DOI: 10.1002/ejoc.201001725

DBU-Promoted Nucleophilic Activation of Carbonic Acid Diesters

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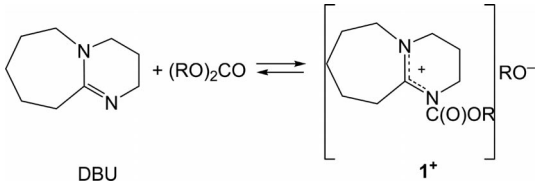
Keywords: Organocatalysis / Reaction mechanisms / Amidine base / Carbonic acid ester

The reactivity of carbonic acid diesters in the presence of the amidine base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) has been investigated for the first time. Organic carbonates can be activated by DBU through the formation of *N*-alkoxycarbonyl ketene aminal **2** as the ultimate product. The latter species may form through deprotonation of the corresponding *N*-alkoxycarbonyl-amidinium cation **1**$^+$ by the amidine base. We have for the first time isolated and characterized, both in the solid state (X-ray crystal structure determination, IR) and in solution (NMR), a few **1**$^+$ chloride salts and studied their reactivity towards the organic base. The reactivity of both **1**$^+$ and **2** with methanol has also been explored. Ketene aminal **2** behaves as a "CO_2R" carrier, as it can selectively transfer the alkoxycarbonyl group to the alcohol and regenerate the amidine base.

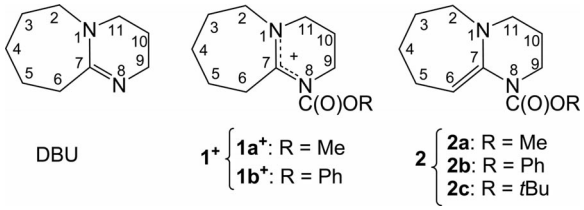
Introduction

The ability of amidine bases, such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), to act as nucleophiles towards a variety of electrophiles has been well established in the last few years.[1,2] Recently, it has been proposed that DBU can act as a nucleophile and react with electrophilic substrates, such as carbonic acid diesters [dimethyl carbonate (DMC) and dibenzyl carbonate], and activate them by forming the cationic intermediate *N*-alkoxycarbonyl DBU derivative **1**$^+$ [Equation (1)].[3] It is proposed that the latter species plays a key role in several important DBU-catalyzed synthetic processes, such as esterification of carboxylic acids with DMC, methylation of phenols, indoles, and benzimidazoles with DMC, benzylation of the N, O, and S atoms with dibenzyl carbonate,[3] and in perhaps some recently described carbonylation processes.[4a,4c] However, the reactivity of carbonic acid diesters in the presence of DBU has never been investigated. Direct evidence supporting equilibrium (1) is still lacking. Furthermore, the chemistry of the **1**$^+$ adduct is practically unknown, as **1**$^+$ salts have never been isolated nor characterized.



(1)

Herein, for the first time, we report the isolation and full characterization, both in the solid state (X-ray crystal structure determination, IR) and in solution (NMR), of a few **1**$^+$ chloride salts (**1a**, R = Me; **1b**, R = Ph), and the conversion of the *N*-alkoxycarbonyl-amidinium adduct **1**$^+$ (Scheme 1) into the ketene aminal **2** (Scheme 1) in the presence of the amidine base DBU. As a part of our studies devoted to exploring new ways to activate carbonic acid diesters,[4] we also focus on the direct reaction of dialkyl, diaryl, and aryl alkyl carbonates with DBU. We demonstrate that ketene aminal **2** forms, as the ultimate product, from the addition of DBU to carbonic acid diesters by an equilibrium process likely involving intermediate **1**$^+$. The reactivity of both **1**$^+$ and their conjugated bases **2** with methanol is also described. The behavior of ketene aminal **2** as a "CO_2R" carrier is highlighted.



Scheme 1. Numbering system in DBU, **1**$^+$, and **2**.

Results and Discussion

Isolation and Characterization of *N*-Alkoxycarbonyl-Amidinium Chloride Salts 1a (R = Me) and 1b (R = Ph)

Chloride salts **1a** and **1b** were prepared by treating DBU with the corresponding chloroformate [Equation (2)] at

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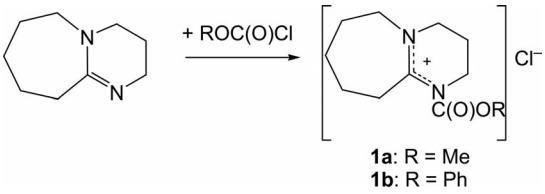
293 K in ethereal solvents. Depending on the reaction conditions, the product precipitated along with variable amounts of DBU·HCl. Both compounds were hygroscopic, and **1a** was isolated as the monohydrate salt **1a**·H_2O.



(2)

Figures 1 and 2 show the crystal structures of **1a**·H_2O and **1b** as determined by X-ray single crystal analysis. As expected, atoms C12, O1, O2, and N8 lie in the same plane [root-mean-square deviations: 0.006 Å (for **1b**), 0.003 Å (for **1a**·H_2O)]. The plane is rotated with respect to that of C7, N8, N1, C6, C11, and C2 and with a rotation angle reversed in the two adducts [**1b**: –47.68(4), **1a**·H_2O: 42.79(6)]. Consequently, in **1b** the C12–O1 bond is almost perpendicular to the mean plane individuated by C6, C5, C3, and C2, but is parallel to the above plane in **1a**·H_2O. The root-mean-square deviation from the mean plane of C7, N8, C12, and C9 is only 0.022 Å in **1b** and 0.033 Å in **1a**·H_2O, showing that N8 retains a noteworthy sp^2-hybridized character in both adducts. The plane is twiddled [20.51(5)° in **1b**, 17.90(5)° in **1a**·H_2O] with respect to that of C7, N8, N1, C6, C11, and C2 but is rotated [32.19(5)° in **1b**, 29.79(6)° in **1a**·H_2O] with respect to the plane containing the carbonyl bond (N8, C12, O1, and O2). The latter feature is intriguing as it suggests in both salts that the N8 atom conjugates preferentially with the atoms C7 and N1 of the amidine moiety rather than with the carbonyl group. Accordingly, in both salts, the N8–C12 bond length is longer than usually reported in the literature for carbamate compounds,[5,6] but the N8–C7 bond is shorter than expected for a CN single bond.[7]

