X-Ray Crystal Structures of the Enolate of *tert*-Butyl α-Cyanoacetate with Li^+ or Protonated 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU-H^+) as Gegenion. N–H Hydrogen Bridge from DBU-H^+ to the Enolate Oxygen Atom

Gernot Boche*, Ira Langlotz, Michael Marsch, and Klaus Harms

Fachbereich Chemie der Universität Marburg,
D-35032 Marburg, Germany

Received April 29, 1994

Key Words: Enolate of *tert*-butyl cyanoacetate with Li^+ or DBU-H^+ as gegenions / Hydrogen bridge from DBU-H^+ to the enolate oxygen atom / Enolates of cyanoacetates, reaction with electrophiles

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For the first time a solid-state structure with protonated 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU-H^+) as the gegenion of an "organic" anion, namely *tert*-butyl α-cyanoacetate (2^-), is determined. The DBU-H^+ N–H bond forms a hydrogen bridge to the enolate oxygen atom of 2^-, the first N–H bridge to an enolate oxygen atom ever characterized. The structure of 2^- DBU-H^+ is compared with that of the corresponding lithium compound $[2^- Li^+ \cdot TMEDA]_2$ in which the cations are bound to the N atoms of the cyano groups and the enolate O atoms forming a twelve-membered ring. Literature reports on the rather different chemistry of anions like 2^- having alkali metal ions or DBU-H^+, respectively, as the gegenions can be understood by means of the two new solid-state structures disclosed in this publication.

X-ray crystal structures especially of alkali metal enolates have extensively been studied by Seebach et al.[1] and Williard et al.[2]. Since these compounds are prepared in most cases from the corresponding carbonyl species by deprotonation with an alkali metal amide, it was interesting to find crystals of a lithium enolate in which not only the oxygen atoms of the enolate but also the nitrogen atoms of the amine formed from the amide are bound to lithium: the pinacolone lithium enolate **1** crystallizes together with *N,N,N'*-trimethylethylenediamine (TriMEDA) as the [**1** · TriMEDA]$_2$ complex[1c]. A section of [**1** · TriMEDA]$_2$ is given in Figure 1.

1 $H_2C{=}C(OLi){-}C(CH_3)_2{-}CH_3$

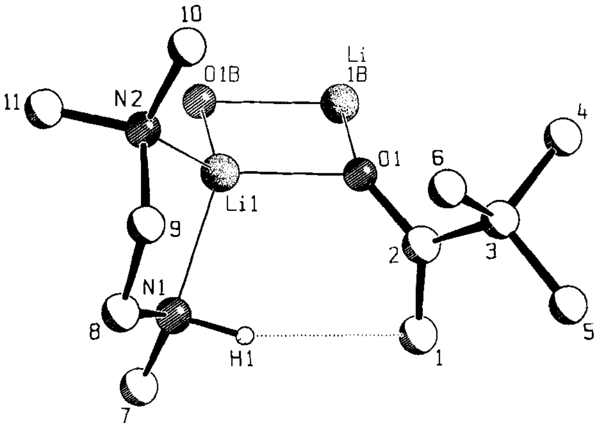
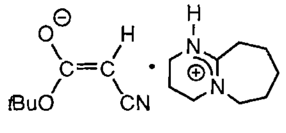


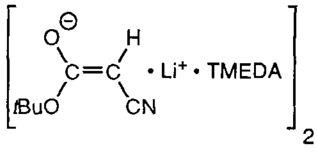
Figure 1. Section of the crystal structure of [**1** · TriMEDA]$_2$[1c]

Most significantly, H1, whose position had to be calculated, forms a hydrogen bridge to the enolate C1 atom. Such an N–H hydrogen bridge is strengthened by the polarization of the N1–H1 bond resulting from the coordination of N1 to Li1. The orientation of the N1–H1 bridge towards C1 is due to the particular geometrical constraints in [**1** · TriMEDA]$_2$. The crystal structure of [**1** · TriMEDA]$_2$ is thus in agreement with observations according to which deuteration (alkylation) of amin-containing lithium enolates often leads to high yields (up to 94%) of the *protonated* carbonyl compound[1,3]. Although the details of this reaction are not fully understood yet[1,3] (as this is the case with protonations of carbanions in general[4]) the N–H proton in the crystals of [**1** · TriMEDA]$_2$ indicates to be "ready to jump" on the enolate carbon atom.

