Carbene Precursors

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Intramolecular "Hydroiminiumation" of Alkenes: Application to the Synthesis of Conjugate Acids of Cyclic Alkyl Amino Carbenes (CAACs)**

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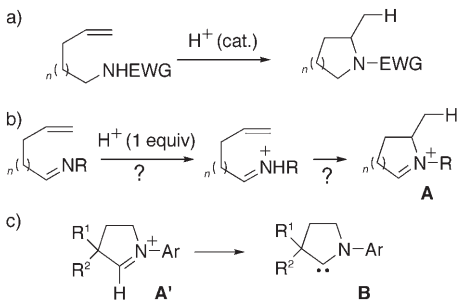
Nitrogen-containing heterocyclic systems have attracted considerable interest over the years because they form the core structures, and are key intermediates, of natural products.[1] One of the most appealing synthetic approaches for their preparation is the intramolecular hydroamination of alkenes, in which the nitrogen–carbon bond is formed by addition of an amine to an olefin.[2] Various catalysts have been used to effect this transformation, which include alkali metals,[3] early[4] and late transition metals,[5] and f-block elements.[6] Interestingly, despite the buffering effect of amines, intramolecular[7] and even intermolecular[8] acid-catalyzed hydroaminations have recently been developed. Schlummer and Hartwig[7a] reported the cyclization of amino alkenes bearing an electron-withdrawing group on the nitrogen atom by catalysis with triflic or sulfuric acid (20 mol%; Scheme 1). A mechanistic study of this process suggested that in contrast to similar transformations using various electrophiles as promoters (for example, iodine-,[9] bromine-,[10] and selenium-based electrophiles[11]), the first step was protonation of the amine, followed by intramolecular transfer of the proton to the double bond in the rate-determining step, and lastly trapping of the generated cation by the amino group. Accordingly, in the absence of electron-withdrawing groups on the nitrogen atom, the cyclization does not occur because of the excessive basicity of the amino group, which prevents the transfer of the proton to the olefin.



Scheme 1. a) Schematic representation of acid-catalyzed intramolecular hydroamination; EWG = electron-withdrawing group, $n = 1,2$. b) The hydroiminiumation reaction as a potential synthetic route to cyclic iminium salts **A**. c) CAAC/H^+ salts **A′**, the precursors of CAACs **B**; $R^1, R^2 \neq H$, Ar = bulky aryl group.

Imines are certainly less basic than amines, and therefore it was decided to investigate the feasibility of "hydroiminiumation" reactions, which would be an atom-economical route to cyclic iminum salts **A** (Scheme 1). Providing there is a bulky aryl substituent on the nitrogen atom and that there is a quaternary carbon atom in the position α to the aldiminium carbon atom, salts **A′** are the direct precursors of stable cyclic alkyl amino carbenes (CAACs) **B**.[12] We have shown that CAACs can compete with N-heterocyclic carbenes (NHCs)[13] as ligands for transition-metal-based catalysts,[12a] and also allow the preparation of very low coordinate transition-metal centers.[12b] We report herein our preliminary results on the scope of the thermally induced hydroiminiumation reaction and its application to the synthesis of a variety of CAAC precursors.

To establish the viability of this hydroiminiumation methodology, the synthesis of the previously reported CAAC/H^+ compound **4a**[12a] was chosen as an initial test. Deprotonation of aldimine **1a**, derived from 2,6-diisopropylaniline ($DippNH_2$) and cyclohexane carboxaldehyde, with lithium diisopropylamide (LDA) leads to the corresponding 1-aza-allyl anion, which readily reacts at room temperature with 3-bromo-2-methylpropene (or 3-chloro-2-methylpropene) to afford the alkenyl aldimine **2a** in 94% yield (Scheme 2). Addition of a stoichiometric amount of a 2 M solution of HCl/Et_2O to a toluene solution of **2a** at −78 °C resulted in the immediate formation of a white precipitate. After 15 minutes at −78 °C, the mixture was allowed to warm to room temperature and stirring was continued for an additional 15 minutes. After filtration and recrystallization from chloroform, a new compound **3a** was isolated as white crystals in 92% yield. The ionic character of **3a** was apparent from its low solubility in toluene, while its acyclic nature was revealed by the presence of a ^{13}C NMR signal at $\delta =$ 117.0 ppm from an ethylenic CH_2 fragment. The protonation of the nitrogen atom was indicated by a ^1H NMR signal at $\delta =$ 15.5 ppm, and by the deshielding of the N=CH ^{13}C and

