The 1 : 1 Adduct of 1,3-Diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-ylidene and Nitrous Oxide

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The nucleophilic carbene 1,3-diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-ylidene (**7**) captures nitrous oxide under formation of both *syn*- (**8**) and *anti*-1,3-diisopropyl-4,5-imidazolium diazotate (**9**). The *syn*-isomer is the thermodynamically more stable form. As shown by X-ray crystallography, the two isomers are statistically distributed in the crystalline state.

Key words: *N*-Heterocyclic Nucleophilic Carbenes, Nitrous Oxide, Stereochemistry, X-Ray Crystallography

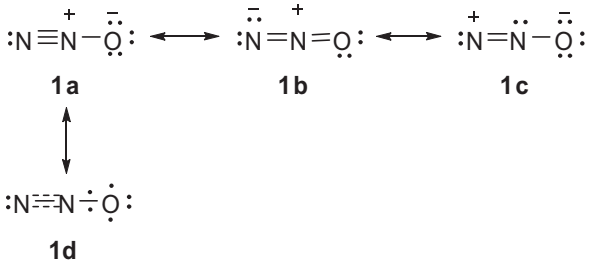
Introduction

The present interest in the chemistry of nitrous oxide is mainly focussed on its role as an atmospheric trace gas in global warming and destruction of the stratospheric ozone layer [1, 2]. Furthermore, the formation and decomposition of nitrous oxide by enzymes of anaerobic bacteria is part of the global nitrogen cycle (denitrification process) [3]. The interaction of N_2O with the metal centers of the active sites of the involved enzymes stimulated an increased interest in the chemistry of N_2O-metal complexes [4]. The catalytic purification of N_2O-polluted waste gases [4] and the utilization of N_2O as oxidant in metal-catalyzed conversions [5] enhanced the research activities in the field of N_2O-metal complexes further. Compared to these activities newer examples for the application of nitrous oxide as reagent in metal-free reactions are scarce.

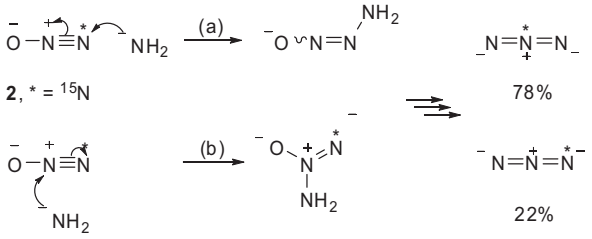
The bonding situation in nitrous oxide can be qualitatively represented by mixing the zwitterionic VB structures **1a**–**c**. The increased-valence structure **1d** [6] with one electron π_x(NO) and π_y(NO) bonds and two fractional π_x(NN) π_y(NN) bonds has also been suggested to describe the N_2O geometry and chemical behavior. The qualitative VB treatment indicates electrophilic character at both N atoms (Scheme 1).

The reactivity of N_2O towards nucleophilic compounds has been known for a long time and is briefly summarized with the following examples. The reaction of alkali metal amide melts with N_2O yields alkali metal azides (Wislicenus reaction) [7]. By means of ^{15}N-labelled nitrous oxide **2**, Clusius *et al.* [8, 9] elucidated the mechanism of this process of industrial importance as a combination of nucleophilic attack at both, the terminal (a) and the central N atom (b). Likewise the deprotonation products of anilines give aryl azides on reaction with N_2O [10] (Scheme 2).

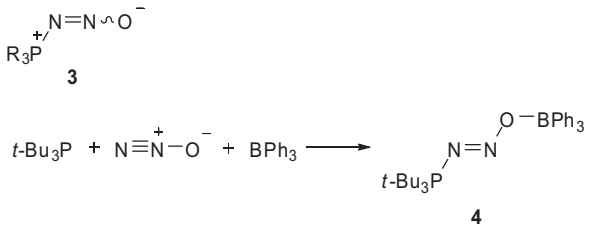
Phosphanes react with nitrous oxide under oxygen transfer to the phosphorus atom [11]. The phosphane-N_2O adduct **3** which decomposes under N_2 extrusion was suggested as an intermediate. The initial nucleophilic attack of the phosphane at the terminal N atom of nitrous oxide is supported by the combined action of t-Bu_3P and Ph_3B or $(C_6F_5)_3B$ as so-called "frustrated Lewis pair" systems which yields the complex **4** in 76% yield [12, 13]. In this reaction the dichotomous character of N_2O with electrophilic properties at the terminal N atom and nucleophilic properties at the O atom is elegantly exploited (Scheme 3).



