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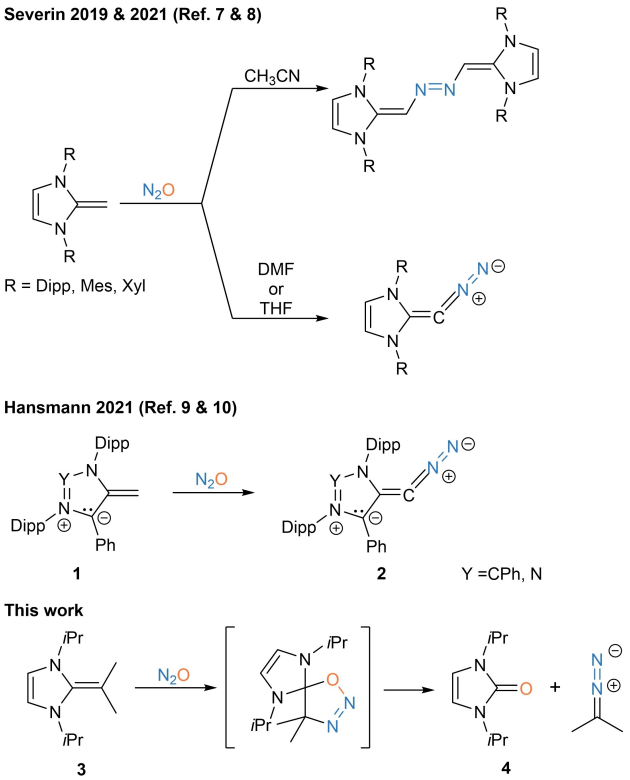
Facile (3+2) Cycloaddition between an *N*-Heterocyclic Olefin and Nitrous Oxide at Ambient Conditions

Jama Ariai,[a] Jonathan Becker,[b] and Urs Gellrich*[a]

We report that a *gem*-dimethylated *N*-heterocyclic olefin (NHO) reacts with N_2O at ambient pressure and room temperature to give an imidazolone and an azine formed from intermediately generated 2-diazopropane. The *in situ* formation of transient diazopropane was indirectly proven by its engagement in a facile cycloaddition with norbornene. According to our studies, the reaction sequence consists of a rate-determining (3+2) cycloaddition between the NHO and N_2O, followed by a cycloreversion that releases the diazoalkane. This mechanistic proposal is supported by DFT calculations. Eyring analysis using temperature-variable ^{1}H NMR spectroscopy allowed us to determine the activation parameters of the initial (3+2) cycloaddition ($\Delta^{\ddagger}H = 11.2(4)$ kcal/mol, $\Delta^{\ddagger}S = -39.8(13)$ e.u., 293–308 K). Frontier molecular orbital analysis shows that the polarization of the π-bond of the NHO decisively facilitates the cycloaddition.

Introduction

The valorization of atmospherically troublesome small molecules such as N_2O is relevant for developing sustainable synthetic methods.[1] The activation of the kinetically inert N_2O molecule by transition metal complexes[2] and, more recently, by p-block compounds such as frustrated Lewis pairs[3] and bismutidenes[4] has attracted considerable attention. Moreover, reactions of strong organic σ-donors with N_2O have been reported. Severin and co-workers showed that N_2O binds to *N*-heterocyclic carbenes (NHC) at ambient conditions to form a stable end-on adduct that decomposes at thermal or photochemical conditions.[5] Furthermore, the $AlCl_3$-mediated synthesis of azoimidazolium dyes from N_2O, NHCs, and arenes was reported.[6] In 2019, Severin and co-workers reported the formation of azo-bridged dimers of *N*-heterocyclic olefins (NHOs) upon exposure of N_2O to substituted NHOs in acetonitrile (Scheme 1).[7] In DMF or THF, however, a stable and isolable diazoalkene is formed.[8] At the same time, Hansmann and co-workers reported that exposure of the mesoionic NHO **1** to N_2O yields the diazoalkene **2**.[9] All the reported reactions between NHOs and N_2O are assumed to proceed *via* attack of the nucleophilic NHO to the *N*-terminus of N_2O. Subsequent proton migration(s) from the exocyclic CH_2 group and elimination render the azo-bridged dimer or diazoalkene.[10] Considering these results, we wondered what course the reaction of an NHO with N_2O would take if the subsequent proton migrations were not possible, for example, due to a dimethylated exocyclic methylene group.



Scheme 1. Reported formation of NHO dimers and diazoalkenes upon exposure of N_2O to imidazole based NHOs bearing exocyclic CH_2 groups (Dipp = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl, Xyl = 2,6-dimethylphenyl).

