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Biomimetic Building-up of the Carbamic Moiety: the Intermediacy of Carboxyphosphate Analogues in the Synthesis of N-Aryl Carbamate Esters from Arylamines and Organic Carbonates Promoted by Phosphorus Acids.

Michele Aresta*, Chiara Berloco and Eugenio Quaranta

Dipartimento di Chimica, Università di Bari, Campus Universitario, 70126, Bari, Italy

and

Centro CNR-MISO, Via Amendola, 173, 70126, Bari, Italy

Abstract: The reaction of aromatic amines with dimethyl carbonate (DMC) or diphenyl carbonate (DPC) in the presence of organo-phosphorus acids [$Ph_2P(O)OH$ (**1**); $(PhO)_2P(O)OH$ (**2**); $(BuO)_2P(O)OH$/$(BuO)P(O)(OH)_2$ equimolar mixture (**3**)] affords carbamate esters, $ArNHC(O)OR$ (R = Me, Ph) with high selectivity. The catalytic role played by the P-acid has been investigated and rationalized in terms of a reaction mechanism involving the intermediate formation of a carbonic-phosphinic(phosphoric) anhydride $X_2P(O)OC(O)OR$ (X = Ph, PhO; R = Me, Ph). The proposed mechanism shows intriguing analogies with the mechanism of formation of carbamate anion in living systems by carbamoyl phosphate synthetase (CPS) enzyme.

INTRODUCTION

Carbamate esters[1] represent a very interesting class of organic compounds because of their widespread utilization in several fields (pharmacolgy, agriculture and chemical industry).[2] They are usually synthesized by: *(a)* reaction of phosgene with an alcohol, followed by aminolysis of the intermediate chloroformate; *(b)* reaction of an alcohol with isocyanates, usually obtained from phosgene.[1,3] However, both methods require the utilization of toxic and harmful compounds and much effort is currently lavished by several researchers on setting up new alternative clean synthetic methodologies based on the use of less dangerous starting materials.

Among the methods that avoid the use of phosgene or isocyanates, homogeneous catalytic carbonylation of nitroaromatics[4] and oxidative carbonylation of amines[5] have received considerable attention. Carbon dioxide also represents a good substitute for phosgene for the synthesis of carbamate esters[6] that can be easily prepared from amines, CO_2 and alkyl halides under very mild conditions.[7]

The reaction of organic carbonates with amines (eq. 1)[8] represents another attractive synthetic way to carbamates that has gained growing attention in the last few years in view of the fact that non-phosgene routes to organic carbonates are now available. Nowadays, in fact, dimethyl carbonate (DMC) can be produced on

$$RR'NH + R''OC(O)OR'' \text{ --------> } RR'NC(O)OR'' + R''OH \qquad (1)$$

R, R' = H, alkyl or aryl
R'' = alkyl or aryl

large-scale by oxidative carbonylation of methanol[9] and other organic carbonates can be easily obtained by transesterification of DMC or diethyl carbonate with phenols[10] or high-boiling alcohols.[11]

Reaction 1 usually needs a suitable catalyst in order to observe good conversion rates and selectivities. Lewis acids, such as $AlCl_3$, $SnCl_2$, $ZnCl_2$, $Zn(O_2CCH_3)_2{\cdot}2H_2O$, $FeCl_3$, or metal (Rh, Ru) complexes, can catalytically promote the selective formation of *N*-propyl ethyl carbamate from *n*-propylamine and diethyl carbonate.[12] Recently, we have demonstrated that CO_2 itself is an effective catalyst for the synthesis of *N*-alkyl methyl carbamates from aliphatic amines and DMC.[13] Attempts to extend this reaction to the carbomethoxylation of aromatic amines failed, most probably because of the lower nucleophilicity of aromatic amines.

Carboalkoxylation of anilines, and more generally of aromatic amines, has been achieved using catalysts such as Zn, Co, Sn, Al, or Ti derivatives,[14] as well as strong bases (alkali alkoxides) in drastic conditions.[15] These processes seem to involve either the activation of an aromatic amine by a base or activation of the organic carbonate by a Lewis acid.