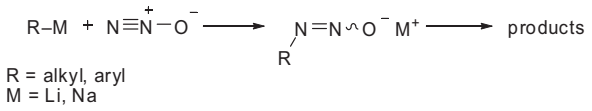
Scheme 1.



Scheme 2.



Scheme 3.

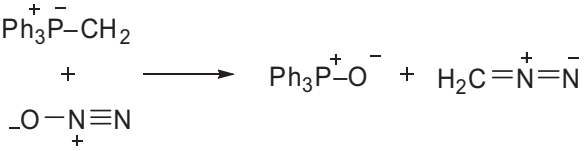


Scheme 4.

Organolithium compounds [14–16] and triphenylmethylsodium [17] react with N_2O to give alkane(arene) diazotates as initial products, which depending on the substituent R are further transformed into a variety of compounds (Scheme 4).

In a formally Wittig-like reaction triphenylphosphonium methylide and N_2O produce diazomethane in low yields [18] (Scheme 5).

Nucleophilic carbenes are powerful neutral C nucleophiles, and their reactivity towards a variety of electrophiles is well-documented in the literature [19–25]. In a recent communication Severin *et al.* [26] described the covalent capture of nitrous oxide by the



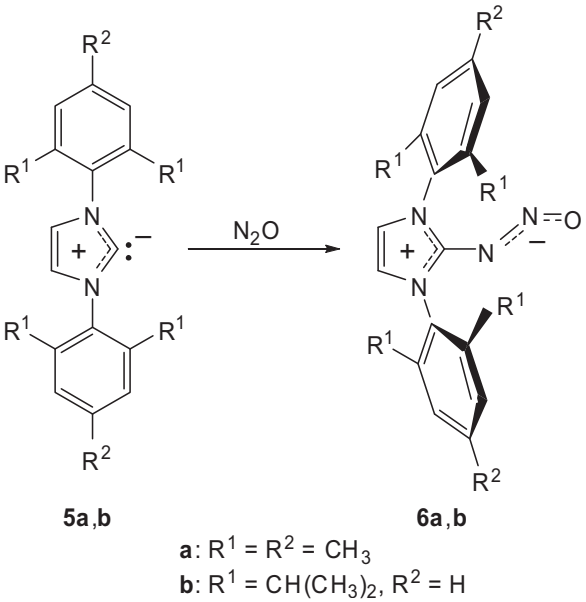
Scheme 5.

N-heterocyclic carbenes **5a**, **b**. This article prompted us to report on our study concerning the reaction of 1,3-diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-ylidene (**7**) with N_2O.

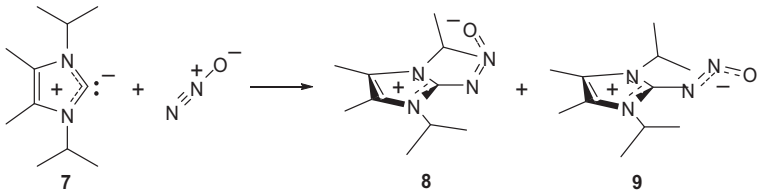
Results and Discussion

The *N*,*N*′-dimesityl and *N*,*N*′-diisopropylphenyl-substituted nucleophilic carbenes **5a**, **b** react with N_2O to give the *anti*-imidazolium diazotates **6a**, **b** [26] (Scheme 6).

Similarly, introduction of nitrous oxide into a solution of 1,3-diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-ylidene (**7**) in toluene furnished a 1 : 1 adduct as a yellow precipitate. However, the stereochemistry of the product formed from **7** differs remarkably. Structure elucidation has indicated that both, *syn*-(**8**) and *anti*-1,3-diisopropyl-4,5-dimethylimidazolium diazotate (**9**) are simultaneously obtained with the *syn*-adduct being the main isomer (Scheme 7).



Scheme 6.



Scheme 7.