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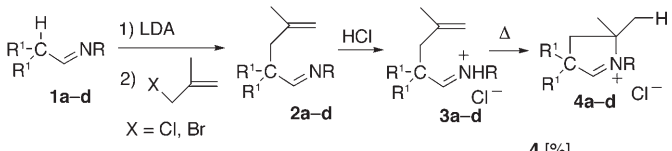


	T [°C][a]	t [h][a]	4 [%] (from 2)[b]
1a–4a: R = Dipp, CHR¹R¹ = Cy	50	18	88
1b–4b: R = Dipp, R¹ = Me	50	24	92
1c–4c: R = Mes, R¹ = Me	70	24	87
1d–4d: R = *t*Bu, R¹ = Me	110	n.r.[c]	0

Scheme 2. Influence of the nature of the R and R¹ substituents on the rate of the hydroiminiumation reaction; Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$; Mes = 2,4,6-Me$_3$C$_6$H$_2$. [a] Time and temperature required for complete conversion of **3**. [b] Yield of isolated product, without isolation of **3**, and using a twofold excess of HCl. [c] n.r. = no reaction.

^{1}H NMR signals (**2a**: $\delta = 173.6$ and 7.6 ppm; **3a**: $\delta = 189.8$ and 8.0 ppm). A single-crystal X-ray diffraction study unambiguously proved the alkenyl aldiminium structure of **3a** (Figure 1).[14] Pleasingly, it was noted that heating an aceto-

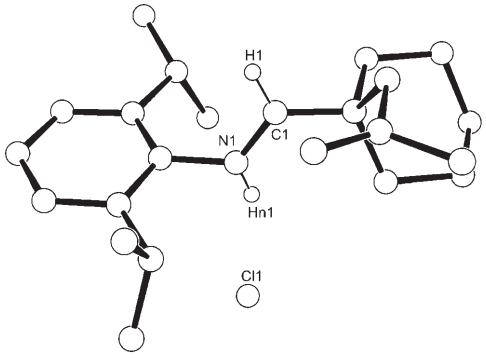
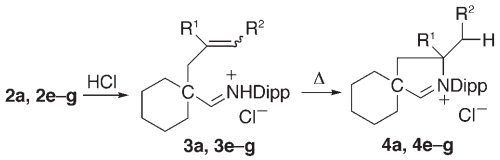


Figure 1. Molecular structure of **3a** in the solid state.

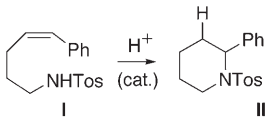
nitrile solution of **3a** in a tube sealed by a teflon stopcock at 50 °C for 18 h afforded the desired cyclic iminium salt **4a** in 88 % yield. Obviously, the last two steps of the synthesis (**2a**→**4a**) can be performed in situ, and the best results (88 % yield of isolated product) were obtained when a twofold excess of HCl was used. The overall transformation (**1a**→**4a**) can thus be done in 83 % yield, which compares extremely favorably with the previously reported method (48 % yield); moreover, the new route uses the same precursor **1a**, but avoids the use of the costly reagents 1,2-epoxy-2-methylpropane and trifluoromethane sulfonic anhydride.

