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Superbase-promoted direct N-carbonylation of pyrrole with carbonic acid diesters

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Abstract

Carbonic acid diesters have been investigated as *carbonylating agents* in the direct reaction with pyrrole (HetNH). In the presence of superbases (DBU, P_1-*t*-Bu, BTPP) as catalysts, the heteroaromatic substrate can be N-carbonylated by *direct* reaction with carbonic acid diesters under not-severe experimental conditions. The carbonylation reaction makes accessible pyrrole *N*-carbonyl derivatives (HetNC(O)OR, $(HetN)_2CO$) selectively through a simple straightforward way, which offers a safe eco-friendly alternative to the traditional synthetic methods based on hazardous phosgene or phosgene-derivatives.

Keywords: Organic carbonates; Catalysis; Pyrrole; Carbonylation; Phosgene substitution

The development of environmentally improved new synthetic routes, which are as much direct as possible and resort to the use of safe and nontoxic starting materials, is a major target of modern chemistry of synthesis. Due to worldwide awareness of environmental hazards of phosgene and governmental policies for environment protection, a series of efforts are currently being focussed on replacing $COCl_2$ in organic synthesis.

Organic carbonates are nowadays obtainable through phosgene-free routes even on industrial scale[1a] and are receiving growing attention as eco-friendly safe and nontoxic phosgene substitutes in carbonylation reactions of amines for the synthesis of carbamates, isocyanates, and ureas.[1] However, much less is known on their use for direct carbonylation of N-heteroaromatic compounds.[2] In principle, this approach (Eqs. 1 and 2) is an attractive route to the synthesis of pyrrole *N*-carbonyl derivatives, HetNC(O)Z (HetNH = pyrrole; Z = OR, OAr, HetN), well-known compounds widely

$$\mathrm{HetNH} + (\mathrm{RO})_2\mathrm{CO} \rightarrow \mathrm{HetNC(O)OR} + \mathrm{ROH} \quad (1)$$

$$2\mathrm{HetNH} + (\mathrm{RO})_2\mathrm{CO} \rightarrow (\mathrm{HetN})_2\mathrm{C(O)} + 2\mathrm{ROH} \quad (2)$$

used as intermediates or starting materials in the synthesis of a variety of fine chemicals, drugs and biologically active substances (epibatidine and derivatives, tropane alkaloids, etc.).[3–6] Such compounds are traditionally synthesized from toxic and harmful phosgene[5] or $COCl_2$-derivatives (dicarbonates,[7] alkyl-azidoformates,[8] 1,1′-carbonyldiimidazole,[6,9] chloroformates[10]) through procedures which, often, require the preliminary conversion of pyrrole into a more nucleophilic metal pyrryl salt.[5,8,10] A more recent and complex synthetic approach, requiring two moles of pyrrole per mole of HetNC(O)Z product, is based on the activation of pyrrole-1-carboxylic acid.[11]

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So far, the *direct* reaction of pyrrole with carbonic acid diesters has received very poor attention.[†] In this work organic carbonates, including industrially relevant dimethyl carbonate (DMC), methyl phenyl carbonate (MPC) and diphenyl carbonate (DPC), have been investigated as *carbonylating agents* in the direct reaction with pyrrole to obtain HetNC(O)Z derivatives. This reaction requires a suitable catalyst and, herein, we also show that superbases, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or phosphazenes, are effective catalysts for the relevant carbonylation process.

The direct reaction of pyrrole with DPC has never been studied in the past. No significant reaction has been observed when pyrrole and DPC (1:3.9 mol/mol) were heated at 393 K for 8 h. However, addition of DBU modified the reactivity of the system. In fact, under very mild conditions, DBU can promote effectively the direct carbonylation of pyrrole with DPC to give both HetNC(O)OPh (**1**) and $(HetN)_2CO$ (**2**) (Eqs. 1 and 2, R = Ph) in relative yields, which depend on the working conditions. Figure 1 illustrates the results obtained, at 293 K, using a homogeneous 2:2:1 (mol/mol) mixture of pyrrole, DBU and DPC. The conversion of pyrrole was not complete even after a long time (≈50% after 24 h) and **1** was obtained as main product. Figure 1 also suggests that an equilibrium state is likely reached under the used conditions. Accordingly, the use of a great excess of pyrrole versus DPC increased the formation of **2** with respect to **1**. For instance, after 24 h at 293 K, **1** and **2** were obtained in approximately equimolar amounts, when pyrrole (14.41 mmol), DBU (2.95 mmol) and DPC (1.45 mmol) were allowed to react in a 10:2:1 molar ratio. Under the working conditions, the conversion of DPC was practically quantitative in less than 6 h. Work-up of reaction mixture afforded **2** in 48% yield. To date, this is the sole example of synthesis of **2** through a route that avoids the use of phosgene[5] or a phosgene derivative such as 1,1′-carbonyldiimidazole.[6,9]