We have been interested in the question whether it is possible to crystallize an enolate with *a hydrogen bridge to the enolate oxygen* atom. Since enolates in general are *O*-protonated to give enols[5], which normally rearrange very quickly to the carbonyl isomer, such a structure would correspond to a point on the reaction coordinate[6] of the protonation of enolates. In the following we report on the crystal structure of the enolate of *tert*-butyl cyanoacetate 2^- with protonated 1,8-diazabicyclo[5.4.0]undec-7-ene DBU-H^+, 2^- DBU-H^+ (Figure 2), compare it with the structure of the lithiated enolate $[2^- Li^+ \cdot TMEDA]_2$ (Figure 5), and discuss the consequences for the chemistry of such species.



2^- DBU-H^+



$[2^- Li^+ \cdot TMEDA]_2$

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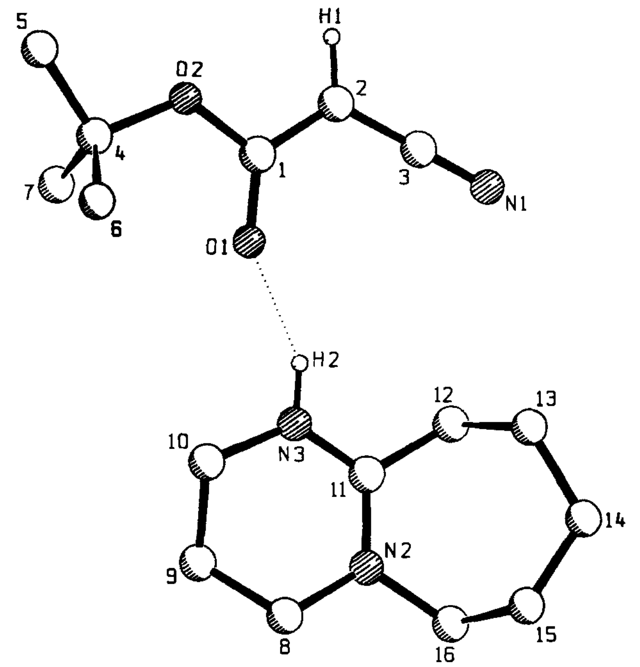


Figure 2. X-ray crystal structure of 2^- DBU-H$^+$. Selected bond lengths [pm] and angles [°]: C1–O1 124.1(2), C1–O2 136.8(2), C1–C2 138.7(3), C2–C3 140.0(3), C3–N1 115.8(3); O1–C1–O2 120.6(2), O2–C1–C2 112.4(2), O1–C1–C2 127.0(2), C2–C3–N1 179.1(2); C10–N3 146.1(3), N3–C11 131.0(3), C11–N2 132.2(2), N3–O1 269.6(2); N3–H2–O1 150(2)

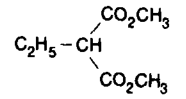
1. *tert*-Butyl Cyanoacetate$^-$ DBU-H$^+$ (2^- DBU-H$^+$)

