Synthesis of Organic Super-Electron-Donors by Reaction of Nitrous Oxide with N-Heterocyclic Olefins

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Supporting Information Placeholder

ABSTRACT: The reaction of nitrous oxide (N_2O) with N-heterocyclic olefins (NHOs) results in cleavage of the N-O bond and formation of azo-bridged NHO dimers. The latter represent very electron-rich compounds with a low ionization energy. Cyclic voltammetry studies show that the dimers classify as a new organic super-electron-donors, with a reducing power similar to what is found for tetraazafulvalene derivatives. Mild oxidants are able to convert the neutral dimers into radical cations, which can be isolated. Further oxidation gives stable dications.

N-Heterocyclic carbenes (NHCs) are able to form covalent adducts with CO_2 (Scheme 1a).[1,2] The resulting imidazolium-2-carboxylates have been used as organocatalysts for different reactions,[3] and they represent easy-to-handle NHC transfer reagents for the synthesis of metal carbene complexes.[4]
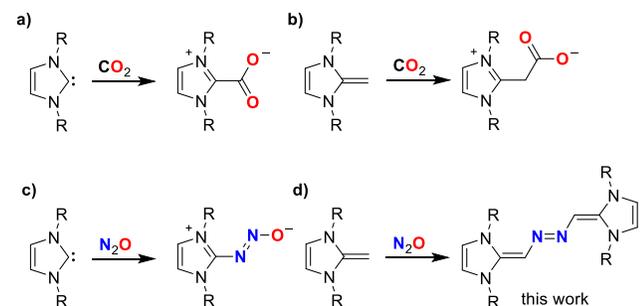
Scheme 1. Reactions of NHCs and NHOs with CO_2 or N_2O.

N-Heterocyclic olefins (NHOs) are alkylidene derivatives of NHCs.[5] The exocyclic C=C double bond is strongly polarized, and the high charge density at the C_α atom makes NHOs strongly Lewis-basic compounds. Similar to NHCs, NHOs react with CO_2 to give zwitterionic covalent adducts (Scheme 1b). These adducts are of key importance in CO_2 sequestration reactions with NHOs.[6]

Nitrous oxide (N_2O) is isoelectronic to CO_2, and likewise a chemically inert compound.[7] Despite its inert character, N_2O is able to form stable covalent adducts with NHCs under ambient conditions (Scheme 1c).[8] So far, NHC-N_2O adducts have not been used in the context of catalytic reactions, but they were shown to act as mild and selective oxidants for metal complexes,[9] and as precursors for azo dyes.[10]

The results summarized above prompted us to explore if NHOs would also react with N_2O. A chemical activation of N_2O with an NHO can indeed be achieved under mild conditions. Instead of a simple 1:1 adduct, we observed the formation of an azo-bridged NHO dimers (Scheme 1d). These dimers represent new super-electron-donors, as evidenced by cyclic voltammetry and reactions with aryl iodides. Details of these investigations are given below.

For our investigations, we have used NHOs with 2,6-iPr$_2$C$_6$H$_3$ (Dipp), 2,4,6-Me$_3$C$_6$H$_2$ (Mes), and 2,6-Me$_2$C$_6$H$_3$ (Xyl) substituents.[11] When concentrated solutions of these compounds in CH_3CN were exposed to an atmosphere of N_2O at room temperature, a gradual color change to orange/red was observed. After 48 h, strongly colored precipitates had formed (**1–3**, Scheme 2), which were isolated and washed with CH_3CN.

The products displayed a reduced symmetry when compared to the starting NHOs, as evidenced by the presence of a double set of NMR signals for the N-aryl groups. This observation indicated that **1–3** are not simple NHO-N_2O adducts.

Analysis of **1** and **3** by single crystal X-ray crystallography showed that azo-bridged NHO dimers had formed (for details, see the Supporting Information, SI). The formation of these dimers can be rationalized by assuming that the reactions proceed via zwitterionic NHO-N_2O adducts of type **A** (Scheme 2), which can tautomerize to the diazohydroxides **B**. A condensation reaction with remaining NHO then provides the dimers **1–3**. Presumably, the condensation reaction is initiated by N–O bond rupture of the diazohydroxide **B**,[12] forming either a vinyl diazonium compound or a diazoalkene.[13]
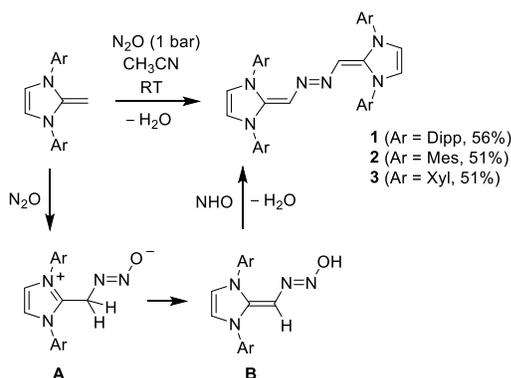
Scheme 2. Reaction of NHOs with N_2O.