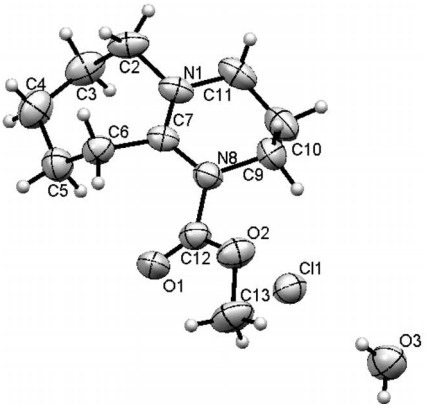


Figure 1. ORTEP view of the salt **1a**·H_2O (displacement ellipsoids are set at 50%). The hydrogen labels are omitted for clarity. Selected bond lengths [Å] and angles [°]: O1–C12 1.192(2), O2–C12 1.327(2), O2–C13 1.454(2), N8–C9 1.486(2), N8–C7 1.359(2), N8–C12 1.414(2), N1–C11 1.477(3), N1–C7 1.309(2), N1–C2 1.484(2), C12–O2–C13 114.39(16), N8–C12–O2 109.37(15), N8–C12–O1 124.49(16), O2–C12–O1 126.15(17), C9–N8–C7 119.19(14), C9–N8–C12 120.12(14), C7–N8–C12 120.60(14), C11–N1–C7 124.36(16), C11–N1–C2 114.61(15), C7–N1–C2 121.03(16), O1–C12–N8–C7 27.60(26), C9–N8–C7–N1 13.91(22), N8–C7–N1–C11 5.51(24), C6–C7–N1–C2 2.69(23), O2–C12–N8–C9 31.89(21), O1–C12–N8–C9 –148.95(18), O2–C12–N8–C7 –151.55(15), O1–C12–N8–C7 27.60(26).

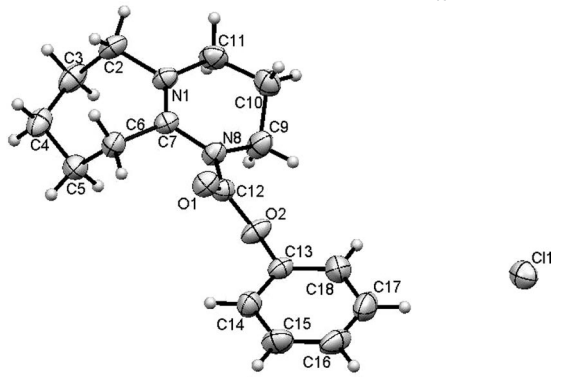


Figure 2. ORTEP view of the salt **1b** (displacement ellipsoids are set at 50%). The hydrogen labels are omitted for clarity. Selected bond lengths [Å] and angles [°]: O1–C12 1.1900(14), O2–C12 1.3379(14), O2–C13 1.4080(13), N8–C9 1.4799(15), N8–C7 1.3642(14), N8–C12 1.4162(14), N1–C11 1.4776(16), N1–C7 1.3036(14), N1–C2 1.4868(15), C12–O2–C13 119.39(9), N8–C12–O2 107.19(9), N8–C12–O1 125.91(10), O2–C12–O1 126.87(10), C9–N8–C7 119.55(9), C9–N8–C12 119.03(9), C7–N8–C12 121.13(9), C11–N1–C7 124.26(10), C11–N1–C2 114.0(1), C7–N1–C2 121.57(10), O1–C12–N8–C7 –30.19(17), C9–N8–C7–N1 –13.94(16), N8–C7–N1–C11 –1.38(17), C6–C7–N1–C2 3.06(13), O2–C12–N8–C9 –34.67(13), O1–C12–N8–C9 143.58(12), O2–C12–N8–C7 151.56(98), O1–C12–N8–C7 –30.19(17).

In both structures the C=O bond is slightly shorter than found in related systems.[5,8] Accordingly, the C=O IR frequency (Table 1) is higher than normally observed for carbamate esters.[8]

In addition, both salts were characterized in solution by NMR spectroscopy (Table 1 and Exp. Section). The resonance of the iminium C7 is characteristic and located at approximately 172 ppm. The value measured for C7 in **1a**

Table 1. Selected IR[a] and NMR[b] spectoscopy data for the salts **1a**–**b** and ketene aminals **2a**–**b**.

	ν(C=O)	ν(C=N)	ν(C=C)	δ_H(H6)	δ_H(H5)	δ_C(CO_2)	δ_C(C6)	δ_C(C7)
1a[c]	1748	1639	–	3.29	[d]	152.80	33.77	172.62
1b[c]	1764	1633	–	3.31	[d]	150.89	34.04	172.69
2a[e]	1701, 1716[f]	–	1663	4.71[g]	1.98	155.43	105.27[h]	143.19
2b	1709[i]	–	[j]	4.89[g]	2.01	153.18	106.04[h]	142.83

[a] ν [cm^{-1}]. [b] In $CDCl_3$. δ [ppm]. [c] IR done in Nujol. [d] See Exp. Section. [e] IR done neat. [f] Shoulder. [g] br. t, $^3J_{H,H}$ = 6 Hz, 1 H. [h] dm, $^1J_{C,H}$ = 159–160 Hz. [i] In $CDCl_3$. [j] Masked.

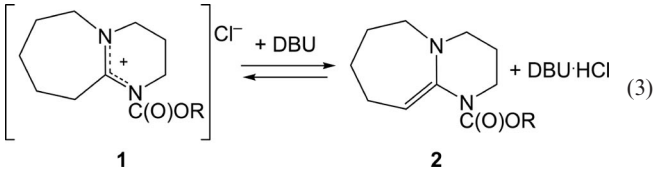
(172.62 ppm) is close to that (171.5 ppm) reported by Shieh,[3a] who obtained **1a** in situ by reacting MeOC(O)Cl with an excess amount of DBU.[9]

Conversion of Amidinium Cation 1^+ into Ketene Aminal 2 (2a, R = Me; 2b, R = Ph)

By using the reaction of DBU with MeOC(O)Cl, we were able to isolate and fully characterize the unprecedented ketene aminal **2a** (Table 1).

To the best of our knowledge, the literature reports only a few examples of *N*-alkoxycarbonyl-substituted ketene aminals.[10] In the ^{13}C NMR spectrum of **2a** the imine C7 atom resonates at 143.19 ppm, while the doublet of multiplets at 105.27 ppm ($^1J_{C,H}$ = 159 Hz) is due to the sp^2-hybridized C6 with only one H atom directly bound. The attached H6 proton absorbs at 4.71 ppm (br. t, $^3J_{H,H}$ = 6 Hz, 1 H) and is coupled with the vicinal H5 protons, which produce a pseudo-quartet at higher fields (δ =1.98 ppm).

