Carbonic Acid Diester Activation by Polymer-Bound DBU and Its Relevance to Catalytic N-Carbonylation of N-Heteroaromatics: Direct Evidence for an Elusive N-Carboxy-Substituted Amidinium Cation Intermediate

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**S** *Supporting Information*

ABSTRACT: Polymer-bound DBU (PS-DBU, DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene) is an effective and selective catalyst for solventless N-phenoxycarbonylation of N-heteroaromatics (pyrrole (**1**), indole (**2**), and carbazole (**3**)) with diphenyl carbonate (DPC), used as an eco-friendly active carbonyl species in place of phosgene-derivatives. The immobilized catalyst is less active than unsupported DBU but can be recovered easily at the end of catalytic run and recycled effectively. Dedicated studies have demonstrated that DBU can react as a nucleophile with DPC even when it is anchored on the polymeric matrix, and provided the first direct evidence (FTIR and solid-state ^{13}C NMR) of formation of a 8-carboxy-substituted 1,8-diazabicyclo[5.4.0]undec-7-enium cation in DBU-promoted nucleophilic activation of carbonic acid diesters.

KEYWORDS: *carbamate, carbonylation, DBU, diphenyl carbonate, N-heteroaromatics, organic carbonate, organocatalysis, phosgene substitution*
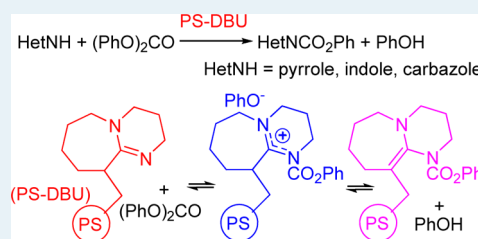
1. INTRODUCTION

As a part of our studies devoted to exploring new ways of activation of carbonic acid diesters,[1,2] currently obtainable through phosgene-free routes,[3−10] and utilizing these compounds as active carbonyl species succedaneous of phosgene in carbonylation processes,[11−18] we have recently reported on a new approach to N-carbonylation of N-heteroaromatics (HetNH) such as pyrrole (**1**), indole (**2**), and carbazole (**3**), which is based on the use of diphenyl carbonate (DPC) as a carbonylating agent (eq 1).[18] In the presence of catalytic
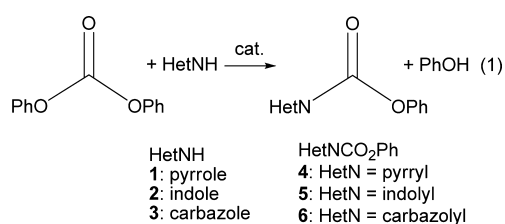
amounts of DBU (≥1 mol % vs HetNH), reaction 1 provides a straightforward selective high-yield entry into heterocarbamates HetNCO₂Ph (**4−6**)[19] through a fully halogen-free synthetic route, which is a safe ecofriendly alternative to classic protocols implying the use of phosgene-derivatives,[32] such as dicarbonates,[23,33a] alkylazidoformates,[33b] 1,1′-carbonyldiimidazole,[34] and

chloroformates.[35] The developed synthetic methodology does not require severe temperature conditions (333−433 K, depending on catalyst load and used substrate) and is solventless, as the organic carbonate, which was reacted in excess with respect to HetNH, served as reactant and solvent. The excess of DPC can be recovered from the reaction mixture in high yield.[18] However, catalyst recycling was not as effective, because DBU catalyst was recovered from reaction mixture in moderate yield and not in a pure form.

In the process (eq 1, cat. = DBU), DBU can act not only as a base catalyst, by activating the HetNH substrate to the relevant more nucleophilic HetN⁻ anion (Scheme 1),[18] but also as a nucleophile,[31,36−41] by activating DPC through the formation of ketene aminal **7a** (Scheme 2).[2,18]

We have documented experimentally that ketene aminals **7** behave as effective "CO₂R" carriers toward NuH pronucleophiles (eq 2) and are more active carbonylating agents not only than the organic carbonate from which they can be generated but also than the relevant alkoxycarbonyl amidinium cation **8** from which they can plausibly form by deprotonation at C6 (Scheme 3).[2,18] DBU itself can act as a proton acceptor, as

Scheme 1. Base Catalysis
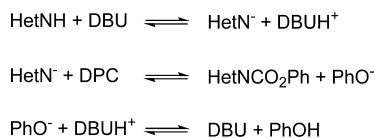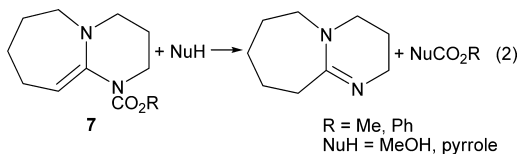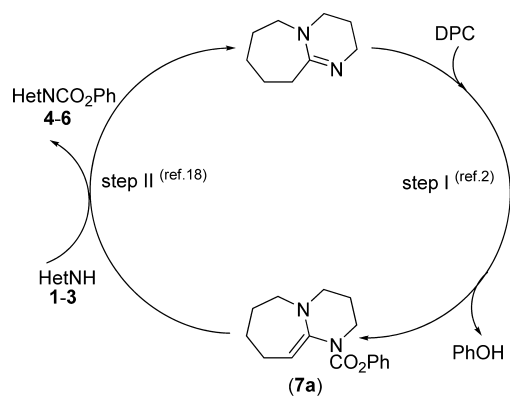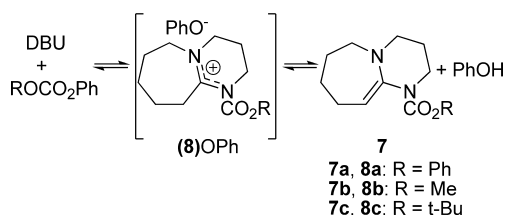