To study the influence of various steric and electronic factors on the hydroiminiumation reaction, several different alkenyl aldimines **2b–h** were prepared (Schemes 2, 3, and 4). Without exception, the protonation occurred smoothly at the nitrogen atom, and the ensuing alkenyl aldiminium salts **3b–h** were obtained in good to excellent yields. The cyclization process occurs slightly more easily when bulky substituents are used on both sides of the NCC fragment (Scheme 2). Indeed, when two methyl groups were used in place of the cyclohexyl group of **3a**, the formation of **4b** required 24 h at 50 °C, whereas for derivative **3c** (Ar = Mes, CR¹R¹ = CMe$_2$) 24 h at 70 °C are necessary to achieve complete conversion. Not surprisingly, a limitation to the methodology was found when an electron-donating *tert*-butyl group was placed on the nitrogen atom. Here, because of the high basicity of the nitrogen center, no trace of the cyclic iminium salt **4d** was detected when a toluene solution of **3d** was heated at 110 °C for 24 h.

Use of alkenyl aldiminium salts **3a** and **3e–g** allowed study of the influence of the substitution pattern of the carbon–carbon double bond on the fate of the hydroiminiumation reaction, especially with regard to its regioselectivity (Scheme 3). The temperature required for cyclization was



	T [°C][a]	t [h][a]	4 [%] (from 2)[b]
2a–4a: R¹ = Me, R² = H	50	18	88
2e–4e: R¹ = R² = H	70	48	90
2f–4f: R¹ = H, R² = Me	90	14	93
2g–4g: R¹ = H, R² = Ph	150	72[c]	61[d]



Scheme 3. Influence of the nature of the alkene substituents R¹ and R² on the rate and regioselectivity of the hydroiminiumation reaction. Tos = toluene-4-sulfonyl. [a] Time and temperature required for complete conversion of **3**. [b] Yield of isolated product, without isolation of **3**, and using a twofold excess of HCl. [c] The reaction did not go to completion and was stopped after 72 h. [d] Yield as measured by NMR spectroscopy.

found to increase along the series **3a** < **3e** < **3f** < **3g**. More importantly, in all cases five-membered heterocycles **4** resulting from *exo* cyclization were obtained, with no trace of the six-membered-ring isomers being detected. Strikingly, the cyclization of **3g** affords exclusively five-membered heterocycle **4g** (Figure 2), despite the presence of a phenyl group at the terminal carbon atom of the olefin, which would

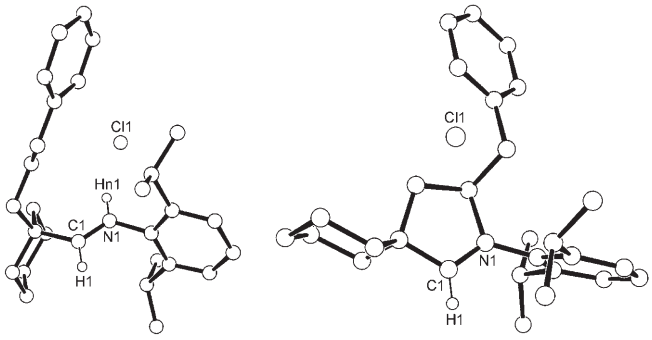
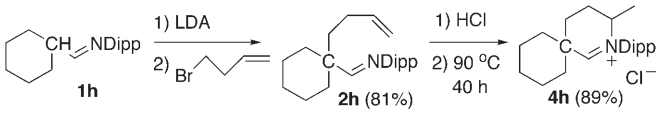


Figure 2. Molecular structures of **3g** (left) and **4g** (right) in the solid state.

be expected to stabilize a benzylic carbocation intermediate. Together these observations favor a mechanism in which the proton would be transferred intramolecularly to the double bond in the rate-determining step, similarly to the mechanism proposed by Schlummer and Hartwig for the acid-catalyzed hydroamination reaction.[7a] When compared to the latter reaction involving alkenyl amine **I**, for which the formation of the six-membered ring **II** was observed, our result suggests that the addition of N–H across the double bond has a greater "concerted" character[15] in the hydroiminiumation than in the hydroamination reaction.[7a]

Six-membered heterocyclic aldiminium salts can also be accessed as shown by the preparation of **4h** (Scheme 4). However, as observed in the hydroamination reaction,[7a] the cyclization to **4h** is more difficult than for the homologous five-membered ring **4e**.