Although "the number of synthetic applications of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is hardly to survey"[7], an X-ray crystal structure investigation of an "organic" anion with the protonated base DBU-H$^+$ as the gegenion has not been reported yet[8]. Despite the similarity of the acidities in acetonitrile of DBU-H$^+$ (pK_{BH^+} = 24.32) and cyanoacetates ($pK_A \approx 24$)[7], we were able to isolate the crystalline 2^- DBU-H$^+$ when we deprotonated *tert*-butyl cyanoacetate **2** with DBU in tetrahydrofuran. As shown in Figure 2, the enolate 2^- is bound to DBU-H$^+$ via the hydrogen bridge N3–H2···O1. The distances within the hydrogen bridge are as follows: N3–H2 87(2), H2···O1 190.3(19), and N3–O1 269.6(2) pm. The angle N3–H2···O1 amounts to 150(2)°. As always if the bridging H atom is localized by X-ray crystallography, bonds like N3–H2 are too short (≈10 pm) and H2···O1 too long (≈10 pm)[9]. The mean values for N–H hydrogen bridges to carbonyl oxygen atoms are calculated to be[9] H···O 195.9 pm for >N–H and 188.8 pm for $\geqslant\overset{+}{\text{N}}$–H, N–O (intermolecular H bridge) 289.2(3) pm, and N–H···O 162.1(4)° (>N–H) and 159.9° ($\geqslant\overset{+}{\text{N}}$–H). In the case of four ammonium picrates the mean value of the N–O distance (289.1 pm)[8a] agrees with the aforementioned N–O distance. A comparison of these mean values with the data of 2^- DBU-H$^+$ reveals that the H2···O1 bond in 2^- DBU-H$^+$ is significantly shorter than the H···O bond in the case of the >N–H- (16 pm) and $\geqslant\overset{+}{\text{N}}$–H-bridged (9 pm) carbonyl compounds. Similarly, the N3–O1 distance in 2^- DBU-H$^+$ is much shorter (19 pm) and the N3–H2···O1 angle much smaller than in N–H-bridged carbonyl species [12° (>N–H) and 10° ($\geqslant\overset{+}{\text{N}}$–H)]. The N–O distance in 2^- DBU-H$^+$ is also much shorter than the same distance in ammonium picrates [269.6(2) versus 289.1 pm, see above]. This is undoubtedly due to the electrostatic attraction between the cationic N–H donor DBU-H$^+$ and the anionic hydrogen bridge acceptor 2^-. Finally, it should be mentioned that the N3–H2···O1 hydrogen bridge in 2^- DBU-H$^+$ is the first example of an ("ammonium") N–H or an O–H hydrogen bridge to an oxygen atom of an enolate anion[10]. In agreement with the correlation principle[6], in the crystals of 2^- DBU-H$^+$ everything is ready for the *O*-protonation of the enolate 2^- to give the corresponding enol. A systematic study of the related α-cyano-α-phenylacetic acid keto-enol system in solution has recently been published[11]. In the crystal structure of the tetrabutylammonium salt of the enolate of ethyl cyanoacetate C–H hydrogen bridges to the anionic moiety are observed[12].

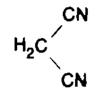
The bond lengths and angles of 2^-, which are similar to those of 2^- in the lithium enolate [2^- Li$^+$ · TMEDA]$_2$, will be discussed in Section 2.

2. [*tert*-Butyl Cyanoacetate$^-$ Li$^+$ · *N,N,N',N'*-Tetramethylethylenediamine]$_2$ [2^- Li$^+$ · TMEDA]$_2$

Before the crystal structure of [2^- Li$^+$ · TMEDA]$_2$ is outlined in more detail we will briefly discuss the crystal structure of a metallated β-dicarbonyl compound (**3**) as well as of a metallated malononitrile (**4**). Since [2^- Li$^+$ · TMEDA]$_2$ contains both a carbonyl and a cyano group the question arises about the effects of these groups on the structure of [2^- Li$^+$ · TMEDA]$_2$.


$C_2H_5-CH(CO_2CH_3)_2$

3


$H_2C(CN)_2$

4

A section of the crystal structure of [(sodium dimethyl 2-ethylmalonate)$_4$ · (DMSO)$_6$] [(3^- Na$^+$)$_4$ · (DMSO)$_6$][13a] is given in Figure 3.

