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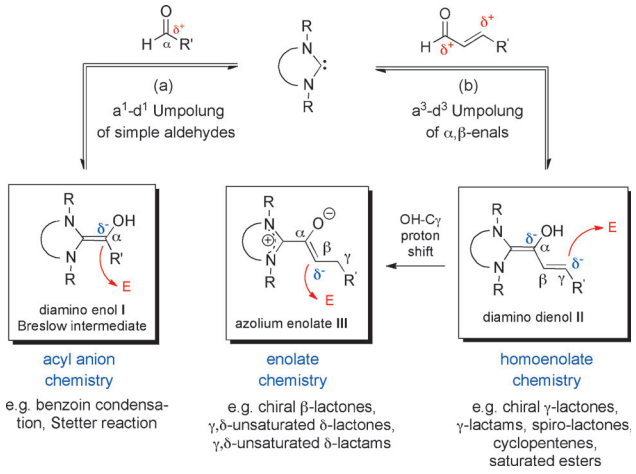
Characterization of the Key Intermediates of Carbene-Catalyzed Umpolung by NMR Spectroscopy and X-Ray Diffraction: Breslow Intermediates, Homoenolates, and Azolium Enolates**

Albrecht Berkessel, Veera Reddy Yatham, Silvia Elfert, and Jörg-M. Neudörfl*

In enzymes as well as in organocatalytic umpolung, catalysis by N-heterocyclic carbenes hinges on the reversible formation of Breslow intermediates[1,2] (chemically: (di)amino enols) **I** (Scheme 1a) in which the innate polarity of, for example, an



Scheme 1. Carbene-catalyzed umpolung of a) simple aldehydes and b) α,β-unsaturated aldehydes.

aldehyde substrate is inverted from electrophilic to nucleophilic.[3–5] In Seebach's terminology, the aldehyde undergoes a^1-d^1 umpolung.[6] Postulated in 1958,[1,2] the first successful generation of diamino enols from aldehydes and carbenes, and their characterization by in situ NMR spectroscopy was reported by us in 2012.[7] Earlier attempts to isolate intermediates resulted in the characterization of C2-hydroxymethyl azolium salts by Teles et al.[8] and hydroxybenzyl azolium salts by O'Donoghue, Smith et al.,[9] the keto form of Breslow intermediates and spiro-dioxolanes (i.e. 1:2 carbene–aldehyde adducts) by our group,[10] aza analogues of the Breslow intermediate by Rovis et al.,[11] and O-methylated amino enols by Mayr et al.[12] and ourselves.[7] With our method for the generation of 2,2-diamino enols in hand, we were able to characterize their solution structures and reactivity by in situ NMR spectroscopy. Most importantly, we could show that 2,2-diamino enols **I** (Scheme 1a) indeed act as acyl anion equivalents, and selectively form cross-benzoin adducts with additional aldehyde.[7] Whereas our NMR study provided proof for the existence and d^1 reactivity of 2,2-diamino enols for the first time, NMR spectroscopy could neither provide information on the geometric parameters of the crucial 2,2-diamino enol C=C double bond, nor on its subtle responses to changes in electron density.

In contemporary carbene organocatalysis, probably the most fascinating and proliferative area is a^3-d^3 umpolung ("conjugate umpolung"), that is, reaction sequences originating from the interaction of an α,β-unsaturated aldehyde with a carbene (Scheme 1b).[13,14] Again, a Breslow-type intermediate is assumed to be pivotal, namely the diamino dienol **II**. In the latter, the γ-position (β-position of the former enal) carries a partial negative charge, and the diamino dienols **II** consequently react as homoenolate equivalents. A subsequent OH–Cγ proton shift[15] in the diamino dienol **II** leads to the azolium enolate **III**. In the latter, the β-position (α-position of the former enal) carries a partial negative charge, and the azolium enolates **III** are therefore considered as enolate equivalents. Note that the formation of the intermediate **II** and/or **III** is assumed to be the decisive branching point for product formation in enal conjugate umpolung, for example, for formation of γ,δ-unsaturated δ-lactones vs. formation of cyclopentenes (Scheme 1b). Quite substantial effort has been invested to optimize reaction parameters (solvent, base etc.) such that one pathway is favored over the other.[16–18] In sharp contrast to their pivotal character in conjugate umpolung, no homoenolate **II** appears to have ever been characterized. Azolium enolates **III** have been accessed by addition of carbenes to ketenes.[19,20]

Herein we now report the crystallization of three 2,2-diamino enols **I**, their X-ray crystal structures, and the effects of electron density modulation on their structural parameters, in particular around the reactive enol C=C bond. Furthermore we disclose the first characterization, by X-ray structure analysis and NMR spectroscopy, of two diamino dienols **II** and two azolium enolates **III**, together with NMR monitoring of the tautomerization of a diamino dienol (**II**) to an azolium enolate (**III**). Finally, we show that the protonation of a diamino dienol (**II**) affords a cationic azolium enol.