Solutions of **1**–**3** in THF appear dark orange. The absorption in the visible range is in line with the solid state structures of **1** and **3**, which both show a co-planar arrangement of the two heterocycles and the divinyldiazene bridge, allowing for efficient π-conjugation. Linear-response time-dependent density functional calculations further confirm this observation, indicating for the main band of **1** a ππ* character located over the heterocycles and the divinyldiazene bridge (see SI for computational details).

The reducing power of **1** was assessed by cyclic voltammetry (CH_3CN, 0.1 M NBu_4PF_6). Two well-separated, reversible redox transitions were observed at $E_{1/2} = -1.34$ and -0.73 V, referenced versus an external Fc/Fc^+ redox couple. Similar values were obtained for the azo compounds **2** and **3** (see SI). The first oxidation potential is comparable to what has been observed for some tetraazafulvalene derivatives, for example **C** and **D** (Figure 1), which are referred to as organic super-reducing-agents.[14–17]

Density functional theory (DFT) calculations using the exchange/correlation functional ωB97X-D[18] were performed to gain further insight into the electronic structure of the new compounds, using **1** as representative example (for details, see SI). The calculations revealed a gas phase vertical ionization energy (vIE) of 4.49 eV, and an adiabatic ionization energy (aIE) of 4.16 eV. Upon inclusion of an implicit solvent model for CH_3CN in the calculation, the ionization energies are lowered to values of 4.19 eV (vIE) and 3.24 eV (aIE), respectively. Calculating the aIE of the tetraazafulvalene derivative **C** using the same computational protocol (DFT/ωB97X-D/IEFPCM), gives a value of 3.34 eV, close to the one obtained for **1**.

It is worth discussing the structurally related compound **E²⁺**, **F** and **G** (Figure 1). **E²⁺** was described by Hünig and co-workers.[19] Electrochemical investigations showed that the corresponding neutral form **E** is formed at $E_{1/2} = -1.00$ V,[18] but isolation of the neutral compound was not attempted. The lower reducing power of **E** compared to **1** is likely related to the presence of annulated benzene rings.[15] The dipnictenes **F** and **G** were recently reported by Ghadwal and co-workers.[20] These compounds were obtained by reaction of phenyl-substituted NHOs with ECl_3 (E = P, As), followed by reduction. Electrochemical

investigations for **F** indicated that the first oxidation occurs at $E_{1/2} = -1.36$ V.[20a]
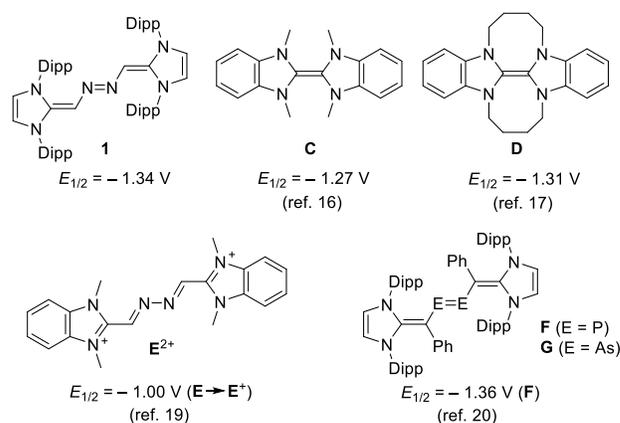
Figure 1. The redox potential for the first oxidation of **1** in comparison to the values of structurally related compounds reported in the literature. The values are based on CV measurements in CH_3CN (for **F**: CH_2Cl_2) with respect to the Fc/Fc^+ redox couple.[17]

The chemical reactivity if the new azo-bridged NHOs was investigated using again compound **1** as representative example. The large difference between the first and the second oxidation potential allows for a selective one-electron oxidation of **1**. The oxidation can be accomplished using chloroform, benzyl bromide, or silver triflimide as oxidants (Scheme 3). The resulting salts **4a**–**c** were isolated in yields between 40 and 72%.

In the absence of air, the salts are stable in solution (THF) and in the solid state.[21] Crystallographic analyses of **4a**–**c** revealed that the single-electron oxidation had resulted in a lengthening of the C1-C2 and the N1-N1' bonds, and a shortening of the C2-N1 bond (Table 1).
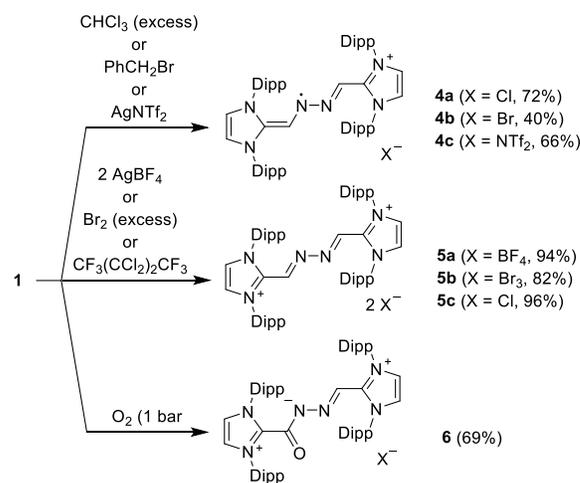
Scheme 3. Reaction of **1** with different oxidants.