The FAB mass spectrum of the precipitate obtained in the reaction of **7** with N_2O (3-nitrobenzylic alcohol as matrix) shows the $[M+H]^+$ ion ($m/z = 225$) as base peak and the $M^{+\bullet}$ ion ($m/z = 224$, rel. int. 40 %). Both, $M^{+\bullet}$ and $[M+H]^+$ expel NO under formation of ions with $m/z = 195$ (rel. int. 95 %) and $m/z = 194$ (rel. int. 65 %). The elimination of NO from $[M+H]^+$ is an exception from the "even electron rule" enabled by the high stability of the NO radical. A further fragment at $m/z = 181$ (rel. int. 45 %) corresponds to the imidazolium ion formed by transfer of the added proton of $[M+H]^+$ to C-2 and N_2O elimination. In addition to the $M^{+\bullet}$ ion ($m/z = 224$, rel. int. 66 %) the FD mass spectrum exhibits cluster ions of the composition $M_2^{+\bullet}$ ($m/z = 448$, rel. int. 10 %) and $[M + \text{imidazolium}]^+$ ($m/z = 405$, rel. int. 100 %).

The X-ray structural analysis of the adduct crystallized from toluene (Fig. 1) has indicated substantial disorder in the crystalline state caused by the presence of two stereoisomers which are statistically distributed with the imidazolium units occupying identical positions. Although the disordering prevents the determination of meaningful bond lengths from the electron density distribution, Fig. 1 clearly shows that the two isomers are *syn*- and *anti*-imidazolium diazotates with the N_2O units in a near orthogonal position in relation to the five-membered ring. A *syn* : *anti* ratio of 70 : 30 can be estimated from the electron densities.

The position of the oxygen atom also influences the orientation of the isopropyl substituents attached at N-2. To avoid steric strain, the methyl groups (C-10, C-11) of the *syn*-adduct **8** are directed away from the oxygen atom O-1.

In accordance with the X-ray data, the ^1H NMR spectra of the adduct in [D_6]benzene, [D_8]toluene, [D_2]dichloromethane, D_2O, and [D_6]acetone shows two sets of signals in ratios of 77 : 23, 76 : 34, 85 : 15, 75 : 25 and 79 : 21. The doubling of the signals is also evident in the ^{13}C NMR spectra. An important observation could be made when the NMR spectra in D_2O were recorded immediately after the solutions had been prepared. At the beginning a *syn*/*anti* ratio of 51.5 : 48.5 was found. This ratio steadily increased over 24 h to 75 : 25. When the solution was kept at 80 °C for 10 min a ratio of 77.6 : 24.4 was obtained.

Obviously, the adduct precipitating in the reaction of **7** with N_2O originally consists of an approximate 1 : 1 mixture of the isomers **8** and **9**, which in solution equilibrate to isomeric mixtures varying from 75 to 85 % in the *syn*-adduct depending on the solvent. From the solvents tested, D_2O is the only one in which the equilibration is slow enough to be detected by simple NMR measurements.

The indiscriminate formation of both isomers means that the energy of the transition state is practically not affected by the orientation of the O atom. However, the dominance of the *syn*-isomer in the equilibrium mixtures indicates that this isomer is the thermodynamically more stable form. This is remarkable because in arene diazotates, the anionic counterparts of the zwitterionic imidazolium diazotates, the *anti*-isomers are more stable [27]. Furthermore, the problem remains to explain the contradictory stereochemical results, when the capturing of N_2O by the nucleophilic carbene **7** is compared with the analogous reactions of **5a** and **b**.

The exclusive formation of the *anti*-adduct in the reactions of **5a**, **b** at one hand in contrast to the formation of *syn*/*anti*-mixtures from **7** at the other hand are probably the results of different steric interactions of the substituents located at the N atoms. The orientation of the bulky aryl groups in **6a**, **b** nearly perpendicular to the five-membered ring allows the introduced diazotate unit to adopt dihedral angles of 25.4 and 39.5°, respectively [26]. Thus, resonance stabilization between the N_2O unit and the imidazolium ring should still be possible to some extent. By way of contrast, the isopropyl substituents of the *syn*- (**8**) and *anti*-adduct (**9**) force the diazotate moiety towards orthogonality with respect to the plane defined by the imidazolium ring. In this geometry, resonance between the diazotate unit