As we reported earlier,[7] the saturated imidazolidinylidene SIPr (**1**) reacts smoothly with a variety of aldehydes **2** in

[*] Prof. Dr. A. Berkessel, V. R. Yatham, S. Elfert, Dr. J.-M. Neudörfl
Cologne University, Department of Chemistry
Greinstrasse 4, 50939 Cologne (Germany)
E-mail: berkessel@uni-koeln.de
Homepage: http://www.berkessel.de

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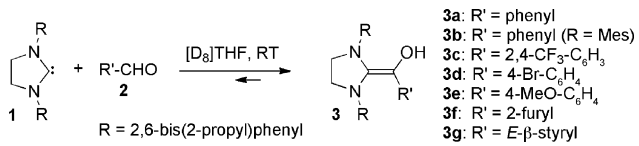
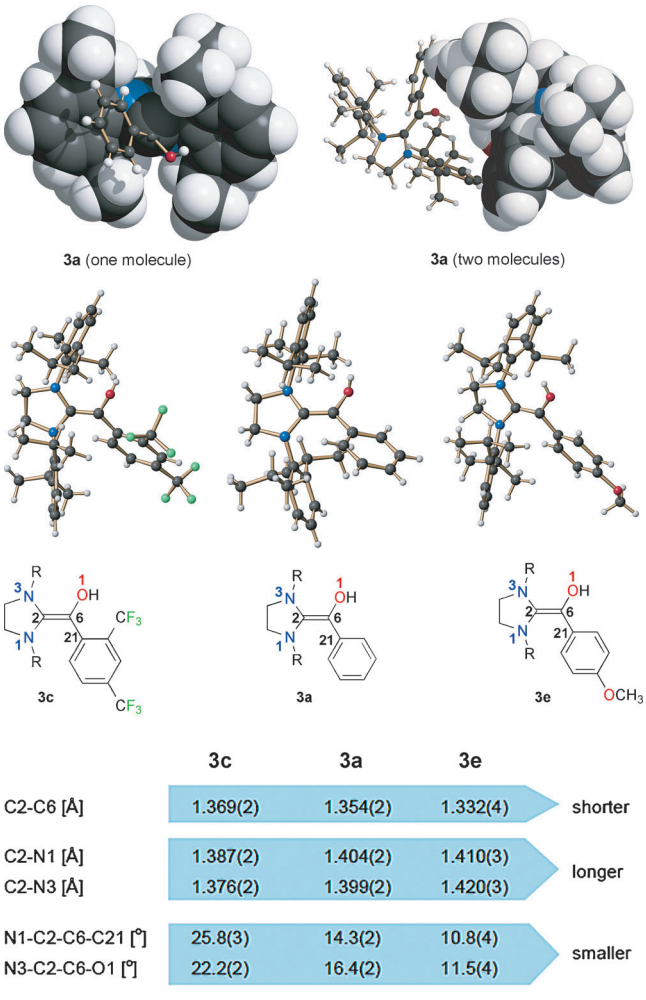


Scheme 2. Saturated imidazolidinylidenes such as SIPr (**1**) react with aldehydes **2** to afford 2,2-diamino enols **3**.