Equilibrium (3) may offer a plausible rationale for the formation of **2a**. Accordingly, the addition of DBU (0.2 equiv.) to a $CDCl_3$ solution of **1a** prompted the rapid formation of **2a**, with easily identifiable ^1H NMR resonances in the spectrum of the reaction mixture. At 293 K in $CDCl_3$, **1b** was also treated with DBU to readily give **2b** according to Equation (3). The NMR spectrum of the reaction mixture (DBU/**1b**, 0.5 mol/mol) showed the appearance of new signals from DBU·HCl and ketene aminal **2b** (R = Ph). The spectroscopic features of **2b** agreed fully with those exhibited by **2a** (Table 1 and Exp. Section). Equilibrium (3) lies to the right. In fact, the addition of more DBU (overall DBU/**1b** molar ratio: 1) favored the production of **2b** and DBU·HCl, and resulted in the disappearance of the resonances due to **1b**. Accordingly, in the IR spectrum of the solution, the carbonyl absorption of **1b** at 1760 cm^{-1} was replaced by that of **2b**, centered at 1709 cm^{-1}. These findings clearly show that $\mathbf{1^+}$ is not a stable species in the presence of free DBU, which can act as an effective base to the cation and abstract one of the acidic H6 protons.[2c,11,12]



1 2 (3)

Reaction of DBU with Carbonic Acid Diesters

The above data provide the key for rationalizing the chemistry of organic carbonates in the presence of DBU.[3,4a,4c] Herein, we show that DBU can interact with carbonic acid diesters to give ketene aminal **2** as the ultimate product.

For instance, at room temperature the alkyl aryl carbonates MeOC(O)OPh (**3a**) or *t*BuOC(O)OPh (**3c**), or the diaryl carbonate $(PhO)_2CO$ (**3b**), were treated with the amidine base to afford ketene aminals **2a**, **2c**, and **2b**, respectively (Table 2).

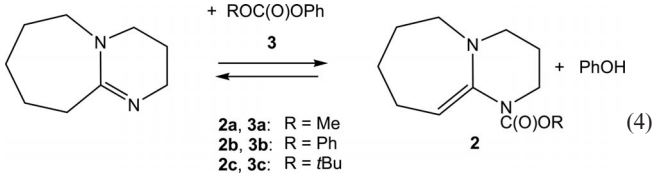
Table 2. Reaction of DBU with ROC(O)OPh (**3**; **3a**, R = Me; **3b**, R = Ph; **3c**, R = *t*Bu) at 293 K, and selected IR[a] spectroscopy data and yields for products **2**.

R	**3**/DBU [mol/mol]	DBU [μL]	THF[b] [mL]	**2**	ν(C=O)	**2**[c] [%]
Me	4	150	–	**2a**	1701 (vw)	17
Me	1	300	–	**2a**	1701 (m) 1716 (m)[d]	18
*t*Bu	4	120	–	**2c**	[e]	6
*t*Bu	1	300	–	**2c**	1705 (w)	8
*t*Bu	0.25	640	–	**2c**	1694 (m) 1701 (m)[d]	25
Ph	3	140	2	**2b**	[f]	20
Ph	1	190	0.3	**2b**	1716 (m) 1732 (m)[d]	25
Ph	0.25	870	–	**2b**	1717 (ms) 1732 (ms)[d]	70

[a] Liquid film, *v* [cm^{-1}]. [b] Used as solvent. [c] NMR yields, based on the limiting reagent. Normally, yields of **2** were measured after a reaction time of 4–8 h and did not change significantly after 20–24 h. [d] Poor or unresolved. [e] Not observed. [f] Not measured.

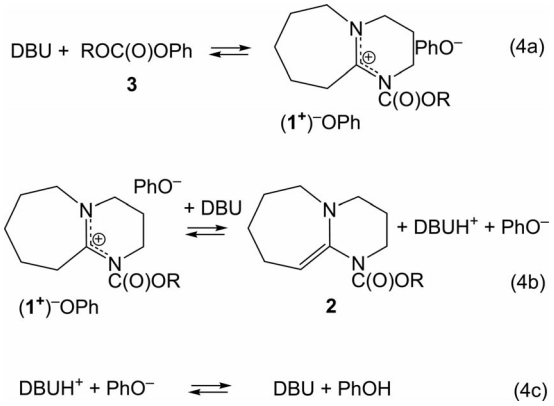
Besides the signals from the carbonate and DBU, the IR spectra of the reaction mixtures showed new weak to medium absorptions between 1700 and 1730 cm^{-1}, consistent with the formation of **2**. NMR spectroscopy was much more informative. ^1H NMR decoupling experiments of the solutions, and analysis in those regions of the spectra not obscured by other resonances (**3**, DBU, PhOH), allowed us to locate most of ketene aminal resonances, such as the very characteristic ones due to H6 and H5 (see Exp. Section). In the ^{13}C NMR spectra of the mixtures, all the signals for **2a**–**c** were easily identifiable, and the diagnostic resonances due to C6, C7, and CO_2 were found in the expected ranges (see Exp. Section).

As a whole, the spectroscopic data support the establishment of equilibrium (4). Equilibrium (4) lies to the left and its position depends on the nature of R and the molar ratio of carbonate/DBU (Table 2).



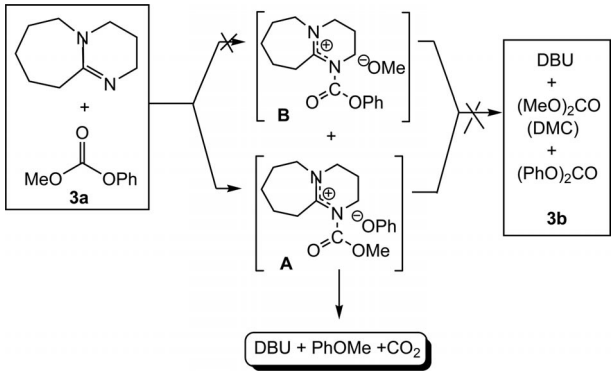
2 (4)

Ketene aminals **2a**–**c** may form from the intermediate ionic species $(\mathbf{1^+})^-$OPh (R = Ph, Me, *t*Bu), ensuing from the nucleophilic attack of DBU on the carbonyl group of **3** [Scheme 2, Equation (4a)].[3a] However, the NMR spectra did not show any detectable amount of $(\mathbf{1^+})^-$OPh, in accordance with the fact that once $\mathbf{1^+}$ formed, it easily converted into **2** in the presence of free DBU.



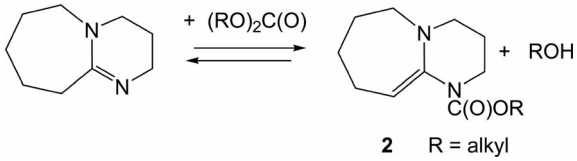
Scheme 2. Plausible reaction pathway to ketene aminal **2**.