Scheme 2. Nucleophilic Catalysis

$$\text{7} + \text{NuH} \longrightarrow \text{7} + \text{NuCO}_2\text{R} \quad (2)$$

R = Me, Ph
NuH = MeOH, pyrrole

Scheme 3. Reactivity of DBU with Carbonic Acid Diesters[2]

(8)OPh

7
7a, 8a: R = Ph
7b, 8b: R = Me
7c, 8c: R = t-Bu

supported by the reactivity of a few **8** chloride salts toward the amidine base. In fact, we have isolated and fully characterized both salts (**8a**)Cl and (**8b**)Cl·H$_2$O (synthesized by reaction of DBU with the relevant chloroformate), and shown that they can easily convert, respectively, into **7a** and **7b** upon reaction with DBU (Scheme 4).[2,41] However, while ketene aminal **7** can be easily detected spectroscopically (FTIR, NMR) in DBU/

Scheme 4. Synthesis of (8)Cl Salts and Their Reactivity with DBU[2]

(8)Cl

(8a)Cl R = Ph
(8b)Cl R = Me

7
7a R = Ph
7b R = Me
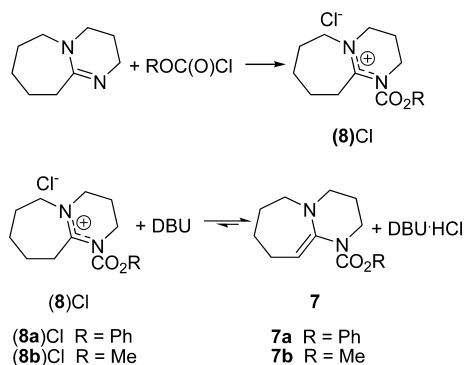
ROC(O)OPh mixtures at the equilibrium with PhOH, the amidine reactant and the relevant carbonic acid diester (Scheme 3), cation **8** still remains a spectroscopically elusive intermediate, in accordance with the fact that **8**, once formed from DBU and the organic carbonate, easily converts into **7** in the presence of free DBU.[2]

As well-known, catalyst anchoring on a suitable polymeric support[42] may facilitate recovery of the catalyst from the reaction mixture and, in principle, may provide a suitable strategy to trap and detect intermediate species bound at the polymeric matrix. We have, therefore, focused on commercially available polystyrene-supported DBU[43−46] (PS-DBU, Chart 1)

Chart 1. Polymer-Bound DBU (PS-DBU) and its N-Phenoxycarbonyl Derivatives A and B
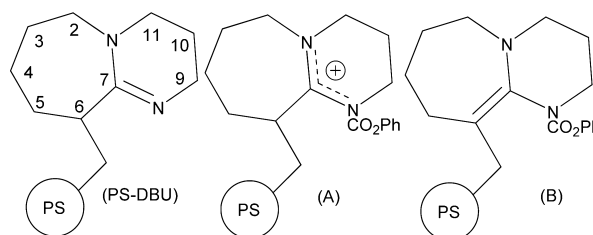
as a potential catalyst of reaction 1. Herein, we report on the catalytic activity of PS-DBU in the carbonylation process (eq 1). We also describe the reactivity of PS-DBU toward DPC, documenting that the amidine catalyst can nucleophilically activate the organic carbonate even when it is immobilized on the polymeric matrix, and, for the first time, provide direct evidence of the formation of a N-carboxy-substituted amidinium cation, like **A**, in the amidine-promoted activation of carbonic acid diesters.

2. EXPERIMENTAL SECTION

2.1. General Methods. Unless otherwise stated, all manipulations were carried out under an inert atmosphere by using vacuum line techniques. All solvents were dried according to conventional methods (P$_2$O$_5$; Na/benzophenone)[47] and stored under N$_2$. DPC, **1**, **2**, and **3** were commercial products. **1** was dried over CaH$_2$, filtered, distilled in vacuo over fresh CaH$_2$, stored and manipulated under N$_2$. PS-DBU (50−100 mesh; 1.83 mmol N/g; 1% cross-linked with divinylbenzene) was from Aldrich and was stored under an inert atmosphere to prevent contamination by atmospheric CO$_2$ and/or moisture.[44,48] In the supported catalyst, DBU is anchored through C6 at the polystyrene matrix (Chart 1). Products **4−6** can be isolated as described elsewhere,[28] after removing the catalyst by filtration (section 2.3).