THF at room temperature, affording 2,2-diamino enols **3** (Scheme 2). Attempts to crystallize the 2,2-diamino enols **3** from THF solutions met, with no exception, with frustration. To our delight, when we changed the solvent to benzene and maintained strictly anaerobic conditions, we obtained crystalline samples of **3a**, **3c**, and **3e** suitable for X-ray structural analysis. The crystal structures of the 2,2-diamino enols **3a**, **3c**, and **3e** are shown in Figure 1, together with selected bond lengths and dihedral angles relevant to the 2,2-diamino enol moiety (see the Supporting Information for ORTEP and further space-filling representations, as well as crystal packing diagrams). Note that the OH hydrogen atom could be located in all three X-ray diffraction studies. Contrary to what may



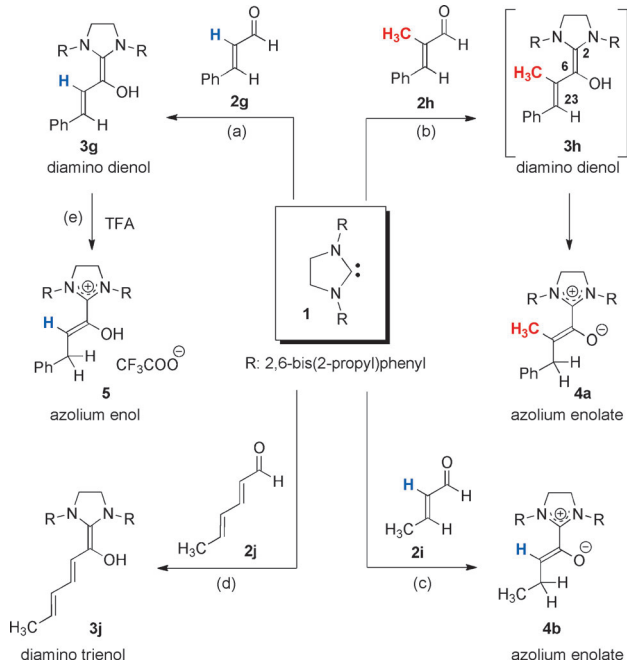
	3c	3a	3e	
C2-C6 [Å]	1.369(2)	1.354(2)	1.332(4)	shorter
C2-N1 [Å]	1.387(2)	1.404(2)	1.410(3)	longer
C2-N3 [Å]	1.376(2)	1.399(2)	1.420(3)	
N1-C2-C6-C21 [°]	25.8(3)	14.3(2)	10.8(4)	smaller
N3-C2-C6-O1 [°]	22.2(2)	16.4(2)	11.5(4)	

Figure 1. X-ray crystal structures of the 2,2-diamino enols **3a**, **3c**, and **3e** [R = 2,6-bis(2-propyl)phenyl]; top row: combined ball-and-stick/space-filling representation of one (left) and two (right) molecules of 2,2-diamino enol **3a**, as observed in the crystal.

have been expected, there is neither inter- nor intramolecular hydrogen bonding to or from the enol OH group (see Figure 1, top row, for a combined ball-and-stick/space-filling representation of one (left) and two (right) molecules of the 2,2-diamino enol **3a**, as observed in the crystal). The crystal packing of the 2,2-diamino enols **3a**, **3c**, and **3e** appears to be based solely on dispersive hydrocarbon interactions.[21] Note that our DFT calculations on the diamino enol **3a** (and the diamino dienol **3g**) reproduce their molecular structure in the crystal quite well (see the Supporting Information).

In the series **3c**–**3a**–**3e**, there is increasing electron density in the enol double bond due to the nature of the substituents on the benzene ring. As a consequence, the enol C=C bond (C2=C6) lengths decrease in the same order, with a simultaneous increase in the length of the 2,2-diamino enol C–N bond (C2–N1 and C2–N3). For the 2,2-diamino enol **3c** with the weakest C2–C6 double bond, the deviation of the enol moiety from planarity is greatest (dihedral angles N1-C2-C6-C21 = 25.8° and N3-C2-C6-O1 = 22.2°). The strengthening of the C2=C6 bond, effected by higher electron density, is accompanied by diminished deviation from planarity, as evidenced by the lower N1-C2-C6-C21 and N3-C2-C6-O1 dihedral angles, for example, for the phenyl derivative **3a** (14.3° and 16.4°), and in particular for the *p*-methoxyphenyl 2,2-diamino enol **3e** (10.8° and 11.5°). Similar effects of the substituent pattern on the length of the C=C bond have been observed for stilbenes. For example, in *E*-stilbene itself, $d_{C=C} = 1.338$ Å,[22] whereas for 4,4′-dimethoxy-*E*-stilbene $d_{C=C} = 1.316$ Å.[23] Di[2,4-bis(trifluoromethyl)]stilbene appears to be an unknown compound.