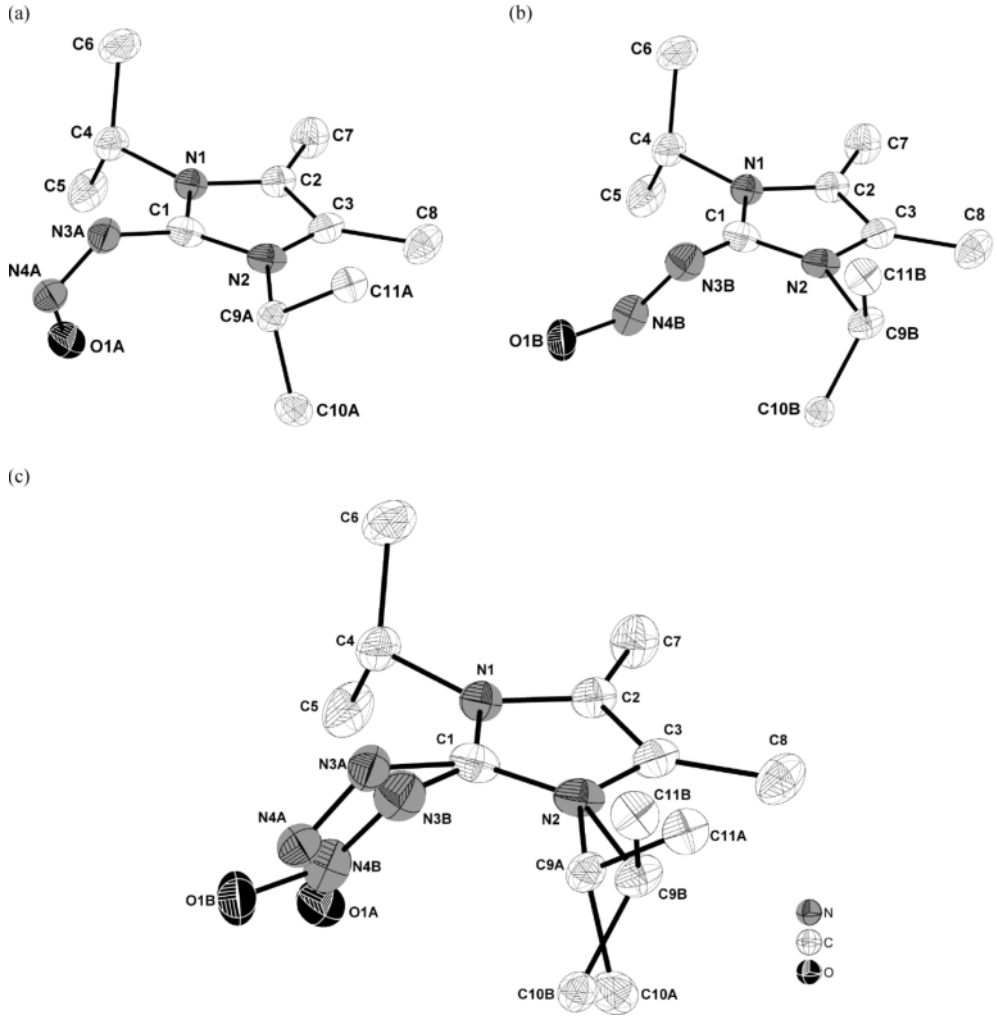
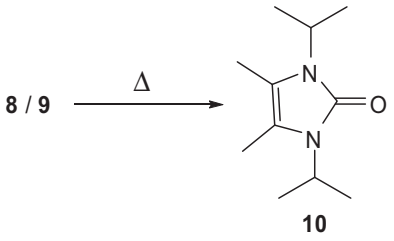


Fig. 1. Molecular structure of 1,3-diisopropyl-4,5-imidazolium diazotates **8** and **9** showing the two refined positions in the disordered parts [upper left (a) and right (b)] and (c) the superposition of the two possibilities. Displacement ellipsoids are at 25 % probability level, hydrogen atoms are omitted for clarity.

and the imidazolium ring is interrupted, however, the *syn*-configuration may gain some extra-stabilization by Coulomb interaction between the negatively charged O atom and the positive charge of the imidazolium ring. This may cause the reversal in the order of stability and, thus, favor **8** over **9**.