Table 1. Selected bond lengths for 1, 3, 4a-c, and 5b as determined by X-ray crystallography.[a]
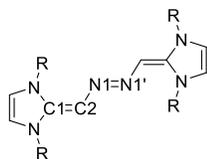
Compound	C1-C2	C2-N1	N1-N1'
1	1.3692(14)	1.3703(14)	1.2907(16)
3	1.3685(14)	1.3713(13)	1.2902(16)
4a	1.408(3)	1.324(2)	1.327(3)
4b	1.4108(18)	1.3214(17)	1.333(2)
4c	1.4109(15)	1.3237(14)	1.3300(18)
5b	1.450(3)	1.271(3)	1.400(3)

[a] All structures show a crystallographic inversion center.

The presence of a radical cation in **4** was confirmed by EPR spectroscopy (Figure 3a). The complex hyperfine coupling indicates that the radical is delocalized over the planar π-system. Such a delocalization is in accordance with the results of DFT calculations, which show that the spin density is distributed over the two heterocycles and the divinyldiazene bridge (Figure 3b).
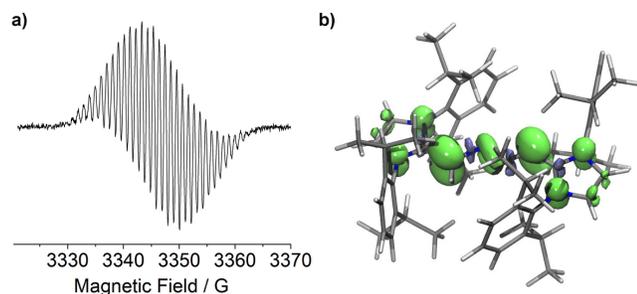
Figure 3. EPR spectrum of **4a** (a), and calculated spin density of the radical cation (b).

Solutions of **4** are strongly colored, and the UV-Vis spectrum (THF) shows absorption bands at 661 nm and 736 nm in addition to a main band at λ_{max} = 516 nm. The occurrence of low-energy bands is typical for π-conjugated radicals.[22]

The addition of two equivalents of AgBF$_4$, an excess of bromine, or 2,2,3,3-tetrachlorohexafluorobutane to a solution of **1** resulted in the formation of imidazolium salts **5a–c**, which could be isolated in high yield (Scheme 3). A crystallographic analysis of **5b** showed that the double oxidation had led to further lengthening of the C1-C2 and the N1-N1' bonds, and shortening of the C2-N1 bond (Table 1).

When a solution of **1** in a mixture of diethyl ether and hexane (2:1) was exposed to dioxygen, we observed the formation of a brown-yellow oily solid. Work-up allowed isolation of the salt **6** in 69% yield (Scheme 3). As evidenced by mass spectrometry and single crystal X-ray crystallography (see SI), the reaction with O$_2$ had resulted

in oxidation of one of the C$_\alpha$ atoms of the azo-bridged dimer.[23]

To qualify as an organic super-reducing-agent, a compound should be able to reduce aryl iodides.[14] We have examined the reaction of **1** with the aryl iodides **7** and **9** (Scheme 4).[24] When a solution of **7** and **1** in a mixture of DMF and toluene (1:1) was heated to 100°C, cyclization to the indoline **8** was observed. The latter could be isolated in 89% yield. The more challenging substrate **9** could also be reduced. However, (benzyloxy)benzene (**10**) was only formed in 43% yield, and incomplete conversion was observed.
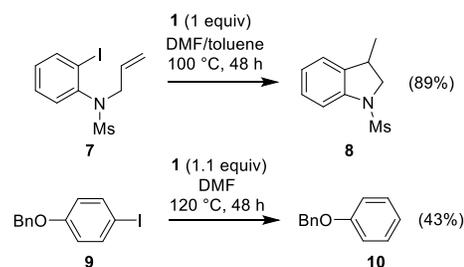
Scheme 4. Reactions of aryliodides with **1**.

In summary, we have examined the reaction of N-heterocyclic olefins with nitrous oxide. Instead of simple N$_2$O adducts, we observed N-O bond cleavage and formation of azo-bridged NHO dimers (**1**–**3**). These dimers are very strong electron donors, which can be converted into a stable radical cations or a dicationic imidazolium salts. The first oxidation potentials are similar to what is observed for some tetraazafulvalenes, allowing the reduction of aryl iodides. Consequently, **1**–**3** classify as new super-electron-donors. Tetraazafulvalenes have been used as potent reducing agents in synthetic chemistry,[14] and similar applications can be envisioned for the new diazenes.

ACKNOWLEDGMENT

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(25) A reaction between **7** and **1** in toluene at room temperature resulted in the precipitation of the radical cation (**1$^{•+}$**)(I$^-$) (= **4d**), the structure of which was characterized by X-ray diffraction. For details, see SI.

TOC graphic:

Super-electron-donors
Three stable redox states