Moreover, in experiments with **3a** or **3c**, no evidence for the formation of **2b** was found. This suggests that the nucleophilic attack of DBU on an unsymmetrical carbonate ROC(O)OPh results in the selective expulsion of PhO^-. In accordance with the selective formation of intermediate **A** with respect to **B** (Scheme 3), we found that, at a higher temperature (393 K, 24 h) and with 0.25 equiv. of DBU, **3a** was decarboxylated to anisole,[4c] but we did not observe the disproportionation of **3a** to dimethyl carbonate and diphenyl carbonate (**3b**).



Scheme 3.

No spectroscopic (IR, NMR) evidence has been obtained for the formation of ketene aminal **2** when dialkyl carbonates, such as dimethyl, dibenzyl, or diethyl carbonate, were treated with DBU at 293 K. Moreover, no resonances attributed to **2a** were observed when DMC/DBU mixtures (1 mol/2 mol) were monitored by ^1H NMR at temperatures between 293 and 343 K.[13] Nevertheless, on the basis of the reactivity exhibited by diaryl and aryl alkyl carbonates, we cannot exclude in the latter cases the presence of the $(1^+)^-OR$ and/or **2** species in the reaction mixture at very low concentrations. There may be a twofold explanation for the behavior observed with dialkyl carbonates. Dialkyl carbonates are much less reactive species than **3a**–**c**,[14] and reversible formation of the $(1^+)^-OR$ salt from the combination of DBU and $(RO)_2CO$ [see Equation (1), R = alkyl] may suffer from a higher energy barrier. Moreover, equilibrium (5) may lie to the left more than equilibrium (4), because of the tendency of the alcohol, ROH, to react with **2** and give back DBU and $(RO)_2CO$, as we have ascertained in the case for the reaction of **2a** with MeOH (see below).

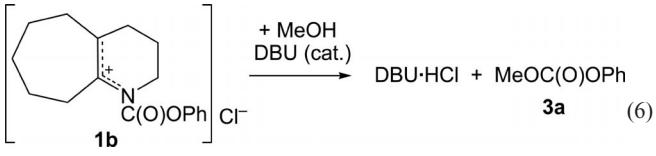


(5)

Reactivity of 1^+ and 2 Towards Methanol

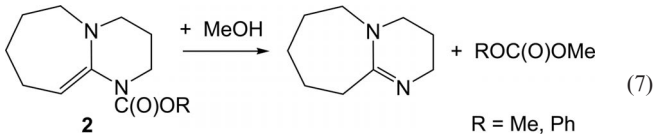
In principle, both the amidinium cation 1^+ and its respective ketene aminal **2** are potential carbonylating substrates. This fact prompted us to explore their reactivity as carbonylating agents[4,14] and ascertain if 1^+ and/or **2** formed by reaction of the carbonate with DBU are really activated forms of that original organic carbonate. In this study we focused on methanol, a relatively weak nucleophilic species, as the reference nucleophile.

We found that after a long time period (17 h) at 293 K in $CDCl_3$, neither **1b** nor **3b** showed any significant reactivity with a 2-fold molar excess amount of MeOH. However, a drastic change in reactivity was observed when, under the same reaction conditions, **1b** was treated with 2 molar equiv. of MeOH in the presence of a catalytic amount of DBU (approximately 20 mol-% relative to $\mathbf{1b}^+$). As a matter of fact, the amidine base promoted the smooth formation of DBU·HCl and **3a**; see Equation (6). The conversion of **1b** was complete within about 1 h.



(6)

We cannot exclude that the catalytic effect observed upon addition of DBU may be ascribed to the formation of methoxide ion, which even in low concentrations (as the pK_a values of MeOH and DBU suggest),[15,16] is a stronger nucleophile than MeOH. However, soon after adding the base to the $CDCl_3$ solution of **1b** and MeOH, we also noted that the NMR spectrum of the reaction mixture showed the presence of ketene aminal **2b**. The signals of both **2b** and **1b** rapidly quenched within about 1 h, because of the formation of the products. This fact suggests that the ketene aminal may be a catalytically active intermediate in the carbonylation process shown in Equation (6), which may involve the reaction of **2b** (R = Ph) with the alcohol as the final step; see Equation (7).



(7)

Further support of this hypothesis was obtained by investigating the reactivity of **1a** and **2a** with MeOH.

Likewise **1b**, even after reaction times as long as 16 h and with 7 molar equiv. of MeOH in $CDCl_3$, **1a**·H_2O did not exhibit any appreciable reactivity towards the alcohol. In addition, under comparable conditions (293 K; $CDCl_3$; MeOH/**3a**, 1.8 mol/mol; 20 h), **3a** did not react significantly with MeOH.

Compared to amidinium cation $\mathbf{1a}^+$ and carbonate **3a**, the corresponding ketene aminal **2a** was a more reactive species and a more active carbonylating agent. At 293 K in $CDCl_3$ (MeOH/**2a**, 1.7 mol/mol), **2a** readily transferred the methoxycarbonyl group to the alcohol producing DMC and the regenerated amidine base; see Equation (7), R = Me. Under the working conditions, the methoxycarbonylation reaction shown in Equation (7), R = Me, was relatively fast (**2a** conversion as high as 77%, after only 2 h) and quantitative (Figure 3). The process was also very selective, as no side products were detected in the reaction mixture.

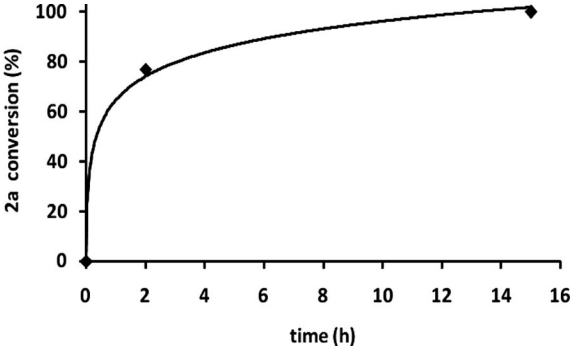


Figure 3. Reaction of **2a** (153.0 mg, 0.73 mmol) with methanol (0.050 mL, 1.23 mmol; MeOH/**2a**, 1.7 mol/mol) in $CDCl_3$ (1 mL) at 293 K. Conversion of **2a** (determined by ^1H NMR) versus time.

The above results are very enlightening and demonstrate clearly that DBU can activate carbonic acid diesters through the formation of *N*-alkoxycarbonyl ketene aminal **2** which can behave as a carrier of the CO_2R group.