It is also well known that several carboxylating enzymes (carbamoyl phosphate synthetase CPS, biotin dependent carboxylases, phosphoenolpyruvate carboxylase) use bicarbonate, a poor electrophile that is activated through the formation of a carboxyphosphate species, $^-OC(O)OP(O)O_2^{2-}$, resulting from the interaction of HCO_3^- anion with ATP (eq. 2).[16] Very interestingly, in natural systems CPS also promotes the

$$ATP + HCO_3^- \text{------>} ADP + {}^-OC(O)OP(O)O_2^{2-} \qquad (2)$$

reaction of $^-OC(O)OP(O)O_2^{2-}$ with ammonia (eq. 3) to produce carbamate anion, which is phosphorylated

$$^-OC(O)OP(O)O_2^{2-} + NH_3 \text{------>} H_2NCO_2^- + HOP(O)O_2^{2-} \qquad (3)$$

in a subsequent step.[17]

With the idea that carbonic acid diesters could be activated towards nucleophilic attack in an analogous way, we have extended our previous investigations on the aminolysis of organic carbonates[13] to the reaction of aromatic amines with DMC or diphenyl carbonate (DPC) using organo-phosphorus Brœnsted acids as promoters. In this paper we describe the synthesis of a few *N*-aryl-carbamates from arylamines and DPC or DMC in the presence of organo-phosphorus acids. The catalytic role played by the P-acid in promoting the formation of carbamate esters has been investigated and the reactivity of isolated phosphocarbonates, potential intermediates in the reaction, studied. Such species have been postulated by several researchers, but very few spectroscopic data are available in the literature.[16]

RESULTS AND DISCUSSION

Synthesis of N-arylcarbamate esters

The direct reaction of aniline with DMC at 363 K (≥ 9 days) does not produce organic carbamate: after 4 days, only modest amounts (< 2%) of methylation products (PhMeNH, $PhNMe_2$) were formed. At the same

temperature, DPC reacts with aniline to give very low yield of PhNHC(O)OPh (2.2 %, after 5 days) together with little diphenylurea. The formation of both these products is totally repressed at 343 K.

Aromatic amines show a poorer reactivity towards both DMC and DPC than the aliphatic ones, whose reactivity towards DMC we have described in detail in a previous paper.[13a] DPC also reacts with aliphatic amines. For example, DPC and benzylamine at 293 K in THF give *N*-benzyl phenyl carbamate in 80 % isolated yield.[18]

Table 1 reports the results of the reaction of DPC with aniline in the presence of $Ph_2P(O)OH$ (**1**) (THF as solvent). At 343 K, PhNHC(O)OPh is obtained with 50-60 % yield and practically 100 % selectivity (entry 1, Table 1). Working at an higher temperature (363 K) in the presence of an excess of aniline increases the yield to 70 % and shortens the reaction time (entry 3, Table 1). At 393 K, in the presence of a modest excess of DPC, the conversion of aniline into the carbamate is almost quantitative in 15 h and the reaction is still very selective (> 99 %) (entry 5, Table 1). We have found that prolonging the reaction time at a given temperature increases the conversion yield, that approaches 100 %, but depletes the selectivity due to formation of DPU (entry 4 and 6, Table 1) according to reaction 4 (if an excess of aniline is present) and/or 5.

$$\text{PhNHC(O)OPh} + \text{PhNH}_2 \xrightarrow{\text{Ph}_2\text{P(O)OH}} \text{PhNHC(O)NHPh} + \text{PhOH} \qquad (4)$$

$$2\ \text{PhNHC(O)OPh} \xrightarrow{\text{Ph}_2\text{P(O)OH}} \text{PhNHC(O)NHPh} + \text{PhOC(O)OPh} \qquad (5)$$

Compound **1** is also an active catalyst for the synthesis of *N*-1-naphthyl phenyl carbamate from 1-aminonaphthalene and DPC. Because of the poorer reactivity of 1-aminonaphthalene with respect to aniline, lower carbamate yields were observed. In fact, in THF solution, *N*-1-naphthyl phenyl carbamate was isolated as a pure violet microcrystalline solid with yields ranging from 30 to 40 % according to the temperature and reaction time.