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Results and Discussion

To address the above-mentioned question, we synthesized the *gem*-dimethylated NHO **3** and exposed a solution of it to an N_2O atmosphere. Complete conversion of **3** was observed overnight at room temperature. We monitored the reaction by ^{1}H NMR spectroscopy and observed a new set of signals that were tentatively assigned to the imidazolone **4** (Figure 1). Furthermore, two new singlets emerged at 1.83 ppm and 1.80 ppm indicating the formation of the azine **5**. After full characterization by NMR spectroscopy (^{1}H, ^{13}C, HH COSY, ^{1}H–^{13}C HMBC, ^{1}H–^{13}C HSQC, ^{1}H–^{15}N HMBC), we analyzed the reaction mixture by infrared (IR) spectroscopy (see the Supporting Information for details). Based on DFT computations of the harmonic vibrational frequencies scaled to account for anharmonicity (PBE0-D3(BJ)/def2-TZVP),[11,12,13,14,15] we simulated the IR spectra for a mixture of imidazolone **4** and acetone azine **5**.

Comparison of the computed and experimental IR spectra substantiated the formation of imidazolone **4** and azine **5**. Most significantly, we observed indicative IR bands at 1677 and 1637 cm^{-1} which we assigned to ν (C=O) of imidazolone (DFT scaled: 1715 cm^{-1}) and ν (C=N) of acetone azine (DFT scaled: 1665 cm^{-1}). The *in situ* yield, determined by quantitative ^{1}H NMR using mesitylene as internal standard, is 60% for imidazolone **4** and 27% for azine **5** (Scheme 2).

The imidazolone **4** was isolated in 53% yield after aqueous workup with HCl. However, under these conditions, acetone azine **5** is not isolable. Thus, we synthesized **5** independently following a procedure from Day and Whiting and unequivocally confirmed its formation during the reaction of NHO **3** and N_2O by NMR spiking experiments (see the Supporting Information).[16] At this point, we assumed that the reaction yields initially imidazolone **4** and 2-diazopropane, which disproportionates to acetone azine and dinitrogen under the reaction conditions (Scheme 2). The decomposition of diazoalkanes in the presence of base/nucleophiles is well documented in the literature.[17] NMR analysis of the reaction mixture also showed the formation of a by-product. While the yields of **4** and **5** are relatively insensitive to the concentration of NHO **3** (0.07–0.3 M), the formation of this by-product is favored at higher concentrations. Therefore, we performed the reaction at higher concentration, which allowed to isolate the by-product by column chromatography in 15% yield. Based on ^{1}H, ^{13}C and ^{15}N NMR spectroscopy, we were able to identify the by-product as azine **6**. Compound **6** exhibits an intense IR band at 1560 cm^{-1} assigned to the ν (C=N) of the azine moiety (DFT scaled: 1591 cm^{-1}). We were thus able to assign all IR bands appearing in the reaction mixture to compounds **4**, **5** and **6**. Screening the reaction conditions, we found that the reaction tolerates the presence of bases. This allows the formation of **3** *in situ* from the bench-stable imidazolium iodide salt **7** (Scheme 3).

Screening different bases (see the Supporting Information), we found that typical bases used for the formation of NHOs, such as KHMDS and KO*t*Bu, work well in this reaction. The 2:1 ratio, at which imidazolone **4** and azine **5** are obtained, indicates that 2-diazopropane is conserved as acetone azine. To further support the initial formation of 2-diazopropane during the reaction of **3** with N_2O, we intended to trap this diazo compound by an 1,3-dipolar cycloaddition with norbornene. Thus, we carried out the reaction in the presence of one equivalent of norbornene at the identical conditions, *i.e.*, 1 atm N_2O at room temperature (Scheme 4).

Under these conditions, the yield of the imidazolone **4** is maintained (62%) while only traces of acetone azine are present according to quantitative ^{1}H NMR. Instead, the cycloaddition product **8** is formed in moderate yield (49%).[18] The conversion of norbornene (61%) is limited by the yield of imidazolone and the associated yield of 2-diazopropane (see Scheme 2). Similar results are obtained when the NHO is formed *in situ* with KHMDS. We note that while established protocols for the