Conclusions

This study sheds light on the reactivity of carbonic acid diesters in the presence of an amidine base such as DBU. We have demonstrated unambiguously that DBU, by reacting as a nucleophile with organic carbonates, can generate through an equilibrium process reactive ketene aminal **2** as the ultimate product. The latter species may reasonably form by deprotonation of a *N*-alkoxycarbonyl-amidinium cation $\mathbf{1}^+$ with the amidine base. We have shown this by isolating and characterizing, for the first time, a few $\mathbf{1}^+$ chloride salts, and studying their reactivity towards the organic base. Upon treatment with DBU, organic carbonates are activated towards nucleophilic attack by the formation of ketene aminal **2**, which can act as a carrier of the CO_2R group. These findings are of interest for their implications in catalysis and open the way to a more accurate understanding of the role played by the amidine base in DBU-catalyzed acylation reactions.[3,4a,4c]

Experimental Section

General Methods: Unless otherwise stated, all reactions and manipulations were conducted under an inert gas atmosphere by using vacuum line techniques. All solvents were dried according to conventional methods (P_2O_5, Na/benzophenone)[17] and stored under N_2. Carbonate **3a** was prepared according to the literature.[18] Carbonate **3b** was recrystallized from diethyl ether at 253 K before use. DBU, ROC(O)Cl (R = Me, Ph), and the other organic carbonates were used as received. DBU was stored under an inert atmosphere. IR spectra were recorded with a Shimadzu FTIR Prestige 21 spectrophotometer or a Perkin–Elmer FTIR 1710 instrument. NMR spectra were recorded with a Varian Inova 400 spectrometer. Chemical shifts are in δ (ppm) and measured relative to residual solvent peaks. GC analyses were recorded with a HP 5890 Series II gas chromatograph (capillary column: Heliflex AT-5, 30 m × 0.25 mm, 0.25 μm film thickness). GC–MS analyses were recorded with a Shimadzu GC-17A linked to a Shimadzu GC–MS QP5050 selective mass detector (capillary column: Supelco MDN-5S, 30 m × 0.25 mm, 0.25 μm film thickness). Analyses of gases were performed with a Dani 8610 GC equipped with a TCD 866. Single-crystal X-ray analyses were carried out with a Bruker X8 Apex II diffractometer equipped with an APEX-II CCD detector.

Isolation and Characterization of 8-Methoxycarbonyl-1,8-diazabicyclo[5.4.0]undec-7-enium Chloride Monohydrate (1a·H_2O): DBU (1 mL, 6.7 mmol) in diethyl ether (15 mL) was added dropwise to an excess amount of MeOC(O)Cl (3 mL, 38.7 mmol) dissolved in the same solvent (5 mL). The solution was stirred for 1 h. The resulting solid precipitate was filtered, washed with diethyl ether, and redissolved in CH_2Cl_2. The CH_2Cl_2 solution was treated with THF (tetrahydrofuran) and cooled to 253 K. The resulting suspension was filtered, and the solid DBU·HCl, the major component, was removed. After addition of diethyl ether and more THF to the solution, a white solid was obtained which was recrystallized repeatedly from CH_2Cl_2/THF to give **1a**·H_2O (170 mg, 10%). ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ = 1.72–1.86 (br. m, 6 H, 3-H, 4-H, and 5-H), 2.23 (quint, $^3J_{H,H}$ = 6 Hz, 2 H, 10-H), 3.29 (br. m, 2 H, 6-H), 3.87 (s, 3 H, OMe), 3.95 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, 9-H or 11-H), 4.08 (pseudo-t overlapped with the signal of 2-H, 2 H, 9-H or 11-H), 4.10 (br. m, 2 H, 2-H) ppm.[19] $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ = 20.87, 21.93, 25.12, 28.06, 33.77 (C-6), 44.08, 52.04, 55.41 (OMe), 57.64, 152.80 (CO_2), 172.62 (C-7) ppm. IR (Nujol): $\tilde{\nu}$ = 1748 (s, C=O), 1639 (s, C=N), 1219, 1200, 1155 cm^{-1}. $C_{11}H_{21}ClN_2O_3$ (264.74): calcd. Cl 13.39; found Cl 13.24.

Isolation and Characterization of 8-Phenoxycarbonyl-1,8-diazabicyclo[5.4.0]undec-7-enium Chloride (1b): A solution of DBU (2 mL, 13.4 mmol) in THF (10 mL) was added dropwise to PhOC(O)Cl (1.7 mL, 13.6 mmol) which was dissolved in the same solvent (10 mL). The solution was stirred for 1 h at ambient temperature. The resulting white precipitate was filtered, washed with THF, and recrystallized from CH_2Cl_2/diethyl ether to give **1b** (2.48 g, 60%). ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ = 1.73 (unresolved br., 6

H, 3-H, 4-H, and 5-H), 2.29 (quint, $^3J_{H,H}$ = 6 Hz, 2 H, 10-H), 3.31 (br. m, 2 H, 6-H), 3.97 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, 9-H or 11-H), 4.08 (br. m, 2 H, 2-H), 4.18 (pseudo-t, $^3J_{H,H}$ = 6 Hz, 2 H, 9-H or 11-H), 7.08 (dm, 2 H, *ortho*-H), 7.19 (m, 1 H, *para*-H), 7.31 (m, 2 H, *meta*-H) ppm.[19] $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ = 20.85, 21.54, 24.86, 27.85, 34.04 (C-6), 44.56, 52.36, 57.84, 120.72 (C-*ortho*), 126.88 (C-*para*), 129.64 (C-*meta*), 149.61 (C-*ipso*), 150.89 (CO_2), 172.62 (C-7) ppm. IR (Nujol): $\tilde{\nu}$ = 1764 (s, C=O), 1633 (s, C=N), 1277, 1221, 1192 cm^{-1}. $C_{16}H_{21}ClN_2O_2$ (308.79): calcd. Cl 11.48; found Cl 11.35.