Only scant information is found in the literature on the acylation of aromatic amines by unactivated arylcarbonates to give *N*-aryl aryl carbamates.[14d] Metal (Zn, Sn) halides or salts[14d] or 2-hydroxypyridine[19] have been used as catalysts. In general, a major problem concerns the selectivity of the reaction because of the side-production, among other products, of substituted ureas ArNHC(O)NHAr. Our results show that aminolysis of DPC by aromatic amines can successfully be accomplished with 100 % selectivity using **1**. Moreover, the catalyst can be easily and quantitatively recovered as arylammonium salt at the end of the reaction and recycled. Thereof, the carbamate is not contaminated by phosphorus. These features make reaction 6 (R = Ph; P-acid = $Ph_2P(O)OH$) very attractive from a practical point of view.

$$\text{ArNH}_2 + \text{ROC(O)OR} \xrightarrow{\text{P-acid}} \text{ArNHC(O)OR} + \text{ROH} \qquad (6)$$

These results prompted us to investigate the utilization of **1** and other organo-phosphorus acids as promoters in the reaction of arylamines with the less reactive dimethyl carbonate (DMC).

Table 1. Formation of PhNHC(O)OPh from Diphenyl carbonate (DPC) and Aniline in the Presence of $Ph_2P(O)OH$ (1).[a]

Entry	DPC (mmol)	$PhNH_2$ (mmol)	THF (mL)	$PhNH_2/(1)$[b]	$PhNH_2/DPC$[c]	$DPC/(1)$[d]	T (K)	time (h)	$PhNHCO_2Ph$[c] % yield	PhNHC(O)NHPh % yield
1	5.37	5.48	5	16.4	1.02	16.1	343	45	51[e]	*f*
2	10.9	11.4	20	21.1	1.04	20.3	363	20	50[e](55)[g]	*f*
3	1.10	10.9	5	159	9.96	16.0	363	4.5	70[g]	*f*
4	1.10	10.9	5	159	9.96	16.0	363	76	85[g]	8[g]
5	3.27	1.20	5	15.8	0.37	42.7	393	15	98[g]	*f*
6	3.27	1.20	5	15.8	0.37	42.7	393	48	90[g]	10[g]

[a] All runs were carried out in THF, under N_2 (0.1 MPa). [b] $PhNH_2/Ph_2P(O)OH$ molar ratio. [c] $PhNH_2/DPC$ molar ratio. [d] $DPC/Ph_2P(O)OH$ molar ratio. [e] Isolated yield. [f] Traces. [g] HPLC yield.

Table 2. Formation of PhNHC(O)OMe from Dimethyl carbonate (DMC) and Aniline in the Presence of Organo-Phosphorus Acids ("P").[a]

Entry	"P"	DMC (mL)	$PhNH_2$ (mmol)	$PhNH_2/"P"$[b]	T (K)	time (d)	$PhNHCO_2Me$[c] % yield	Carb/"P"[d]	Ph(Me)NH[c] % yield	$PhNMe_2$[c] % yield
1	$(BuO)_2P(O)OH/BuOP(O)(OH)_2$[e]	22	21.9	11.4	363	4	15	1.7	*f*	*g*
2	$(BuO)_2P(O)OH/BuOP(O)(OH)_2$[e]	22	21.9	5.7	363	4	20	1.2	*f*	*g*
3	$(BuO)_2P(O)OH/BuOP(O)(OH)_2$[e]	22	21.9	5.7	363	8.5	36	2.1	*f*	*g*
4	$(BuO)_2P(O)OH/BuOP(O)(OH)_2$[e]	22	21.9	5.7	343	8	0.1	-	*f*	*g*
5	$Ph_2P(O)OH$	5	5.5	15.7	363	4	16	2.5	2.1	0.4
6	$(PhO)_2P(O)OH$	5	5.5	15.7	363	4	5.5	0.88	2.1	0.4

[a] All runs were carried out under N_2 (0.1 MPa). [b] Aniline/"P"-acid molar ratio. [c] GC yield based on aniline. [d] Mol of PhNHC(O)OMe formed *per* mol of "P"-acid used. [e] A commercial equimolar mixture of acids was used. [f] Traces as determined by GC-MS. [g] Traces as determined by GC-MS.