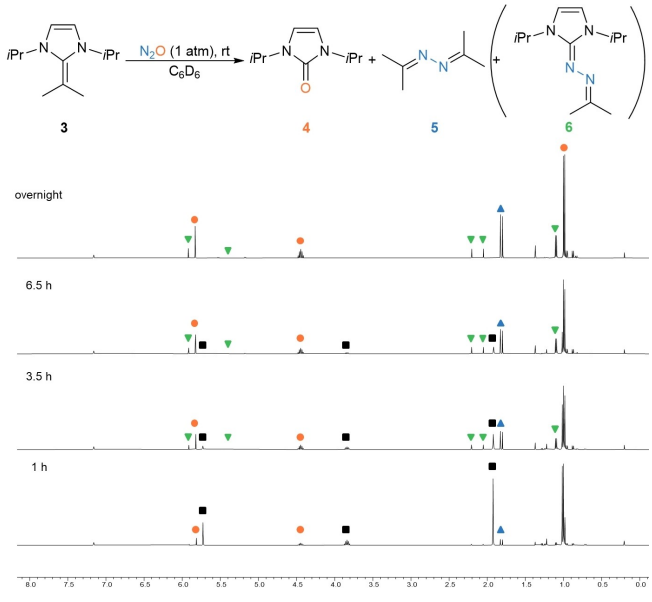
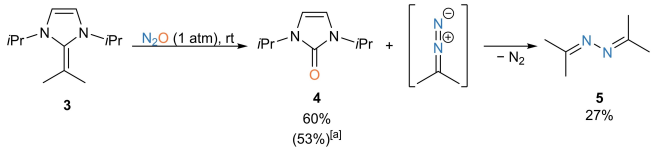
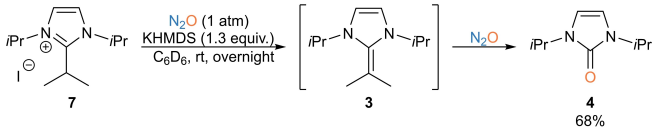


Figure 1. Reaction of NHO **3** with N_2O (1 atm) at room temperature monitored by ^{1}H NMR (400 MHz, C_6D_6). Black squares, orange circles, blue triangles pointing up, and green triangles pointing down highlight the signals assigned to NHO **3**, imidazolone **4**, azine **5**, and azine **6**, respectively. (*Vide infra* for details regarding the broadened heptet of **6** at 5.39 ppm).



Scheme 2. Reaction of **3** with N_2O and the proposed intermediate formation of 2-diazopropane. Conversion and yields according to quantitative ^{1}H NMR unless stated otherwise.[a] Yield of isolated compound at preparative scale.



Scheme 3. *In situ* formation of the NHO by deprotonation in the presence of ambient N_2O in C_6D_6. Yield according to quantitative ^{1}H NMR.

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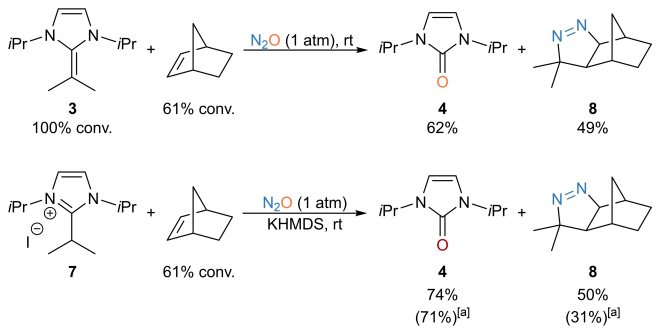

Scheme 4. Trapping of 2-diazopropane, generated by exposure of NHO **3** to N_2O, by 1,3-dipolar cycloaddition with norbornene. Conversion and yields according to quantitative ^{1}H NMR.[a] Yields of isolated products are given in parenthesis.

valorization of N_2O focus on its use as oxidant,[4,19] the reaction described herein is a rare example of the formation of a diazoalkane from N_2O.[2b,20] To gain insight into the reaction mechanism, we investigated the kinetics of the reaction of **3** with N_2O by temperature-variable ^{1}H NMR spectroscopy in C_6D_6 (Figure 2).

This study revealed a first-order dependence for the reaction rate with respect to NHO **3** and allowed us to determine the activation parameters by Eyring analysis: $\Delta^{\ddagger}H = 11.2(4)$ kcal/mol and $\Delta^{\ddagger}S = -39.8(13)$ e. u.[21] The highly negative activation entropy is indicative of an ordered transition state as in a cycloaddition reaction. Thus, we assume that the reaction of NHO **3** with N_2O commences with a (3 + 2) cycloaddition, followed by a cycloreversion that liberates the 2-diazopropane. The (3 + 2) cycloaddition between olefins and N_2O has been reported previously but requires usually harsh and technically demanding reaction conditions.[22] Even the reaction with highly reactive strained cycloalkynes requires an elevated N_2O pressure (15–75 bar).[20c] In this regard, it is remarkable that the cycloaddition between the NHO **3** and N_2O reported herein takes place already at room temperature at ambient pressure. To rationalize the facility of the 1,3-dipolar cycloaddition between NHO **3** and N_2O, we considered the frontier Kohn-Sham orbitals (Figure 3).[23,24] By inspection of the orbital levels, it is evident that the reaction proceeds by interaction of the lowest unoccupied molecular orbital (LUMO) of N_2O with the highest occupied molecular orbital (HOMO) of NHO **3**. The largest coefficient of the LUMO of N_2O is on the *N*-terminus. The HOMO of the NHO is strongly polarized towards the exocyclic carbon and thereby reflects the ylidic nature of the NHO. This is in contrast to ordinary alkene/alkyne functional groups, which lack this orbital polarization.