The reactivity of system was directed towards the selective formation of **1** by modifying suitably the experimental conditions. At 333 K, a 1:1:3.9 (mol/mol) mixture of pyrrole, DBU and DPC afforded **1** in high yield and selectively (⩾99%) within short times (3 h; Table 1, entry 1).[‡] 1,1′-carbonyldipyrrole, $(HetN)_2CO$, formed only in trace amounts. Table 1 (entries 2 and 3) shows clearly that the carbonylation process is promoted also by catalytic amounts (10 mol %) of the amidine base. Under the latter conditions, however, quantitative conversion to **1** required longer reaction times and higher temperatures. Product **1** has been isolated in high yield (≈90%). Moreover, most of the excess of DPC (up to 90%) can be recovered.

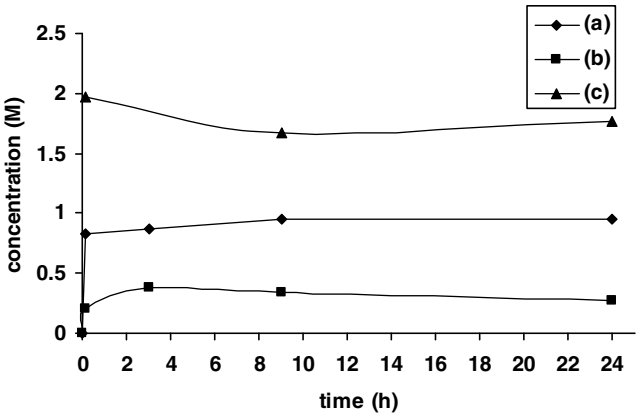


Fig. 1. Reaction of pyrrole (9.51 mmol) with DPC (4.72 mmol) in the presence of DBU (9.37 mmol) at 293 K. (a): **1**; (b): **2**; (c) pyrrole.

Table 1
Carbonylation of HetNH (pyrrole, indole, carbazole) to HetNC(O)OPh with DPC (HetNH/DPC ≈ 1:4 mol/mol) in the presence of DBU[a]

Entry	HetNH	mmol of			T[b] (K)	t (h)	HetNH GC-conversion[c] (%)
		HetNH	DPC	DBU			
1	Pyrrole	3.60	14.12	3.68	333	3	97
2	Pyrrole	3.60	14.00	0.335	343	24	62
3	Pyrrole	3.60	14.04	0.335	393	24	98
4	Indole	3.69	14.07	3.68	333	3	100
5	Carbazole	3.59	14.03	3.68	333	3	100

[a] Selectivity to HetNC(O)OPh was ⩾99% in all the runs. $(HetN)_2CO$, if any, formed in trace amounts.
[b] The reaction mixture was homogeneous at the working temperature.
[c] *n*-Dodecane was used as internal standard.

Also indole and carbazole were easily converted in high yield into the corresponding *N*-phenoxycarbonyl derivatives by reaction with DPC, under conditions analogous to those employed for pyrrole. Entries 4 and 5 in Table 1 summarize the results obtained when DBU has been used in equimolar ratio with respect to the heteroaromatic substrate HetNH (indole, carbazole). Both 1-phenoxycarbonyl indole (**3**) and 9-phenoxycarbonyl carbazole (**4**) have been isolated in good yield (76% and 80%, respectively).[§] The

[†] A few early works have dealt with the reaction of HetNM salts (M = K, Na, Li, MgBr) with DMC[12a] or $(EtO)_2CO$[10c,12a] or $^tBuOC(O)OPh$.[12b] Recently, as a part of a study on the use of DMC as *methylating agent* of N-heterocyclic compounds,[13] it has been briefly reported that $(Bu_4N)Br$ (8 mol %) catalyzes the reaction of pyrrole with DMC to give 1-methylpyrrole (HetNMe) and HetNC(O)OMe as major products. After 24 h at 393 K total conversion of pyrrole was attained, but the reaction was not selective (HetNC(O)OMe: 51%; HetNMe: 36%). At 383 K, the process was more selective (HetNC(O)OMe: 92%; HetNMe: 4%), but the conversion rate of pyrrole was divided by two.