Table 2 shows that, at 363 K, the formation of *N*-phenyl methyl carbamate from DMC and aniline can be promoted by organo-phosphorus Brœnsted acids ("P"), such as **1**, $(PhO)_2P(O)OH$ (**2**) or, even, a commercial equimolar mixture of $(BuO)_2P(O)OH$ and $(BuO)P(O)(OH)_2$ (**3**). The conversion rate may appear, at a first glance, of modest relevance from a practical point of view. Nevertheless, the high selectivity (practically 100 %) makes this class of catalyst attractive as methylation is repressed. Moreover, the phosphorus catalyst is recovered and does not contaminate the final product. Among the acids we tested until now, the best catalytic activity was shown by **1**.

Reaction 6 (Ar = Ph; R = Me) has usually been carried out under an inert gas atmosphere (N_2), using DMC as solvent, under homogeneous conditions at 363 K. At this temperature, in fact, the anilinium salt of the P-acid is soluble in DMC, while separates at room temperature (293 K). At intermediate temperatures, anilinium salt solubilization may be incomplete and this results in lower yield of the carbamate ester (entry 4, Table 2).

Role of the P-acid

In order to shed light on the role played by the P-acid, we have investigated the reactivity of aniline towards DMC or DPC in the presence of other Brœnsted acids.

Aniline (2 mL, 21.9 mmol) and DMC (20 mL) do not afford the carbamate in the presence of $PhNH_3Cl$ (11.0 mmol) at 363 K after 9 days. Only traces of *N*-phenyl methyl carbamate were formed when aniline (0.5 mL, 5.48 mmol) and DMC (5 mL) were homogeneously reacted in the presence of triflic acid (0.925 mmol, $PhNH_2/CF_3SO_3H$ molar ratio = 5.9) at 363 K. Conversely, after 7 days at this temperature the reaction produced *N*-methylaniline (19 %) and *N,N*-dimethylaniline (4 %). Formation of carbamate ester was observed in low yield using trifluoroacetic acid as promoter. After 8 days at 363 K the reaction of aniline (0.5 mL, 5.48 mmol) with DMC (5 mL) in the presence of $CF_3C(O)OH$ (0.348 mmol, $PhNH_2$/acid molar ratio = 15.7) afforded organic carbamate (6.2 %), *N*-methylaniline (3.4 %) and *N,N*-dimethylaniline (0.5 %). However, degradation of the catalyst took place under the working conditions as it was converted into *N*-phenyltrifluoroacetamide, $CF_3C(O)NH(Ph)$. These results account for the specificity of the catalytic role of the organo-phosphorus acids.

Figure 1 shows the kinetics of formation of PhNHC(O)OPh from aniline and DPC in the presence of various Brœnsted acids at 363 K. The experimental data confirm that strong acids, such as HCl or triflic acid, are not very effective catalysts. It is reasonable to suppose that, under the working conditions (excess of aniline), these species convert into the respective anilinium salts (eq. 7) that, as we have discussed above, are poor catalysts:

$$HX + PhNH_2 \text{ ------> } PhNH_3X \qquad (7)$$

$$X = Cl^-, CF_3SO_3^-$$

Indeed, the kinetics observed in the presence of HCl or triflic acid are very similar. These results are reminiscent of the modest catalytic effect played by pyrrolidinium ion, when added as perchlorate salt, in the aminolysis of phenyl or *p*-chlorophenyl *p*-nitrobenzoate by pyrrolidine.[20] If the operating mechanism were the same, the anilinium ion should accelerate the reaction of DPC with aniline by donating a proton to the

departing phenolic oxygen and assisting the collapse of the tetrahedral intermediate generated by the interaction of the amine with DPC.