We further studied the reaction of **3** with N_2O computationally with the revised spin-component-scaled double-hybrid functional revDSD-PBEP86[25] in conjunction with the D4 dispersion correction[26] and the quadruple-zeta basis set def2-QZVPP (Figure 4). Solvent effects were considered implicitly using the SMD model for benzene.[27] Lowest energy conformations of all minima and transition state structures were obtained by automated exploration of conformational chemical space using CREST.[28] We assumed initial formation of the van-der-Waals complex **vdW1**. According to the computations, the end-on addition of the NHO **3** to N_2O that yields zwitterion **10** is endergonic and requires a high kinetic barrier of 28.0 kcal mol^{-1}. The (3 + 2) cycloaddition between N_2O and the double bond of **3** in which the exocyclic CMe_2 group binds to the terminal nitrogen of N_2O ($\mathbf{TS_{vdW1/9}}$) is with 23.3 kcal mol^{-1} kinetically preferred. The computed activation barrier for this initial cycloaddition is in excellent agreement with the kinetic barrier of $\Delta^{\ddagger}G_{298} = 23.0$ kcal mol^{-1} determined by Eyring analysis (Figure 2). The transition state structure shows a bent N_2O unit (143°) with the formation of the C–N bond (2.11 Å) preceding the C–O bond (2.92 Å) formation. This dominant C–N interaction is in agreement with the FMO-representation and supports the interpretation that the reaction is controlled by orbital interactions (Figure 3). The formation of the spirocyclic intermediate **9** is only slightly exergonic relative to **vdW1**. However, its fragmentation *via* a retro (3 + 2) cycloaddition

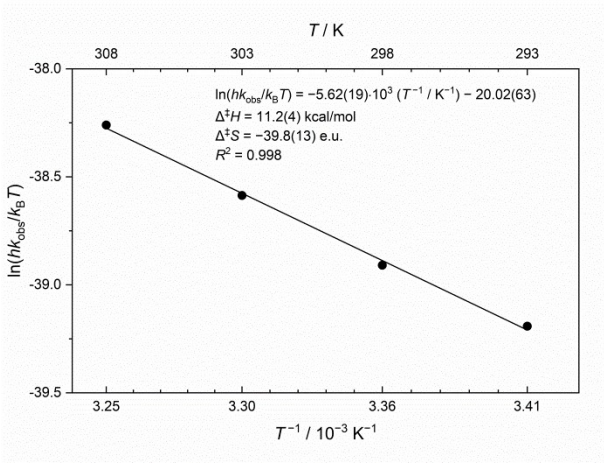

Figure 2. Determination of the activation enthalpy $\Delta^{\ddagger}H$ and activation entropy $\Delta^{\ddagger}S$ according to Eyring equation. Rate constants were obtained by variational temperature ^{1}H NMR analysis (293–308 K, C_6D_6) of the first-order decay of NHO **3** exposed to N_2O using mesitylene as internal standard.

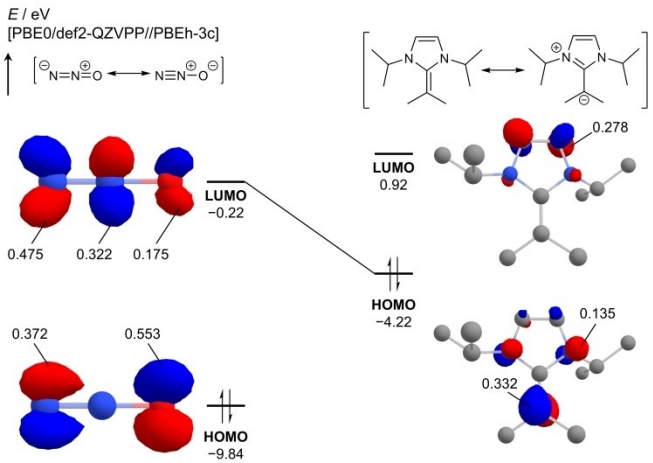

Figure 3. Canonical Kohn–Sham molecular orbitals and atomic coefficients computed at PBE0/def2-QZVPP//PBEh-3c level of theory. For brevity, degenerate orbitals of N_2O are omitted. Colour code for the depiction of the molecular structures: C in grey, N in blue, O in red, and H omitted for clarity.