In the course of our in situ NMR studies on the interaction of aldehydes with imidazolidinylidenes such as SIPr (**1**), we already noted the clean formation of the diamino dienol **3g** from *E*-cinnamic aldehyde **2g** (Scheme 2 and Scheme 3a).[7] The reaction of this aldehyde with carbene **1** in benzene provided crystals of **3g** suitable for X-ray structural analysis, and the crystal structure of **3g** is shown in Figure 2a. The diene moiety is virtually planar, with a torsion angle C2-C6-C21-C22 of 177.4(3)°. The lengths of the two C=C bonds are 1.362(4) Å (C2=C6) and 1.356(3) Å (C21=C22), whereas the length of the connecting C–C single bond (C6–C21) amounts to 1.424(3) Å. As in the case of the 2,2-diamino enols **3a**, **3c**, and **3e**, the crystal packing of the diamino dienol **3g** did not indicate the involvement of the hydroxy group in hydrogen bonding (see the Supporting Information). When α-methyl *E*-cinnamic aldehyde (**2h**) was reacted with SIPr (**1**) at room temperature in benzene, crystallization did not yield the analogous diamino dienol **3h**, but the azolium enolate **4a**. As illustrated in Scheme 3b, the formation of the azolium enolate **4a** can be explained by O-to-Cγ proton shift in the initially formed diamino dienol **3h**. The X-ray crystal structure of the azolium enolate **4a** is shown in Figure 2b. The enolate moiety is almost planar, with a dihedral angle O1-C6-C21-C22 of −173.0(2)°. At the same time, the enolate moiety is arranged almost perpendicular to the imidazolidinium ring, as evidenced by dihedral angles O1-C6-C2-N3 of 51.3(3)° and O1-C6-C2-N1 of −122.7(2)°. The saturation of the γ-carbon atom is clearly revealed by its tetrahedral geometry. As mentioned in the introduction, azolium enolates



Scheme 3. SIPr (**1**) reacts with aldehydes **2g** and **2j** to afford the diamino di/trienols **3g** and **3j** (a and d); SIPr (**1**) reacts with aldehydes **2h** and **2i** to give the azolium enolates **4a** and **4b** (b and c); diamino dienol **3g** is protonated by TFA to give the azolium enol **5** (e).

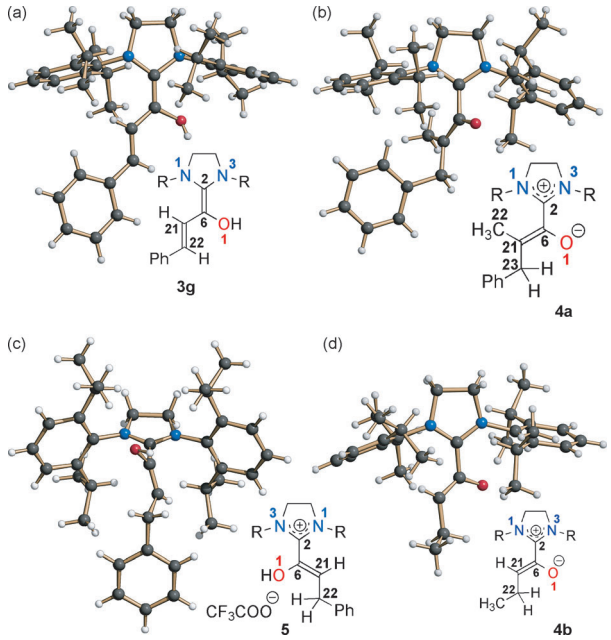


Figure 2. X-ray crystal structures of the diamino dienol **3g**, the azolium enolates **4a** and **4b**, and the azolium enol **5** (TFA anion not shown); R = 2,6-bis(2-propyl)phenyl.

have been observed upon addition of NHCs to ketenes,[19,20] but never before from the reaction of α,β-unsaturated aldehydes, as in our case.

