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Research Article

On the Reactivity of N-*tert*-Butyl-1,2-Diaminoethane: Synthesis of 1-*tert*-Butyl-2-Imidazoline, Formation of an Intramolecular Carbamate Salt from the Reaction with CO_2, and Generation of a Hydroxyalkyl-Substituted Imidazolinium Salt

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N-*tert*-Butyl-1,2-diaminoethane was shown to react rapidly with atmospheric carbon dioxide to generate the zwitterionic ammonium carbamate salt $CO_2N(H)C_2H_4N(H)_2{}^tBu$ (**1**). Reaction of N-*tert*-butyl-1,2-diaminoethane with triethylorthoformate gave 1-*tert*-butyl-2-imidazoline (**2**) in 24% yield after fractional distillation, and the hydroxyalkyl-tethered imidazolinium salt $[HOC(Me)_2CH_2NC_2H_4N(CH)^tBu][Cl]$ (**3**) was synthesised from the sequential reaction of N-*tert*-butyl-1,2-diaminoethane with isobutylene epoxide, HCl, and triethylorthoformate.

1. Introduction

1,2-Diamines, exemplified by ethylenediamine and its derivatives, are produced on a large scale and are used for many purposes including coordination chemistry [1] and CO_2 capture [2–6]. Chiral diamines are also well known and have been utilised in the production of various chiral catalysts [7–9]. N-substituted ethylenediamines can also function as precursors to 1-substituted-2-imidazolines (dihydroimidazoles) [10, 11], with the synthesis of unsymmetrical saturated N-heterocyclic carbenes (NHCs) one potential application for these compounds [12, 13]. Examples of 2-imidazolines that are widely used in the synthesis of unsymmetrical saturated NHCs include those with mesityl (2,4,6-$Me_3C_6H_2$) and 2,6-diisopropylphenyl (Dipp: 2,6-${}^iPr_2C_6H_3$) substituents [12,13]. 1-Ethyl-2-imidazoline and 1-benzyl-2-imidazoline are known compounds [14], but the *tert*-butyl derivative, to the best of our knowledge, has not been reported. If the N-3 position is subsequently substituted with a hydrocarbon linker terminating with a donor atom, then these compounds represent useful precursors to tethered saturated NHCs [15], which have been extensively explored by Arnold and coworkers [16–20]. We have recently reported on the use of

N-substituted-1,2-diaminoethanes to form fluorenyl tethered diamines [21], which then acted as useful precursors to a tethered N-heterocyclic stannylene (NHSn) with a Dipp substituent [21]. During this research we noted the reactivity of N-*tert*-butyl-1,2-diaminoethane [22] with air, which encouraged us to explore the reactivity of this diamine further. In this publication, we characterise the reaction product of N-*tert*-butyl-1,2-diaminoethane with carbon dioxide, the synthesis of 1-*tert*-butyl-2-imidazoline, and the formation of a hydroxyalkyl imidazolinium salt with an N-*tert*-butyl substituent.