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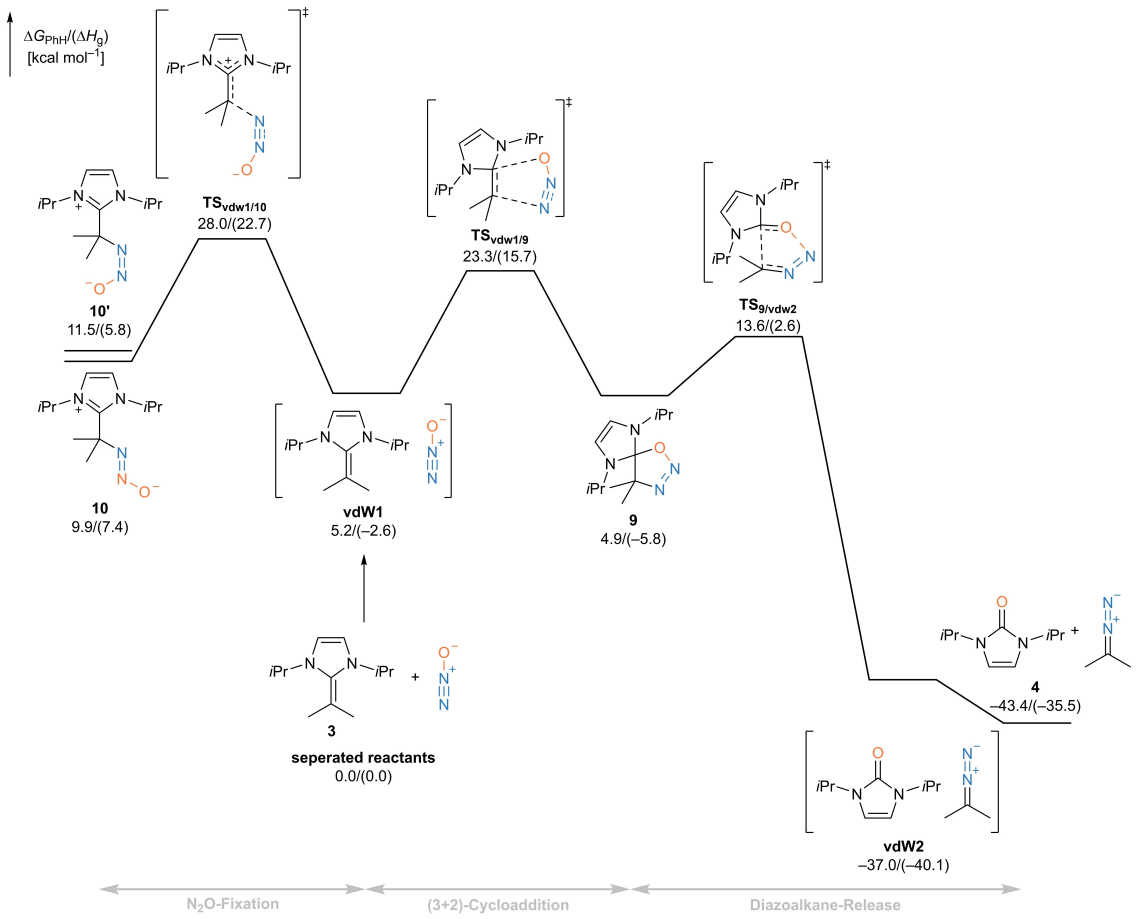

Figure 4. Gibbs free energies in benzene and gas phase enthalpies of the formation of 2-diazopropane upon exposure of **3** to N_2O computed at revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c level. Solvent effects were implicitly considered with the SMD model.

requires only a moderate activation barrier of less than 10 kcal mol^{-1}. Regarding the transition state structure (**TS$_{9/vdW2}$**), the diazoalkane moiety is bent by 133° and the scission of the N–O bond (2.10 Å) is more developed than the C–C scission (1.79 Å). Furthermore, this elementary step, that yields the imidazolone **4** and 2-diazopropane, is according to the computations highly exergonic. The overall kinetic barrier of the reaction between the separated reactants and the transition state of the (3 + 2) cycloaddition is computed to be 23.3 kcal mol^{-1}. Finally, we noted that the reaction described herein is sensitive regarding the substitution pattern of the NHO: When an NHO with 2,6-diisopropylphenyl instead of the isopropyl substituents at nitrogen is exposed to N_2O, no reaction is observed. The barrier of the cycloaddition of such an NHO with 2,6-diisopropylphenyl substituents at nitrogen with N_2O is 29.1 kcal/mol and therefore increased by 5.8 kcal/mol compared to the isopropyl derivative **3**. Likewise, NHOs with an imidazolidine backbone do not show any reactivity towards N_2O.

