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Heterocycle syntheses with anionic N-heterocyclic carbenes.

Ring transformations of sydnone imine anions

Tyll Freese,^[a] Ana-Luiza Lücke,^[a] Jan C. Namyslo,^[a] Martin Nieger,^[b] and Andreas Schmidt^{*[a]}

Abstract: Sydnone imines were deprotonated at C4 to give lithium-stabilized anions which proved to be stable for several months in solution. These anions are elements of the intersection of the substance classes of N-heterocyclic carbenes and mesomeric betaines and can be formulated as anionic N-heterocyclic carbenes. The negative charge translates into high-field shifts of the ¹³C NMR resonance frequencies of C4 in comparison to other NHCs. Similar to the chemistry of N-heterocyclic carbenes reactions with isocyanates and isothiocyanates gave 4-(N-carbamoyl)-benzoylsydnone imines in trapping reactions. As a result of ring transformations involving the characteristic π -architecture of the mesoionic framework, however, imidazolidine-2,4-dithiones, imidazolin-2,4-diones and 1,2,4-triazol-5-ones were formed depending on the substitution pattern of the starting materials and the reaction conditions.

the high degree of positive charge on N3, whereas the negative partial charge on the exocyclic nitrogen atom is reflected in its basicity.^[7] The electron density on C4 is thought to determine the mode of electrophilic substitution reactions.^[7]

Scheme 1. Some canonical formulae of sydnones **1** and of sydnone imines **2**.

Introduction

Sydnones **1** (1,2,3-oxadiazolium-5-olates) represent the most prominent structural type of 228 theoretically predicted mesoionic compounds.^[1] They are members of the class of conjugated mesomeric betaines (CMB) and belong to class 1B according to a recent classification of heterocyclic mesomeric betaines.^[2] The term mesomeric betaine summarizes all molecules which can exclusively be described by a number of dipolar or tetrapolar resonance forms which delocalize the positive and negative charges within a common π -electron system. As examples, sydnones can be described by canonical forms such as **1(I)**, **1(II)** and **1(III)**. The latter two are in agreement with the bond lengths of the exocyclic C-O bond which corresponds to a double bond.^[3] Sydnones have proven to be versatile 1,3-dipoles for cycloaddition reactions^[4] and have displayed various biological activities.^[5] In contrast to sydnones, the much lesser examined class of sydnone imines **2** (1,2,3-oxadiazolium-5-aminides) formally possess an exocyclic imine bond as analogously represented by the canonical forms **2(II)** and **2(III)**.^[6] The chemistry of sydnone imines such as their hydrolytic or thermal decomposition has been associated with

In view of the current interest in anionic heterocyclic carbenes^[8] we became interested in studying the anions of sydnones **3** and of O-ethyl sydnones **4**.^[3] Similar to the parent compound, the anions have to be described by several mesomeric forms. Concerning **3**, the structures of anionic NHCs and of abnormal anionic NHCs are among the canonical formulae as shown (Scheme 2). By contrast, the deprotonated O-ethylsydnone **4** can be defined as abnormal N-heterocyclic carbene. The fact that the delocalization of the negative charge of **3** include the site of deprotonation, *i.e.* C4, sets these systems apart from most known anionic N-heterocyclic carbenes. Connectivity analyses^[2] of sydnone anions reveal that C4 is a starred (active) position and, correspondingly, large atomic orbital coefficients of the highest occupied molecular orbitals (HOMO) were calculated to be located on C4, resulting in an ESP partial charge of -0.94 and considerable high-field shifts of the ¹³C NMR signals.

Scheme 2. Sydnone anions **3** and the NHC of O-ethyl sydnone **4**. Charge distribution according to the resonance forms (I) and connectivity analysis (II).

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The anions of sydnone form palladium complexes which are catalytically active in cross-coupling reactions.^{[3],[9]} These derivatives of mesoionic compounds are elements of the interesting intersection of the substance classes of mesomeric betaines and N-heterocyclic carbenes. A first review is available.^[10] Very recently, a quantitative analysis of factors influencing the ease of formation and σ -bonding strength of N-heterocyclic carbenes, including those derived from mesomeric betaines, was developed.^[11] According to this analysis, N-phenylsydnone has CREF factor (carbene relative energy of formation) of 0.572 which means that deprotonation occurs easier than in diphenylimidazolium-4-olate (CREF = 0.600).^[11] In continuation of our interest in mesomeric betaines,^[12] N-heterocyclic carbenes^[13] and the combination of both classes^[14] we report here on new and unexpected reactions of sydnone imine anions which prove their Janus-type character.

Results and Discussion

The sydnone imine hydrochlorides **6a,b** were prepared from the amines **5a,b** by nucleophilic substitution with haloacetonitriles in reasonable yields according to modified literature procedures concerning the cyclohexyl derivative,^[15] followed by N-nitrosation and ring closure reaction on treatment with gaseous hydrochloric acid. Final benzoylation gave the sydnone imines **7a,b** as stable, brownish to yellow-colored compounds which we used as starting materials for further syntheses. The sydnone imine **7c** was prepared by a slightly different method which we described in an earlier paper.^[16]

Scheme 3. Reaction conditions starting from **5a**: A) 1.1 eq. of ClCH₂CN, 2.2 eq. of K₂CO₃, MeCN, 20 h, reflux (79 %)^[39]; B) 2.4 eq. of amyl nitrite, Et₂O, 20 h, rt, then HCl(g), 1.5 h, rt (88 %); C) 1.2 eq. of PhCOCl, CH₂Cl₂, -10 °C, then 2.4 eq. of NEt₃ (96 %). Reaction conditions starting from **5b**: A) 1.2 eq. of BrCH₂CN, 1.2 eq. of NaOAc, EtOH, 24 h, reflux (73 %); B) 2.4 eq. of amyl nitrite, Et₂O, 20 h, rt, then HCl(g), 1.5 h, rt (82 %); C) 1.2 eq. of PhCOCl, CH₂Cl₂, -10 °C, then 2.4 NEt₃ (76 %). Reaction conditions starting from **5c**: D) BrCH₂CN, NaOAc, EtOH, reflux (83%); E) NaNO₂, HCl, 0 °C (92%); F) HCl(g), Et₂O, 20 °C (99%); G) PhCOCl, CH₂Cl₂, -10 °C, then NEt₃ (80%).

Sydnone imines are known to be photochemically and thermally sensitive.^[17] Nevertheless we obtained single crystals of sydnone imine **7a** by slow evaporation of a chloroform-ethyl acetate mixture in the dark and subjected them to a single crystal X-ray analysis. The exocyclic C–N bond was found to be 131.56(14) pm which resembles the C(sp²)=N double bond length of oximes and imines (128 pm) rather than the C(sp²)–N single bond length of formamide (138 pm).

Figure 1. Molecular drawing of **7a** (displacement parameters are drawn at 50% probability level). Selected bond lengths [pm] (crystallographic numbering): N2–N3: 129.71 (13), N3–C4: 134.70 (13), C4–C5: 138.63 (15), C5–N6: 131.56 (14), C7–O7: 123.75(13), O7–H4: 238.3 pm.

