties. The chemical and physical properties of mesomeric betaines are strongly dependent on their types of conjugation which define five distinct classes of mesomeric betaines. Two of them have not been recognized before 2013.[1] As summarized in 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 (PCCMB) are widely applied as stable precursors of normal N-heterocyclic carbenes (nNHC).[3] Scheme 1 shows the PCCMB imidazolium-2-carboxylate **1**, which gives **2** on decarboxylation.[4] Other suitable PCCMBs for the generation of nNHCs are pyrazolium-3-carboxylates,[5] indazolium-3-carboxylates[6] 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 **3**[8] and imidazolium-4-aminide **4**[9] are in tautomeric equilibrium with their corresponding NHCs. The anionic N-heterocyclic carbenes **5**[10] and **6**[11] are deprotonated sydnones and sydnonimines, respectively, whereas the carbene **7** was generated from an ylide.[12] By contrast, carbene **8**[13] 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 NHCs[15]) 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 on treatment with boranes.



Scheme 1.

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 between δ = 11.22 (**11a**) and 10.95 ppm (**11b**) in DMSO-d_6. 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). On betaine formation, the resonance frequency of the OH groups of **11a,b** disappears while the signals of 2-*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 higher field. The betaine tautomers **12a,b(A)** proved to be stable in polar protic solvents such as methanol (E_T^N = 0.762). In aprotic, less polar solvents such as DMSO (E_T^N = 0.444) or THF (E_T^N = 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 tautomer 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 THF in the presence of sulfur and selenium, respectively, gave the triazolethiones **13a,c** and triazoleselenones **13b,d** in acceptable to good yields.



reaction conditions: A) KOH, MeOH. B) potassium 2-methylbutan-2-olate, S_8, THF, 0 °C, 30 min, then 100 °C, 3 h. C) potassium 2-methylbutan-2-olate, Se, THF, 0 °C, 30 min, then 100 °C, 3 h. D) S_8, toluene, reflux, 8 h [**13a**, **13c**]

Scheme 2.

Suitable single crystals of the salt **11b** were obtained by slow evaporation of a concentrated solution in ethanol (Figure 1). The phenol substituent is twisted by 56.24(19)° (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 (s. Supporting Information).

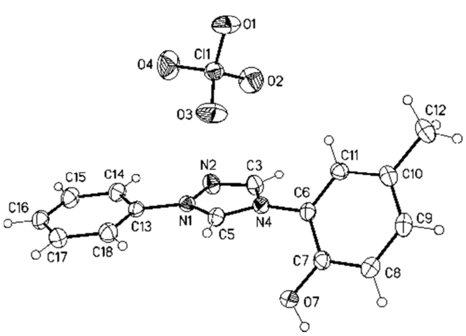


Fig. 1. Molecular drawing of triazolium salt **11b** (displacement parameters are drawn at 50% probability level).

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 (Figure 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 °), 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) °; 192(2) pm / 163(3) °). In contrast to the corresponding salt **11b**, the phenol substituent is twisted only slightly by -7.4(3) ° (C3-N4-C12-C17) from the plane of the triazolium ring. On deprotonation, the C-O bond of the phenol shortens by approximately 6 pm (s. Supporting Information).

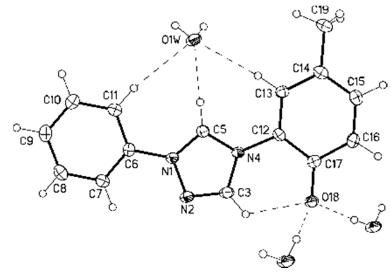
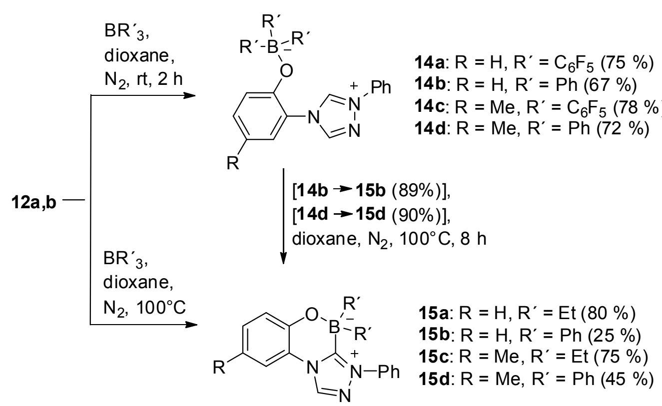


Fig. 2. Molecular drawing of triazolium betaine **12b(A)** showing the hydrogen bond pattern (displacement parameters are drawn at 50% probability level).