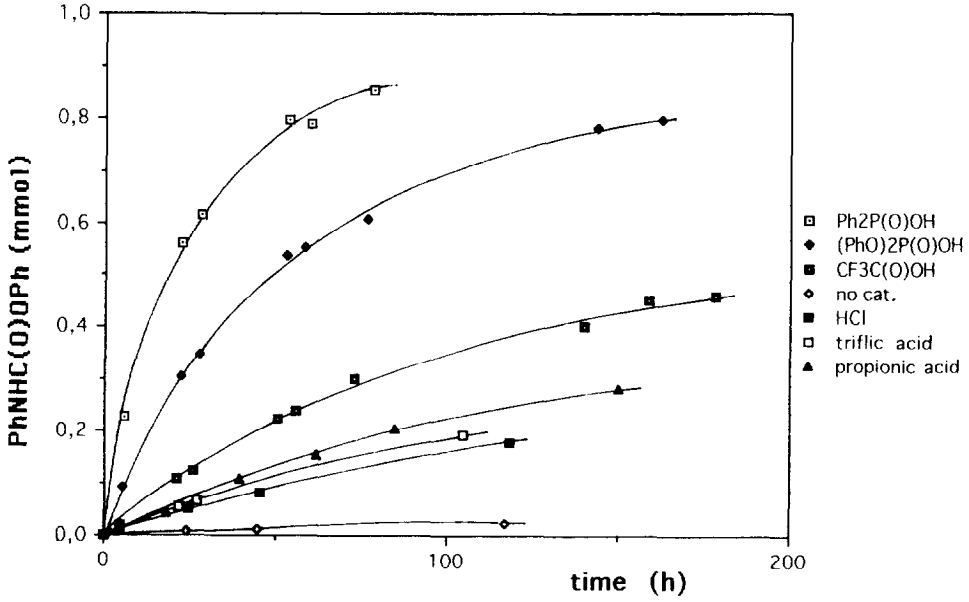
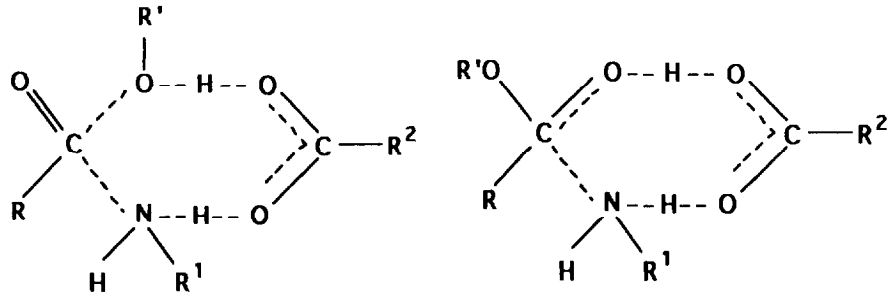


Fig. 1 Kinetics of formation of PhNHC(O)OPh from aniline (0.11 mL, 1.20 mmol) and DPC (1.10 mmol) in the presence of various Brœnsted acids [363 K; solvent: THF (5 mL)]. ⊡ Catalyst: 1; $PhNH_2$/1 molar ratio = 17.6. ◆ Catalyst: 2; $PhNH_2$/2 molar ratio = 17.6. ◘ Catalyst: $CF_3C(O)OH$; $PhNH_2/CF_3C(O)OH$ molar ratio = 18.5. ▲ Catalyst: $C_2H_5C(O)OH$; $PhNH_2/C_2H_5C(O)OH$ molar ratio = 18.0. □ Catalyst: CF_3SO_3H; $PhNH_2/CF_3SO_3H$ molar ratio = 17.7. ■ Catalyst: HCl (added to the reactant solution as $PhNH_3Cl$ (0.067 mmol); $PhNH_2$/HCl molar ratio = 18.6. ◇ No catalyst.