Next we performed a base screening to obtain the anions of sydnone imines for further examinations. The CREF index of 5-(acetylmino)-3-methyl-sydnone as a model compound was calculated to be 0.574.^[11] Ring cleavages of sydnone imines are known to occur under basic conditions^[18] or in water to give N-nitrosoaminoacetamides and α -(N-nitrosobenzylamino)acrylonitrile, respectively.^[19] In addition, *N*-acyl-substituted sydnone imines form 4-hydroxy-1,2,3-triazoles^[20] or pyrazolinones^[21] on treatment with hydroxide or aqueous ammonia by means of ring transformations. In the past, *n*BuLi has been used to initiate several electrophilic attacks at C4,^[22] however, these reactions suffer from rapid decompositions at elevated temperatures.^[23] In the course of our base screenings we found that 1M lithium bis(trimethylsilyl)amide in THF at rt is the best base to accomplish quantitative deprotonations at C4 of sydnone imines (Scheme 4). Again, several canonical formulae describe the systems, among those mesomeric forms of anionic NHCs, anionic abnormal NHCs as well as by a structure which displays two negative charges on C4. According to the understanding of mesomerism concerning the distribution of charges in conjugated systems, one of these two negative charges at C4 is due to the exocyclic sp² orbital, and the other represents the delocalized negative charge within the π -conjugated system.

Scheme 4. Sydnone imine anions and their canonical forms.

The deprotonated sydnone imines **8a–c** are stable in THF solutions for several months in the absence of water. ¹³C NMR spectra show a down field shift at the C4 position (**8a**: 152.0 ppm, **8b**: 154.8 ppm, **8c**: 159.8 ppm) in comparison to the starting materials. These values, however, are considerably shifted high-field in comparison to other N-heterocyclic

carbenes.^[10] The role of the lithium cation is crucial for the stabilization of the anions, as potassium ions trigger decomposition. According to a DFT calculation at the B3LYP/6-31G(d,p) level the lithium cation is located between the carbene carbon atom and the carbonyl oxygen atom. The 2-methoxyphenyl substituent is twisted out of planarity. We calculated the HOMO-1, HOMO and LUMO energies of **8c** to be -6.39 eV, -5.46 eV and -1.85 eV, respectively. The HOMO-1 includes the σ lone pair, whereas the HOMO and LUMO are π orbitals, respectively (Fig. 2).

Figure 2. HOMO-1 (above left), HOMO (above right) and LUMO (below) of **8c**.

In order to study the covalent bond character of the C-Li bond, we performed ^7Li NMR measurements of **8c**. Literature suggests a rising covalent C-Li bonding character with increasing downfield shifts in the ^7Li NMR spectra.^[24] The ^7Li NMR shift of **8c** was determined to be +0.6 ppm (THF-[D]₈, rt), whereas the chemical shift for LHMDS is +0.1 ppm (THF-[D]₈, rt, ext. ref. LiBr). Comparison of literature known chemical shifts in THF (nBuLi: +1.2 ppm at rt;^[25] tBuLi: +0.3 ppm at -95 °C;^[26] LiAlH₄: -0.2 ppm at rt^[27]) indicates a covalent bond character between tBuLi and nBuLi for the Li-C bond of the carbene **8c**. Sydnone imine anions form gold and palladium complexes^[16] and undergo reactions with S^[28] and Se.^[16] To the best of our knowledge, however, the trapping reaction with CO₂, isocyanates and isothiocyanates have not yet been described. They are trapping reactions of N-heterocyclic carbenes such as imidazole-2-ylidene,^[29] pyrazol-3-ylidene,^[30] indazol-3-ylidene^[31] as well as several organo lithium compounds. Thus phenyl lithium reacts with isocyanates,^[32] isothiocyanates,^[33] and carbon dioxide^[34] similarly; the non-complexed phenyl anion was calculated to have a significant carbene character.^[35] To study the behavior of sydnone imine anions toward heterocumulenes we reacted freshly prepared samples of deprotonated sydnone imines with tolyl isocyanate, tolyl isothiocyanate and p-chlorophenyl isocyanate. Starting from sydnone imine **7a** the anticipated amides **9,11** and the thioamide **10** were formed at rt in high yields (Scheme 5). Higher temperatures (< 50 °C) gave identical products in similar yields.

Scheme 5. Amides and thioamides from sydnone imine **7a**.

When starting from the 3-aryl substituted sydnone imines **7b,c**, however, the 5-arylhydrazono-imidazolidine-2,4-diones or -dithiones **12 - 17** and the triazoles **18,19** were formed in moderate yields on reaction with the aforementioned iso(thio)cyanates (Scheme 6). The outcome of the reactions is dependent on the substitution patterns of the substrates, the iso(thio)cyanates, the stoichiometry, and the reaction temperature. Details are summarized in Table 1. The yellow hydrazones **12** and **14** can be isolated when performing the reaction at -30 °C with subsequent quenching with water, whereas the corresponding triazoles **18** and **19** were formed slowly while warming the reaction mixture to rt. Thus, the p-chlorophenyl-substituted sydnone **7b** reacted with isocyanates to give the triazoles **18** and **19** (Table 1, entries 7,8), whereas the less reactive isothiocyanate gave the hydrazone **17** (Table 1, entry 6).

Scheme 6. Formation von arylhydrazones from sydnone imines **7b,c**.

Table 1. Substitution pattern of compounds **12 - 19**, reaction times, temperatures and yields.

Entry	educt	product	R ¹	R ²	R ³	X	t	T	yield
1	7b	12	H	Cl	Me	O	8 h	-30°C	30%
2	7b	13	H	Cl	Me	S	5 h	rt	47%
3	7b	14	H	Cl	Cl	O	8 h	-30°C	26%
4	7c	15	OMe	H	Me	O	5 h	rt	36%
5	7c	16	OMe	H	Me	S	5 h	rt	43%
6	7c	17	OMe	H	Cl	O	5 h	rt	40%
7	7b	18	H	Cl	Me	-	5 h	rt	26%
8	7b	19	H	Cl	Cl	-	5 h	rt	26%

A single crystal X-ray study of **15** helped to determine the structure (Fig. 3) and displays hydrogen bondings between O4-N7-H and O14-N7-H, resulting in a planar conformation between the o-methoxyphenyl and the imidazolidine ring fragments. The NH-proton is localized at the N7-nitrogen atom in the crystal structure and this is also true in solutions and can be proven by HMBC NMR spectra at rt. The hydrazones show intense yellow (diones) to violet colors (dithiones) with extinction coefficients from 15500 (**13**) to 33900 (**10**) L/mol*cm.

Figure 3. Molecular drawing of **15** (displacement parameters are drawn at 50% probability level). Selected bond lengths [pm] (crystallographic numbering): N1-C2: 137.98(14), N1-C5: 141.06(13), C2-O2: 121.33(13), C2-N3: 141.04(14), N3-C4: 138.98(14), C4-O4: 121.92(14), C4-C5: 146.93(15), C5-N6: 128.63(14), N6-N7: 134.11(13), O4-H7: 212(1), O14-H7: 227(1) pm.

We propose the following mechanism for the formation of **12** - **17** (Scheme 7). The sydnone imine carbenes **7b,c** are subsequently trapped by two molecules of isocyanates (**A** → **B**). The negative charge of the isocyanate residue of **B** induce a ring cleavage of the sydnone imine to give **C**, the enolate moiety of which attacks the azo group to give **D**. Formation of benzoyl isocyanate yielded the isolated products **12** - **17**.

Scheme 7. Proposed mechanism for the formation of **12** - **17** by ring transformation.

According to a DFT calculation at the B3LYP/6-31G(d,p) level the HOMO and LUMO of intermediate **7cB** are separated. The HOMO has indeed a large atomic orbital coefficient at the negatively charged nitrogen atom of the northern carbamoyl(2-methoxyphenyl)amidate moiety, whereas the LUMO has a large coefficient at C4 of the sydnone imine moiety. This step therefore resembles intramolecular charge neutralizations of cross-conjugated mesomeric betaines.^[36] Likewise, the HOMO of intermediate **7cC** has large coefficients at the enolate carbon atom, whereas at the azo group large coefficients of the LUMO were calculated.