GC analyses were performed 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 carried out 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). IR spectra were taken on a Shimadzu FTIR Prestige 21 spectropho-tometer or a Perkin-Elmer FTIR 1710 instrument. [13]C cross-polarization magic angle scanning (CP MAS) measurements were performed at 151 MHz on a Bruker AVANCE 600 apparatus equipped with a MAS II Pneumatic Unit, using total suppression of sideband (TOSS) technique. Solid sample was

packed in a 4 mm zirconia rotor with a Kel-F cap and spinned at 11 kHz during the analysis (delay time = 4 s).

2.2. PS-DBU Catalyzed Carbonylation of HetNH with DPC: General Procedure. Typically, into a 30 mL Schlenk tube, containing the catalyst (PS-DBU),[49] DPC and the substrate (HetNH) were added. The reaction mixture was heated in an oil bath to the working temperature, allowed to react for a given time (for further details see Tables 1−4 and

Table 1. Carbonylation of HetNH (1−3) to HetNCO$_2$Ph (4−6) with DPC in the Presence of PS-DBU Catalyst at 393 K

entry	HetNH (mmol)	DPC/HetNH (mol/mol)	catalyst load[a] (%)	t (h)	HetNH conversion (%)
1	**1** (1.20)	3.9	9.8	24	90
2	**2** (1.26)	3.7	8.9	3	96
3	**2** (0.62)	4.2	9.6	3	98
4	**3** (1.13)	4.0	9.9	3	∼100

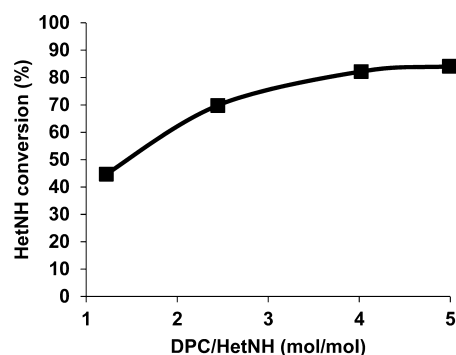[a]Catalyst load = [mol of supported DBU/mol of HetNH]100.

Figure 1. Reaction of HetNH (**3**) with DPC in the presence of PS-DBU: influence of DPC/**3** molar ratio.[50] Reaction conditions: catalyst load, 4.7 ± 0.2 mol %; T, 393 K; reaction time, 2 h. Carbamate selectivity was ≥99% in all the runs.

the legends[50] of Figure 1 and 2), and then cooled to ambient temperature. The solidified mixture was treated with diethyl ether or THF and the liquid phase analyzed by GC (internal standard = n-dodecane) or GC-MS.

2.3. Catalyst Recovery and Recycling. At the end of the catalytic run (section 2.2) the reaction mixture was cooled to room temperature, suspended in diethyl ether or THF, and filtered. The catalyst, which was not soluble in the solvent used, was repeatedly washed with more solvent, and, after drying in vacuo, was reusable for a new run (Figure 3 and Table 5).

2.4. Reaction of PS-DBU with DPC: Typical Procedure. A solventless mixture of PS-DBU and DPC (excess) was stirred at a given temperature (393−443 K) for a measured time, cooled to room temperature and, then, suspended in diethyl ether. The suspension was filtered and the solid material was repeatedly washed on filter with small volumes of diethyl ether, dried in vacuo and analyzed by spectroscopic methods (Figures 5−7). The GC analysis of the combined mother and washing solutions showed the formation of phenol. For further details, see the legends of Figures 5−7.

2.5. Reactivity of DPC-Pretreated PS-DBU with HetNH (Indole). To 87.2 mg of DPC-pretreated PS-DBU (spectrum a, Figure 8), isolated as reported in section 2.4, an excess of **2**

(0.1074 g, 0.90 mmol) was added. The mixture was stirred at 393 K for 3 h, cooled to ambient temperature and suspended in THF. The suspension was filtered and the solid material was repeatedly washed on filter with small volumes of THF to remove unreacted indole, dried in vacuo and analyzed by FTIR spectroscopy (spectrum b, Figure 8). The filtered solution, analyzed by GC-MS, contained, in addition to the excess of **2**, also **5**, (HetN)$_2$CO (HetN, indolyl; MS (70 eV), m/z 260 [M$^+$], 144 [M$^+$ − HetN], 116 [M$^+$ − HetNCO, (base peak)], 89, 69, 57, 44), PhOH, and DPC.

2.5. Reactivity of DPC-Pretreated PS-DBU with HetNH (Pyrrole). To 94.3 mg of DPC-pretreated PS-DBU (spectrum a, Figure 9), isolated as reported in section 2.4, an excess of **1** (0.200 mL, 2.88 mmol) was added. The mixture was stirred at 333 K for 4 h, cooled to ambient temperature and suspended in THF. The suspension was filtered and the solid material, after washing with more THF, was dried in vacuo and analyzed by FTIR spectroscopy (spectrum b, Figure 9). The GC-MS analysis of the filtered solution showed the formation of **4**, (HetN)$_2$CO (HetN, pyrryl; MS (70 eV), m/z 160 [M$^+$], 94 [M$^+$ − HetN], 66 [M$^+$ − HetNCO], 39),[28] PhOH, and DPC.