Most importantly, the two enolate oxygen atoms O101 and O102 are in a cisoid conformation. Furthermore, C101, C102, and C103 are planarly coordinated and form essentially one plane, which allows ideally a six-membered ring chelation with Na1. The C–C and C–O bond lengths in the malonate anion are as follows: C101–C102 139 pm, C102–C103 141 pm, C101–O101 125 pm, C103–O102 124 pm. The following bond angles have been determined: O101–C101–C102 130°, C101–C102–C103 119°, C102–C103–O102 130°. In contrast, with a larger nonchelating cation as, e.g., the hexamethylguanidinium cation, dimethyl 2-ethylmalonate (3^-) prefers the transoid conformation with the more favorable dipole-dipole interactions. The bond lengths in the transoid malonate anion are essentially the same as in the above-mentioned cisoid sodium

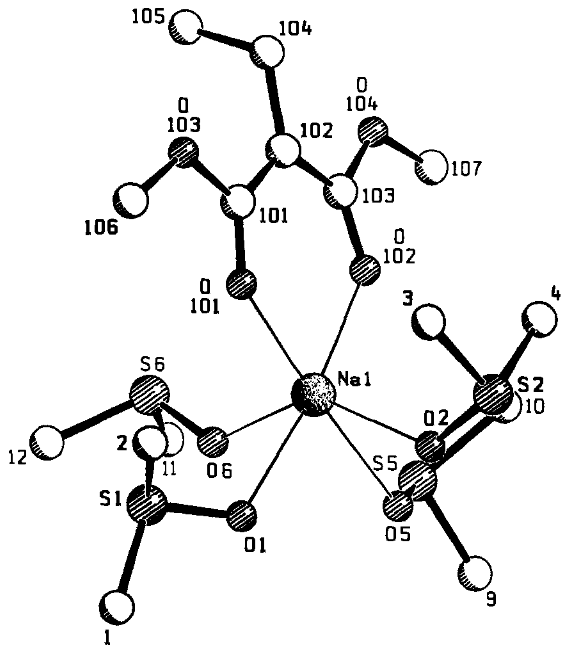


Figure 3. Section of the crystal structure of [(sodium dimethyl 2-ethylmalonate)$_4$ · (DMSO)$_6$] [(3$^-$ Na$^+$)$_4$ · (DMSO)$_6$][13a]

complex[13a]. A completely different situation arises in the case of metallated malononitriles as shown by the crystal structure of [Li$_3$(12-crown-4)$_2$(HC(CN)$_2$)$_3$]$_\infty$ [(4$^-$ · Li$^+$)$_2$(12-crown-4)$_2$]$_\infty$ in Figure 4[14a]. The essentially linear C−C−N structural elements (178.6−179.3°) of the anionic carbon atom and the cyano groups do not allow an intramolecular chelation of the metal ion. Rather, polymeric structures are favored with the lithium ions being coordinated to the cyano N atoms. The C−C bond lengths in the C−C−N units are between 137.2 and 140.9 pm, while the C−N distances amount to 114.0−116.8 pm. The C−C−C bond angles at the anionic carbon atoms are close to 120° (119.2−121.4°).

As one can see from Figure 5 the crystal structure of the lithiated *tert*-butyl cyanoacetate [**2**$^-$ Li$^+$ · TMEDA]$_2$ is a

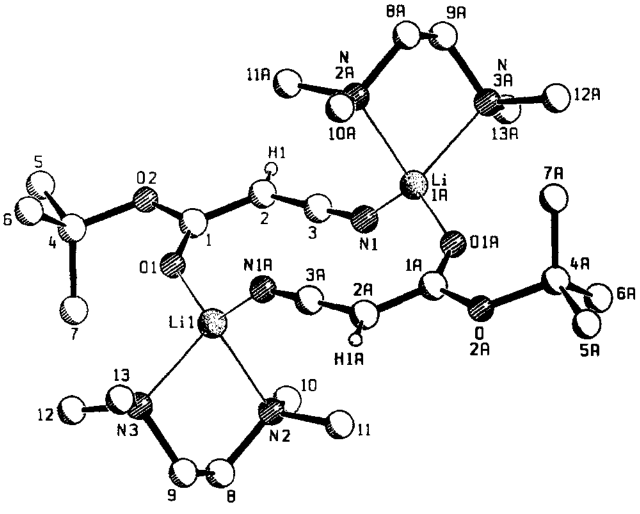


Figure 5. X-ray crystal structure of [**2**$^-$ Li$^+$ · TMEDA]$_2$. Selected bond lengths [pm] and angles [°]: O1−Li1 186.9(4), N1A−Li1 200.4(4), O1−C1 124.9(3), C1−C2 138.8(3), C2−C3 138.6(3), C3−N1 116.1(3), C1−O2 137.1(3); O1−C1−C2 126.9(2), C1−C2−C3 120.6(2), C2−C3−N1 178.8(2)