We also undertook a DFT study of the tautomerization of **3h** to **4a**, and the reaction path is shown in Figure 3. In line with results obtained by Sunoj et al.,[15] intramolecular proton

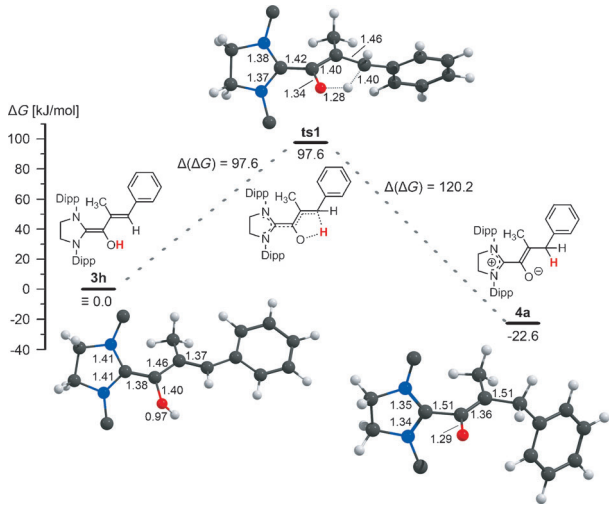


Figure 3. Relative free energies [kJ mol^{-1}] of the stationary points involved in the formation of the azolium enolate **4a** from the diamino dienol **3h** by means of an intramolecular 1,4-proton shift (gas phase, 298 K). For clarity, only the *ipso* C atoms of the 2,6-bis(2-propyl)phenyl (Dipp) groups are drawn. Selected bond lengths and distances are given in [Å].

transfer appears feasible at room temperature. Note that the diene moiety in the computed optimized structure of the diamino dienol **3h** is only slightly distorted, as evidenced by the dihedral angle C2-C6-C21-C23 of 164° (cf. 177.4° in **3g**).[24]

As an example of a nonaromatic enal, (*E*)-crotonic aldehyde (**2i**) was subjected to the same reaction and crystallization conditions. In [D$_8$]THF, the product displayed a characteristic triplet in its ^{1}H NMR spectrum at $\delta =$ 3.46 ppm ($^3J_{HH} = 6.6$ Hz, 1H, H21) and ^{13}C NMR resonances at $\delta = 172.4$ (C2), 102.9 (C21), 18.0 (C22) ppm, features consistent with the azolium enolate **4b** (Scheme 3c; see the Supporting Information for the complete NMR characterization). Again, crystallization from benzene was successful, and the X-ray crystal structure of the azolium enolate **4b** is shown in Figure 2d. As in the case of the azolium enolate **4a**, the enolate partial structure is almost planar, with a dihedral angle O1-C6-C21-C22 of 3.4(9)° and 1.0(10)°, respectively (two independent molecules per unit cell). We were delighted to see that the *Z* configuration of the enolate typically assumed (based on calculations) for reaction intermediates of this type[15,17,18] is indeed present in the crystal structures of both **4a** and **4b**, and thus proven experimentally for the first time. Close inspection of the crystal structure of **4b** furthermore indicates that the enolate C–H hydrogen atom is oriented towards the plane of the "left-hand" benzene ring. For the two independent molecules of **4b** present in the unit cell, the distances of the enolate C–H hydrogen atom from the centroid of the benzene ring are 2.864 Å and 3.365 Å, respectively. This type of CH–π interaction[26] has recently been postulated to be crucial for high (stereo)selectivity in a number of N-heterocyclic carbene catalyzed hetero-Diels–Alder reactions.[18]

As an example for the interaction of a dienal with SIPr (**1**), (*E*,*E*)-sorbic aldehyde **2j** (Scheme 3d) was employed. No crystalline material could be obtained, but NMR monitoring

of the reaction ([D_8]THF, room temperature) clearly revealed the quantitative formation of the diamino trienol **3j**. In this context, the ^{1}H NMR resonance at $\delta = 3.68$ ppm (OH) is indicative, together with ^{13}C NMR signals at $\delta = 142.7$ (C2) and 112.8 (C6) ppm (see the Supporting Information for full NMR characterization of **3j**). In the absence of oxygen, the diamino trienol **3j** was stable and did not show any tendency towards further reaction, for example, tautomerization to the corresponding azolium enolate.