Scheme 4. Synthesis of six-membered heterocyclic aldiminium salt **4h**.

Besides the easy preparation of a wide variety of CAAC/H^+ compounds, the intramolecular hydroiminiumation reported here features some distinct advantages when compared to the intramolecular hydroamination reaction. The resulting iminium ions are very reactive, potentially allowing for the subsequent addition of a large range of nucleophiles, and since they are often prochiral, this chemistry offers the possibility of facile construction of a new stereogenic center α to the nitrogen atom. The extension of this work to other protonated sp^2-nitrogen-containing species is under active investigation.

Experimental Section

All manipulations were performed under argon by using standard Schlenk techniques and oven-dried, argon-flushed glassware. Dry, oxygen-free solvents were employed. ^1H and ^{13}C NMR spectra were recorded on Varian Inova 300 and Bruker Avance 300 spectrometers.

Representative procedure for the synthesis of alkenyl imines **2**: A solution of LDA (1.18 g, 11.0 mmol) in Et_2O (20 mL), cooled to −78 °C, was added to a solution of aldimine **1a** (3.00 g, 11.0 mmol) in Et_2O (20 mL) at −78 °C. After 15 minutes the mixture was left to warm to room temperature and stirring was continued for an additional two hours. The volatiles were then removed under vacuum to afford an oily yellow-orange residue, which was dissolved in Et_2O (30 mL) and cooled to −78 °C. 3-Bromo-2-methylpropene (1.11 mL, 11.1 mmol) was then slowly added. After 15 minutes the solution was warmed to room temperature and stirring was continued for an additional 12 h. Removal of the volatiles under vacuum and extraction with hexanes afforded alkenyl aldimine **2a** as a light-yellow oil in 94% yield. $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, 25 °C): $\delta = 173.6$ (N=CH), 149.1 (C_{ipso}), 142.3 (*C*=CH_2), 137.7 (C_{ortho}), 123.9 (C_{para}), 123.0 (C_{meta}), 115.5 (=CH_2), 46.6 (C_{Cy}), 44.5 (CH_2), 33.5 (H_2C_{Cy}), 27.7 (*C*HCH$_3$), 26.1 (H_2C_{Cy}), 25.6 (*C*H$_3$C=), 23.8 and 23.6 (CH*C*H$_3$), 22.8 ppm (H_2C_{Cy}); ^1H NMR (300.0 MHz, $CDCl_3$, 25 °C): $\delta = 7.60$ (s, 1H, CH=N), 7.18–7.09 (m, 3H, H_{aro}), 4.95 (s, 1H, C=CH_2), 4.80 (s, 1H, C=CH_2), 3.06 (sept, $J_{HH} = 6.8$ Hz, 2H, C*H*CH$_3$), 2.35 (s, 2H, CH_2), 1.96 (m, 2H, H_2C_{Cy}), 1.86 (s, 3H, CH$_3$C=), 1.71–1.44 (m, 8H, H_2C_{Cy}), 1.21 ppm (d, $J_{HH} = 6.8$, 12H, CHC*H*$_3$); MS (EI): *m*/*z*: 326 $[M+H]^+$.