Conclusions

In summary, we have documented that NHO **3** reacts with N_2O at ambient conditions to give an imidazolone and a transient diazoalkane. According to our kinetic and computational studies, this reaction proceeds *via* a sequence of (3 + 2)-cycloaddition and cycloreversion. FMO analysis shows that the orbital polarization of the NHO enhances the orbital interactions with N_2O, promoting the rate-determining cycloaddition. The reaction also works when the NHO is formed *in situ* by deprotonation of a bench-stable imidazolium salt. This reaction pathway is unlocked by a *gem*-dimethyl substitution at the reactive exocyclic carbon atom, which prevents proton migration within an NHO–N_2O adduct. Complementary to established protocols for the valorization of N_2O which focus on its use as oxidant, this reaction is a rare example of the formation of a diazoalkane from N_2O. We expect this discovery to stimulate the development of synthetic protocols for the valorization of N_2O.

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Experimental Section

General procedure for the activation of N_2O: In a nitrogen-filled glovebox, NHO **3** (9.5 mg, 0.05 mmol) was dissolved in 0.4 mL C_6D_6 and transferred to an NMR tube with J. Young valve. In a fume hood, the solution was degassed by three freeze-pump-thaw cycles. A balloon, connected to a vacuum line and an N_2O cylinder *via* a three-way valve, was purged multiple times with N_2O. The NMR tube, connected to the filled balloon and a vacuum line *via* three-way valve, was exposed to the N_2O atmosphere for a short duration after multiple purging. The reaction proceeded in a closed tube under a static N_2O atmosphere and full conversion was achieved overnight. For *in situ* formation of NHO **3**, 1,2,3-triisopropylimidazolium iodide **7** (16 mg, 0.05 mmol) was suspended in a KHMDS (13 mg, 1.3 equiv.) solution of 0.4 mL C_6D_6 in an NMR tube with J. Young valve.

Trapping of 2-Diazopropane with Norbornene: In a nitrogen-filled glovebox, NHO **3** (9.2 mg, 0.047 mmol), norbornene (4.5 mg, 0.049 mmol), and mesitylene (6.96 μL, 0.050 mmol) were dissolved in 0.4 mL C_6D_6 and transferred to an NMR tube with J. Young valve. In a fume hood, the solution was degassed by three freeze-pump-thaw cycles. A balloon, connected to a vacuum line and an N_2O cylinder *via* a three-way valve, was purged multiple times with N_2O. The NMR tube, connected to the filled balloon and a vacuum line *via* a three-way valve, was exposed to the N_2O atmosphere for a short duration after multiple purging. The reaction proceeded in a closed tube under a static N_2O atmosphere and full conversion was achieved overnight. The NMR data are consistent with literature reports.[18]

1,3-Diisopropyl-2-(1-methylethylidene)imidazoline 3: To a 250 mL round-bottom flask equipped with a stir bar, septum, Schlenk-frit, joined to a Schlenk flask containing a stir bar, KH (30% in mineral oil, 17.2 g, 129 mmol, 2 equiv.) was added using a Pasteur pipette. The suspension was washed four times with *n*-pentane (ca. 10 mL) to remove the mineral oil. Then, washed KH was suspended in 100 mL diethyl ether. While stirring, 1,2,3-triisopropylimidazolium iodide **7** (17.73 g, 55.0 mmol, 1.0 equiv.) was added and the reaction mixture was vigorously stirred for two days in the absence of light. Then, the solvent was removed *in vacuo* at 0 °C. The residue was suspended in *n*-pentane, filtrated, and extracted with *n*-pentane. The resulting red solution was concentrated *in vacuo* at 0 °C to remove *n*-pentane. The obtained liquid was transferred and distilled (70–71 °C/2.0 mbar) to afford 1,3-diisopropyl-2-(1-methylethylidene)imidazoline **3** (7.630 g, 71%) as a yellowish liquid, which was stored in the freezer of a glovebox in the absence of light at −36 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 5.73 (s, 2H, CH=CH), 3.84 (hept, J = 6.6 Hz, 2H, N–C<u>H</u>$(CH_3)_2$), 1.93 (s, 6H, C=C$(CH_3)_2$), 1.01 (d, J = 6.7 Hz, 12H, N–CH(C<u>H</u>$_3)_2$). ^{13}C NMR (101 MHz, C_6D_6) δ 147.9 (<u>C</u>=C$(CH_3)_2$), 114.2 (CH=CH), 72.8 (C=<u>C</u>$(CH_3)_2$), 49.7 (N–<u>C</u>H$(CH_3)_2$), 21.7 (C=C(<u>C</u>H$_3)_2$), 20.5 (N–CH(<u>C</u>H$_3)_2$). HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{23}N_2$ 195.1856; found 195.1853.