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 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[*e*]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 starting from **14b,d** by heating in excellent yields. 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 on ring closure to **15b,d**.



Scheme 3.

Suitable single crystals of **14c** were obtained by slow evaporation of a concentrated solution in DMSO. The bond lengths 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) ° (C5-N1-C6-C7) and 148.59(15) ° (C5-N4-C12-C17) [-35.7(2)° (C5-N4-C12-C13)] from the plane of the triazolium ring (Fig. 3).

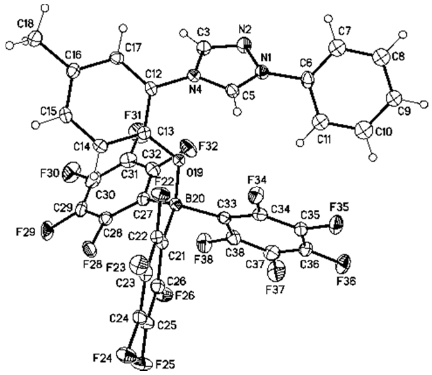


Fig. 3. Molecular drawing of triazolium phenoxytriphenylborate **14c** (displacement parameters are drawn at 50% probability level).

Finally, suitable single crystals of the new ring system **15a** were obtained by slow evaporation of a concentrated solution in ethanol (Fig. 4). In the elemental cell two molecules are connected *via* one molecule of water which forms hydrogen bonds to the oxygen atoms of the central [1,4,2]oxazaborininium-4-ide cores, respectively [H…O / O-H-…O: 188(2) pm / 178(2) ° and 195(2) pm/ 162(2) °] (*c.f.* Fig. 5, Supporting Information). The phenyl rings are twisted by 46.13(18)° (N5-N4-C18-C23) -42.7(2)° (N105-N104-C118-C123) from the plane of the triazolium ring. The oxazaborininium ring is twisted. Thus dihedral angels of -28.57(16)° [24.48(17)°] (O1-B2-C3-N7) and 46.77(15)° [-46.84(16)°] (C13-O1-B2-C3) were measured. The bond lengths $O_{phenolate}$-B and $C_{carbene}$-B were determined to be 154.26(17) pm [154.27(19) pm] and 163.9(2) pm [164.2(2) pm], respectively, whereas the bond connecting the boron atom with the two remaining ethyl groups are shorter (160.6(2) and 162.7(2) pm [160.3(2) pm and 161.8(2) pm)]. In imidazodiazaboroloindoles, trapping products of anionic imidazole-2-ylidenes, the B–$C_{carbene}$ bond is longer [165.2(2) pm] than in **15a**.[17] The angle N-$C_{carbene}$-N in **15a** (N4-C3-N7) was determined to be 103.40(12)°. In the BH_3 adduct of 2-phenyl-pyrrolo[2,1-*c*]-[1,2,4]triazol-3-ylidene the bond length $C_{carbene}$-B is 161.1(3) pm, the angle N-$C_{carbene}$-N is 102.0(2) ° and the N-$C_{carbene}$ bond lengths 136.3(3) pm and 137.0(3), respectively.[18] Borane adducts of 1,2,4-triazolium-3-ylidenes are quite rare. One literature-known example is the trapping reaction of 2,4,5-triphenyl-[1,2,4]triazol-3-ylidenes with $BH_3 \cdot THF$.[19]

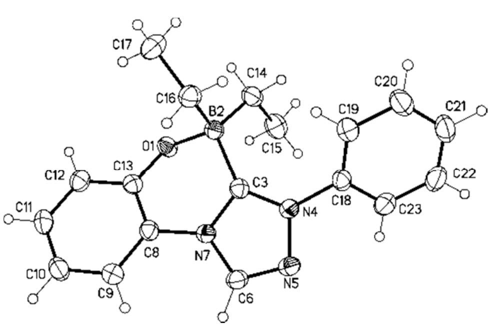


Fig. 4. Molecular drawing of the new heterocyclic ring system **15a** (displacement parameters are drawn at 50% probability level).

In summary, 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 on trapping with boranes.

Notes and references

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† Electronic Supplementary Information (ESI) available: crystallographic data of **11b**, **12b**, **14c**, and **15a** in cif-format.
Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1027080 (**11b**), CCDC1027081 (**12b**), CCDC 1027082 (**14c**), and CCDC 1027083 (**15a**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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