[‡] DPC has been used as reagent and reaction medium: the reaction mixture, heterogeneous at 293 K, became rapidly homogeneous at 333 K. In the present study, solvent-free conditions have been employed deliberately in view of the current widespread attention for solventless processes.

[§] 1-Phenoxycarbonyl indole is a well-known compound, which is traditionally synthesized by reaction with phenyl chloroformate,[14a,d] or by reaction of indole with 1,1′-carbonyldiimidazole and phenol in the presence of DMAP,[14c] or by coupling of PhONa with indole-1-carboxylic acid anhydride according to the method developed by Patel.[14b] To the best of our knowledge, the carbazole derivative **4** is a new compound which has been fully characterized by spectroscopic methods (IR, NMR, MS).

Table 2
Carbonylation of pyrrole (HetNH) to HetNC(O)OR with carbonic acid diesters in the presence of superbases

Entry	Carbonate	Base	mmol of			Molar ratio (mol/mol)			T (K)	t (h)	Yield[a] (%)
			HetNH	Base	Carbonate	HetNH	Base	Carbonate			
1	DMC	DBU	3.60	3.68	11.88	1	1	3.3	293	27	15
2	DMC	DBU	0.706	0.709	2.38	1	1	3.4	393	1.5	30
3	DMC	P_1-*t*-Bu	0.706	0.071	11.88	1	0.1	16.8	393	3	60
4	DMC	BTPP	0.706	0.072	11.88	1	0.1	16.8	393	3	66
5	DMC	BTPP	0.706	0.072	11.88	1	0.1	16.8	393	6.5	68
6	DBzC	BTPP	0.706	0.072	6.37	1	0.1	9.0	393	5.5	32
7	DBzC	BTPP	0.360	0.036	6.00	1	0.1	16.7	393	7	42
8	DBzC	BTPP	0.360	0.036	5.82	1	0.1	16.2	393	24	65
9	MPC	DBU	0.706	0.736	3.15	1	1	4.5	293	28.5	75[b,c]
10	MPC	DBU	0.706	0.736	3.15	1	1	4.5	333	5	88[c]
11	MPC	DBU	0.706	0.074	3.15	1	0.1	4.5	333	24	23[c]
12	MPC	DBU	0.706	0.074	3.15	1	0.1	4.5	363	24	40[d]
13	MPC	DBU	0.706	0.074	3.15	1	0.1	4.5	393	24	47[e]
14	*t*-BuPC	DBU	0.706	0.736	3.15	1	1	4.4	293	93	⩽1[b]
15	*t*-BuPC	DBU	0.706	0.736	3.15	1	1	4.4	333	24	7
16	*t*-BuPC	DBU	0.706	0.736	3.15	1	1	4.4	363	44	35[f]
17	*t*-BuPC	DBU	0.706	0.736	3.15	1	1	4.4	393	25	Traces[g]
18	*t*-BuPC	BTPP	0.360	0.327	1.57	1	1	4.4	293	41	21[b]
19	*t*-BuPC	BTPP	0.360	0.327	1.57	1	1	4.4	363	25	78
20	*t*-BuPC	BTPP	0.360	0.327	1.57	1	1	4.4	393	12	2[h]

[a] HetNC(O)OR GC-yield (internal standard: *n*-dodecane).
[b] Under comparable conditions, but in the absence of any catalyst, no reaction was observed.
[c] Yield of **1**: <1%.
[d] Yield of **1**: 2%.
[e] Yield of **1**: 12%.
[f] After 24 h, **8** yield was 26%.
[g] Pyrrole conversion was equal to 35%. After 1 h at 393 K, minor amounts of **8** were clearly evident in the reaction mixture.
[h] Pyrrole conversion was 6%. After 3 h at 393 K, the yield of **8** was equal to 41%.

studies in progress are turned to make possible both the quantitative recovery and the recycling of catalysts.