Besides the neutral diamino dienol **3g** (Figure 2a) and the two neutral, but zwitterionic azolium enolates **4a** and **4b** (Figure 2b and d), we were also able to generate and crystallize the γ-protonation product of the diamino dienol **3g**, that is, the cationic azolium enol **5** (Scheme 3e). Upon treatment of the diamino dienol **3g** with trifluoroacetic acid (TFA), we observed the instantaneous disappearance of the signals characteristic of **3g** (e.g. ^{1}H NMR doublets at $\delta =$ 6.08 ppm, $^3J_{HH} = 15.2$ Hz, 1H, H21, and $\delta = 5.53$ ppm, $^3J_{HH} =$ 15.2 Hz, 1H, H22), with concomitant formation of a new product characterized by a triplet at $\delta = 4.81$ ppm ($^3J_{HH} =$ 7.2 Hz, 1H, H21) and a doublet at $\delta = 3.37$ ppm ($^3J_{HH} =$ 7.2 Hz, 2H, H22). Similarly indicative were the changes in the ^{13}C NMR spectrum with the C2 and C22 signals moving from 145.0 to 166.1 ppm, and 111.0 to 30.8 ppm, respectively (see the Supporting Information for full NMR characterization of **5**). Crystallization of the azolium enol **5** could be achieved from benzene/*n*-hexane (1:1), and its X-ray crystal structure is shown in Figure 2c. The enol is *Z*-configurated and, as indicated by the dihedral angle N1-C2-C6-O1 of −60.5(2)°, the enol substructure is almost orthogonal to the heterocyclic ring.[27]

Note that the above γ-protonation of the diamino dienol **3g** to the azolium enol **5**, in an intermolecular fashion by an external proton source (here TFA), corresponds to the decisive step in the mechanism of redox esterification of α,β-enals formulated by Bode et al.[17,25] and by Scheidt et al.[28] However, at room temperature and throughout the 12 h of our measurement, the azolium enol **5** did not show any tendency to tautomerize to the corresponding acyl azolium cation, the subsequent step typically formulated for redox esterification.[17,25,28]

In our crystallization experiments, the azolium enolate **4a** was identified as the product resulting from the interaction of the carbene SIPr (**1**) with α-methyl *E*-cinnamic aldehyde **2h** (X-ray structure of **4a**: Figure 2b). NMR monitoring of this reaction ([D_8]THF) revealed that the formation of the azolium enolate **4a** is preceded by that of the diamino dienol **3h** (Figure 4a, Scheme 3b). Indicative NMR features of the diamino dienol **3h** are ^{1}H NMR singlets at $\delta = 6.14$ ppm (H23) and $\delta = 4.18$ ppm (OH), and ^{13}C NMR resonances at $\delta = 144.5$ (C2), 118.8 (C23), 116.5 (C6) ppm (see the Supporting Information for COSY, HMQC, HMBC, and NOESY data). At 25 °C, the maximum concentration of **3h** was reached at about 6 h. After roughly 2 h, the formation of the azolium enolate **4a** was noticeable and its concentration increased over time. Characteristic resonances of the azolium enolate **4a** are the ^{1}H NMR singlet at $\delta = 3.12$ ppm (2H, H23), and the ^{13}C NMR signals at $\delta = 173.1$ (C2) and 35.7 (C23) ppm (see the Supporting Information for further NMR

