



Anionic N-heterocyclic carbenes by decarboxylation of sydnone-4-carboxylates

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ABSTRACT

Unstable N-heterocyclic carbenes can be masked and stabilized as pseudo-cross-conjugated hetarenium-carboxylates which decarboxylate on warming. This study deals with the decarboxylation of carboxylates of mesoionic compounds to generate anionic N-heterocyclic carbenes. Lithium sydnone-4-carboxylates were therefore prepared via 4-bromosydnonones by halogen-lithium exchange with nBuLi and subsequent treatment with carbon dioxide. Protonation gave the corresponding sydnone-4-carboxylic acids. Thermogravimetric measurements in addition to temperature dependent IR spectroscopy proved the decarboxylation of lithium sydnone-4-carboxylates and formation of the corresponding sydnone anions which can be represented as anionic N-heterocyclic carbenes. In DMSO-d₆ solution, water favors the decarboxylation. Calculations have been performed to elucidate the mechanism of the decarboxylation in the absence and presence of water.

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1. Introduction

In the past years anionic N-heterocyclic carbenes (anionic NHC) have risen from laboratory curiosities to an innovative emerging field. Consequently, recent results concerning chemistry, properties and applications have been summarized in a first comprehensive review.¹ Anionic N-heterocyclic carbenes can be tripolar zwitterionic or anionic π -conjugated. For example, the N-heterocyclic carbene **1** bearing a borate at N1 is a zwitterionic anionic N-heterocyclic carbene.² Its negative charge is not in π -conjugation with the heterocycle (Scheme 1). Borate ligands can also be joined to the 4-position of imidazole-2-ylidene,³ to the 2-position of imidazole-4-ylidene,⁴ or to two N1 positions of two imidazole-2-ylidenes which form a B-bridged biscarbene.⁵

Aluminates,⁶ gallates,⁷ and other species also belong to this type of N-heterocyclic carbenes. Carbenes with one or more coordinating tethered anionic ligands such as **2** can also be termed zwitterionic anionic N-heterocyclic carbenes, because the sp³-

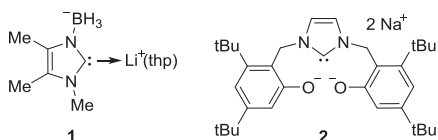
hybridized carbon atoms interrupt the conjugation between carbene and anionic moieties.⁸

In order to generate conjugated anionic N-heterocyclic carbenes, it has been shown that mesomeric betaines are suitable starting materials. Application of Ramsden's betaine classification theory⁹ leads to several subclasses of conjugated anionic N-heterocyclic carbenes. A review summarizes knowledge which has been gained to date.¹⁰ Thus, the deprotonation of mesoionic compounds such as imidazolium olate **3** (X=O)¹¹ or imidazolium aminide **3** (X=N)¹² give π -conjugated anionic N-heterocyclic carbenes such as **4**. Other examples have been described.¹³ In these systems, the HOMO is joined to the diaminocarbene partial structure through an active atomic orbital coefficient. Cross-conjugated anionic N-heterocyclic carbenes such as **6** have been prepared from Kappe's betaine **5** by deprotonation.¹⁴ In carbene **6** the diaminocarbene moiety is joined to the anionic backbone through phase inversions (nodal positions; inactive positions) of the corresponding HOMO which cause a π -electronic charge-separation in the ground state.¹⁵ Thus, systems such as **6** have to be distinguished from the former mentioned species (Scheme 2).

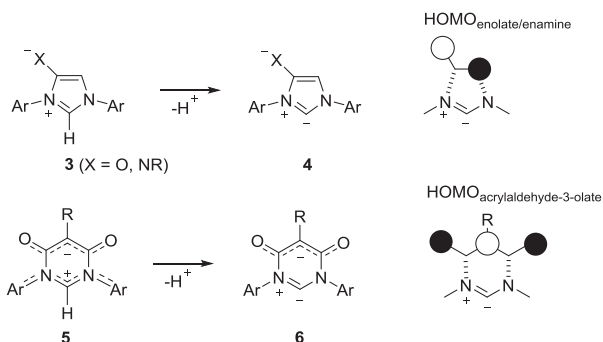
The anions **8(I)** – **8(III)** of sydnones **7** (1,2,3-oxadiazolium-5-olates¹⁶) delocalize their negative charge within the π -conjugated

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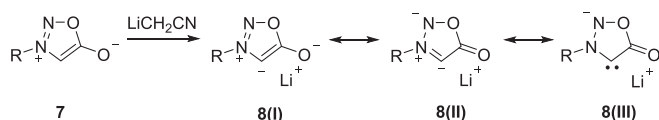
Scheme 1. Examples of zwitterionic anionic N-heterocyclic carbenes.