Figure 4. Frontier orbital profile of the intermediates **7cB** and **7cC**.

Further investigation showed the possibility to directly react the hydrazone **12** into the triazole **18** starting from the anion of **12** (Scheme 8). This is generated by LHMDS at rt and undergoes a [2+3]-cycloaddition with isocyanate and subsequent ring cleavage of the imidazoledione moiety. Extrusion of one molecule of isocyanate gave the triazole **18** after quenching the reaction mixture. A blind probe was also carried out without addition of isocyanate. Under these conditions, reaction temperatures up to 50 °C induced no reaction at all.

Scheme 8. Transformation of the hydrazone **12** into triazole **18**.

Conclusions

Sydnone imine anions are elements of the intersection between mesomeric betaines and N-heterocyclic carbenes. They have to be represented by several canonical formulae, among those the structures of anionic NHCs and abnormal anionic NHCs. The sp^2 hybrid orbital at C4 containing the pair of electrons governs its carbene character, whereas the architecture of π -electrons translates into a mesomeric betaine-like chemical behavior. A large atomic orbital coefficient of the HOMO at C4 leads to considerable high-field shifts of the ^{13}C NMR resonance frequencies. Sydnone imine anions were generated by LHMDS in THF at rt. They proved to be stable under exclusion of light and moisture. Depending on the substitution pattern they reacted with isocyanates and isothiocyanates to give (arylcarbamoyl)-3-cyclohexyl-sydnone imines, 1,3-diaryl-5-(2-arylhydrazono)-imidazolidine-2,4-diones or 1-aryl-3-(N-arylcarbamoyl)-4-aryl-4,5-dihydro-1,2,4-triazol-5-ones as a result of the symphony of σ (carbene) and π electrons (mesomeric betaine).

Experimental Section

General consideration

Flash-chromatography was performed with silica gel 60 (0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance 400 and Bruker Avance III 600 MHz. ^1H NMR spectra were recorded at 400 MHz or 600 MHz and ^{13}C NMR spectra were measured at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH , CH_3); - = down (CH_2). The numbering of the compounds is not necessarily in accordance with IUPAC rules to allow comparisons ("spectroscopic numbering"). FT-IR spectra were obtained on a Bruker Vector 22 in the range of 400 to 4000 cm^{-1} . Melting points were measured by differential scanning calorimetry (DSC) using

a DSC 6 apparatus (Perkin Elmer). The electrospray ionization mass spectra (ESIMS) were taken with an Agilent LCMSD series HP 1100 with APIES at a fragmentor voltage of 30 V unless otherwise noted. Samples were dissolved in MeOH and sprayed from MeCN at 4000 V capillary voltage. The HR-MS spectra were measured on a Bruker Daltonik Tesla-Fourier transform-ion cyclotron resonance mass spectrometer with electrospray ionisation. Yields are not optimized.

Crystal structure determination

The single-crystal X-ray diffraction study was carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) (**7a**) or Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) (**15**). Direct Methods (SHELXS-97)^[37] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2).^[38] Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(N) free). Semi-empirical absorption corrections and extinction corrections were applied (see cif-file for details).

7a: colorless crystals, $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_2$, $M = 271.32$, crystal size $0.32 \times 0.16 \times 0.08 \text{ mm}$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.7085(4) \text{ \AA}$, $b = 17.9600(7) \text{ \AA}$, $c = 7.7222(3) \text{ \AA}$, $\beta = 103.236(1)^\circ$, $V = 1310.71(9) \text{ \AA}^3$, $Z = 4$, $\rho(\text{calc}) = 1.375 \text{ Mg m}^{-3}$, $F(000) = 576$, $\mu(\text{CuK}\alpha) = 0.76 \text{ mm}^{-1}$, 11915 reflections ($\theta_{\text{max}} = 72.2^\circ$), 2559 unique [$R_{\text{int}} = 0.020$], 182 parameters, $R1$ (for 2449 $I > 2\sigma(I)$) = 0.033, $wR2$ (all data) = 0.086, $S = 1.05$, largest diff. peak and hole 0.29 and $-0.19 \text{ e \AA}^{-3}$.

15: yellow crystals, $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_3$, $M = 414.45$, crystal size $0.24 \times 0.20 \times 0.12 \text{ mm}$, triclinic, space group $P-1$ (no. 2), $a = 7.7786(4) \text{ \AA}$, $b = 12.1357(8) \text{ \AA}$, $c = 12.5091(8) \text{ \AA}$, $\alpha = 117.631(2)^\circ$, $\beta = 99.457(2)^\circ$, $\gamma = 92.632(2)^\circ$, $V = 1021.83(11) \text{ \AA}^3$, $Z = 2$, $\rho(\text{calc}) = 1.347 \text{ Mg m}^{-3}$, $F(000) = 436$, $\mu(\text{MoK}\alpha) = 0.09 \text{ mm}^{-1}$, 41247 reflections ($\theta_{\text{max}} = 27.5^\circ$), 4695 unique [$R_{\text{int}} = 0.030$], 287 parameters, 1 restraint, $R1$ (for 4117 $I > 2\sigma(I)$) = 0.038, $wR2$ (all data) = 0.101, $S = 1.03$, largest diff. peak and hole 0.40 and $-0.29 \text{ e \AA}^{-3}$.

CCDC 1588012 (**7a**), and 1588013 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Calculations.

All density-functional theory (DFT)-calculations were carried out by using the current Spartan Software (Spartan'16, Wavefunction, Inc., Irvine, CA. Available from: <http://www.wavefun.com>) running on an Intel® Core™ i7-6950X deca-core system equipped with 64 GB RAM main memory and sufficient solid-state disc space. MMFF optimized structures were used as starting geometries. Then, the B3LYP density functional and the 6-31G(d,p) basis set was used. All final structures were proven to be true minima by the absence of

imaginary frequencies or transition states by the occurrence of a negative frequency.

Synthesis of sydnone imine hydrochloride 6a: Cyclohexylamine (**5a**) (5.00 g, 50.4 mmol), chloroacetonitrile (4.19 g, 55.5 mmol), potassium carbonate (13.94 g, 101 mmol) and 50 mL of acetonitrile were combined in a 100 mL flask and refluxed for 20 h. Afterwards the reaction mixtures were poured into 250 mL of water. The aqueous phase was extracted with dichloromethane three times, respectively. The combined organic phases were dried over MgSO_4 and the solvent was removed under reduced pressure. Further purification of the black liquid was not necessary for the follow-up reaction. Yield: 5.50 g (79%) of a black oil of N-cyclohexyl-aminoacetonitrile. ^1H NMR (400 MHz, CDCl_3): δ = 3.63 (s, 2H, 5-H), 2.68 (tt, $J_{\text{H,H}1}$ = 10.2 Hz, $J_{\text{H,H}2}$ = 3.8 Hz, 1H, 1-H), 1.83-1.88 (m, 2H, 2/2'-H), 1.72-1.78 (m, 2H, 3/3'-H), 1.60-1.67 (m, 1H, 4-H), 1.25-1.36 (m, 2H, 3/3'-H), 1.14-1.23 (m, 1H, 4-H), 1.04-1.14 (m, 2H, 2/2'-H) ppm. Spectroscopic data are in agreement with those reported in the literature.^[39] A solution of N-cyclohexyl-aminoacetonitrile thus prepared (5.50 g, 39.8 mmol) in 35 mL Et_2O (abs.) in a two-necked flask was treated with isopentyl nitrite (12.9 mL, 95.5 mmol) and stirred at rt for 20 hours. Afterwards the solution was treated with gaseous hydrochloric acid for 90 minutes. The resulting precipitation was filtered off and washed generously with Et_2O and DCM. Yield: 7.13 g (88%) of a white solid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 9.87 (s, 2H, 6-H), 8.17 (s, 1H, 4-H), 4.88 (tt, $J_{\text{H,H}1}$ = 11.3 Hz, $J_{\text{H,H}2}$ = 3.8 Hz, 1H, 7-H), 2.17-2.20 (m, 2H, 8/8'-H), 1.81-1.91 (m, 4H, 8/8'-H + 9/9'-H), 1.62-1.65 (m, 1H, 10-H), 1.36-1.47 (m, 2H, 9/9'-H), 1.19-1.30 (m, 1H, 10-H) ppm. Spectroscopic data are in agreement with those reported in the literature.^[40]