Isolation and Characterization of Methyl 1,8-Diazabicyclo[5.4.0]-undec-6-ene-8-carboxylate (2a): A solution of DBU (2.0 mL, 13.4 mmol) in THF (10 mL) was added dropwise to MeOC(O)Cl (1.05 mL, 13.6 mmol) which was dissolved in the same solvent (10 mL). The reaction mixture was stirred for 1 h, cooled to 253 K for 3 h, and then filtered. Evaporation in vacuo of the solution gave ketene aminal **2a** (0.710 g) as a colorless viscous oil. ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ = 1.44 (m, $^3J_{4\text{-}H,3\text{-}H}$ = 6.2 Hz, 2 H, 4-H), 1.61 (m, $^3J_{3\text{-}H,4\text{-}H}$ = 6 Hz, 2 H, 3-H), 1.69 (m, $^3J_{H,H}$ = 6 Hz, 2 H, 10-H), 1.98 (pseudo-q, $^3J_{5\text{-}H,6\text{-}H}$ = 6.2 Hz, 2 H, 5-H), 2.82 (m, 2 H, 9-H or 11-H), 2.91 (m, 2 H, 2-H), 3.41 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, 9-H or 11-H), 3.54 (s, 3 H, OMe), 4.71 (br. t, $^3J_{6\text{-}H,5\text{-}H}$ = 6 Hz, 1 H, 6-H) ppm.[19] $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K): δ = 23.43, 24.46, 26.03, 28.33, 43.34, 49.00, 52.40 (OMe), 52.91, 105.27 (C-6), 143.19 (C-7), 155.44 (CO_2) ppm. In the proton-coupled spectrum, the signals at 52.40 ppm (OMe) and 105.27 ppm (C-6) split, respectively, into a quartet ($^1J_{C,H}$ = 145 Hz) and a doublet of multiplets ($^1J_{C,H}$ = 159 Hz). IR (neat): $\tilde{\nu}$ = 1717 (shoulder), 1701 (s, C=O), 1663 (ms, C=C), 1273, 1213, 1184, 1167, 1122 cm^{-1}. MS (70 eV): *m*/*z* (%) = 210 $[M]^+$, 195 $[M - CH_3]^+$, 181, 179 $[M - OCH_3]^+$, 151 $[M - CO_2CH_3]^+$, 123, 98, 68, 54, 41. $C_{11}H_{18}N_2O_2$ (210.26): calcd. C 62.83, H 8.63, N 13.32; found C 62.63, H 8.84, N 13.15.

Reaction of 1b with DBU in $CDCl_3$: The addition of DBU (0.030 mL, 1 equiv.) to a solution of **1b** (0.0583 g, 0.189 mmol) in $CDCl_3$ resulted in disappearance of the NMR resonances of the salt and the appearance of the new signals corresponding to **2b** (phenyl 1,8-diazabicyclo[5.4.0]undec-6-ene-8-carboxylate) and DBU·HCl. The characterization data is for the reaction mixture. ^1H NMR (400 MHz, $CDCl_3$, 293 K, **2b**): δ = 1.46 (m, $^3J_{4\text{-}H,3\text{-}H}$ = 6 Hz, 2 H, 4-H), 1.64 (m, $^3J_{3\text{-}H,4\text{-}H}$ = 6 Hz, 2 H, 3-H), 1.77 (quint, $^3J_{H,H}$ = 6 Hz, 2 H, 10-H), 2.01 (pseudo-q, $^3J_{5\text{-}H,6\text{-}H}$ = 6.2 Hz, 2 H, 5-H), 2.90 (m, 2 H, 9-H or 11-H), 2.96 (m, 2 H, 2-H), 3.52 (br. t, $^3J_{H,H}$ = 6.2 Hz, 2 H, 9-H or 11-H), 4.89 (br. t, $^3J_{6\text{-}H,5\text{-}H}$ = 6 Hz, 1 H, 6-H), 6.98 (dm, 2 H, *ortho*-H), 7.03 (m, 1 H, *para*-H), 7.20 (m, 2 H, *meta*-H) ppm.[19] ^1H NMR (400 MHz, $CDCl_3$, 293 K, DBU·HCl): δ = 1.52–1.59 (unresolved m, 3-H, 4-H, and 5-H), 1.83 (quint, $^3J_{H,H}$ = 6 Hz, 10-H), 2.69 (m, 6-H), 3.23 (t, $^3J_{H,H}$ = 6 Hz, 9-H), 3.31 (t, $^3J_{H,H}$ = 6 Hz, 11-H), 3.32 (m, 2-H partially overlapped with the signal of 11-H), 11.22 (br. s, NH) ppm.[19] $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K, **2b**): δ = 23.38, 24.46, 25.88, 28.26, 43.75, 48.97, 52.88, 106.04 (C-6), 121.31 (C-*ortho*), 124.71 (C-*para*), 128.76 (C-*meta*), 142.83 (C-7), 151.25 (C-*ipso*), 153.18 (CO_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K, DBU·HCl): δ = 19.89, 24.20, 26.87, 28.82, 33.05, 39.11, 48.26, 53.66, 164.58 (C-7) ppm. In both the ^1H NMR and ^{13}C NMR spectra of DBU·HCl, the chemical shifts were sensitive to the used DBU/**1b** molar ratio.

General Procedure for the Reaction of 3a with DBU: To the organic carbonate a measured volume of the amidine base (Table 2) was added. The reaction mixture was stirred at ambient temperature for a given time (4–5 h) and analyzed by NMR (^1H and ^{13}C), using $[D_6]$DMSO (deuterated dimethyl sulfoxide, contained in a coaxial capillary tube) as an external reference, and FTIR. For more details, see Table 2. Besides NMR signals from the reactants **3a** and DBU, there were also signals in the spectra from the products **2a** and phenol (see below). Herein, we report in detail the spectroscopic characterization of the equimolar mixture of **3a** (260 μL, 2.07 mmol)/DBU (300 μL, 2.01 mmol). The characterization data is for the reaction solution. ^1H NMR (400 MHz, 293 K, **3a**): δ = 3.25 (s, OMe), 6.66–6.70 (overlapped m, *para*-H and *ortho*-H), 6.83 (m, *meta*-H) ppm. ^1H NMR (400 MHz, 293 K, DBU): δ = 0.92 (br. m, 3-H), 1.03 (br. m, 4-H and 5-H), 1.15 (quint, 10-H), 1.84 (br. m, 6-H), 2.53 (m, 2-H), 2.56 (t, 9-H or 11-H), 2.71 (t, 9-H or 11-H) ppm. ^1H NMR (400 MHz, 293 K, **2a**): δ = 4.36 (br. t, $^3J_{H,H}$ = 6 Hz, 6-H), 3.09 (s, OMe), 2.99 (t, $^3J_{H,H}$ = 6.8 Hz, 9-H or 11-H), 2.46 (m, 2-H), 2.34 (t, $^3J_{H,H}$ = 6 Hz, 9-H or 11-H), 1.58 (pseudo-q, $^3J_{5\text{-}H,4\text{-}H}$ = 6.2 Hz, 5-H), 1.20 (quint, $^3J_{H,H}$ = 6 Hz, 10-H) ppm. The 3-H and 4-H resonances of **2a** were masked by the signals at 1.15 ppm and 1.03 ppm for DBU, respectively, as ascertained by decoupling experiments. ^1H NMR (400 MHz, 293 K, PhOH): δ = 6.16 (m, *para*-H), 6.35 (dm, *ortho*-H), 6.62 (m, *meta*-H), 13.56 (br., OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, **2a**): δ = 23.10, 24.36, 25.82, 28.27, 42.87, 48.35, 51.51 (OMe), 52.51, 103.73 (C-6), 143.51 (C-7), 154.60 (CO_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, **3a**): δ = 54.36 (OMe), 120.47 (C-*ortho*), 125.25 (C-*para*), 128.84 (C-*meta*), 150.84 (C-*ipso*), 153.36 (CO_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, DBU): δ = 22.17, 25.57, 27.94, 29.05, 35.95, 43.27, 47.43, 51.72, 159.55 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, PhOH): δ = 115.49 and 116.04 (C-*ortho* and C-*para*), 128.44 (C-*meta*), 160.43 (C-*ipso*) ppm. In the proton-coupled spectrum the **2a** resonances assigned to C-6 and OMe were, respectively, a doublet of multiplets ($^1J_{C,H}$ = 158 Hz) and a quartet ($^1J_{C,H}$ = 146 Hz). The FTIR spectrum (liquid film) of the reaction solution showed, besides the signals of **3a** (1767 cm^{-1}, C=O) and DBU (1620 cm^{-1}, C=N), new poorly resolved medium absorptions at 1701 and 1716 cm^{-1} (C=O) due to **2a**.