DBU also promoted the carbonylation of pyrrole with DMC to HetNC(O)OMe (**5**). At 293 K, the methoxycarbonylation was very selective (100%) but proceeded slowly in low yield (Table 2, entry 1). At more elevated temperatures (Table 2, entry 2) **5** formed in higher yield, but less selectively (83%) because of significant side-production of 1-methylpyrrole (**6**) since the beginning of the run.

We have focussed, therefore, on base catalysts other than DBU. We have found that, in the temperature range explored (293–393 K), phosphazenes, such as tBuN = P(NMe$_2$)$_3$ (P_1-*t*-Bu) and tBuN = P(NC$_4$H$_8$)$_3$ (BTPP), are effective and selective catalysts for the direct methoxycarbonylation of pyrrole with DMC. Entries 3 and 4 (Table 2) summarize the results obtained at 393 K in the presence of a catalytic amount (10 mol %) of phosphazene and using DMC both as a reagent and solvent (DMC/pyrrole = 17 mol/mol). Besides **5**, HetNMe also formed as the side-product, but in very low amounts as long as reaction times were short. At 393 K (Table 2, entries 3 and 4), **5** can be obtained in good yields (60–66%) and with high selectivity (⩾98%) within ≈3 h. To our knowledge, these results do not find any better precedent in the literature. BTPP was found to be a more effective catalyst than P_1-*t*-Bu, in accordance with the fact that BTPP is both a stronger base and a more powerful nucleophile than P_1-*t*-Bu.[15]

The selectivity of N-methoxycarbonylation diminished with time because of the progressive formation of **6**.[¶] For instance, entry 5 in Table 2 shows that, after 6.5 h at 393 K, in the presence of BTPP as the catalyst, the yield of **5** was only slightly higher (68%), but selectivity was less satisfactory (95%). The phosphazene catalyst deactivated by converting into OP(NR$_2$)$_3$ (NR$_2$ = NMe$_2$ or NC$_4$H$_8$), without any catalytic activity. At 393 K (Table 2, entries 3 and 4), the deactivation of phosphazene was still modest for short reaction times. In fact, after 2–3 h, most of the catalyst was still active and, after stopping the catalytic run, can be separated from the reaction mixture to be reused.[‖]

[¶] The reaction of pyrrole with DMC, used as *methylating* substrate in place of harmful conventional methylating agents such as CH_3I or dimethyl sulfate,[16] is currently under study as eco-friendly way to the synthesis of **6**. For instance, we have found that, after 23 h at 393 K, a mixture of pyrrole (0.708 mmol), DMC (11.87 mmol) and P_1-*t*-Bu (0.708 mmol) gave **6** in 97% yield.

[‖] The recovery of BTPP, which is less volatile than P_1-*t*-Bu, was easily achieved by distilling in vacuo, at 293 K, the reaction mixture. The distillate contained **5**, with unreacted pyrrole and DMC as main components, but not BTPP (by GC), which, together with minor amounts of OP(NC$_4$H$_8$)$_3$, was the major component of the poorly volatile distillation residue.

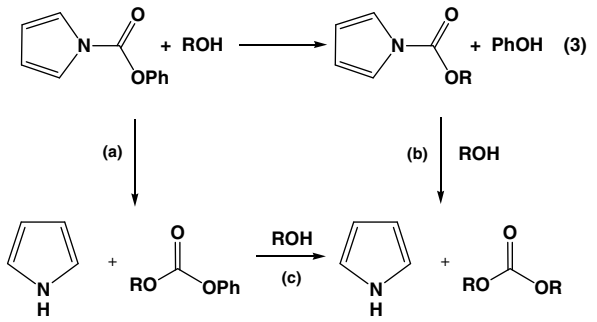
BTPP, in catalytic amount (10 mol %), also promoted the N-benzyloxycarbonylation of pyrrole with dibenzyl carbonate. At 393 K, depending on the working conditions (Table 2, entries 6–8), 1-benzyloxycarbonyl pyrrole (**7**) has been obtained in 32–65% yield. Remarkably, 1-benzylpyrrole did not form under the employed conditions.

We have also investigated the reaction of pyrrole with a few alkyl aryl carbonates. In the presence of an equimolar amount of DBU, pyrrole reacted with an excess of MPC (MPC/pyrrole = 4.5 mol/mol), under very mild conditions (293–333 K), to give HetNC(O)OMe (**5**) in good yield (75–88%) within reasonable times (Table 2, entries 9 and 10). The formation of **5** was also promoted by catalytic amounts of DBU versus pyrrole (Table 2, entries 11–13).