Synthesis of sydnone imine hydrochloride 6b: p-Chloroaniline (10.00 g, 78.4 mmol), bromoacetonitrile (11.28 g, 94.1 mmol), sodium acetate trihydrate (12.80 g, 94.1 mmol) and 40 mL of ethanol were combined in a 100 mL flask and refluxed for 24 h. Afterwards the reaction mixture was poured into 250 mL of iced water. The resulting precipitate was filtered off, washed with water and dried *in vacuo*. Purification was achieved by recrystallization from EtOH . Yield: 9.53 g (73%) of a white solid consistent of N-(p-chlorophenyl)-aminoacetonitrile. ^1H NMR (400 MHz, CDCl_3): δ = 7.19-7.23 (m, 2H, 2/2'-H), 6.60-6.64 (m, 2H, 3/3'-H), 4.06 (s, 3H, 4-H + 5-H) ppm. Spectroscopic data are in agreement with those reported in the literature.^[41] A solution of N-cyclohexyl-aminoacetonitrile thus prepared (3.76 g, 22.5 mmol) in 35 mL of Et_2O (abs.) in a two-necked flask was treated with isopentyl nitrite (7.3 mL, 54.1 mmol) and stirred at rt for 20 hours. Afterwards the solution was treated with gaseous hydrochloric acid for 90 minutes. The precipitation was filtered off and washed generously with Et_2O . Yield: 4.28 g (82%) of a white solid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.22 (s, 2H, 6-H), 8.75 (s, 1H, 4-H), 8.10-8.13 (m, 2H, 8/8'-H), 7.85-7.87 (m, 2H, 9/9'-H) ppm. Spectroscopic data are in agreement with those reported in the literature.^[18b]

General procedure for the benzylation of sydnone imine hydrochlorides 6a-c: A suspension of the sydnone imine hydrochloride, 1.2 eq. of benzoyl chloride and DCM (abs.) was cooled to -10°C . Then under vigorous stirring a solution of 2.4 eq. of triethylamine in 5 mL of DCM (abs.) was added slowly. The mixture was then slowly warmed to rt and stirred for 16 h. Afterwards 100 mL of water were added. The aqueous phase was extracted with dichloromethane three times. The combined organic phases were dried over MgSO_4 and the solvent was finally removed under reduced pressure.

3-Cyclohexyl-6-benzoylsydnone imine 7a: N-Cyclohexyl-sydnone imine hydrochloride (2.00 g, 9.82 mmol), benzoyl chloride (1.37 mL, 11.78 mmol), triethylamine (3.28 mL, 23.57 mmol) and 30 mL of DCM (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM:MeOH = 30:1). Yield: 2.55 g (96%) of a brownish solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.27-8.29 (m, 2H, 9/9'-H), 8.20 (s, 1H, 4-H), 7.46-7.51 (m, 1H, 11-H), 7.41-7.45 (m, 2H, 10/10'-H), 4.52 (tt, $J_{\text{H,H}1}$ = 11.8 Hz, $J_{\text{H,H}2}$ = 3.9 Hz, 1H, 12-H), 2.27-2.31 (m, 2H, 13/13'-H), 1.96-2.01 (m, 2H, 14/14'-H), 1.83-1.94 (m, 2H, 13/13'-H), 1.76-1.81 (m, 1H, 15-H), 1.41-1.52 (m, 2H, 14/14'-H), 1.24-1.35 (m, 1H, 15-H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 174.4 (o, C-5), 174.2 (o, C-7), 137.1 (o, C-8), 129.3 (+, C-11), 129.3 (+, C-9/9'), 127.9 (+, C-10/10'), 104.0 (+, C-4), 64.6 (+, C-12), 32.2 (-, C-13/13'), 24.6 (-, C-14/14'), 24.5 (-, C-15) ppm. Spectroscopic data are in agreement with those reported in the literature.^[15]

3-(p-Chlorophenyl)-6-benzoylsydnone imine 7b: N-(p-Chlorophenyl)-sydnone imine hydrochloride (0.30 g, 1.29 mmol), benzoyl chloride (0.18 mL, 1.55 mmol), triethylamine (0.43 mL, 3.10 mmol) and 10 mL DCM (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM:MeOH = 30:1). Yield: 0.29 g (76%) of a yellow solid, mp: 191°C (decomposition). ^1H NMR (400 MHz, CDCl_3): δ = 8.65 (s, 1H, 4-H), 8.26-8.29 (m, 2H, 9/9'-H), 7.79-7.84 (m, 2H, 13/13'-H), 7.58-7.61 (m, 2H, 14/14'-H), 7.48-7.52 (m, 1H, 11-H), 7.41-7.45 (m, 2H, 10/10'-H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 174.5 (o, C-5), 174.3 (o, C-7), 139.5 (o, C-15), 136.8 (o, C-8), 132.2 (o, C-12), 131.7 (+, C-11), 130.8 (+, C-14/14'), 129.5 (+, C-9/9'), 128.0 (+, C-10/10'), 122.8 (+, C-13/13'), 104.3 (+, C-4) ppm; IR (ATR): 3187, 3066, 1627, 1553, 1489, 1432, 1314, 1293, 1093, 1067, 1011, 971, 946, 832, 729, 707, 690, 681, 662, 642, 516, 497 cm^{-1} ; MS (ESI 30 V) m/z (%) = 300.0 (30) $[\text{M}+\text{H}]^+$. HR-ESI-MS: calcd for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_2\text{Cl}_1^+$ 300.0540. Found 300.0540.

General procedure for the sydnone imine deprotonations: Under an inert atmosphere a dry sample of the sydnone imine in an NMR tube was dissolved in anhydrous THF- d_8 . Then 1.2 eq. of a 2M solution of LHMDs in THF was added to give the lithium adduct in quantitative yields.

4-Lithium-3-cyclohexyl-6-benzoylsydnone imine 8a: 3-Cyclohexyl-6-benzoylsydnone imine (0.021 g, 0.077 mmol) and a 2M solution of LHMDs in THF (0.046 mL, 0.093 mL) were used for the deprotonation experiment. ^1H NMR (600 MHz, THF-

δ : 8.33–8.35 (m, 2H, 9/9'-H), 7.30–7.35 (m, 3H, 10/10'-H + 11-H), 4.45–4.50 (m, 1H, 12-H), 2.15–2.18 (m, 2H, Cy-H), 1.96–2.03 (m, 2H, Cy-H), 1.88–1.92 (m, 2H, Cy-H), 1.73–1.78 (m, 1H, Cy-H), 1.45–1.54 (m, 2H, Cy-H), 1.22–1.30 (m, 1H, Cy-H) ppm; ^{13}C NMR (150 MHz, THF- d_8): δ = 185.6 (o, C-5), 170.2 (o, C-7), 152.0 (o, C-4), 141.1 (o, C-8), 130.1 (+, C-11), 129.8 (+, C-9/9'), 127.8 (+, C-10/10'), 64.3 (+, C-12), 34.4 (-, C-Cy), 26.1 (-, C-Cy), 25.9 (-, C-Cy) ppm.