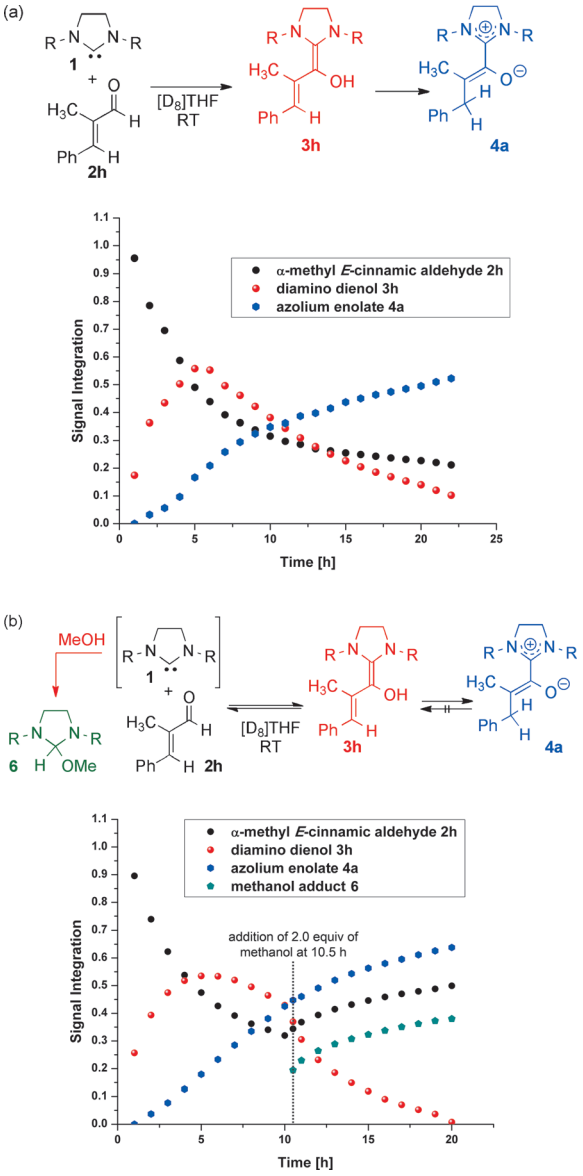


Figure 4. a) Time course of the tautomerization of the diamino dienol **3h** to the azolium enolate **4a**. b) Time course of the same reaction as in (a), but with addition of methanol after a reaction time of 10.5 h; R = 2,6-bis(2-propyl)phenyl.

data of **4a**). Note that the diamino dienol **3g**, derived from the same carbene SIPr (**1**) and *E*-cinnamic aldehyde (**2g**), that is, just lacking the α-methyl group, did not undergo tautomerization to an azolium enolate in solution under the same conditions.

When 2 equiv of methanol was added to the **3h/4a** mixture present after 10.5 h reaction time, the concentration of the diamino dienol **3h** dropped sharply, with concomitant regeneration of α-methyl *E*-cinnamic aldehyde (**2h**) and formation of the methanol adduct of SIPr (**6**, Figure 4b). In contrast, the concentration profile of the azolium enolate **4a** was basically unaffected by the addition of methanol; that is, the concentration increased steadily with time. Figure 4b summarizes our mechanistic interpretation: The formation of diamino dienol **3h** from aldehyde **2h** and carbene **1** is

reversible, and addition of methanol results in a shift to the left, presumbly driven by the formation of the carbene's methanol adduct **6**. In contrast, the tautomerization of **3h** to the azolium enolate **4a** appears to be largely irreversible. Note that alcohols such as methanol may additionally accelerate the tautomerization of **3h** to **4a**, by proton shuttling, within a seven-membered cyclic enol–alcohol aggregate. According to our DFT calculations on this process (see the Supporting Information), the transition state of the tautomerization of **3h** to **4a** is lowered in energy by approximately 18 kJ mol^{-1} when one molecule of methanol is involved (see Figure 3 for the noncatalyzed proton shift). Thus, even with a decreasing concentration of diamino dienol **3h**, the concentration–time profile of azolium enolate **4a** is virtually unchanged.

As mentioned earlier, the addition of TFA to the diamino dienol **3g** derived from *E*-cinnamic aldehyde (**2g**) did *not* result in retro-cleavage to *E*-cinnamic aldehyde (**2g**) and azolium trifluoroacetate, but in protonation to the azolium enol **5**.[29] Taken together, these observations nicely parallel conclusions from recent studies by Bode et al. on N-mesityl triazolylidenes, namely that the formation of the diamino dienol from α-methyl *E*-cinnamic aldehyde (**2h**) is reversible, whereas the analogous transformation of *E*-cinnamic aldehyde (**2g**) is irreversible.[30]

In summary, the selective generation and characterization[31] of diamino enols, diamino dienols, azolium enolates, and an azolium enol reported herein for the first time puts the mechanistic analysis of NHC-catalyzed a^1-d^1 and a^3-d^3 umpolung on a solid structural basis. Thus, a number of hitherto postulated reaction intermediates were prepared and characterized. The wealth of structure and reactivity data disclosed will surely aid in the design of novel NHC-catalyzed umpolung reactions, and in the in-depth understanding of the existing ones.

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Keywords: carbenes · NMR spectroscopy · reaction mechanisms · umpolung · X-ray diffraction

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[20] Upon acceptance of this manuscript, we were notified of a related publication by Mayr and Maji discussing the synthesis and ambident reactivity of azolium enolates derived from NHCs and methyl phenyl ketene: B. Maji, H. Mayr, *Angew. Chem.* **2013**, DOI: 10.1002/ange.201303524; *Angew. Chem. Int. Ed.* **2013**, DOI: 10.1002/anie.201303524.
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