In an analogous experiment, 46.8 mg of an aged sample of DPC-pretreated PS DBU (spectrum b, Figure 7) were reacted with an excess of **1** (0.200 mL, 2.88 mmol), at 333 K for 4 h. The reaction mixture was worked up as described above. The solid material isolated by filtration did not show any more significant absorptions between 1700 and 1750 cm^{-1} (spectrum d, Figure 7). Also in this case the GC-MS analysis of the filtered solution showed the formation of **4**, (HetN)$_2$CO (HetN, pyrryl), PhOH, and DPC.

3. RESULTS AND DISCUSSION

3.1. Carbonylation of 1−3 with Diphenyl Carbonate: Catalytic Activity of PS-DBU. In this study the activity of PS-DBU as the catalyst of reaction 1 was investigated under solventless conditions (see Introduction). At the working temperature, low-melting DPC (mp = 353 K) acted as reactant and solvent.

Table 1 shows that PS-DBU is an active catalyst for N-phenoxycarbonylation of **1−3** with DPC, albeit less active (Table 2) than unsupported DBU. Under the working conditions (Table 1), both **2** and **3** were carbonylated quantitatively and selectively (≥99%) within a short time (3 h), while selective (∼99%) high yield carbonylation of less reactive pyrrole required longer times (entry 1, Table 1). Immobilization of the amidine catalyst on the polymeric support did not produce any significant decrease of carbamate

Table 2. Carbonylation of HetNH (1−3) to HetNCO$_2$Ph (4−6) with DPC at 393 K: PS-DBU vs DBU Catalytic Activity

entry	HetNH (mmol)	catalyst	DPC/HetNH (mol/mol)	catalyst load (%)	t (h)	HetNH conversion (%)
1	**1** (1.20)	PS-DBU	4.0	9.9[a]	8	61
2	**1** (3.60)	DBU	3.9	9.3[b]	8	83
3	**2** (1.30)	PS-DBU	3.8	9.2[a]	0.5	56
4	**2** (1.24)	DBU	3.8	9.7[b]	0.5	82
5	**3** (1.20)	PS-DBU	3.9	9.2[a]	0.5	54
6	**3** (1.24)	DBU	3.8	9.2[b]	0.5	87

[a][mol of supported DBU/mol of HetNH]100. [b][mol of DBU/mol of HetNH]100.

selectivity relative to unsupported DBU. In fact, ureidic species $(HetN)_2CO$, if any, formed only in trace amounts.

Using **3** as the reference substrate we have investigated the influence of a few reaction parameters on the productivity of the process. Figure 1 illustrates the change of carbazole conversion against the DPC/HetNH (HetNH = **3**) molar ratio, when the reaction was carried out at 393 K, for 2 h, with a DBU load close to 5 mol %. The use of a DPC/HetNH molar ratio higher than 4 did not offer any substantial benefit as it effected only a very modest variation of substrate conversion to carbamate. Conversely, substrate conversion diminished sensibly when using DPC/HetNH molar ratios lower than 4. The observed trend justifies the use of DPC/HetNH molar ratios close to 4 in the present work.

Carbonylation of **3** can be effectively promoted by a catalyst load as low as 1 mol %. Curve a in Figure 2 illustrates the
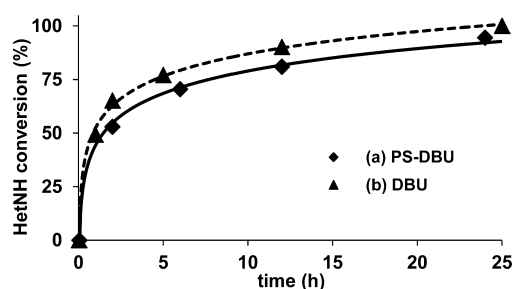

Figure 2. Reaction of HetNH (**3**) with DPC at 393 K.[50] (a) catalyst: PS-DBU; DPC/**3** = 4.0 ± 0.1 mol/mol; catalyst load = 1.0 ± 0.1 mol %. (b) catalyst: DBU; DPC/**3** = 3.9 ± 0.1 mol/mol; catalyst load = 1.1 ± 0.1 mol %. Carbamate selectivity: ≥ 99% in all the runs.

conversion of **3** as a function of time, at 393 K, when using a DPC/HetNH/(supported)DBU molar ratio close to 4:1:0.01. Under the working conditions, carbazole was carbonylated selectively (>99%) and with high yield (95%) within a time as long as 24 h. The carbonylation process proceeded more slowly than with unsupported DBU (curve b in Figure 2).

At the same temperature (393 K), under otherwise similar reaction conditions, indole exhibited a behavior close to that of carbazole (entry 2, Table 3). However, at a markedly lower temperature, carbonylation of **2** (mp: 326 K) or **3** (mp: 520 K) was excessively slow (see, for instance, entry 1 in Table 3, for the specific case of indole). We, therefore, explored the use of higher temperatures. At 433 K, both **2** and **3** were selectively and quantitatively carbonylated within 4 h (entry 4 and 6,

Table 3. N-Phenoxycarbonylation of HetNH (1−3) with DPC Promoted by PS-DBU: Influence of Temperature

entry	HetNH (mmol)	DFC/HetNH (mol/mol)	catalyst load[a] (%)	T (K)	t (h)	HetNH conversion[b] (%)
1	**2** (1.22)	3.9	0.89	343	24	34
2	**2** (2.48)	4.0	0.97	393	24	87
3	**2** (1.56)	4.0	1.0	433	2	91
4	**2** (1.22)	3.9	1.3	433	4	>99
5	**3** (1.51)	4.3	1.1	433	2	93
6	**3** (1.53)	3.8	0.99	433	4	100
7	**1** (1.80)	4.0	0.99	433	24	37
8	**1**(4.86)	4.0	1.0	473	24	81[c]

[a][mol of supported DBU/mol of HetNH]100. [b]Selectivity ≥99%. [c]The reaction was carried out in a steel autoclave.