4-Lithium-3-(p-chlorophenyl)-6-benzoylsydnone imine 8b: 3-(p-Chlorophenyl)-6-benzoylsydnone imine (0.015 g, 0.050 mmol) and 2M solution of LHMDS in THF (0.030 mL, 0.060 mL) were used for the deprotonation experiment. ^1H NMR (600 MHz, THF- d_8): δ = 8.29–8.31 (m, 2H, 9/9'-H), 8.14–8.16 (m, 2H, 13/13'-H), 7.53–7.56 (m, 2H, 14/14'-H), 7.29–7.32 (m, 1H, 11-H), 7.24–7.27 (m, 2H, 10/10'-H) ppm. ^{13}C NMR (150 MHz, THF- d_8): δ = 186.5 (o, C-5), 171.2 (o, C-7), 154.8 (+, C-4), 139.8 (o, C-15), 140.7 (o, C-8), 136.4 (o, C-12), 130.4 (+, C-11), 130.2 (+, C-14/14'), 130.0 (+, C-9/9'), 127.9 (+, C-10/10'), 123.9 (+, C-13/13'), ppm.

4-Lithium-3-(o-methoxyphenyl)-6-benzoylsydnone imine 8c: 3-(o-Methoxyphenyl)-6-benzoylsydnone imine (0.022 g, 0.075 mmol) and 2M solution of LHMDS in THF (0.045 mL, 0.089 mL) were used for the deprotonation experiment. ^1H NMR (600 MHz, THF- d_8): δ = 8.25–8.24 (m, 2H, 9/9'-H), 7.48–7.51 (m, 1H, 15-H), 7.46–7.47 (m, 1H, 17-H), 7.22–7.25 (m, 1H, 11-H), 7.19–7.20 (m, 1H, 14-H), 7.13–7.16 (m, 2H, 10/10'-H), 7.05–7.07 (m, 1H, 16-H), 3.73 (s, 3H, 19-H) ppm.^[16] ^{13}C NMR (150 MHz, THF- d_8): δ = 185.4 (o, C5), 170.4 (o, C7), 159.8 (o, C4), 154.9 (o, C13), 140.8 (o, C8), 131.8 (+, C15), 130.8 (o, C12), 130.1 (+, C11), 129.8 (+, C9/C9'), 128.2 (+, C17), 127.9 (+, C10/C10'), 121.0 (+, C16), 113.4 (+, C14), 56.1 (+, C19) ppm. ^7Li NMR (233 MHz, THF- d_8): δ = 0.58 ppm.

General procedure for the sydnone imine carbene generation and subsequent reaction with isocyanates / isothiocyanates: Under an inert atmosphere the sydnone imines were solved in THF (abs.) and treated with a 2M solution of LHMDS in THF. After stirring for 10 minutes at rt the isocyanates/isothiocyanates were added. An immediate change of color was observed. The reaction mixture was stirred for 5 h, then combined with silica gel and purified by column chromatography.

4-(N-(p-Methylphenyl)carbamoyl)-3-cyclohexyl-6-benzoylsydnone imine 9: 3-Cyclohexyl-6-benzoylsydnone imine (0.271 g, 1.00 mmol), 2 M of LHMDS in THF (0.60 mL, 1.20 mmol), 4-tolyl isocyanate (0.28 mL, 2.20 mmol) and 12 mL THF (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM:MeOH = 100:1). Yield: 0.399 g (99 %) of a white solid, mp: 198 °C (decomposition). ^1H -NMR (600 MHz, CDCl_3): δ = 11.21 (s, 1H, 17-H), 8.24–8.25 (m, 2H, 9/9'-H), 7.55–7.56 (m, 2H, 19/C19'-H), 7.53–7.57 (m, 1H, 11-H), 7.46–7.48 (m, 2H, 10/10'-H), 7.18–7.19 (m, 2H, 20/20'-H), 5.94 (tt, $J_{\text{H,H}1}$ = 11.6 Hz, $J_{\text{H,H}2}$ = 3.6 Hz, 1H, 12-H), 2.37–2.39 (m, 2H, 13/13'-H), 2.35 (s, 3H, 22-H), 1.93–2.01 (m, 4H, 13/13'-H + 14/14'-H), 1.80–1.82 (m, 1H, 15-H), 1.54–1.61 (m, 2H, 14/14'-H),

1.30–1.37 (m, 1H, 15-H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 172.1 (o, C-7), 165.5 (o, C-5), 153.8 (o, C-16), 136.7 (o, C-8), 134.9 (o, C-21), 134.8 (o, C-18), 132.2 (+, C-11), 129.9 (+, C-20/20'), 129.4 (+, C-9/9'), 128.4 (+, C-10/10'), 120.2 (+, C-19/19'), 107.4 (o, C-4), 65.8 (+, C-12), 32.6 (-, C-13/13'), 25.2 (-, C-14/14'), 24.9 (-, C-15), 21.1 (+, C-22) ppm; IR (ATR): 3175, 3116, 3053, 2936, 2853, 1674, 1635, 1606, 1574, 1549, 1512, 1447, 1396, 1369, 1307, 1277, 1261, 1234, 1178, 1035, 1018, 902, 869, 828, 805, 741, 712, 693, 591, 536, 508 cm^{-1} ; MS (ESI 30 V) m/z (%) = 427.1 (30) $[\text{M}+\text{Na}^+]$, 831.5 (100) $[2\text{M}+\text{Na}^+]$. HR-ESI-MS: calcd for $\text{C}_{23}\text{H}_{25}\text{N}_4\text{O}_3^+$ 405.1927. Found 405.1926.

4-(N-(p-Methylphenyl)carbamothioyl)-3-cyclohexyl-6-benzoylsydnone imine 10: 3-Cyclohexyl-6-benzoylsydnone imine (0.271 g, 1.00 mmol), 2 M of LHMDS in THF (0.60 mL, 1.20 mmol), 4-tolyl isothiocyanate (0.328 g, 2.20 mmol) and 12 mL of THF (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM:PE = 10:1). Yield: 0.352 g (84%) of a yellow solid, mp: 171 °C (decomposition). ^1H NMR (400 MHz, CDCl_3): δ = 13.47 (s, 1H, 17-H), 8.15–8.18 (m, 2H, 9/9'-H), 7.64–7.66 (m, 2H, 19/C19'-H), 7.49–7.54 (m, 1H, 11-H), 7.40–7.46 (m, 2H, 10/10'-H), 7.24–7.26 (m, 2H, 20/20'-H), 6.97 (tt, $J_{\text{H,H}1}$ = 11.4 Hz, $J_{\text{H,H}2}$ = 3.5 Hz, 1H, 12-H), 2.44–2.47 (m, 2H, 13/13'-H), 2.39 (s, 3H, 22-H), 1.90–2.00 (m, 4H, 13/13'-H + 14/14'-H), 1.79–1.83 (m, 1H, 15-H), 1.50–1.62 (m, 2H, 14/14'-H), 1.28–1.38 (m, 1H, 15-H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 176.1 (o, C-16), 172.0 (o, C-7), 163.4 (o, C-5), 137.3 (o, C-21), 136.3 (o, C-8), 135.6 (o, C-18), 132.3 (+, C-11), 129.7 (+, C-20/20'), 129.4 (+, C-9/9'), 128.4 (+, C-10/10'), 124.2 (+, C-19/19'), 111.6 (o, C-4), 65.9 (+, C-12), 32.9 (-, C-13/13'), 25.2 (-, C-14/14'), 24.9 (-, C-15), 21.3 (+, C-22) ppm; IR (ATR): 2936, 2855, 1640, 1600, 1564, 1506, 1448, 1392, 1307, 1253, 1231, 1045, 1020, 817, 756, 737, 708, 571, 505, 449 cm^{-1} ; MS (ESI 30 V) m/z (%) = 443.1 (100) $[\text{M}+\text{Na}^+]$, 863.5 (80) $[2\text{M}+\text{Na}^+]$. HR-ESI-MS: calcd for $\text{C}_{23}\text{H}_{25}\text{N}_4\text{O}_2\text{S}_1^+$ 421.1698. Found 421.1700.