In principle, the reaction of pyrrole with MPC may afford the methylation of heteroaromatic ring or also result in the co-formation of **1**. However, under the conditions used in entries 9–13 (Table 2), we have never observed the formation of methylated pyrroles. Moreover, the formation of **1** is absolutely negligible at the lowest working temperatures (Table 2, entries 9–11), but becomes more important at 393 K (Table 2, entry 13). Elevated temperatures (393 K) also promote the side-production of noticeable amounts of anisole and the formation of DMC and DPC. The incidence of these side-processes was negligible at the lowest temperatures investigated (Table 2, entries 9–11). The formation of anisole implies the decarboxylation of the alkyl aryl carbonate, a well-known process which may be promoted by guanidine bases or also Lewis acids.[17] In an *ad-hoc* experiment, we ascertained the formation of anisole when DBU and MPC (1:4.5 mol/mol) were reacted at 393 K for 24 h.

t-Butyl phenyl carbonate (*t*-BuPC) was less reactive than MPC (in Table 2, compare entries 14 and 15 with entries 9 and 10, respectively). At 363 K, in the presence of an equimolar amount of DBU versus pyrrole, the heteroaromatic substrate reacted with *t*-BuPC to give 1-*t*-butyloxycarbonyl pyrrole (**8**) in modest yield (Table 2, entry 16). Under comparable conditions, BTPP was more efficient than DBU (in Table 2, compare entries 18 and 19 with entries 14 and 16, respectively). In the temperature range 293–363 K (Table 2, entries 14–16, 18 and 19), side-products such as *t*-BuOPh or **1**, if any, were formed only in traces or minor amounts. Whatever catalyst (BTPP or DBU) was used, increasing temperature to 393 K (Table 2, entries 17 and 20) caused a drastic reduction of yield of **8**, which, under the working conditions, further reacted with time to give back pyrrole or to produce other species (including trace amounts of alkylation products of pyrrole (123 *m*/*z*)). The highest temperature (393 K) also promoted the extended decarboxylation of the organic carbonate.[††]

All the described carbonylation reactions (Eqs. 1 and 2) were very regioselective. In no case we have found any evidence of formation of C-carbonylation products (2-pyrrole esters, 1,2′-dipyrrylketone, etc.). This feature deserves attention as such species may form in variable amounts depending on the conditions employed, when HetNM salts are reacted stoichiometrically with organic carbonates[10c,12a] or chloroformates.[10c]



Scheme 1.

The easy selective access to 1-phenoxycarbonyl pyrrole, HetNC(O)OPh (Eq. 1, R = Ph), prompted us to explore also the reactivity of **1** with alcohols (Eq. 3, Scheme 1). In principle, reaction (3) offers another potential solution for the synthesis of 1-alkoxycarbonyl pyrroles, which may prove a useful synthetic route when the direct way (Eq. 1) is less convenient or not at all practicable (for instance, if the relevant organic carbonate is not readily accessible). To date, we have found no examples of transesterification reactions of HetNC(O)Z (HetNH = pyrrole; Z = OR, OAr) compounds with alcohols. Herein, we focus on the reactions of **1** with a few alcohols, such as MeOH, $PhCH_2OH$ and the more sterically crowded *t*-BuOH, which allow to emphasize different types of reactivity. Moreover, the relevant –C(O)OR (R = Me, $PhCH_2$, *t*-Bu) groups are often used to protect the N-atom of pyrrole in a variety of reactions.[3,4]

At 293 K, in the absence of any catalyst, **1** reacted readily with anhydrous MeOH (MeOH/**1** = 500 mol/mol) to give **5** selectively (100%). Under the working conditions, the conversion of **1** was already as high as 96% after 7 h and practically quantitative (≈100%) within 22 h. The absence of by-products, such as pyrrole and methyl phenyl carbonate or DMC, is noteworthy as it indicates (see Scheme 1) that (i) the attack of MeOH to **1** causes the selective expulsion of phenoxo- instead of pyrryl-group and (ii) **5** does not react with MeOH in the absence of any catalyst.