Representative procedure for the synthesis of alkenyl iminium salts **3**: A solution of HCl in Et_2O (1.54 mL, 2.0 M, 3.1 mmol) was added to a solution of alkenyl aldimine **2a** (1.00 g, 3.1 mmol) in hexane (10 mL) at −78 °C. Precipitation of a white powder was immediately observed. After 15 minutes the mixture was warmed to room temperature and stirring was continued for an additional 15 minutes. Filtration of the white precipitate, washing with hexanes (2 × 10 mL), and drying under vacuum afforded the alkenyl iminium salt **3a** in 92% yield. M.p. 83 °C (decomp); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, 25 °C): $\delta = 189.8$ (NH=CH), 143.0 (C_{ortho}), 140.5 (*C*=CH_2), 135.4 (C_{ipso}), 130.4 (C_{para}), 124.5 (C_{meta}), 117.0 (=CH_2), 46.7 (C_{Cy}), 45.7 (CH_2), 34.0 (H_2C_{Cy}), 28.7 (*C*HCH$_3$), 25.1 (*C*H$_3$C=), 25.0 (H_2C_{Cy}), 24.0 (CH*C*H$_3$), 22.6 ppm (H_2C_{Cy}); ^1H NMR (300.0 MHz, $CDCl_3$, 25 °C): $\delta = 15.50$ (s, 1H, NH), 7.98 (s, 1H, CH=N), 7.37 (t, $J_{HH} = 8.1$ Hz, 1H, H_{para}), 7.22 (d, $J_{HH} = 8.1$ Hz, 2H, H_{meta}), 4.99 (s, 1H, C=CH_2), 4.82 (s, 1H, C=CH_2), 2.99 (sept, $J_{HH} = 6.8$ Hz, 2H, C*H*CH$_3$), 2.68 (s, 2H, CH_2), 2.42 (m, 2H, H_2C_{Cy}), 1.90 (m, 2H, H_2C_{Cy}), 1.84 (s, 3H, CH$_3$C=), 1.73 (m, 2H, H_2C_{Cy}), 1.58 (m, 4H, H_2C_{Cy}), 1.24 ppm (d, $J_{HH} = 6.8$ Hz, 12H, CHC*H*$_3$); MS (FAB): *m*/*z*: 326 $[M]^+$.

Representative procedure for the hydroiminiumation reaction leading to **4**: A solution of alkenyl iminium salt **3a** (1.00 g, 2.8 mmol) in acetonitrile (10 mL) in a tube sealed by a teflon stopcock was heated at 50 °C for 18 h. The volatiles were removed under vacuum to afford **4a** as a white powder in 88% yield. Alternatively, a solution of HCl in Et_2O (3.08 mL, 2.0 M, 6.2 mmol) was added to a solution of alkenyl aldimine **2a** (1.00 g, 3.1 mmol) in acetonitrile (10 mL) at −78 °C. The solution was warmed to room temperature and sealed with a teflon stopcock, then heated at 50 °C for 18 h. The volatiles were removed under vacuum to afford **4a** as a white powder in 88% yield. M.p. 168 °C; $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, 25 °C): $\delta = 193.0$ (N=CH), 144.6 (C_{ortho}), 131.9 (C_{para}), 129.0 (C_{ipso}), 125.4 (C_{meta}), 82.9 (*C*CH$_3$), 53.6 (C_{Cy}), 45.6 (CH_2), 33.8 (H_2C_{Cy}), 30.0 (*C*HCH$_3$), 29.1 (CH_3), 26.8 (CH_3), 24.2 (H_2C_{Cy}), 22.3 (CH_3), 21.3 ppm (H_2C_{Cy}); ^1H NMR (300.0 MHz, $CDCl_3$, 25 °C): $\delta = 10.69$ (s, 1H, CH=N), 7.42 (t, $J_{HH} = 7.8$ Hz, 1H, H_{para}), 7.23 (d, $J_{HH} = 7.8$ Hz, 2H, H_{meta}), 2.57 (sept, $J_{HH} = 6.7$ Hz, 2H, C*H*CH$_3$), 2.37 (s, 2H, CH_2), 1.80–1.34 (m, 10H, H_2C_{Cy}), 1.47 (s, 6H, CCH$_3$), 1.25 (d, $J_{HH} = 6.7$ Hz, 6H, CHC*H*$_3$), 1.13 ppm (d, $J_{HH} = 6.7$ Hz, 6H, CHC*H*$_3$); MS (FAB): *m*/*z*: 326 $[M]^+$. All spectroscopic data are comparable to those observed for the corresponding triflate salt.[12a]

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