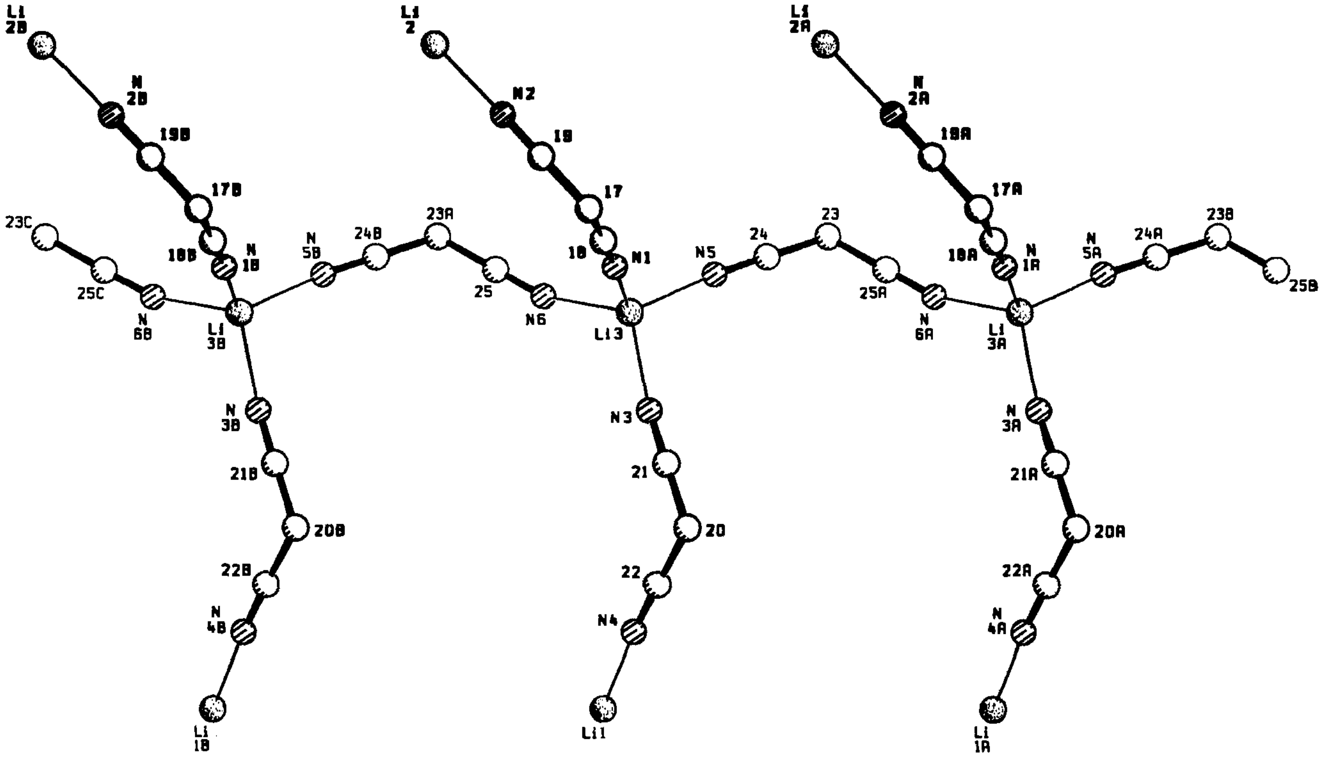


Figure 4. Section of the crystal structure of [Li$_3$(12-crown-4)$_2$(HC(CN)$_2$)$_3$]$_\infty$ [(4$^-$ Li$^+$)$_2$(12-crown-4)$_2$]$_\infty$[14a]

compromise between the structures of metallated β-dicarbonyl compounds and metallated malononitriles.