2. Results and Discussion

N-*tert*-Butyl-1,2-diaminoethane was synthesised as previously described [21, 22]; however, we noticed that it rapidly reacts with atmospheric CO_2 forming a zwitterionic alkylammonium carbamate (**1**, Scheme 1). This was confirmed by X-ray crystallographic analysis of a single crystal formed by the reaction of the parent diamine and showed the structure to be an intramolecular alkylammonium carbamate salt resulting from nucleophilic attack of CO_2 followed by
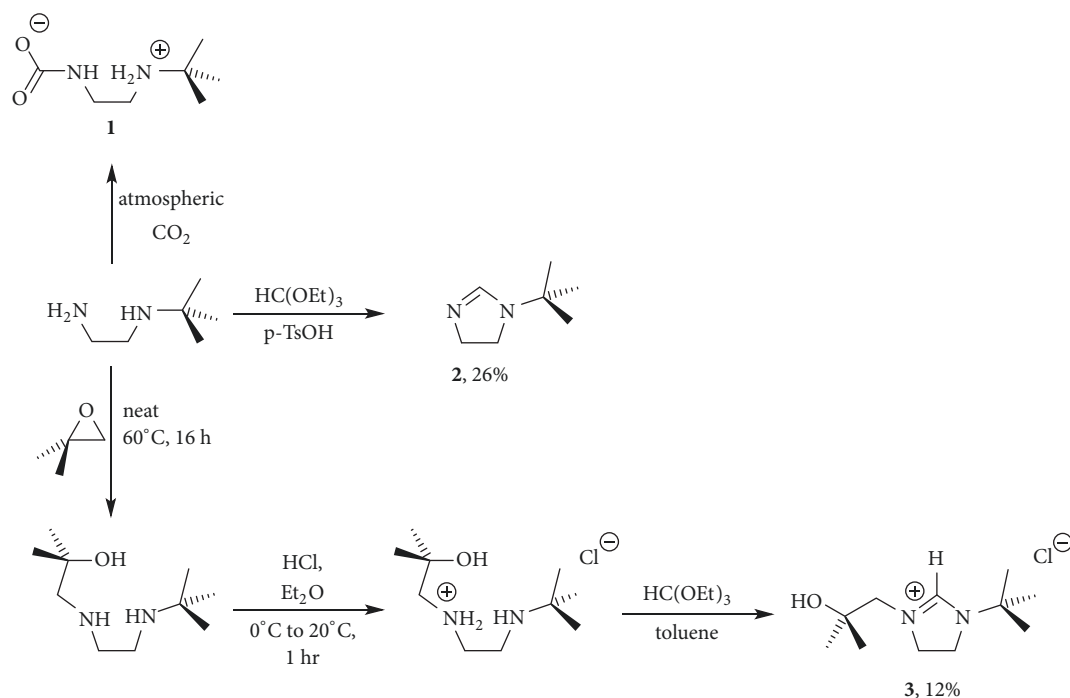
Scheme 1: Reactions of N-*tert*-butyl-1,2-diaminoethane.

the formal deprotonation of the NH_2 by the $N(H)^t Bu$ unit (Figure 1).

The solid-state structure of **1** shows dimeric units formed from H-bonding between the two H atoms of the two different N atoms towards O2 of the carbamate group. An $R_2^2(8)$ graph set ring motif is constructed from H-bonding between the remaining O atom of the carbamate group and the second H atom on N2. The C-O bond lengths are almost identical and C1 has a planar geometry. The molecular structure is similar to that observed for $MeN(H)_2C_2H_4N(H)CO_2$, which was observed to be H-bonding to additional water molecules [5]. Long and coworkers have structurally characterised several intramolecular ammonium carbamates based on N-substituted ethylene diamines from *in situ* reactions of CO_2 with a Mg-based metal-organic framework containing the bound diamine [6].

The synthesis of 1-*tert*-butyl-2-imidazoline (**2**) was achieved by the acid-catalysed reaction of the diamine with triethylorthoformate (Scheme 1). Careful fractional distillation yielded the product in low yield (24%). The H atom at the 2-position was observed at δ 7.03 ppm by ^{1}H NMR spectroscopy as a triplet due to $^4J_{H-H}$ coupling to one of the backbone CH_2 groups via coupling through the C=N bond. The $^{13}C\{^1H\}$ NMR spectroscopic resonance for C-2 was also observed at high frequency (154.6 ppm). Accurate mass spectrometry observed the parent molecular ion at 126.11510 Da. **2** reacts with moisture in the air so should be stored and handled under N_2. The attempted reaction with isobutylene epoxide (70°C, 5 days) did not yield the desired hydroalkyl-functionalised carbene (or the related zwitterionic alkoxy-imidazolinium tautomer that was seen with imidazoles) [23–27], so a different synthetic route to