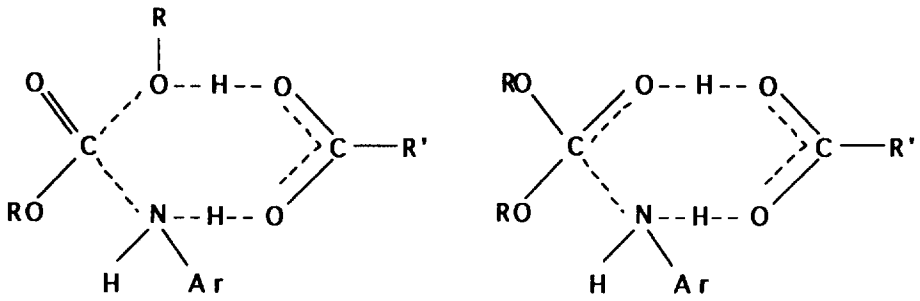
Carboxylic acids, such as propionic acid (pKa = 4.87)[21] and trifluoroacetic acid[22] (pKa = 0.52),[23] show a modest catalytic activity.

The ability of carboxylic acids to promote the aminolysis of esters, or other acid derivatives, is well documented in the literature.[24] As far their role is concerned, either an "acid" or a "bifunctional" catalysis could be invoked. The latter requires the formation of an eight-membered cyclic transition state [(**A**) or (**B**)]



(A) (B)

involving the carboxylic acid, the attacking amine and the carbonylic substrate. Such mechanism could take place also in the aminolysis of DPC by aniline in the presence of catalytic amounts of RC(O)OH [see (**C**) or (**D**)]. The hypothesis that a "pure acid catalysis" is operating (trifluoroacetic acid is a better catalyst for



(C) R = Me, Ph (D)

reaction 6 (R = Ph) than the weaker propionic acid) is ruled out by the fact that a stronger acid such as HCl has almost no catalytic activity.

Phosphorus-acids are by far better catalysts, and **1** and **2** are particularly active. The behaviour of **1** has been investigated in greater detail. Figure 2 shows some kinetic results for the formation of