Table 3). Under analogous experimental conditions, **1**, the least reactive of the substrates investigated, converted into **4** with very modest yield (entry 7, Table 3). Higher conversions of **1** into **4** were achieved by increasing temperature to 473 K (entry 8, Table 3). Under more moderate temperature conditions, good to high conversion of pyrrole into *N*-phenoxycarbonyl pyrrole required either longer times (entry 1, Table 4) or higher catalyst loadings (entries 2−4, Table 4).

Table 4. N-Phenoxycarbonylation of Pyrrole (1) with DPC Promoted by PS-DBU

entry	**1** (mmol)	DFC/**1** (mol/mol)	catalyst load[a] (%)	T (K)	t (h)	HetNH conversion[b] (%)
1	1.84	4.0	1.0	443	48	77
2	1.05	4.0	3.4	443	24	73
3	1.22	4.0	3.4	443	36	97
4	1.20	3.9	9.8	393	24	90

[a][mol of supported DBU/mol of HetNH]100. [b]Selectivity ≥ 99%.

3.1.1. Catalyst Recycling. At the end of the reaction, the catalyst can be easily recovered quantitatively (section 2.3). The recovered catalyst, when reused, displayed a catalytic activity and selectivity comparable with that of fresh PS-DBU, as shown in Figure 3.
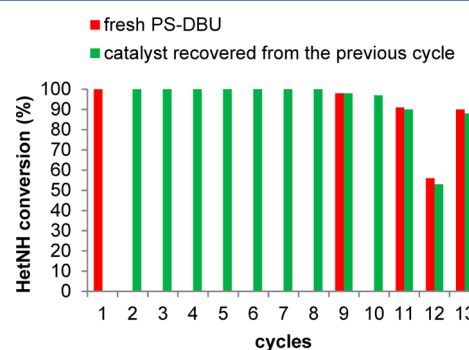
Figure 3. Catalytic N-phenoxycarbonylation of **1**-**3** with DPC: catalyst recycling. Reaction conditions: 393 K, DPC/HetNH ≈ 4 mol/mol, catalyst load = 9−10 mol % vs HetNH. Cycles 1−8: Used HetNH was **3**, reaction time = 3 h. Cycles 9−12: Used HetNH was **2**; cycles 9 and 10, reaction time = 3 h. Cycle 11: Reaction time = 2 h. Cycle 12: Reaction time =0 .5 h. Cycle 13: Used HetNH was **1**, reaction time 24 h. Carbamate selectivity ≳ 99%.

Figure 4 shows the FTIR spectrum of fresh PS-DBU and those of catalyst recovered from a few catalytic runs (see entry 3 in Table 4 and entry 2 in Table 5). The fresh catalyst (spectrum a) displays, in addition to the characteristic bands at 696, 754, and around 1600 cm^{-1} due to the phenyl rings of the polymeric matrix, a poorly resolved absorption around 1616 cm^{-1} assigned to C=N stretching of the anchored DBU moieties. The latter band is found at 1618 cm^{-1} in the FTIR spectrum of neat DBU. Relative to that of fresh PS-DBU, the spectra of the recovered catalysts show a few evident alterations in the region of C=O stretching (1700−1750 cm^{-1}) and in the range 1230−1160 cm^{-1}. The appearance of these new bands, which are related with a structural modification of the catalytic system, and the persistence of the absorption around 1616 cm^{-1} suggest that a few of the anchored DBU molecules may have undergone a phenoxycarbonylation reaction at the iminic

Figure 4. FTIR spectra (2200−500 cm^{-1}, KBr) of (a) PS-DBU, (b) catalyst recovered from run 3 in Table 4, and (c) Catalyst Recovered from Run 2 in Table 5

Table 5. Catalytic N-Phenoxycarbonylation of pyrrole (1) with DPC[a]

run	1 (mmol)	DPC (mmol)	catalyst (g)		1 conversion[b] (%)
			PS-DBU	recovered catalyst	
1	5.81	23.2	0.2151[c]		97
2	5.81	23.1		0.2164[d]	95

[a]Reaction conditions: DPC/HetNH ≈ 4 mol/mol; T = 443 K; reaction time = 36 h. [b]Selectivity to carbamate ≥ 99%. [c]Catalyst load ([mol of supported DBU/mol of HetNH]100): 3.3 mol %. [d]Mass of catalyst recovered from run 1 and reused.

N8 atom by DPC. This prompted us to investigate this issue more deeply, in order to ascertain whether also PS-DBU can nucleophilically activate the organic carbonate as unsupported DBU does.

3.2. PS-DBU-Promoted Activation of DPC. PS-DBU was reacted with an excess of DPC under solventless conditions comparable with those employed in the catalytic runs. The solid material isolated as described in section 2.3 was studied both spectroscopically and from the reactivity point of view.