a substituted imidazolinium salt was attempted based on literature precedent (Scheme 1) [16]. In consecutive steps, isobutylene epoxide, HCl, and triethylorthoformate were reacted with N-*tert*-butyl-1,2-diaminoethane to yield an oil that was purified by crystallisation from acetone in low yield (12%). Unfortunately, changing the anion to $[I]^-$ or $[BF_4]^-$ did not aid crystallisation and did not result in an improved synthesis. The product was characterised by X-ray crystallography (Figure 2), multinuclear NMR spectroscopy, and elemental analysis. The molecular structure of **3** showed a 5-membered imidazolinium ring with a *tert*-butyl substituent and a hydroxyalkyl chain. The Cl counter anion is H-bonded to the imidazolinium C-H as well as the O-H, and there are several close contacts to other C-H atoms as well. The C-N bond lengths in the ring are similar (C1-N1 = 1.311(3) Å and C1-N2 = 1.323(3) Å) and C2-C3 is a single bond (1.530(4) Å). ^{1}H NMR spectroscopic analysis revealed the expected signals based on the X-ray structure, with the imidazolinium CH as a singlet at 9.54 ppm. The C-2 resonance was observed at δ 158.0 ppm by $^{13}C\{^1H\}$ NMR spectroscopy.

3. Conclusions

N-*tert*-Butyl-1,2-diaminoethane was found to be a convenient starting material for the synthesis of 1-*tert*-butyl-2-imidazoline (**2**) as well as the hydroxyalkyl-tethered imidazolinium salt **3**. However, N-*tert*-butyl-1,2-diaminoethane was found to react with atmospheric CO_2 to give the alkylammonium carbamate **1**, and 1-*tert*-butyl-2-imidazoline was also found to be unstable in the presence of atmospheric
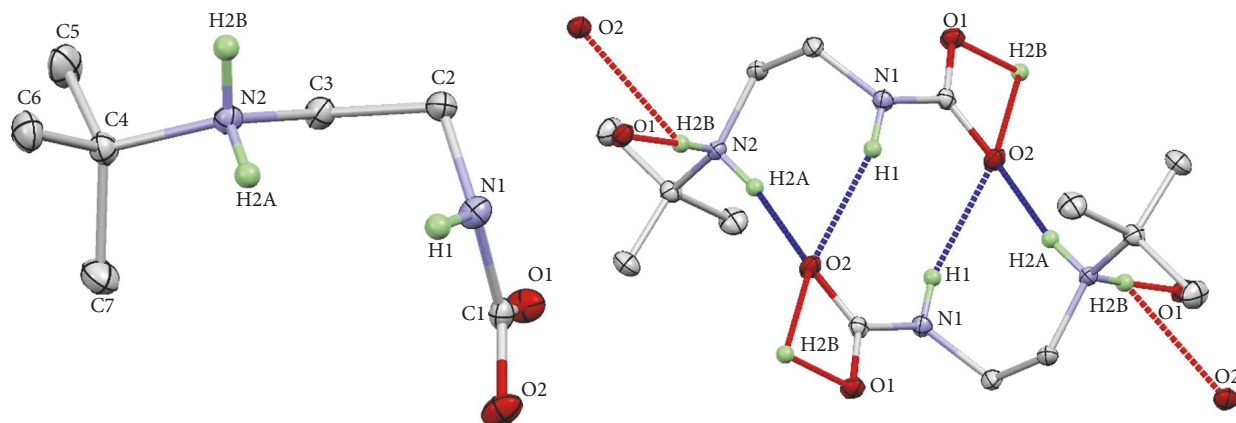
FIGURE 1: Molecular structure of ${}^{t}BuN(H)_2C_2H_4N(H)CO_2$ (**1**, left) forming dimeric units and an extended structure through H-bonding (right). Thermal ellipsoids set at 50% probability. Hydrogen atoms except for those attached to N atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): O1-C1 1.267(1), O2-C1 1.277(1), N1-C1 1.400(1), N1-C2 1.464(1), O1-C1 O2 123.98(8), C1-N1-C2 120.32(7).
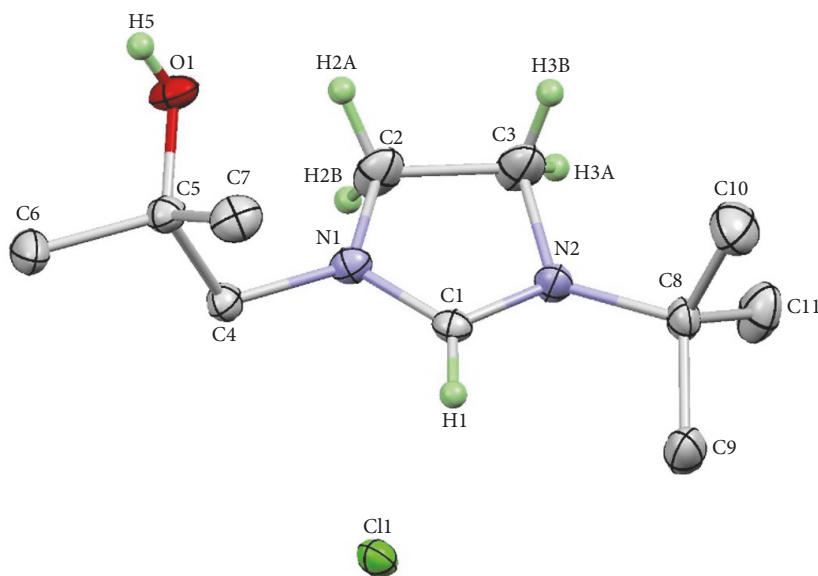