General Procedure for Reaction of 3c with DBU: To the organic carbonate a measured volume of the amidine base (Table 2) was added. The reaction mixture was stirred at ambient temperature for a given time (5–8 h) and analyzed by NMR (^1H and ^{13}C), using $[D_6]$DMSO (contained in a coaxial capillary tube) as an external reference, and FTIR. For more details, see Table 2. Besides NMR signals from the reactants **3c** and DBU, there were also signals in the spectra from the products **2c** (8-*tert*-butyl 1,8-diazabicyclo[5.4.0]undec-6-ene-8-carboxylate) and phenol (see below). Herein, we report in detail the spectroscopic characterization of the 1:4 (mol/mol) mixture of **3c** (200 μL, 1.08 mmol)/DBU (640 μL, 4.28 mmol). The characterization data is for the reaction solution. ^1H NMR (400 MHz, 293 K, **3c**): δ = 1.12 (s, Me), 6.78 (dm, *ortho*-H), 6.81 (m, *para*-H), 6.98 (m, *meta*-H) ppm. ^1H NMR (400 MHz, 293 K, DBU): δ = 1.01 and 1.18 (br. m, 3-H, 4-H, and 5-H), 1.28 (quint, 10-H), 1.91 (m, 6-H), 2.72–2.79 (overlapped signals, 2-H, 9-H, and 11-H) ppm. ^1H NMR (400 MHz, 293 K, **2c**): δ = 4.38 (br. t, $^3J_{H,H}$ = 6 Hz, 6-H), 3.04 (t, $^3J_{H,H}$ = 6.8 Hz, 9-H or 11-H), 2.56 (m, 2-H), 2.48 (t, $^3J_{H,H}$ = 6 Hz, 9-H or 11-H), 1.68 (pseudo-q, $^3J_{5\text{-}H,6\text{-}H}$ = 6.6 Hz, 5-H), 1.35 (quint, $^3J_{H,H}$ = 6 Hz, 10-H), 1.03 (s, Me) ppm. The 4-H resonance was masked by the signal at 1.10 ppm, as ascertained by decoupling experiments, and the resonance due to 3-H was obscured by the signals of DBU around 1.18 ppm. ^1H NMR (400 MHz, 293 K, PhOH): δ = 6.22 (m, *para*-H), 6.34 (dm, *ortho*-H), 6.68 (m, *meta*-H), 11.5 (v br., OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, **2c**): δ = 23.37, 24.76, 27.56 (Me), 27.88, 29.09, 42.34, 48.58, 52.88, 78.05 (CMe_3), 103.94 (C-6), 144.12 (C-7), 153.44 (CO_2) ppm. $^3C\{^1H\}$ NMR (100 MHz, 293 K, **3c**): δ = 26.82 (Me), 81.95 (CMe_3), 120.74 (C-*ortho*), 125.02 (C-

para), 128.85 (C-*meta*), 150.95 (C-*ipso*), 151.05 (CO_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, DBU): δ = 22.58, 25.92, 28.33, 29.34, 36.48, 43.81, 47.68, 51.90, 158.91 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, PhOH): δ = 115.30 and 116.45 (C-*ortho* and C-*para*), 128.44 (C-*meta*), 159.99 (C-*ipso*) ppm. In the proton-coupled spectrum the **2c** resonance assigned to C-6 was a doublet of multiplets ($^1J_{C,H}$ = 158 Hz). In the region of 2000–1600 cm^{-1}, the FTIR spectrum of this mixture showed the signals of **3c** (1759 cm^{-1}, C=O) and DBU (1620 cm^{-1}, C=N), as well as new medium absorptions at 1694 and 1701 cm^{-1} (shoulder), consistent with the formation of **2c**.