Also $PhCH_2OH$ reacted selectively with **1** (ROH/**1** = 29 mol/mol) to give 1-benzyloxycarbonyl pyrrole, but in poor yield (even after 17.5 h at 348 K). The high yield conversion of **1** into **7** can be attained in the presence of a base, like DBU. At 293 K, **1** (0.801 mmol) reacted readily with a modest excess (≈10%) of $PhCH_2OH$ in diethyl ether (1 mL) containing DBU (0.802 mmol). The conversion of **1** was practically quantitative within 6 h and afforded **7** in high yield (80%, isolated). However, the presence of DBU promoted also the formation of other species, such as pyrrole and dibenzyl carbonate. Scheme 1 (see a–c)

[††] The GC–MS analysis of the reaction mixture showed the formation of *t*-BuOPh (150*m*/*z*) and minor amounts of *t*-butyl phenol isomers (150 *m*/*z*).

describes a few plausible reaction pathways for the formation of these species. The GC analysis of the reaction solution also showed the formation of $PhOCH_2Ph$. On the whole, the incidence of these side-reactions was very modest, as, under the working conditions (after 6 h, at 293 K), pyrrole yield did not exceed 7%. By the same method 1-*t*-butyloxycarbonyl pyrrole was also obtained (40% GC yield), but under less mild reaction conditions (24 h at 378 K; *t*-BuOH/DBU/**1** = 147:1:1 mol/mol), as the system *t*-BuOH/**1** was less reactive, even in the presence of the amidine base. The formation of **8** was accompanied by a pronounced formation of pyrrole. These findings show that reaction (3) is very sensitive to the structure of alcohol used. Moreover, DBU can effectively promote the transesterification reaction, but the amidine base may also open other reaction pathways which may reduce the selectivity of the transesterification process.

In summary, for the first time, the reactivity of pyrrole towards carbonylating agents as carbonic acid diesters has been explored. In the presence of superbases (P_1-*t*-Bu, BTPP, DBU) as catalysts, pyrrole (HetNH) can be easily and selectively carbonylated at the N-atom by direct reaction with organic carbonates. The carbonylation reaction does not require severe experimental conditions and makes accessible pyrrole *N*-carbonyl derivatives (HetNC(O)OR, $(HetN)_2CO$)[18] through a simple straightforward way which avoids the traditional phosgene-based methods involving stoichiometric steps and co-production of wasted salts. We have also demonstrated that 1-phenoxycarbonyl pyrrole, easily obtainable from pyrrole and DPC in high yield, is a suitable starting material for the synthesis of alkoxycarbonyl pyrroles by transesterification with alcohols.[18] Further applications of these methods, as well as the mechanistic features of the reported processes, are under investigation.

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18. *Experimental*: 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) and stored under N_2. DMC was dried over 5 A molecular sieves for 24 h, filtered, distilled, and stored under N_2. Pyrrole was dried over CaH_2, filtered, distilled in vacuo over fresh CaH_2 and stored under N_2. The organic carbonates, except for MPC,[19] were commercial products (Fluka, Aldrich). DBU and the phosphazene bases (Fluka, Aldrich) were used as received and stored under an inert atmosphere.
Carbonylation of HetNH (pyrrole, indole, carbazole) with DPC in the presence of DBU: The reaction mixture containing HetNH, DPC and the base, after reacting at the working temperature, was cooled to room temperature, if necessary, and dissolved in diethyl ether. The ethereal solution was washed with water and dried over $MgSO_4$. The product (**1** or **2** or **3**) was isolated by (flash)-chromatography on a silica gel column using, as eluent, 20:1 (v/v) petroleum ether/ethyl acetate for **1**, 10:1 (v/v) petroleum ether/diethyl ether for **2** and 20:1 (v/v) petroleum ether/diethyl ether in the case of **3**. The isolation of **4** required a different procedure. In this case the ethereal solution was evaporated in vacuo. The carbazole derivative **4** was isolated from the residue by washings with methanol, because of limited solubility of **4** in the alcohol solvent.
Carbonylation of pyrrole with dialkyl- or alkyl aryl carbonates in the presence of superbases (DBU, P_1-t-Bu, BTPP). General procedure: Into a 30 mL Schlenk tube, containing pyrrole and the organic carbonate (DMC or MPC, etc.), the catalyst (DBU or phosphazene) and *n*-dodecane (internal standard) were added. The mixture was allowed to react at the working temperature for a measured time and analyzed by GC or GC–MS.
Reaction of 1-phenoxycarbonyl pyrrole with alcohols. General procedure: Into a 30 mL Schlenk tube, containing **1**, the anhydrous alcohol and, if used, DBU and diethyl ether, the internal standard (*n*-dodecane) was added. The reaction mixture was allowed to react at

the working temperature and, at measured intervals of time, analyzed by GC or GC–MS. The product **7** was isolated by fractionating the reaction solution on a silica gel thin layer with petroleum ether/diethyl ether (10:1 v/v).