FIGURE 2: Molecular structure of **3**. Thermal ellipsoids set at 50% probability. Hydrogen atoms except for those attached to C1 – C3 and O1 are omitted for clarity. Selected bond lengths (Å) and angles (°): C1-N1 1.311(3), N2-C1 1.323(3), C2-C3 1.530(4), N1-C1-N2 114.1(2).

moisture, highlighting the greater reactivity of these compounds compared to related literature examples with N-aryl groups.

4. Experimental

All reactions were performed under an oxygen-free (H_2O, O_2 < 0.5 ppm) nitrogen atmosphere using standard Schlenk line techniques or by using an MBRAUN UNIlab Plus glovebox unless otherwise stated. Anhydrous toluene was obtained from an MBRAUN SPS-800 and diethyl ether was distilled from sodium/benzophenone; $CDCl_3$ was dried over molecular sieves (4 Å). All anhydrous solvents were degassed before use and stored over activated molecular sieves. N-*tert*-Butyl-1,2-diaminoethane was synthesised as previously

described [21]. NMR spectra were recorded on Bruker AV300 or AVIII400 spectrometers at 25°C, and the chemical shifts δ are noted in parts per million (ppm) calibrated to the residual proton resonances of the deuterated solvent ($CDCl_3$ δ = 7.27 ppm). X-ray diffraction experiments were performed using a Bruker X8 APEXII diffractometer at 100 K on single crystals of the samples covered in inert oil and placed under the cold stream of the diffractometer, with exposures collected using Mo Kα radiation (λ = 0.71073 Å). Indexing, data collection, and absorption corrections were performed and structures were solved using direct methods (SHELXT) [28] and refined by full-matrix least-squares (SHELXL) [28] interfaced with the programme OLEX2 [29] (Table 1). H atoms were placed using a riding model except for those attached to N or O atoms, which were located in the electron density map and freely refined with a fixed isotropic parameter of 1.2x that of

TABLE 1: Crystallographic data for **1** and **3**.