General Procedure of Reaction of 3b with DBU: To the mixture of the organic carbonate and the amidine base (Table 2) a minimum volume of THF was added, in cases where the mixture was heterogeneous at ambient temperature (Table 2). The solution was stirred at ambient temperature for 5 h and analyzed by NMR (^1H and ^{13}C), using [D_6]DMSO (contained in a coaxial capillary tube) as an external reference, and FTIR. For more details, see Table 2. Besides NMR signals from the reactants **3b**, DBU, and THF, if used, there were also signals in the spectra from the products **2b** and phenol (see below). Herein, we report in detail the spectroscopic characterization of the equimolar mixture of **3b** (0.2700 g, 1.26 mmol)/DBU (190 μL, 1.27 mmol) and THF (0.3 mL). The characterization data is for the reaction solution. ^1H NMR (400 MHz, 293 K, THF): δ = 3.05, 1.11 ppm. ^1H NMR (400 MHz, 293 K, DBU): δ = 0.83 (m, 3-H), 0.89–1.02 (overlapped m, 4-H and 5-H), 1.08 (quint, 10-H), 1.81 (m, 6-H), 2.43 (m, 2-H), 2.46 (t, 9-H or 11-H), 2.67 (t, 9-H or 11-H) ppm. ^1H NMR (400 MHz, 293 K, PhOH): δ = 6.14 (m, *para*-H), 6.33 (dm, *ortho*-H), 6.57 (m, *meta*-H), 13.32 (br., OH) ppm. ^1H NMR (400 MHz, 293 K, **2b**): δ = 4.48 (t, br, $^3J_{H,H}$ = 6 Hz, 6-H), 3.03 [9-H or 11-H, masked by the THF signal at 3.05 ppm; when irradiating at 3.03 ppm, the quintet at 1.18 ppm, due to 10-H (see below), converted into a triplet with $^3J_{H,H}$ = 6 Hz], 2.33 (t, $^3J_{H,H}$ = 5.9 Hz, 9-H or 11-H), 1.56 (pseudo-q, $^3J_{5\text{-}H,6\text{-}H}$ = 6.2 Hz, 5-H), 1.18 (quint, $^3J_{H,H}$ = 6 Hz, 10-H), 0.98 (4-H, masked by DBU multiplet between 0.89 and 1.02 ppm; when irradiating at 0.98 ppm, the pseudo-quartet at 1.56 ppm, due to 5-H, converted into a doublet with $^3J_{5\text{-}H,6\text{-}H}$ = 6.2 Hz) ppm. The 2-H and 3-H resonances could not be assigned, as they were masked, respectively, by the DBU signals at approximately 2.3–2.4 ppm and between 0.8–1.0 ppm. The resonances for the *ortho*-H and *meta*-H overlapped with those of **3b** at 6.61 ppm (*para*-H) and 6.70–6.80 ppm (*ortho*-H and *meta*-H). $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, **2b**): δ = 23.07, 24.28, 25.69, 28.14, 43.32, 48.36, 52.42, 104.67 (C-6), 120.97 (C-*ortho*), 124.12 (C-*para*), 128.32 (C-*meta*), 143.19 (C-7), 151.45 (C-*ipso*), 152.27 (CO_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, **3b**): δ = 120.27 (C-*ortho*), 125.50 (C-*para*), 128.88 (C-*meta*), 150.63 (C-*ipso*), 151.13 (CO_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, DBU): δ = 21.95, 25.40, 27.77, 28.93, 35.50, 42.84, 47.35, 51.65, 160.02 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, PhOH): δ = 115.39 and 116.39 (C-*ortho* and C-*para*), 128.39 (C-*meta*), 160.09 (C-*ipso*) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 293 K, THF): δ = 66.81, 24.91 ppm. In the proton-coupled spectrum the resonance assigned to C-6 of **2b** was a doublet of multiplets ($^1J_{C,H}$ = 160 Hz). In the region of 2000–1600 cm^{-1}, the FTIR spectrum (liquid film) of the solution showed the signals of **3b** (1782 cm^{-1}, C=O) and DBU (1620 cm^{-1}, C=N), as well as medium poorly resolved new absorptions at 1716 and 1732 cm^{-1} (C=O), assigned to **2b**.

Reaction of 1b with MeOH in the Presence of a Catalytic Amount of DBU: To a solution of **1b** (99.1 mg, 0.321 mmol) and MeOH (26 μL, 0.642 mmol) in $CDCl_3$ (1 mL), DBU (10 μL, 0.067 mmol) was added. The reaction mixture was stirred for about 1 h at 293 K and then analyzed by ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopy. The NMR spectra showed complete conversion of **1b**. In the ^{13}C NMR spectrum, the generated organic carbonate **3a** produced a characteristic quartet at 153.83 ppm ($^3J_{C,H}$ = 4 Hz) which was assigned to the carbonyl C atom. Minor amounts of DMC and phenol were slowly formed by further reaction of **3a** with an excess amount of methanol. The GC-MS analysis of the reaction solution further confirmed the formation of all the above products.

Reaction of 2a with MeOH: Methanol (0.050 mL; 1.23 mmol) was added to a solution of **2a** (153.0 mg; 0.73 mmol) in $CDCl_3$ (1 mL), and the mixture was stirred at ambient temperature. The quantitative conversion of **2a** into DMC and DBU was monitored by ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopy (see also Figure 3). In the ^{13}C NMR spectrum the organic carbonate (DMC) produced a characteristic septuplet at 155.59 ppm ($^3J_{C,H}$ = 4 Hz) which was assigned to the carbonyl C atom. The formation of the products was further confirmed by GC analysis. In the range of 2000–1600 cm^{-1}, the FTIR spectrum of the solution showed the characteristic absorptions of DMC and DBU at 1755 (C=O) and 1612 cm^{-1} (C=N), respectively.

X-ray Crystallographic Analyses[20–22]

Salt 1a·H_2O: $C_{11}H_{21}Cl_1N_2O_3$, Mr = 264.75, T = 293 K, monoclinic, space group $P2_1/c$, scan type: ω – ϕ, a = 6.6506(4) Å, b = 15.5432(10) Å, c = 13.2041(10) Å, $\alpha = \gamma$ = 90°, β = 90.237(5)°, V = 1364.92(16) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.29 $g\,cm^{-3}$, crystal size: 0.150 × 0.600 × 0.750 mm^3, F(000) = 464, μ(Mo-K_α) = 0.280 mm^{-1}, min. transmission 0.8702, max. transmission: 1.000, $2\theta_{max.}$ = 61.12°, 11826/3855 measured/independent reflections [R(int) = 0.027], 2457/154 reflection used/number of parameters, refinement against |F|, GOF = 1.017, final R indices were R_1 = 0.042 [$I > 3\sigma(I)$] and wR_2 = 0.047 [$I > 3\sigma(I)$], H atoms isotropically refined, residual electron density 0.25/–0.16 e $Å^3$. Mo-K_α radiation (λ = 0.71073). Structure solution obtained by charge flipping method with SUPERFLIP.[20] Least-squares refinement was carried out by CRYSTAL.[21]

Salt 1b: $C_{16}H_{21}Cl_1N_2O_2$, Mr = 308.81, T = 293 K, monoclinic, space group $P2_1/c$, scan type: ω – ϕ, a = 10.1805(2) Å, b = 14.5849(4) Å, c = 10.3843(2) Å, $\alpha = \gamma$ = 90°, β = 100.4040(10)°, V = 1516.53(6) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.35 $g\,cm^{-3}$, crystal size: 0.265 × 0.400 × 0.900 mm^3, F(000) = 604, μ(Mo-K_α) = 0.258 mm^{-1}, min. transmission: 0.9054, max. transmission: 1.000, $2\theta_{max.}$ = 62.06°, 39738/4837 measured/independent reflections [R(int) = 0.026], 3285/190 reflection used/number of parameters, refinement against |F|, GOF = 1.046, final R indices were R_1 = 0.034 [$I > 3\sigma(I)$] and wR_2 = 0.042 [$I > 3\sigma(I)$], H atoms isotropically refined, residual electron density 0.26/–0.13 e $Å^3$. Mo-K_α radiation (λ = 0.71073). Structure solution obtained by charge flipping method with SUPERFLIP.[20] Least-squares refinement was carried out by CRYSTAL.[21]

Acknowledgments

Università degli Studi di Bari (Fondi di Ateneo) and Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) (PRIN 2008A7P7YJ_002) are acknowledged for financial support.

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Received: December 24, 2010
Published Online: March 16, 2011