1,3-Dihydro-1,3-bis(1-methylethyl)-2*H*-imidazol-2-one 4: In a nitrogen-filled glovebox, NHO **3** (104 mg, 0.535 mmol) was dissolved in 4.0 mL Et_2O and transferred to a 50 mL Schlenk tube with J. Young valve equipped with a stir bar. In a fume hood, the solution was degassed by three freeze-pump-thaw cycles. A balloon, connected to a vacuum line and an N_2O cylinder *via* a three-way valve, was purged multiple times with N_2O. The Schlenk tube, connected to the filled balloon and a vacuum line *via* a three-way valve, was exposed to the N_2O atmosphere for a short duration after multiple purging. The reaction mixture was stirred vigorously overnight in a closed tube under a static N_2O atmosphere. Then, the reaction mixture was poured onto 10 mL HCl (aq, 1 M). After phase separation, the organic phase was washed with water (3×5 mL). The combined aqueous phases were extracted with Et_2O (2×10 mL). The combined organic phases were washed with 10 mL brine (NaCl aq sat), dried over Na_2SO_4, and filtered. After the removal of all volatiles *in vacuo*, the title compound **4** was obtained as colorless/yellowish oil (47 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (s, 2H, CH=CH), 4.39 (hept, J = 6.7 Hz, 2H, –C<u>H</u>$(CH_3)_2$), 1.26 (d, J = 6.8 Hz, 12H, –CH(C<u>H</u>$_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8 (C=O), 106.6 (CH=CH), 44.3 (–CH(<u>C</u>H$_3)_2$), 22.2 (–<u>C</u>H$(CH_3)_2$). ^{15}N NMR (41 MHz, $CDCl_3$) δ −233.5. IR (KBr, film, cm^{-1}): 3174 (w), 3137 (w), 3106 (w), 2975 (s), 2931 (s), 2876 (m), 2855 (m), 1659 (s), 1573 (w), 1461 (s), 1446 (s), 1393 (m), 1371 (m), 1329 (w) 1258 (m), 1224 (s), 1176 (w), 1162 (w), 1134 (m), 1087 (m), 1000 (m), 930 (w), 876 (m), 801 (m), 758 (w), 705 (m), 660 (m). HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_9H_{16}N_2ONa^+$ 191.1155; found 191.1150.

Acetone Azine 5: The compound was synthesized according to an unmodified literature procedure.[16] ^{1}H NMR (400 MHz, C_6D_6) δ 1.83 (s, 6H), 1.80 (s, 6H).

(1,3-Dihydro-1,3,diisopropyl-2H-imidazol-2-one)-2-(1-methylethylene)-hydrazine 6: In a nitrogen-filled glovebox, NHO **3** (108 mg, 0.56 mmol) was dissolved in 1.0 mL Et_2O and transferred to a 50 mL Schlenk tube with J. Young valve equipped with a stir bar. In a fume hood, the solution was degassed by three freeze-pump-thaw cycles. A balloon, connected to a vacuum line and an N_2O cylinder *via* a three-way valve, was purged multiple times with N_2O. The Schlenk tube, connected to the filled balloon and a vacuum line *via* a three-way valve, was exposed to the N_2O atmosphere for a short duration after multiple purging. The reaction mixture was stirred vigorously overnight in a closed tube under a static N_2O atmosphere. Then, the reaction mixture was directly subjected to column chromatography (silica, first EtOAc/*n*-hexane (2:3, R_f 0.0) followed by EtOAc/*n*-hexane (2:3) + 5 vol% Et_3N (R_f 0.4)). After the removal of all volatiles *in vacuo*, the title compound **6** was obtained as a yellow oil (19 mg, 15%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.23 (s, 2H, CH=CH), 5.14 (hept, J = 6.8 Hz, 2H, N–C<u>H</u>$(CH_3)_2$), 1.97 (s, 3H, C_q–CH_3), 1.91 (s, 3H, C_q–CH_3), 1.28 (d, J = 6.7 Hz, 12H, N–CH(C<u>H</u>$_3)_2$). ^{13}C NMR (176 MHz, $CDCl_3$) δ 149.1 (N–C_q-(N)–N), 148.9 (–N=<u>C</u>$_q$–CH_3), 108.6 (CH=CH), 46.7 (N–<u>C</u>H$(CH_3)_2$), 25.0 (C_q–<u>C</u>H_3), 22.1 (N–CH(<u>C</u>H$_3)_2$), 16.1 (C_q–<u>C</u>H_3). ^{15}N NMR (71 MHz, $CDCl_3$) δ −44.3 (–N=$C_q(CH_3)_2$), −241.7 (<u>N</u>–C_q(N)–<u>N</u>). ^{1}H NMR (600 MHz, C_6D_6) δ 5.90 (s, 2H, CH=CH), 5.39 (s br, 2H, N–C<u>H</u>$(CH_3)_2$), 2.22 (s, 3H, C_q–CH_3), 2.06 (s, 3H, C_q–CH_3), 1.10 (d, J = 6.8 Hz, 12H, N–CH(C<u>H</u>$_3)_2$). ^{13}C NMR (151 MHz, C_6D_6) δ 148.7 (N–C_q(N)–N), 147.4 (–N=<u>C</u>$_q$–CH_3), 108.3 (CH=CH), 46.7 (N–<u>C</u>H$(CH_3)_2$), 25.2 (C_q–<u>C</u>H_3), 22.0 (N–CH(<u>C</u>H$_3)_2$), 16.5 (C_q–<u>C</u>H_3). ^{15}N NMR (71 MHz, C_6D_6) δ −41.9 (–N=$C_q(CH_3)_2$), −243.9 (<u>N</u>–C_q(N)–<u>N</u>). IR (ATR, C_6D_6, cm^{-1}): 1560 ν(C=N). HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{23}N_4^+$ 223.1917; found 223.1918.