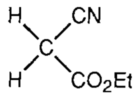
Again, each lithium (e.g. Li1) is coordinated to an enolate oxygen (O1) and to a cyano N atom (N1A). An intramolecular chelation, as in the case of metallated β-dicarbonyl compounds (see Figure 3), is excluded because of the essentially linear structure of the C−C−N units [178.8(2)°]. On the other hand, instead of the polymeric motif, which is the preferred one of lithiated malononitriles (see Figure 4), a twelve-membered ring dimer is the favorable structure here. In addition to the cyanide N and enolate O coordination each lithium atom is bound to a TMEDA molecule. The bond lengths and angles in the anionic units **2**$^-$ of [**2**$^-$ Li$^+$ · TMEDA]$_2$ and **2**$^-$ DBU-H$^+$ are almost identical: O1−C1 124.9(3) versus 124.1(2) pm, C1−C2 138.8(3) versus 138.7(3) pm, C2−C3 138.6(3) versus 140.0(2) pm, C3−N1 116.1(3) versus 115.8(3) pm, O1−C1−C2 126.9(2) versus 127.0(2)°, C1−C2−C3 120.7(2) versus 120.6(2)°, C2−C3−N1 178.8(2) versus 179.1(2)°. The different behavior towards electrophiles of anions as, e.g., **2**$^-$ having different gegenions like alkali metal ions on the one hand and DBU-H$^+$ on the other hand, thus should not be related to the structures of the anions in such compounds. Rather, it must be the different cations which are responsible for the often very different chemistry (see also Section 3).

The bond length in the cyano groups of [**2**$^-$ Li$^+$ · TMEDA]$_2$ [C3−N1 116.1(3) pm] is typical of lithiated cyanides; it is only slightly longer (2−3 pm) than in non-metallated cyanides[15]. C2−C3 [138.6(3) pm] is 2−3 pm longer than the corresponding bonds in lithiated cyanides[15]. In lithiated malononitriles like [(**4**$^-$ Li$^+$)$_2$(12-crown-4)$_2$]$_\infty$ (see Figure 4) this bond amounts to 138−140 pm[14]. The C1−O1 bond [124.9(3) pm] in [**2**$^-$ Li$^+$ · TMEDA]$_2$ is much shorter than comparable C−O bonds in lithium enolates (136 pm[1,2]), however ≈4 pm longer than C−O bonds in lithiated β-dicarbonyl compounds[13]. C1−C2 in [**2**$^-$ Li$^+$ · TMEDA]$_2$ (138.8 pm) is longer than the corresponding C−C bonds in enolates (134 pm[1,2]).

3. Significance of Hydrogen Bridges to Enolate Oxygen Atoms in Synthetic Applications

We have already mentioned the importance of N−H hydrogen bridges to enolate carbon atoms, which are formed with the amine if enolates are prepared by reaction of carbonyl compounds with lithium amides: consecutive reactions with electrophiles are very often hampered by competing protonation reactions[1,3]. Protonation can be avoided by transformation of the amine into the amide by means of an alkyllithium compound[1].

Likewise, N−H hydrogen bridges to enolate oxygen atoms of the type found in the crystal structure of **2**$^-$ DBU-H$^+$ may be significant in alkylation reactions of compounds of the type H_2CX_2 (X = CN, CO_2R) in the presence of a base. Thus, e.g., alkylation of ethyl cyanoacetate (**5**) with ethyl iodide in THF leads to different amounts of mono- and dialkylated products **6** and **7** depending on the nature of the base, which was used, see Table 1[16].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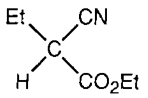
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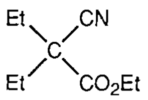
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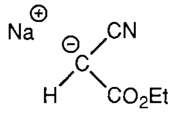
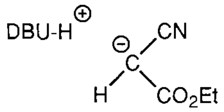
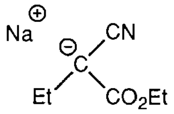