	1	**3**
Empirical formula	$C_7H_{16}N_2O_2$	$C_{11}H_{23}ClN_2O$
Formula weight	160.22	234.76
T/K	100	100
Crystal system	monoclinic	tetragonal
Space group	$P2_1/n$	I-4
a/Å	8.3778(12)	14.6891(14)
b/Å	9.2202(12)	14.6891(14)
c/Å	11.8067(18)	13.2031(14)
$\alpha/°$	90	90
$\beta/°$	104.385(8)	90
$\gamma/°$	90	90
Volume/Å^3	883.4(2)	2848.8(6)
Z	4	8
ρ_{calc}g/cm^3	1.205	1.095
μ/mm^{-1}	0.088	0.250
F(000)	352.0	1024.0
Crystal size/mm^3	$0.65 \times 0.6 \times 0.15$	$0.3 \times 0.2 \times 0.2$
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.386 to 60.266	5.546 to 56.668
Index ranges	$-11 \leq h \leq 11, -13 \leq k \leq 12, -16 \leq l \leq 16$	$-16 \leq h \leq 19, -19 \leq k \leq 19, -17 \leq l \leq 16$
Reflections collected	18629	8173
Independent reflections	2583 [R_{int} = 0.0278, R_{sigma} = 0.0208]	3525 [R_{int} = 0.0337, R_{sigma} = 0.0481]
Data/restraints/parameters	2583/0/112	3525/0/144
Goodness-of-fit on F^2	1.049	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.0891	R_1 = 0.0382, wR_2 = 0.0840
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.0935	R_1 = 0.0454, wR_2 = 0.0880
Largest diff. peak/hole (e Å^{-3})	0.40/-0.20	0.45/-0.21
Flack parameter	N/A	0.48(3)

the atom they are attached to. CCDC deposition numbers were 1871407 (**1**) and 1871406 (**3**). Elemental analyses were conducted using an Exeter CE-440 elemental analyser at Heriot-Watt University by Dr. Koenraad Collart or by Mr. Stephen Boyer at London Metropolitan University. Electron ionization mass spectrometry (EIMS) was performed using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh.

4.1. Synthesis of 1. Freshly distilled N-*tert*-butyl-1,2-diaminoethane was exposed to air and a white solid formed rapidly. ^{1}H NMR (300 MHz, 25°C, D_2O): δ(ppm) 3.28 (2H, m, CH_2), 3.08 (m, 2H, CH_2), 1.31 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.5 MHz, 25°C, D_2O): δ(ppm) 164.86 (NCO_2), 56.53 (CH_2), 43.07 (CH_2), 38.46 (CMe_3) and 24.83 (CH_3).

4.2. Synthesis of 1-tert-butyl-2-Imidazoline (2). N-*tert*-Butyl-1,2-diaminoethane (3.439 g, 29.6 mmol, 1 equiv.) was combined with triethylorthoformate (19.7 cm^3, 118.4 mmol, 4 equiv.) and *para*-toluenesulfonic acid (281 mg, 1.48 mmol, 0.05 equiv.) and then heated under reflux for 16 h. NaOH (10 cm^3 of a 5% solution in H_2O) was added and the

mixture extracted with CHCl$_3$ (3 x 50 cm^3). The organic layer was dried over MgSO$_4$ and CHCl$_3$ and EtOH were removed under reduced pressure. A short path distillation apparatus was used to fractionally distil the resulting liquid. Triethylorthoformate distilled at 50°C, 20 mbar (diaphragm pump) as the first fraction then 1-*tert*-butyl-2-imidazoline at 26 – 30°C at 5 x10^{-1} mbar (rotary vane pump) as the second fraction yielding a moisture sensitive colourless liquid (960 mg, 7.6 mmol, 26%). ^{1}H NMR (300 MHz, 25°C, CDCl$_3$): δ(ppm) 7.00 (t, $^4J_{H-H}$ = 1.8 Hz, 1H, CH), 3.75 (td, $^3J_{H-H}$ = 9.9 Hz, $^4J_{H-H}$ = 1.8 Hz, 2H, CH_2N=CH), 3.23 (t, $^3J_{H-H}$ = 9.9 Hz, 2H, CH$_2$N^{t}Bu), 1.23 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (75.5 MHz, 25°C, CDCl$_3$): δ(ppm) 154.57 (CH), 54.41 (CH$_2$), 51.91 (CMe$_3$), 44.32 (CH$_2$), 28.47 (CH$_3$). HRMS (EI-MS) m/z: [M]$^+$ Calcd for C$_7$H$_{14}$N$_2$ 126.11515; Found 126.11510.