The FTIR spectrum of the polymeric material isolated after a reaction time of 2 h at 393 K (spectrum b, Figure 5) shows a few evident changes between 1150 and 1200 cm^{-1} and new ν(C=O) bands at 1733 cm^{-1} (poorly resolved) and around 1718 cm^{-1}. The latter absorptions agree well with those observed for **7a** (ν(C=O) = 1717 and 1732 cm^{-1} (shoulder)) or **7b** (ν(C=O) = 1702 and 1717 cm^{-1} (shoulder))[2] and indicate that, likewise unsupported DBU, also polymer-anchored DBU can be N-phenoxycarbonylated by reaction with DPC (eq 3). The reaction cogenerates phenol, which was detected by GC and GC-MS.

Figure 5. FTIR spectra (1800−650 cm^{-1}, KBr) of (a) PS-DBU, (b) PS-DBU pretreated with DPC at 393 K for 2 h (PS-DBU 0.1285 g, 0.116 mmol of supported DBU; DPC 0.5007 g, 2.33 mmol), (c) PS-DBU pretreated with DPC at 393 K for 16 h (PS-DBU 0.2286 g, 0.208 mmol of supported DBU; DPC 0.900 g, 4.20 mmol), and (d) PS-DBU pretreated with DPC at 438 K for 12 h (PS-DBU 0.4219 g, 0.384 mmol of supported DBU; DPC 1.6518 g, 7.71 mmol).

For longer reaction times at the same (393 K) or higher (438 K) temperature an absorption can be noted at higher frequency (spectrum c and d, respectively, in Figure 5). The latter absorption falls in the region wherein ν(C=O) was found in (**8a**)Cl (1764 cm^{-1}, with unresolved shoulder at lower wavenumbers) and (**8b**)Cl (1748 cm^{-1}) salts and is compatible with the formation of (**A**)OPh units, which are the reasonable intermediates through which (**B**) moieties may form. Therefore, solid state CP MAS ^{13}C NMR spectroscopy was used as a diagnostic tool to further substantiate the above assignment. Accordingly, the solid state CP MAS ^{13}C NMR-TOSS spectrum (Figure 6) of PS-DBU pretreated with DPC at 438 K for 12 h (FTIR spectrum: d in Figure 5) showed a signal at 171.8 ppm,[51] which is absent in the spectrum of PS-DBU and can be assigned to C7 carbon of (**A**) moieties by comparison

Figure 6. CP MAS ^{13}C NMR-TOSS spectrum (11 kHz) of (a) PS-DBU and (b) PS-DBU pretreated with DPC at 438 K for 12 h (see also IR spectrum d in Figure 5).

with the ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of (**8a**)Cl (δ = 20.85, 21.54, 24.86, 27.85, 34.04 (C6), 44.56, 52.36, 57.84, 120.72 (C-*ortho*), 126.88 (C-*para*), 129.64 (C-*meta*), 149.61 (C-*ipso*), 150.89 (COO), 172.62 (C7) ppm).[2] The above spectroscopic results provide the first sound experimental evidence of the formation of a N-carboxy-substituted amidinium intermediate, like **A**, in the reaction of DBU with an organic carbonate.

Inspection of Figure 5 shows that **A** moieties can accumulate on the polymeric matrix for longer reaction times. This suggests that conversion of **A** into **B** moieties may become less and less facile as reaction 3 proceeds. Nevertheless, **A** → **B** conversion can occur, albeit very slowly, even at ambient temperature, as it can be inferred by comparing the IR spectrum of a freshly isolated sample of DPC-pretreated PS-DBU (spectrum a, Figure 7; bands at 1750 and 1719 cm^{-1} due to **A** and **B** groups, respectively) with that of the same material aged for a few months at room temperature (spectrum b, Figure 7), which, in the carbonyl region, does not show any more the band at 1750 cm^{-1}, but exhibits only absorptions in the range 1710 −1734 cm^{-1} assignable to **B** groups.
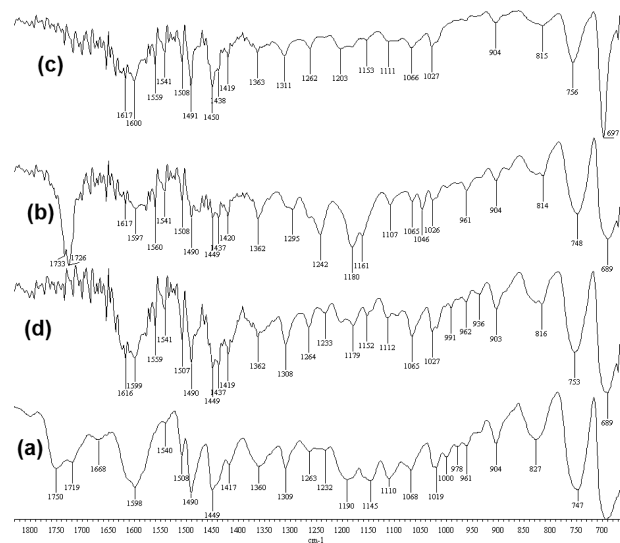

Figure 7. (a) FTIR spectrum (1850−650 cm^{-1}, KBr) of a freshly isolated sample of PS-DBU pretreated with DPC at 443 K for 12 h (PS-DBU 0.271 g, 0.244 mmol of supported DBU; DPC 1.046 g, 4.88 mmol); (b) FTIR spectrum (KBr) of the same material (see above a), after aging for a few months at r.t.; (c) FTIR spectrum (KBr) of the solid material isolated after reacting aged DPC-pretreated PS-DBU (see b) with pyrrole at 333 K for 4 h (section 2.6); and (d) FTIR spectrum (KBr) of PS-DBU.