5$^-$ Na$^+$


5$^-$ DBU-H$^+$


6$^-$ Na$^+$

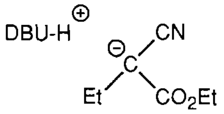

6$^-$ DBU-H$^+$

Table 1. Alkylation of **5** with ethyl iodide and NaH or DBU in THF or DMF[16]

Base	Solvent	Product ratio [%]		
		5	**6**	**7**
DBU	THF	18	72	10
NaH	THF	26	29	45
DBU	DMF	8	64	28
NaH	DMF	9	58	33

While the reaction with sodium hydride in THF results in the formation of large amounts (45%) of dialkylated product **7** this is not so with the base DBU[16] (10% **7**). Apparently, the monoalkylated species **6** is deprotonated much faster by the sodium enolate **5**$^-$ Na$^+$ to give **6**$^-$ Na$^+$ than by the DBU-H$^+$ enolate **5**$^-$ DBU-H$^+$ to give **6**$^-$ DBU-H$^+$. The formation of **6**$^-$ Na$^+$ and **6**$^-$ DBU-H$^+$, respectively, is a prerequisite for the formation of the dialkylated **7**.

If the structures of [**2**$^-$ Li$^+$ · TMEDA]$_2$ (Figure 5) and **2**$^-$ DBU-H$^+$ (Figure 2) indeed are models for those of **5**$^-$ Na$^+$ and **5**$^-$ DBU-H$^+$, one can envisage that in the case of **5**$^-$ DBU-H$^+$ an *intra*molecular proton transfer from DBU-H$^+$ to **5**$^-$ is preferred to the *inter*molecular deprotonation of monoalkylated **6** by **5**$^-$ DBU-H$^+$ to give **6**$^-$ DBU-H$^+$ followed by the formation of the dialkylated **7**. Such a situation corresponds to the favorable *intra*molecular *C*-protonation of the enolate carbon atom by the Li-coordinated amine molecule as outlined in the introductory remarks. A comparable intramolecular protonation reaction, however, does not exist in the case of the sodium species **5**$^-$ Na$^+$. Consequently, its deprotonation reaction of **6** to give **6**$^-$ Na$^+$, followed by the formation of dialkylated **7**, is much more favored. In strongly polar solvents like DMF (instead of THF) the preference for the formation of the monoalkylated **6** is also reduced (Table 1). Now the intramolecular hydrogen bridge from DBU-H$^+$ to the enolate oxygen atom of **5**$^-$ has to compete with a hydrogen bridge from DBU-H$^+$ to the oxygen atom of the solvent DMF. This raises the probability of **5**$^-$ to deprotonate **6** giving **6**$^-$ and thus more **7**.

A further example of an N−H bridge to an enolate oxygen atom is discussed in the case of an ammonium cation and a gold(I)-complexed α-isocanoacetate enolate. The N−H bridged ion pair is involved in the first catalytic enantioselective aldol reaction[17,18].

In summary, we have disclosed the X-ray crystal structures of the α-cyanoacetate enolates **2**$^-$ DBU-H$^+$ and [**2**$^-$ Li$^+$ · TMEDA]$_2$. Although the structures of the enolates **2**$^-$ are very similar in both cases, the structures as a whole are completely different: [**2**$^-$ Li$^+$ · TMEDA]$_2$ forms a twelve-membered ring dimer with Li$^+$ being attached to the nitrile N and enolate O atoms (as well as to TMEDA). On the other hand, an N−H hydrogen bridge to the enolate O atom is observed in **2**$^-$ DBU-H$^+$, the first N−H bridge to an enolate O atom so far structurally characterized. The structure corresponds to a point on the reaction coordinate of the protonation of enolates, which normally leads first to the corresponding enols. The structure of **2**$^-$ DBU-H$^+$ is also in agreement with results in alkylation reactions of enolates of α-cyanoacetates with DBU-H$^+$ and Na$^+$, respectively, as the gegenions, and THF and DMF, respectively, as the solvents: **5**$^-$ in **5**$^-$ DBU-H$^+$ (which corresponds to **2**$^-$ DBU-H$^+$) is less significant in intermolecular deprotonation reactions than **5**$^-$ in **5**$^-$ Na$^+$, apparently due to the N−H hydrogen bridge to the enolate oxygen atom in **5**$^-$ DBU-H$^+$.