In cross-over experiments between the adducts **6a/b** and the complementary free carbenes **5b/a**, no transfer of N_2O was observed [26]. Similarly, the *syn*/*anti* mixture **8/9** shows no N_2O transfer when mixed with the nucleophilic carbene **5a** in [D_8]THF, although, because of the lack of resonance, the bond between C-2 of the imidazolium unit and the diazotate N atom is expected to be weaker in **8/9** compared to **6a**. Therefore, a dissociation-recombination mechanism to explain the observed equilibration between **8** and **9** in solution can be excluded and either rotation about the formal N,N double bonds or inversion at the N atom remain to rationalize the geometrical isomerization.

The adduct **8/9** expels dinitrogen under formation of the urea **10** at temperatures above 60 °C in non-protic solvents. In [D_8]THF the decomposition into **10** reach 81 % after 80 h at 60 °C and in [D_8]toluene 68 % after 50 min at 80 °C. This is in line with what



Scheme 8.

has been found for the analogous compound **6a** [26]. (Scheme 8)

The urea **10** is identical with a specimen independently synthesized by oxidation of 1,3-dihydro-1,3-diisopropyl-4,5-dimethyl-2,3-dihydroimidazole-2-thione with alkaline hydrogenperoxide. The decomposition of **8/9** into the urea **10** is strongly solvent-dependent. In D_2O and [D_4]methanol no reaction could be detected on heating to 80 °C (24 h) and 60 °C (82 h). In these solvents, strong solvation by hydrogen bonding should stabilizes the imidazolium diazotates **8/9**. In the crystalline state the adduct **8/9** endures heating *in vacuo* to 60 °C without the formation of the urea **10**.

Conclusion

1,3-Diisopropyl-4,5-dimethyl-1,3-dihydroimidazol-2-ylidene (**7**) captures N_2O under formation of both, the *syn*- and the *anti*-imidazolium diazotate **8** and **9**. Both stereoisomers are formed under kinetic control in approximately equal amounts, however in solution the *syn*-isomer **8** becomes the dominating species. *syn*/*anti*-Ratios of ∼ 3 : 1 to ∼ 4 : 1 could be detected by ^{1}H NMR spectroscopy depending on the nature of the solvents.

To the best of our knowledge, the parallel formation of the *syn*- and *anti*-isomer in a single reaction step is unique in the chemistry of diazotates. Furthermore, the isomeric pair **8/9** represents the first documented example with the *syn*-form as the thermodynamically more stable diazotate.

Experimental Section

All reactions were carried out under an atmosphere of argon. Solvents were dried using standard procedures and distilled in an argon atmosphere prior to use. 1,3-Diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-ylidene (**7**) was prepared according to literature methods [28].

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AvanceII+400 instrument at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in ppm, multiplicities are labelled s (singulet), d (doublet) and sept (septet).

The FAB mass spectra were recorded on a Finnigan TSQ 70 instrument with 3-nitrobenzylic alcohol as matrix material. FD mass spectra were obtained on a MAT 95 instrument.

*Adducts of nitrous oxide with 1,3-diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-ylidene (**8**, **9**)*