4-(N-(p-Chlorophenyl)carbamoyl)-3-cyclohexyl-6-benzoylsydnone imine 11: 3-Cyclohexyl-6-benzoylsydnone imine (0.200 g, 0.74 mmol), 2 M of LHMDS in THF (0.44 mL, 0.89 mmol), 4-chlorophenyl-isocyanate (0.249 g, 1.62 mmol) and 12 mL of THF (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM:PE = 10:1). Yield: 0.261 g (83%) of a white solid, mp: 182 °C (decomposition). ^1H NMR (400 MHz, CDCl_3): δ = 11.33 (s, 1H, 17-H), 8.20–8.23 (m, 2H, 9/9'-H), 7.60–7.64 (m, 2H, 19/C19'-H), 7.54–7.58 (m, 1H, 11-H), 7.46–7.50 (m, 2H, 10/10'-H), 7.33–7.36 (m, 2H, 20/20'-H), 5.89 (tt, $J_{\text{H,H}1}$ = 11.5 Hz, $J_{\text{H,H}2}$ = 3.6 Hz, 1H, 12-H), 2.37–2.39 (m, 2H, 13/13'-H), 1.92–2.00 (m, 4H, 13/13'-H + 14/14'-H), 1.81–1.84 (m, 1H, 15-H), 1.51–1.63 (m, 2H, 14/14'-H), 1.28–1.40 (m, 1H, 15-H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 172.0 (o, C-7), 165.4 (o, C-5), 153.9 (o, C-16), 136.6 (o, C-8), 136.0 (o, C-18), 132.4 (+, C-11), 130.2 (o, C-21), 129.5 (+, C-20/20'), 129.4 (+, C-9/9'), 128.5 (+, C-10/10'), 121.4 (+, C-19/19'), 107.1 (o, C-4), 66.0 (+, C-12), 32.6 (-, C-13/13'), 25.2 (-, C-14/14'), 24.9 (-, C-15) ppm; IR (ATR): 3234, 3112, 3057, 2933, 2849, 1677, 1640, 1602, 1577, 1548, 1489, 1448, 1395, 1366, 1334, 1307, 1266, 1183, 1169, 1086, 1037, 1021, 898, 870, 825, 762, 708, 689,

584, 507, 454, 439 cm^{-1} ; MS (ESI 30 V) m/z (%) = 447.1 (100) $[\text{M}+\text{Na}^+]$, 871.3 (60) $[2\text{M}+\text{Na}^+]$. HR-ESI-MS: calcd for $\text{C}_{22}\text{H}_{21}\text{N}_4\text{O}_3\text{Cl}_1\text{Na}^+$ 447.1200. Found 447.1200.

1,3-Di-(4-methylphenyl)-5-(2-(4-chlorophenyl)-hydrazono)-imidazolidine-2,4-dione 12: 3-(4-Chlorophenyl)-6-benzoylsydnone imine (0.300 g, 1.00 mmol), 2 M of LHMDS in THF (0.60 mL, 1.20 mmol), 4-tolyl isocyanate (0.28 mL, 2.20 mmol) and 12 mL of THF (abs.) were used. The reaction was stirred at -30°C for 8 h and then quenched with 1 mL of water. Purification was achieved by column chromatography (silica gel, DCM). Yield: 0.127 g (30%) of a yellow solid, mp: 221°C . ^1H NMR (400 MHz, CDCl_3): δ = 11.07 (s, 1H, 17-H), 7.45-7.47 (m, 2H, 7/7'-H), 7.37-7.40 (m, 2H, 12/12'-H), 7.31-7.33 (m, 2H, 8/8'-H), 7.30-7.32 (m, 2H, 13/13'-H), 7.18-7.21 (m, 2H, 20/20'-H), 6.94-6.98 (m, 2H, 19/19'-H), 2.43 (s, 3H, 10-H), 2.41 (s, 3H, 15-H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 156.7 (o, C-4), 150.7 (o, C-2), 141.9 (o, C-18), 138.9 (o, C-14), 138.0 (o, C-9), 130.0 (+, C-8/8'), 129.9 (+, C-13/13'), 129.5 (o, C-6), 129.4 (+, C-20/20'), 127.9 (o, C-11), 126.7 (o, C-21), 126.3 (o, C-5), 126.2 (+, C7/7'), 125.9 (+, C-12/12'), 114.3 (+, C-19/19'), 21.4 (+, C-10 + C-15) ppm; IR (ATR): 3297, 3037, 2921, 1761, 1699, 1616, 1600, 1502, 1406, 1235, 1136, 1093, 943, 898, 817, 806, 762, 736, 642, 582, 509, 420 cm^{-1} ; MS (ESI 30 V) m/z (%) = 471.1 (100) $[\text{M}+\text{H}^+]$. HR-ESI-MS: calcd for $\text{C}_{23}\text{H}_{19}\text{N}_4\text{O}_2\text{Cl}_1\text{Na}^+$ 441.1094. Found 441.1092.

1,3-Di-(4-methylphenyl)-5-(2-(4-chlorophenyl)-hydrazono)-imidazolidine-2,4-dithione 13: 3-(4-Chlorophenyl)-6-benzoylsydnone imine (0.300 g, 1.00 mmol), 2 M of LHMDS in THF (0.60 mL, 1.20 mmol), 4-tolyl isothiocyanate (0.328 g, 2.20 mmol) and 12 mL of THF (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM). Yield: 0.181 g (40%) of a red solid, mp: 273°C (decomposition). ^1H NMR (600 MHz, CDCl_3): δ = 14.41 (s, 1H, 17-H), 7.39-7.41 (m, 6H, 8/8'-H + 12/12'-H + 13/13'-H), 7.27-7.28 (m, 2H, 7/7'-H), 7.22-7.25 (m, 2H, 20/20'-H), 7.04-7.06 (m, 2H, 19/19'-H), 2.48 (s, 3H, 15-H), 2.46 (s, 3H, 10-H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 174.0 (o, C-4), 171.2 (o, C-2), 140.6 (o, C-18), 140.3 (o, C-9), 139.5 (o, C-14), 133.8 (o, C-5), 132.0 (o, C-6), 131.5 (o, C-11), 130.4 (+, C-8/8'), 130.1 (+, C-13/13'), 129.8 (+, C-20/20'), 129.4 (o, C-21), 128.6 (+, C7/7'), 128.4 (+, C-12), 116.4 (+, C-19), 21.6 (+, C-10) 21.6 (+, C-15) ppm; IR (ATR): 3038, 2961, 2919, 2856, 1564, 1511, 1479, 1422, 1389, 1320, 1258, 1218, 1145, 1082, 982, 884, 801, 761, 724, 632, 607, 574, 518, 508, 416 cm^{-1} ; MS (ESI 30 V) m/z (%) = 473.0 (100) $[\text{M}+\text{Na}^+]$. HR-ESI-MS: calcd for $\text{C}_{23}\text{H}_{19}\text{N}_4\text{S}_2\text{Cl}_1\text{Na}^+$ 473.0637. Found 473.0641.