1,2,3-Triisopropylimidazolium Iodide 7: In a two-neck round-bottom flask equipped with a stir bar and a reflux condenser, 2-isopropylimidazole (9.33 g, 84.7 mmol, 1.0 equiv.) was dissolved in 120 mL acetonitrile. While stirring, K_2CO_3 (14.44 g, 104 mmol, 1.2 equiv.) and 2-iodopropane (42 mL, 420 mmol, 5.0 equiv.) were added. The suspension was refluxed at 90 °C under gentle nitrogen flow. Additional portions of 2-iodopropane (8.5 mL, 84.5 mmol, 1.0 equiv.) were added after 1.5 days and another 2.5 days, respectively. After 6 days in total full conversion was achieved according to ESI–MS. The reaction mixture was filtrated. After the removal of the volatiles, the solid residue was triturated in boiling toluene. Then, the product was dissolved in a minimum amount of acetone and precipitated by addition of ethyl acetate (7–10 fold excess). After filtration, the resulting powder was washed with ethyl acetate in several portions until the washing solution was colorless and finally with *n*-hexane once to afford 1,2,3-triisopropylimidazolium iodide **7** as a colorless powder (21.00 g, 68%). Crystals suitable for single crystal X-ray diffraction were obtained by vapor diffusion from either acetone/*n*-pentane or acetone/ether (deposition number 2099774). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 2H, CH=CH), 4.88

(hept, $J = 6.7$ Hz, 2H, N–C<u>H</u>$(CH_3)_2$), 3.90 (hept, $J = 7.3$ Hz, 1H, C–C<u>H</u>-$(CH_3)_2$), 1.51 (d, $J = 6.7$ Hz, 12H, N–CH(C<u>H</u>$_3)_2$), 1.45 (d, $J = 7.3$ Hz, 6H, C–CH(C<u>H</u>$_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7 (C_q), 119.4 (CH=CH), 51.3 (N–<u>C</u>H$(CH_3)_2$), 24.6 (C–<u>C</u>H$(CH_3)_2$), 23.3 (N–CH(<u>C</u>H$_3)_2$), 20.0 (C–CH(<u>C</u>H$_3)_2$). HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{12}H_{23}N_2$ 195.1856; found 195.1764. HRMS (ESI): *m/z* $[M]^-$ calcd for I 126.9050; found 126.9109.

Cycloaddition Product 8: In a nitrogen-filled glovebox, 1,2,3-triisopropylimidazolium iodide (425 mg, 1.3 mmol), KHMDS (345 mg, 1.3 equiv.), and norbornene (122 mg, 1.0 equiv.) were suspended in 10 mL toluene inside a Schlenk tube with J. Young valve. In a fume hood, the suspension was degassed by three freeze-pump-thaw cycles. A balloon, connected to a vacuum line and an N_2O cylinder *via* a three-way valve, was purged multiple times with N_2O. The NMR tube, connected to the filled balloon and a vacuum line *via* three-way valve, was exposed to the N_2O atmosphere for a short duration after multiple purging. The reaction proceeded with the N_2O balloon connected to the Schlenk tube overnight. Then, all volatiles were removed *in vacuo* and the solid residue was extracted with Et_2O and passed through a silica plug (5 g silica gel). The cycloaddition product **8** was eluted with 20% EtOAc/*n*-hexane (50 mL) and then imidazolone **4** was eluted with 40% EtOAc/*n*-hexane with 5 vol% Et_3N (50 mL). After removal of all volatiles *in vacuo*, imidazolone **4** was obtained as a yellowish oil (156 mg, 71%), and the cycloaddition product **8** was obtained as a colorless oil after distillation at 40–50 °C (bath)/oil pump (68 mg, 31%). The ^{1}H NMR data is consistent with literature reports.[18]

Supporting Information

Additional references cited within the Supporting Information.[29–38]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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