A constant flow of nitrous oxide is passed into a solution of 2.328 g (12.91 mmol) of the carbene **7** in 80 mL toluene for 8 h. The solution turns yellow followed by the formation of a yellow precipitate. The solvent is removed *in vacuo*, and unreacted carbene (**7**) is removed by sublimation to afford 2.53 g (87 %) of a yellow solid. – ^{1}H NMR (D_2O, **8**): $\delta = 1.42$ (d, $J = 7.0$ Hz, 12 H, $N_{1,3}$-CH-(CH_3)$_2$), 2.32 (s, 6 H, $C_{4,5}$-CH_3), 4.56 (sept, $J = 7.0$ Hz, 2 H, $N_{1,3}$-CH-(CH_3)$_2$). – ^{13}C NMR (D_2O, **8**): $\delta = 8.5$ ($C_{4,5}$-CH_3), 20.7 ($N_{1,3}$-CH-(CH_3)$_2$), 50.0 ($N_{1,3}$-CH-(CH_3)$_2$), 123.8 ($C_{4,5}$), 145.5 (C_2). – ^{1}H NMR (D_2O, **9**): $\delta = 1.39$ (d, 12 H, $N_{1,3}$-CH-(CH_3)$_2$), 2.29 (s, 6 H, $C_{4,5}$-CH_3), 4.27 (sept, $J = 7.0$ Hz, 2 H, $N_{1,3}$-CH-(CH_3)$_2$). – ^{13}C NMR (D_2O, **9**): $\delta = 8.6$ ($C_{4,5}$-CH_3), 19.9 ($N_{1,3}$-CH-(CH_3)$_2$), 49.9 ($N_{1,3}$-CH-(CH_3)$_2$), 124.2 ($C_{4,5}$), 143.7 (C_2). – ^{1}H NMR (C_6D_6, **8**): $\delta = 1.07$ (d, $J = 6.9$ Hz, 12 H, $N_{1,3}$-CH-(CH_3)$_2$), 1.53 (s, 6 H, $C_{4,5}$-CH_3), 4.58 (sept, $J = 6.9$ Hz, 2 H, $N_{1,3}$-CH-(CH_3)$_2$). – ^{13}C NMR (C_6D_6, **8**): $\delta = 9.4$ ($C_{4,5}$-CH_3), 21.2 ($N_{1,3}$-CH-(CH_3)$_2$), 49.2 ($N_{1,3}$-CH-(CH_3)$_2$), 120.7 ($C_{4,5}$), 153.8 (C_2). – ^{1}H NMR (C_6D_6, **9**): $\delta = 1.09$ (d, $J = 6.9$ Hz, 12 H, $N_{1,3}$-CH-(CH_3)$_2$), 1.48 (s, 6 H, $C_{4,5}$-CH_3), 4.16 (sept, $J = 7.0$ Hz, 2 H, $N_{1,3}$-CH-(CH_3)$_2$). – ^{13}C NMR (C_6D_6, **9**): $\delta = 9.0$ ($C_{4,5}$-CH_3), 20.6 ($N_{1,3}$-CH-(CH_3)$_2$), 49.0 ($N_{1,3}$-CH-(CH_3)$_2$), 121.5 ($C_{4,5}$), 153.4 (C_2). – $C_{11}H_{20}N_4O$: calcd. C 58.9, H 9.0, N 25.0; found C 58.5, H 9.5, N 25.5. FAB- and FD-MS data see text.

*1,3-Diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-one (**10**) by oxidation of 1,3-diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-thione*

Compound **10** was prepared by the method described in ref [29]. An ice-cold solution of 1.0 g (4.71 mmol) thione and six pellets of sodium hydroxide in 35 mL of ethanol and 2 mL of water was mixed with 6 mL of hydrogen peroxide (30 %), and the mixture was stirred at 0 °C for 1 h and was then stored in a refrigerator overnight. After dilution with 40 mL of water and extraction with toluene, the toluene solution was treated with sodium carbonate and evaporated to yield 0.3 g (33 %) of a colorless solid. – ^{1}H NMR (D_2O): $\delta = 1.36$ (d, $J = 7.0$ Hz, 12 H, $N_{1,3}$-CH-(CH_3)$_2$), 2.03 (s, 6 H, $C_{4,5}$-CH_3), 4.29 (sept, $J = 7.0$ Hz, 2 H, $N_{1,3}$-CH-(CH_3)$_2$). – ^{13}C

NMR (D_2O): $\delta = 8.4$ ($C_{4,5}$-CH_3), 20.2 ($N_{1,3}$-CH-(CH_3)$_2$), 45.3 ($N_{1,3}$-CH-(CH_3)$_2$), 114.5 ($C_{4,5}$), 151.8 (C_2). – EI-MS (70 eV): m/z (%) = 196 (41) $[M]^{+\bullet}$, 154 (33) $[M–C_3H_6]^{+\bullet}$, 112 (100) $[M–2\ C_3H_6]^{+\bullet}$, 111 (39), 97 (18).

*Thermolysis of adducts **8**/**9***

The thermal decomposition of **8/9** was performed in deuterated solvents in NMR tubes. The formation of **10** was followed by ^{1}H NMR spectroscopy. For reaction times and temperatures see text.