4.3. Synthesis of 3. N-*tert*-Butyl-1,2-diaminoethane (2.018 g, 17.4 mmol, 1 equiv.) was combined with isobutylene oxide (1.252g, 1.54 mL, 17.4 mmol, 1 equiv.) in an ampoule equipped with a Young's tap and heated to 60°C for 16 h. Dry Et$_2$O (30 cm^3) was then added to the resultant colourless oil and the solution transferred to a Schlenk vessel equipped with

a large stirrer bar. 1 M HCl in Et_2O (17.2 cm^3, 1 equiv.) was added at 0°C forming a white solid which was then stirred for 16 h at room temperature. The supernatant solution was removed by cannula filtration and the white solid dried under vacuum. Toluene (30 cm^3) and triethylorthoformate (10 cm^3) were added and the mixture was heated to 90°C for 7 h. Et_2O (50cm^3) was added which caused a yellow oil to separate and the supernatant solution was removed by cannula. Acetone (ca. 10 cm^3) was added to dissolve the oil, and storage at -25°C gave colourless crystals of the product (488 mg, 2.08 mmol, 12%).

^{1}H NMR (400 MHz, 25°C, CDCl$_3$): δ(ppm) 9.54 (s, 1H, C-H), 5.10 (s, 1H, OH), 4.18 (m, 2H, ^{t}BuNCH$_2$CH$_2$N), 3.96 (m, 2H, ^{t}BuNCH$_2$CH$_2$N), 3.69 (s, 2H, CH$_2$C(CH$_3$)$_2$), 1.44 (s, 9 H, ^{t}Bu), 1.27 (s, 6 H, CH$_2$C(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, 25°C, CDCl$_3$): δ(ppm) 158.0 (C-H), 69.8 (4°C), 57.5 (CH$_2$C(CH$_3$)$_2$), 56.7 (4°C), 51.3 (^{t}BuNCH$_2$CH$_2$N), 45.2 (^{t}BuNCH$_2$CH$_2$N), 28.3 (^{t}Bu), 27.4 (C(CH$_3$)$_2$). Elemental analysis calculated for C$_{11}$H$_{23}$ClN$_2$O (%): C 56.28, H 9.88 N 11.93. Found (%): C 56.18, H 9.95, N 11.86.

Data Availability

In addition to the supporting information (available here), additional research data supporting this publication are available from Heriot-Watt University's research data repository at DOI: 10.17861/ab6d5f14-ee8f-4be1-94c7-3c9fd0eea37a. CIF files for **1** and **3** have been deposited with the CCDC, deposition numbers: 1871407 (**1**) and 1871406 (**3**).

Conflicts of Interest

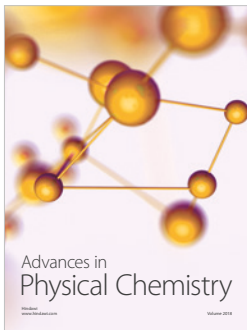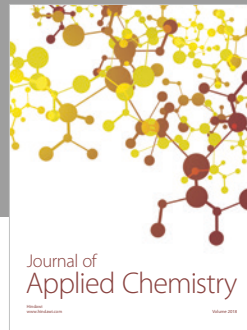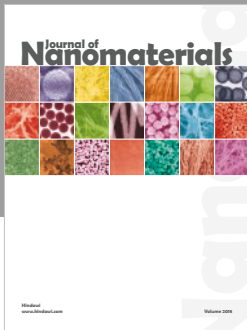The authors declare that they have no conflicts of interest.

Acknowledgments

Supplementary Materials

The supporting information which the authors submitted with the paper gives NMR spectra for the new compounds described in the publication. *(Supplementary Materials)*

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