Experimental

Preparation of Crystalline **2**$^-$ DBU-H$^+$: 140 mg (1.00 mmol) of *tert*-butyl α-cyanoacetate was allowed to react with 140 mg (1.00 mmol) of DBU in 2 ml of THF at −78°C. The colorless precipitate dissolved on warming to 20°C. After 4 d at 4°C crystals of **2**$^-$ DBU-H$^+$ appropriate for X-ray crystallography had formed. Yield: 0.09 g (32%).

Preparation of Crystalline [**2**$^-$ Li$^+$ · TMEDA]$_2$: 140 mg (1.00 mmol) of *tert*-butyl α-cyanoacetate was deprotonated with 0.65 ml (1.04 mmol) of a 1.6 M solution of *n*BuLi in hexane at −78°C in the presence of 228 mg (2.00 mmol) of TMEDA in 1.2 ml of THF. The immediately crystallized [**2**$^-$ Li$^+$ · TMEDA]$_2$ was warmed to 20°C, dissolved, and recrystallized at 4°C. After 2 d monocrystalline [**2**$^-$ Li$^+$ · TMEDA]$_2$ had formed (112 mg, 43%).

Crystal Structure Determination of [**2**$^-$ Li$^+$ · TMEDA]$_2$: $C_{26}H_{52}Li_2N_6O_4$, M = 526.6. Monoclinic space group $P2_1/c$, a = 905.8(1), b = 2257.0(2), c = 839.2(1) pm, β = 101.22(1)°, V = 1686.8(3) pm^3 · 10^6, Z = 2, D_c = 1.037 g · cm^{-3}, μ(Cu-$K_α$) = 5.22 cm^{-1}. Diffractometer: Enraf-Nonius CAD4, Cu-$K_α$ radiation, graphite monochromator, T = 193(5) K, ω scans. 2358 reflections measured ($Θ_{max}$ = 55°), 2112 independent (R_{int} = 0.0539). The structure was solved by direct methods[19] and refined[19] on F with 1805 reflections with $F > 4σ(F)$, all non-hydrogen atoms anisotropic, the hydrogen atoms were located and refined isotropically. Final R values: R = 0.0404, wR = 0.0412 for 277 parameters, weighting scheme: $w^{-1} = σ^2(F)$. The extinction parameter x was 0.0094(7)[19]. All calculations were performed with a MicroVax II and a DEC AXP 3000−300[20−22].

Crystal Structure Determination of **2**$^-$ DBU-H$^+$: $C_{16}H_{27}N_3O_2$, M = 293.4. Monoclinic space group $P2_1/n$, a = 1168.7(2), b = 1246.2(1), c = 1285.3(2) pm, β = 116.23(1)°, V = 1680.0(4) pm^3 · 10^6, Z = 4, D_c = 1.160 g · cm^{-3}, μ(Cu-$K_α$) = 5.83 cm^{-1}. Diffractometer: Enraf-Nonius CAD4, Cu-$K_α$ radiation, graphite monochromator, T = 193(5) K, ω scans. 2368 reflections measured ($Θ_{max}$ = 55°), 2111 independent (R_{int} = 0.0344). The structure was solved by direct methods[19] and refined[19] on F with 1860 reflections with $F > 4σ(F)$, all non hydrogen atoms anisotropically, the hydrogen atoms were located and refined isotropically. Final R values: R = 0.0366, wR = 0.0375 for 272 parameters, weighting scheme: $w^{-1} = σ^2(F)$. The extinction parameter x was 0.0146(6)[19]. All calculations were performed with a MicroVax II and a DEC AXP 3000−300[20−22].

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