1,3-Di-(4-chlorophenyl)-5-(2-(4-chlorophenyl)-hydrazono)-imidazolidine-2,4-dione 14: 3-(4-Chlorophenyl)-6-benzoylsydnone imine (0.300 g, 1.00 mmol), 2 M of LHMDS in THF (0.75 mL, 1.50 mmol), 4-chlorophenyl isocyanate (0.369 g, 2.40 mmol) and 12 mL of THF (abs.) were used. The reaction was stirred at -30°C for 8 h and then quenched with 1 mL of water. Purification was achieved by column chromatography (silica gel, DCM). Yield: 0.119 g (26%) of a yellow solid, mp: 261°C . ^1H NMR (600 MHz, CDCl_3): δ = 11.06 (s, 1H, 15-H), 7.54-7.57 (m,

2H, 7/7'-H), 7.50-7.52 (m, 2H, 8/8'-H), 7.50 (s, 4H, 11/11'/12/12'-H), 7.22-7.25 (m, 2H, 18/18'-H), 6.97-6.99 (m, 2H, 17/17'-H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 156.0 (o, C-4), 150.0 (o, C-2), 141.5 (o, C-16), 134.8 (o, C-13), 133.8 (o, C-6), 130.5 (o, C-9), 129.7 (+, C-11/11'), 129.6 (+, C-18/18'), 129.5 (+, C-7/7'), 129.0 (o, C-10), 127.5 (+, C8/8'), 127.3 (o, C-19), 127.2 (+, C-12/12'), 125.3 (o, C-5), 114.5 (+, C-17/17') ppm; IR (ATR): 3266, 3098, 1754, 1699, 1599, 1491, 1396, 1235, 1133, 1092, 1014, 941, 898, 816, 792, 759, 549, 506, 481 cm^{-1} ; MS (ESI 30 V) m/z (%) = 459.0 (100) $[\text{M}+\text{H}^+]$. HR-ESI-MS: calcd for $\text{C}_{21}\text{H}_{12}\text{N}_4\text{O}_2\text{Cl}_3^+$ 457.0026. Found 457.0023.

1,3-Di-(4-methylphenyl)-5-(2-(2-methoxyphenyl)-hydrazono)-imidazolidine-2,4-dione 15: 3-(2-Methoxyphenyl)-6-benzoylsydnone imine (0.295 g, 1.00 mmol), 2 M of LHMDS in THF (0.60 mL, 1.20 mmol), 4-tolyl isocyanate (0.15 mL, 1.20 mmol) and 12 mL of THF (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM:MeOH = 300:1). Yield: 0.196 g (47%) of a yellow solid, mp: 230°C . ^1H NMR (400 MHz, CDCl_3): δ = 11.35 (s, 1H, 17-H), 7.48-7.51 (m, 2H, 7/7'-H), 7.40-7.42 (m, 2H, 12/12'-H), 7.27-7.33 (m, 5H, 8/8'-H + 13/13'-H + 23-H), 6.86-6.90 (m, 2H, 21-H + 22-H), 6.83-6.85 (m, 1H, 20-H), 3.88 (s, 3H, 25-H), 2.43 (s, 3H, 10-H), 2.40 (s, 3H, 15-H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 156.4 (o, C-4), 150.7 (o, C-2), 146.3 (o, C-19), 138.8 (o, C-14), 137.7 (o, C-9), 132.8 (o, C-18), 130.0 (+, C-13/13'), 129.8 (o, C-6), 129.8 (+, C-8/8'), 128.1 (o, C-11), 126.4 (o, C-5), 126.3 (+, C-7/7'), 126.0 (+, C12/12'), 121.5 (+, C-21), 121.5 (+, C-22), 112.1 (+, C-23), 110.5 (+, C-20), 55.8 (+, C-25), 21.4 (+, C-10 + C15) ppm; IR (ATR): 3292, 2992, 2853, 1743, 1703, 1600, 1512, 1464, 1437, 1394, 1268, 1224, 1173, 1133, 1021, 938, 835, 804, 746, 606, 577, 507, 430 cm^{-1} ; MS (ESI 30 V) m/z (%) = 437.0 (100) $[\text{M}+\text{Na}^+]$. HR-ESI-MS: calcd for $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_3\text{Na}^+$ 437.1590. Found 437.1588.

1,3-Di-(4-methylphenyl)-5-(2-(2-methoxyphenyl)-hydrazono)-imidazolidine-2,4-dithione 16: 3-(2-Methoxyphenyl)-6-benzoylsydnone imine (0.295 g, 1.00 mmol), 2 M of LHMDS in THF (0.75 mL, 1.50 mmol), 4-tolyl isothiocyanate (0.328 g, 2.20 mmol) and 12 mL of THF (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM). Yield: 0.161 g (36%) of a violet solid, mp: 274°C (decomposition). ^1H NMR (600 MHz, CDCl_3): δ = 14.36 (s, 1H, 17-H), 7.42-7.43 (m, 2H, 7/7'-H), 7.39-7.41 (m, 2H, 13/13'-H), 7.38-7.40 (m, 2H, 8/8'-H), 7.29-7.31 (m, 3H, 12/12'-H + 23-H), 7.03-7.05 (m, 1H, 21-H), 6.88-6.91 (m, 2H, 20-H + 22-H), 3.94 (s, 3H, 25-H), 2.48 (s, 3H, 10-H), 2.46 (s, 3H, 15-H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 173.6 (o, C-4), 170.1 (o, C-2), 147.7 (o, C-19), 140.0 (o, C-14), 139.2 (o, C-9), 134.7 (o, C-5), 132.3 (o, C-11), 131.8 (o, C-6), 131.5 (o, C-18), 130.0 (+, C-13/13'), 129.8 (+, C-8/8'), 126.3 (+, C-12/12'), 126.0 (+, C7/7'), 121.5 (+, C-21), 121.5 (+, C-22), 112.1 (+, C-23), 110.5 (+, C-20), 56.1 (+, C-25), 21.6 (+, C-10) 21.6 (+, C-15) ppm; IR (ATR): 3041, 2943, 2842, 1596, 1549, 1511, 1477, 1417, 1391, 1318, 1298, 1255, 1208, 1180, 1151, 1111, 1090, 1040, 1022, 986, 869, 802, 782, 742, 725, 646, 630, 576, 551, 520 cm^{-1} ; MS (ESI 30 V) m/z (%) = 469.1

(100) [M+Na⁺]. HR-ESI-MS: calcd for C₂₄H₂₃N₄O₁S₂⁺ 447.1313. Found 447.1310.