Spectroscopic data. Compound **1**: IR (Nujol, cm^{-1}): 1769vs (CO). ^1H NMR (acetone-d_6, 500 MHz): δ 6.35 (t, 2H, H_β), 7.32–7.39 (m, 3H, H_{para} and H_{ortho}), 7.42 (t, 2H, $J = 2.3$ Hz, H_α), 7.46–7.52 (m, 2H, H_{meta}). ^{13}C NMR (acetone-d_6, 125 MHz): δ 113.75 (C_β), 121.21(C_α), 122.36, 127.23 and 130.41 ($C_{ortho,\ meta,\ para}$), 149.42 (C=O), 151.43 (C_{ipso}). MS (EI, 70 eV) m/z: 187 ($M^{+\cdot}$), 143, 115, 94, 77, 66, 51, 39. Compound **2**: IR (Nujol, cm^{-1}): 1734vs (CO). ^1H NMR ($CDCl_3$, 400 MHz) δ: 6.36 (t, 4H, $J = 2.2$ Hz, H_β), 7.30 (t, 4H, $J = 2.2$ Hz, H_α). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 113.24 (C_β), 121.95 (C_α), 148.01 (C=O). MS (EI, 70 eV) m/z: 160 ($M^{+\cdot}$), 94, 66, 39. Compound **3**: IR (Nujol, cm^{-1}): 1751vs (CO). ^1H NMR (CD_3CN, 500 MHz): δ 6.76 (dd, 1H, $J = 3.7$ and 1 Hz, H3), 7.29 (td, 1H), 7.32–7.39 (m, 4H), 7.49 (m, 2H, H_{meta}), 7.65 (dt, 1H, $J = 8$ Hz, H4), 7.82 (d, 1H, $J = 3.7$ Hz, H2), 8.20 (d, 1H, $J = 8.4$ Hz, H7). ^{13}C NMR (CD_3CN, 100 MHz): δ 109.46, 115.75 and 116.02, 122.16, 122.72, 124.25, 125.53 and 125.59, 126.94 and 127.07, 127.39, 130.61 (slightly br), 131.59, 136.39 (slightly br), 150.28 (slightly br), 151.42. MS (EI, 70 eV) m/z: 237 ($M^{+\cdot}$), 193, 144, 116, 89, 77, 65, 63, 51, 39. Compound **4**: IR (Nujol, cm^{-1}): 3076, 3061, 3042, 3032 (w), 1736vs (C=O), 1599mw, 1485m, 1446s, 1366s, 1332m, 1304m, 1250m, 1219m, 1204s, 1157m, 1115mw, 1070m, 1022mw, 929w, 850w, 754s, 723ms, 692m. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.34–7.44 (m, 5H), 7.47–7.53 (m, 4H), 8.01 (d, 2H, $J = 7.6$ Hz), 8.38 (d, 2H, $J = 8.1$ Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 116.49, 119.77, 121.76, 123.79, 126.22, 126.51, 127.43, 129.74, 138.12, 150.11, 150.79. MS (EI, 70 eV) m/z: 287 ($M^{+\cdot}$), 194, 166, 140, 115, 89, 77, 65, 63, 51, 39. Compound **7**: IR (neat, cm^{-1}): 1748vs (CO). ^1H NMR ($CDCl_3$, 400 MHz): δ 5.37 (s, 2H, OCH_2), 6.25 (t, 2H, $J = 2$ Hz, H_β), 7.31 (t, 2H, $J = 2$ Hz, H_α), 7.36–7.46 (m, 5H, $H_{aromatics}$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 68.81 (OCH_2), 112.46 (C_β), 120.05 (C_α), 128.35, 128.64, 128.67 ($C_{ortho,\ meta,\ para}$), 134.85 (C_{ipso}), 150.23 (C(O)O). MS (EI, 70 eV) m/z: 201 ($M^{+\cdot}$), 157, 123, 110, 91, 77, 65, 51, 39.

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