Scheme 2. Anionic N-heterocyclic carbenes of mesomeric betaines.

system (Scheme 3).¹⁷ They can be represented as abnormal anionic N-heterocyclic carbenes **8(I)**, anionic normal N-heterocyclic carbenes **8(II)** and as electron sextet structures **8(III)**. Thus, syndnone anions, which proved to be quite stable as lithium adducts under exclusion of moisture,¹⁷ are elements of the intersection of the compound classes of mesomeric betaines and anionic N-heterocyclic carbenes. They have been applied in synthetic chemistry¹⁸ and as ligands of catalysts for Suzuki-Miyaura reactions under various conditions.¹⁹ Syndnone imine carbenes have been described recently.²⁰ According to a very recently introduced quantitative analysis of factors influencing the ease of formation of oxa- and thia-N-heterocyclic carbenes, N-phenyl-syndnone has a CREF (carbene relative energy of formation) index value of 0.572 which is between the values of **3** (Ar = Ph; 0.600) and **5** (Ar = Me; 0.547).²¹

In continuation of our studies we became interested in syndnone-4-carboxylates, because a number of hetarenium-carboxylates can behave as masked N-heterocyclic carbenes. Examples are carboxylates of pyridin-2-ylidene derivatives,²² imidazole-2-ylidenes,²³ pyrazolium-3-ylidenes,²⁴ and indazolium-3-ylidenes.²⁵ They were proven to be versatile starting materials for their *in-situ* generation by thermal decarboxylation which is a valuable alternative to deprotonations. Based on these reported developments and our finding that syndnone-4-carboxylates are effective additives for Suzuki-Miyaura reactions in acid,¹⁹ we investigated the decarboxylation and the thermal behavior of syndnone-4-carboxylates in the solid state, in solution, and under ESI mass spectrometric conditions. The mechanism of the decomposition was also examined via DFT computations.



Scheme 3. Selected canonical forms of syndnone anions.

2. Results and discussion

2.1. Syntheses and characterizations of syndnone-4-carboxylates

Lithium syndnone-4-carboxylates **10a,b** were prepared by bromination at the C4 positions of the syndnones **7a,b** based on literature procedures to yield **9a**²⁶ and **9b**.²⁷ This was followed by bromine-lithium exchange and treatment of the resulting species with carbon dioxide. The formed syndnone-4-carboxylate **10a** has already been described in the literature before.²⁸ Finally, the lithium-carboxylates were protonated to give the carboxylic acids **11a,b**. In contrast to the generally applied procedures,^{19,29} hydrochloric acid was replaced by hydrogen tetrafluoroborate as protonating agent in order to obtain better yields (Scheme 4).

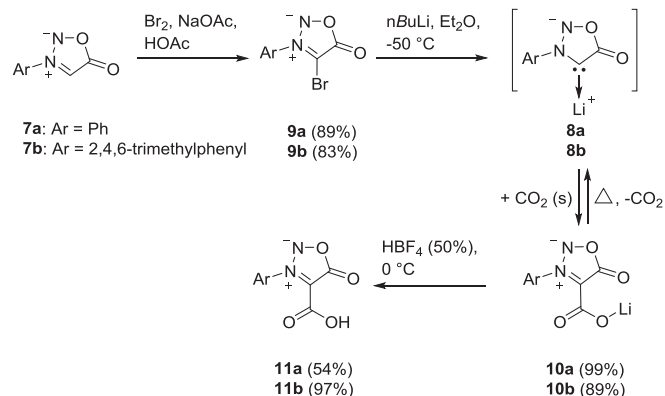
We performed single crystal X-ray analyses on the isolated compounds **7a** and **7b**. We found, that the syndnone moiety and the aryl ring at position N3 are twisted by 104.7° (**7a**)³⁰ and 178.9° (**7b**)¹⁷ from the molecular plane. In addition, single crystals of N-phenylsyndnone-4-carboxylic acid **11a** were grown through slow evaporation of a concentrated solution in ethanol. The monoclinic crystals comprised neither water of crystallization nor solvent molecules (Fig. 1).

In the crystallized form, the N-phenylsyndnone-4-carboxylic acid **11a** forms dimers which are connected via two relatively stable³¹ homo-intermolecular hydrogen bonds³² (Fig. 2).

According to the single crystal analysis, the torsion angle between the syndnone ring and the N3-aryl ring (C12–C10–N3–N2) is 116.0° and the dihedral angle between syndnone and carboxylate group (C5–C4–C7–O9) was measured to be 174.4°. The bond between the carboxylic acid moiety and the syndnone ring (1.44 Å) appears to be longer than in aliphatic carboxylic acids. The carbonyl double bond C7=O has a length of 1.23 Å. The bond length between the carbonyl carbon atom and the hydroxyl group is shortened (1.34 Å), caused by the dimeric structure.³³

2.1.1. Classifications

Syndnones (**I**) are conjugated mesomeric betaines (CMB) constructed of the 1,3-dipole azomethin-imine (**II**) and carbon dioxide (Scheme 5). Their isoconjugated equivalents are even, non-alternant hydrocarbon dianions **III**. Mesoionic compounds of type A such as syndnones are constructed of atoms a-f which contribute electrons to the system as indicated by the superscripts (**IV**). Syndnone-4-carboxylates are anionic tripoles, therefore they are exceptions to the definition of mesomeric betaines in the classical sense.³⁴ Nevertheless they can be described as hybrids of the conjugated mesomeric betaines syndnone and pseudo-cross-conjugated mesomeric betaines (PCCMB), because they possess the



Scheme 4. Synthesis of syndnone-4-carboxylic acids.

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