1,3-Di-(4-chlorophenyl)-5-(2-(2-methoxyphenyl)-hydrazono)-imidazolidine-2,4-dione 17: 3-(2-Methoxyphenyl)-6-benzoylsydnone imine (0.295 g, 1.00 mmol), 2 M of LHMDS in THF (0.60 mL, 1.20 mmol), 4-chlorophenyl-isocyanate (0.338 g, 2.20 mmol) and of 12 mL THF (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM:PE = 10:1). Yield: 0.195 g (43%) of a yellow solid, mp: 259 °C. ¹H NMR (600 MHz, CDCl₃): δ = 11.34 (s, 1H, 15-H), 7.57-7.59 (m, 2H, 12/12'-H), 7.51-7.53 (m, 2H, 8/8'-H), 7.49-7.51 (m, 2H, 11/11'-H), 7.48-7.50 (m, 2H, 7/7'-H), 7.27-7.29 (m, 1H, 21-H), 6.91-6.93 (m, 2H, 19-H + 20-H), 6.86-6.87 (m, 1H, 18-H), 3.90 (s, 3H, 23-H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 155.7 (o, C-4), 150.0 (o, C-2), 146.4 (o, C-17), 134.5 (o, C-6), 133.5 (o, C-10), 132.3 (o, C-16), 130.8 (o, C-13), 129.6 (+, C-11/11'), 129.4 (+, C-7/7'), 129.2 (o, C-9), 127.5 (+, C-12/12'), 127.2 (+, C-8/8'), 125.4 (o, C-5), 122.2 (+, C-19), 121.6 (+, C-20), 112.2 (+, C-21), 110.6 (+, C-18), 55.9 (+, C-23) ppm; IR (ATR): 3275, 3099, 3060, 2942, 2838, 1749, 1704, 1594, 1523, 1493, 1401, 1248, 1215, 1175, 1138, 1091, 1017, 944, 821, 794, 759, 735, 671, 595, 508, 482 cm⁻¹; MS (ESI 30 V) *m/z* (%) = 477.0 (100) [M+Na⁺]. HR-ESI-MS: calcd for C₂₂H₁₆N₄O₃Cl₂Na⁺ 477.0497. Found 477.0492.

1-(4-Chlorophenyl)-3-(N-(4-methylphenyl)carbamoyl)-4-(4-methylphenyl)-4,5-dihydro-1,2,4-triazol-5-on 18: 3-(4-Chlorophenyl)-6-benzoylsydnone imine (0.300 g, 1.00 mmol), 2 M of LHMDS in THF (0.60 mL, 1.20 mmol), 4-tolyl isocyanate (0.30 mL, 2.40 mmol) and 12 mL of THF (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM, then again PE:EE 3:1). Yield: 0.109 g (26%) of a white solid, mp: 236 °C. ¹H NMR (600 MHz, CDCl₃): δ = 8.56 (s, 1H, 16-H), 7.99-8.02 (m, 2H, 7/7'-H), 7.45-7.47 (m, 2H, 18/18'-H), 7.42-7.45 (m, 2H, 8/8'-H), 7.29-7.31 (m, 2H, 12/12'-H), 7.25-7.27 (m, 2H, 11/11'-H), 7.11-7.13 (m, 2H, 19/19'-H), 2.41 (s, 3H, 14-H), 2.31 (s, 3H, 21-H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 152.8 (o, C-15), 151.6 (o, C-3), 139.5 (o, C-13), 138.6 (o, C-5), 135.7 (o, C-6), 135.0 (o, C-20), 133.9 (o, C-17'), 131.8 (o, C-9), 130.1 (o, C-10), 129.9 (+, C-12/12'), 129.6 (+, C-19/19'), 129.2 (+, C-8/8'), 126.9 (+, C-11/11'), 120.3 (+, C-7/7'), 119.9 (+, C-18/18'), 21.3 (+, C-14) 20.9 (+, C-21) ppm; IR (ATR): 3387, 3039, 2922, 2859, 1717, 1699, 1595, 1533, 1516, 1490, 1443, 1403, 1370, 1298, 1238, 1176, 1090, 1010, 887, 837, 806, 728, 718, 594, 579, 511 cm⁻¹; MS (ESI 30 V) *m/z* (%) = 441.0 (100) [M+Na⁺]. HR-ESI-MS: calcd for C₂₃H₁₉N₄O₂Cl₁Na⁺ 441.1094. Found 441.1096.

1-(4-Chlorophenyl)-3-(N-(4-chlorophenyl)carbamoyl)-4-(4-chlorophenyl)-4,5-dihydro-1,2,4-triazol-5-on 19: 3-(4-Chlorophenyl)-6-benzoylsydnone imine (0.300 g, 1.00 mmol), 2 M of LHMDS in THF (0.75 mL, 1.50 mmol), 4-chlorophenyl isocyanate (0.369 g, 2.40 mmol) and 12 mL of THF (abs.) were used. Purification was achieved by column chromatography (silica gel, DCM then again PE:EE 3:1). Yield: 0.121 g (26%) of a white solid, mp: 270 °C. ¹H NMR (600 MHz, CDCl₃): δ = 8.60 (s, 1H, 15-H), 7.98-8.00 (m, 2H, 7/7'-H), 7.53-7.55 (m, 2H,

17/17'-H) 7.48-7.51 (m, 2H, 12/12'-H), 7.45-7.48 (m, 2H, 12/12'-H), 7.33-7.35 (m, 2H, 11/11'-H), 7.30-7.33 (m, 2H, 18/18'-H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 153.0 (o, C-14), 151.4 (o, C-3), 138.0 (o, C-5), 135.7 (o, C-13), 135.5 (o, C-6), 134.9 (o, C-16), 132.4 (o, C-9), 131.2 (o, C-10), 130.7 (o, C-19), 129.7 (+, C-12/12'), 129.5 (+, C-8/8'), 129.4 (+, C-18/18'), 128.7 (+, C-11/11'), 121.4 (+, C-17/17'), 120.6 (+, C-7/7') ppm; IR (ATR): 3387, 3100, 1731, 1703, 1593, 1532, 1489, 1398, 1372, 1302, 1240, 1180, 1089, 1002, 889, 842, 824, 789, 727, 601, 567, 500, 442 cm⁻¹; MS (ESI 30 V) *m/z* (%) = 457.0 (100) [M-H⁺]. HR-ESI-MS: calcd for C₂₁H₁₂N₄O₂Cl₃⁻ 457.0026. Found 457.0026.

From 1,3-Di-(4-methylphenyl)-5-(2-(4-chlorophenyl)-hydrazono)-imidazolidine-2,4-dione (12) to 1-(4-Chlorophenyl)-3-(N-(4-methylphenyl)carbamoyl)-4-(4-methylphenyl)-4,5-dihydro-1,2,4-triazol-5-on 18: Under an inert atmosphere 1,3-di-(4-methylphenyl)-5-(2-(4-chlorophenyl)-hydrazono)-imidazolidine-2,4-dione (0.035 g, 0.084 mmol) was dissolved in 10 mL of THF (abs.), then 2 M LHMDS in THF (0.05 mL, 0.100 mmol) was added. The mixture was stirred for 10 minutes at rt, afterwards 4-tolyl isocyanate (0.01 mL, 0.092 mmol) was added dropwise. Purification was achieved by column chromatography (silica gel, DCM). Yield: 0.024 g (69%) of a white solid.

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Keywords: Betaines • Carbenes • Anions • 1,2,4-Triazolones • Imidazolidine-2,4-diones

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FULL PAPER

Sydnone imine anions combine elements of anionic N-heterocyclic carbenes and mesomeric betaines. Thus, reaction with isocyanates (X = O) or isothiocyanates (X = S) give adducts of the carbene type σ orbitals, whereas ring transformations to give imidazolidine-2,4-dithiones, imidazolin-2,4-diones and 1,2,4-triazol-5-ones result from their characteristic π architecture of betaines.

Anionic N-heterocyclic carbenes

Tyll Freese, Ana-Luiza Lücke, Jan C. Namyslo, Martin Nieger, and Andreas Schmidt*

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Heterocycle syntheses with anionic N-heterocyclic carbenes. Ring transformations of sydnone imine anions