Crystal structure determination

A suitable single crystal was selected and mounted on a Stoe IPDS I diffractometer for data collection (graphite-monochromatized MoK_α radiation, $\lambda = 0.71073$ Å, oscillation scan mode). The structure was solved by Direct Methods and expanded using Fourier difference techniques with the SHELXS/L-97 program package [30, 31] (Table 1). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares refinements on F^2. The hydrogen atom bound to C(4) was found in the Fourier map, all other hydrogen atoms were added in calculated positions, and all were refined isotropically. The isopropyl group bound to N(2) and the diazotate group bound to C(1) were refined with a disorder model in a ratio of 62(1) : 38(1), and 64(1) : 36(1) %, respectively. Selected bond lengths and angles are summarized in Table 2.

CCDC 911586 contains 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.

Table 1. Crystal structure data for 1,3-diisopropyl-4,5-imidazolium diazotate **8/9**.

Formula	$C_{11}H_{20}N_4O$
M_r	224.31
Crystal size, mm^3	0.5 × 0.5 × 0.4
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
a, Å	10.048(1)
b, Å	11.294(3)
c, Å	11.321(2)
β, deg	104.25(2)
V, Å^3	1245.3(4)
Z	4
D_{calcd}, g cm^{-3}	1.20
μ (MoK_α), cm^{-1}	0.8
F(000), e	488
hkl range	±11, ±13, ±13
θ range, deg	2.59 to 25.03
Refl. measured / unique / R_{int}	12357 / 2126 / 0.0388
Param. refined	205
$R1$ / $wR2$[a] [$I > 2\sigma(I)$]	0.0503 / 0.1220
$R1$ / $wR2$[b] (all data)	0.0772 / 0.1344
GoF (F^2)[c]	0.920
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.221 / −0.151

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for 1,3-diisopropyl-4,5-imidazolium diazotate **8/9** with estimated standard deviations in parentheses.

	8/9
Bond lengths	
N(1)–C(1)	1.332(2)
N(1)–C(2)	1.393(2)
N(1)–C(4)	1.486(2)
N(2)–C(1)	1.330(3)
N(2)–C(3)	1.388(3)
N(2)–C(9A)	1.520(5)
N(2)–C(9B)	1.523(8)
C(1)–N(3B)	1.22(1)
C(1)–N(3A)	1.523(6)
C(2)–C(3)	1.361(3)
C(9A)–C(11A)	1.541(9)
C(9A)–C(10A)	1.54(1)
C(9B)–C(11B)	1.48(2)
C(9B)–C(10B)	1.544(2)
O(1A)–N(4A)	1.248(7)
N(3A)–N(4A)	1.250(9)
O(1B)–N(4B)	1.27(2)
N(4B)–N(3B)	1.380(19)
Bond angles	
C(1)–N(1)–C(2)	109.12(16)
C(1)–N(2)–C(3)	109.10(15)
C(1)–N(2)–C(9A)	114.9(3)
C(3)–N(2)–C(9A)	135.9(3)
C(1)–N(2)–C(9B)	139.7(6)
C(3)–N(2)–C(9B)	110.8(6)
C(9A)–N(2)–C(9)B	25.2(4)
N(3B)–C(1)–N(2)	114.6(6)
N(3B)–C(1)–N(1)	136.9(6)
N(2)–C(1)–N(1)	108.42(19)
N(3B)–C(1)–N(3A)	16.9(6)
N(2)–C(1)–N(3A)	126.8(3)
N(1)–C(1)–N(3A)	123.5(3)
C(3)–C(2)–N(1)	106.38(16)
C(2)–C(3)–N(2)	106.97(16)
N(2)–C(9A)–C(11A)	109.2(4)
N(2)–C(9A)–C(10A)	105.7(4)
C(11A)–C(9A)–C(10A)	108.2(7)
C(11B)–C(9B)–N(2)	105.9(8)
C(11B)–C(9B)–C(10B)	114.1(12)
N(2)–C(9B)–C(10B)	108.9(7)
N(4A)–N(3A)–C(1)	115.8(6)
O(1A)–N(4A)–N(3A)	116.0(7)
O(1B)–N(4B)–N(3B)	117.2(14)
C(1)–N(3B)–N(4B)	108.0(10)

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