The reactivity of DPC-pretreated PS-DBU with HetNH (**1**, **2**) is consistent with the above-described chemistry.

For instance, DPC-pretreated PS-DBU (spectrum b, Figure 8) was reacted with an excess of **2** at 393 K for 3 h (section 2.5). The solid material isolated by filtration after suspending the reaction mixture in THF did not show any more significant absorptions in the carbonyl region (spectrum a, Figure 8) and, furthermore, was practically superimposable with that of PS-DBU (spectrum c, Figure 8). Moreover, the GC-MS analysis of the THF solution showed the formation of **5**, together with (HetN)$_2$CO (HetN, indolyl), phenol, and DPC.

Analogous experiments were carried out using pyrrole in place of indole, but under milder conditions (333 K, 4 h, Figure
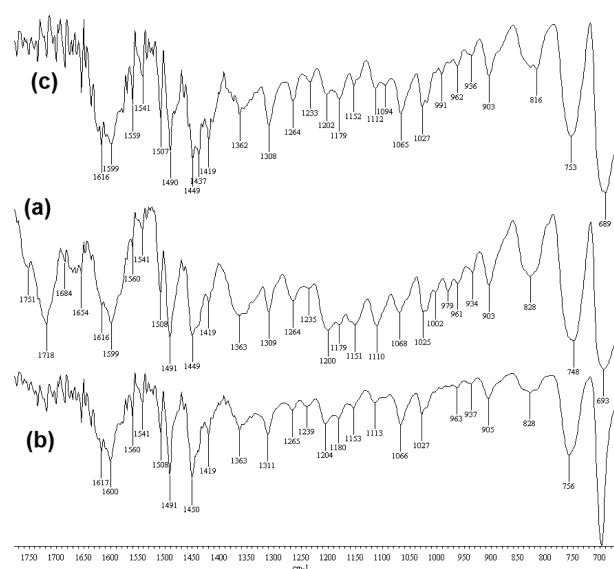

Figure 8. FTIR spectra (1800−650 cm^{-1}, KBr) of (a) PS-DBU pretreated with DPC at 393 K for 16 h (PS-DBU 0.2286 g, 0.208 mmol of supported DBU; DPC 0.900 g, 4.20 mmol), (b) solid material isolated after reacting DPC-pretreated PS-DBU (see a) with indole at 393 K for 3 h (section 2.5), and (c) PS-DBU.

7 and 9). In this case, the GC-MS analysis of the reaction mixtures showed the formation of **4**, in addition to 1,1′-carbonyldipyrrole, PhOH and DPC.
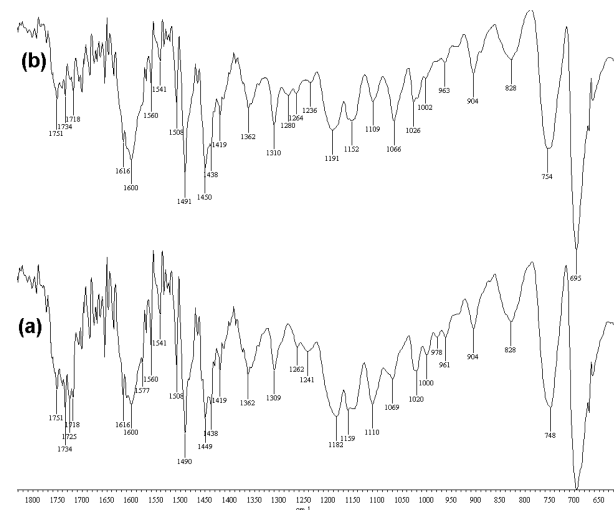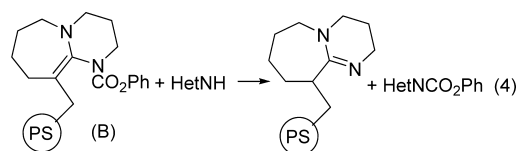

Figure 9. FTIR spectra (1850−600 cm^{-1}, KBr) of (a) PS-DBU pretreated with DPC at 438 K for 12 h (PS-DBU 0.4219 g, 0.384 mmol of supported DBU; DPC 1.6518 g, 7.71 mmol) and (b) solid material isolated after reacting DPC-pretreated PS-DBU (see a) with pyrrole at 333 K for 4 h (section 2.6).

Reaction 4, implying direct N-carbonylation of HetNH by (**B**)-moieties, as well as reaction 5 (which may be promoted by

supported DBU molecules[28]) and the reactivity summarized in Scheme 3, describe plausible ways to the formation of the observed products. We note that reaction 4 is reminiscent of step (II) in Scheme 2 and finds sound experimental support in reaction 2, which we have documented elsewhere.[2,18]
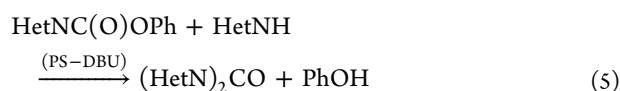
$$\text{HetNC(O)OPh} + \text{HetNH}$$
$$\xrightarrow{\text{(PS-DBU)}} (\text{HetN})_2\text{CO} + \text{PhOH} \qquad (5)$$

Figure 9 deserves an additional comment. In the spectrum of the solid isolated after reaction with pyrrole (spectrum b) the relative intensities of the residual absorptions assigned to **A** (1751 cm^{-1}) and **B** moieties ($1700-1734 \text{ cm}^{-1}$) changed with respect to those observed in the starting material (spectrum a), suggesting that, under the mild (333 K) working conditions used, **B** residues react more easily than **A** moieties. This agrees well with our previous findings showing that ketene aminal **7** is a more active carbonylating agent of pyrrole than the corresponding N-alkoxycarbonyl amidinium cation (**8**).[2,18]

As a whole, the body of the above results demonstrates unambiguously that also PS-DBU, likewise unsupported DBU, can nucleophilically activate the organic carbonate and can act as a nucleophile catalyst in reaction 1 (see Scheme 2). However, considering the well-known ability of PS-DBU to act as a proton acceptor,[42] we cannot exclude, also in the present case, the co-occurrence of a basic mechanism involving the activation of HetNH substrate, as described in Scheme 1 for the unsupported catalyst. It is reasonable to expect that DBU anchorage at the polymeric matrix may hamper, for steric reasons,[42-45] the nucleophilic pathway (Scheme 2) more markedly than the proton transfer reaction between the HetNH substrate and the immobilized base. This may offer a plausible rationale for the lower activity exhibited by PS-DBU compared to the unsupported catalyst.

4. CONCLUSIONS

The activity of polymer-bound DBU as catalyst for carbonylation of N-heteroaromatics, such as pyrrole, indole and carbazole, with diphenyl carbonate has been investigated under solventless conditions. PS-DBU is an efficient and selective catalyst for N-phenoxycarbonylation of **1−3** but is less active than unsupported DBU. However, immobilization of DBU allows the quantitative recovery of the catalytic system which can be reused without any substantial decrease both of activity and selectivity. The easy quantitative recovery of the catalyst, as well as its effective reutilization, markedly improve the greenness of the synthetic method, and make profitable the use of more massive catalyst loadings, which allow to conjugate the achievement of very high conversions within reasonable reaction times with more moderate energy inputs.

Ad hoc studies have demonstrated that DBU can nucleophilically activate DPC even when the amidine base is supported on the polymeric matrix and provided, for the first time, direct evidence of the intermediacy of a N-carboxy-substituted amidinium cation in the DBU-promoted activation of a carbonic acid diester.

ASSOCIATED CONTENT

ⓢ Supporting Information

Spectroscopic characterization of compounds **4−6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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(19) HetNCO$_2$R (R = alkyl, aryl) carbamates are important synthetic intermediates for the preparation of a variety of chemicals, including pharmaceutically relevant substances (epibatidine and derivatives; epiboxidine and other 7-azabicyclo[2.2.1]heptanes), biologically active compounds (alkaloids) and more complex heterocyclic systems.[20−26] Under suitable conditions, N-phenoxycarbonyl derivatives HetN-CO$_2$Ph (HetNH = **1−3**) can act as carbonylating agents and are converted easily into unsymmetrical ureas HetNC(O)NR$_2$[27] or, by transesterification with alcohols, into HetNCO$_2$R compounds,[28] which are useful precursors of the corresponding N-alkyl derivatives HetNR (R = alkyl).[29−31]
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(49) mmol of supported DBU = $[(m(g)_{PS-DBU}) \bullet (1.83 \text{ mmol N/g})]/2$.

(50) The experimental points in Figure 1 and 2 have been obtained according to the protocol described in section 2.2. The legends of the figures report the mean values of the DPC/HetNH molar ratio or the catalyst load ([mol of (supported) DBU/mol of HetNH]100).

(51) The signal at 151.8 ppm (Figure 6) can be attributed to carbonyl carbon of **A** or **B** moieties. Herein, we report, as a comparison, also the ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **7a**: δ = 23.38, 24.46, 25.88, 28.26, 43.75, 48.97, 52.88, 106.04 (C6), 121.31 (C-*ortho*), 124.71 (C-*para*), 128.76 (C-*meta*), 142.83 (C7), 151.25 (C-*ipso*), 153.18 (COO) ppm.[2] By comparison with the ^{13}C spectrum of

PS-DBU, the resonance at 158.8 ppm is assigned to C7 of unreacted polymer-bound DBU molecules, the presence of which is also supported by the absorption around 1616 cm^{-1} (section 3.1.1) in the FTIR spectrum of the isolated material. The strong signals at 145.9, 128.2, ~50, 41.2, and 40.6 ppm are due to the carbons (aromatic and aliphatic) of the polymeric matrix (PS), while the resonances at 65.9 and 15.3 ppm (masking signals formerly present in the spectrum of PS-DBU) may be due to residual amounts of diethyl ether, used in the workup of the reaction mixture (section 2.4).