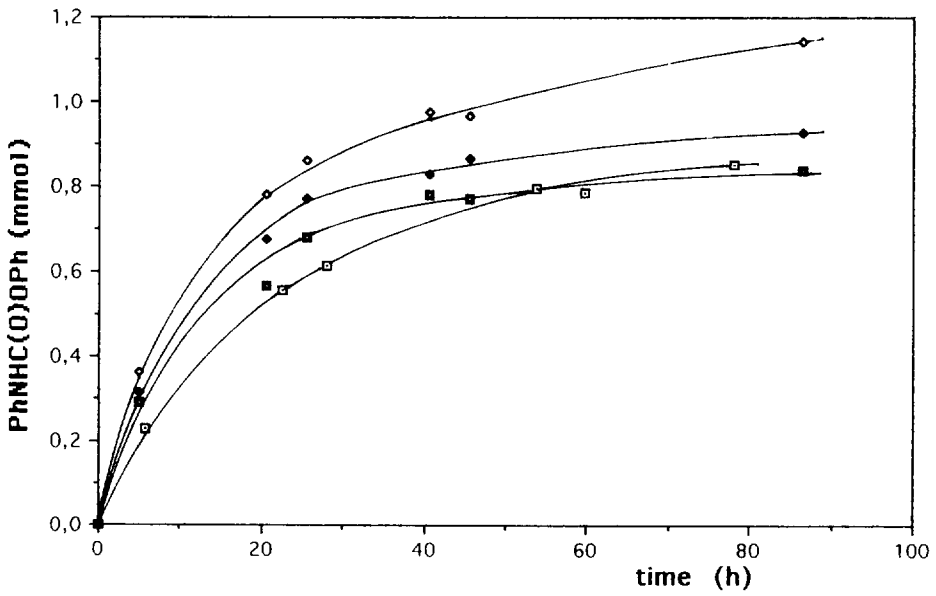


Fig. 2. Kinetics of formation of PhNHC(O)OPh from aniline and **1** in THF (5 mL) at 363 K. Working conditions: ⊡ $PhNH_2$ (1.20 mmol), DPC (1.10 mmol), **1** (0.068 mmol). ◆ $PhNH_2$ (2.40 mmol), DPC (1.10 mmol), **1** (0.068 mmol). ■ $PhNH_2$ (1.20 mmol), DPC (1.10 mmol), **1** (0137 mmol). ◇ $PhNH_2$ (1.20 mmol), DPC (2.20 mmol), **1** (0.068 mmol).

PhNHC(O)OPh from aniline, DPC and **1**, in THF (5 mL) at 363 K, as function of the molar ratio of the three reactants. The data show that the reaction rate depends on the concentration of each of the reagents.

In principle, both **1** and **2** might act as "bifunctional" catalysts, likewise carboxylic acids. However, the fact that they show a catalytic activity markedly higher than $CF_3C(O)OH$ and $CH_3CH_2C(O)OH$, despite their acid strength (in water)[25] is roughly intermediate between that exhibited by the two carboxylic acids considered, suggests that P-acids promote carbamate formation through a different reaction pathway.

Scheme 1 summarizes a plausible alternative mechanism for the aminolysis of organic carbonates in the presence of the organo-phospho-acids we have investigated.

Scheme 1

$$X_2P(O)OH + PhNH_2 \text{ ====== } X_2P(O)O^- {}^+H_3NPh \quad (8)$$

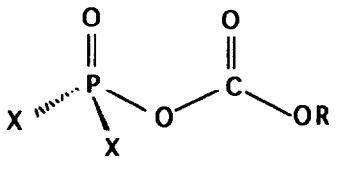
$$X_2P(O)O^- {}^+H_3NPh + (RO)_2C{=}O \text{ ---> } X_2P(O)OC(O)OR + ROH + PhNH_2 \quad (9)$$

$$PhNH_2 + X_2P(O)OC(O)OR \text{ -----> } X_2P(O)OH + PhNHC(O)OR \quad (10)$$

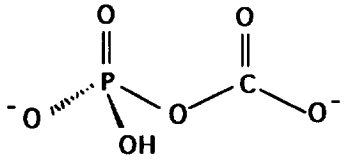
R = Ph, Me; X = Ph, PhO

This mechanism calls for a specific role of the conjugated base of the acid, through the intermediate formation of a carbonic diphenyl-phosphinic(phosphoric) mixed anhydride $X_2P(O)OC(O)OR$, that, upon reaction with the free aromatic amine, converts into the carbamate ester, regenerating, thus, the acid catalyst, $X_2P(O)OH$.[28]

The proposed mechanism shows interesting analogies with that suggested for several enzymatic reactions involving HCO_3^- as carboxylating agent. As shown below, the mixed anhydride $X_2P(O)OC(O)OR$ (**G**) is structurally reminiscent of carboxyphosphate $(HO)OP(O)OCO_2^{2-}$ (**H**), that represents the key



(G)



(H)

intermediate involved in living systems in the carboxylation reactions using HCO_3^- instead of CO_2, as a source of carbon. Interestingly, $X_2P(O)OC(O)OR$ and $(HO)OP(O)OCO_2^{2-}$ represent the activated form of $(RO)_2C{=}O$ and HCO_3^-, respectively. Furthermore, reaction 10 of Scheme 1 involves the building-up of a carbamic function through a route that reminds the synthesis of carbamate anion from ammonia and $(HO)OP(O)OCO_2^{2-}$ by CPS enzyme.

The suggested mechanism (Scheme 1), based on "nucleophilic catalysis", provides a rationale for explaining both the higher activity of P-acids with respect to common Broensted acids and carboxylic acids, and the better performance of **1** with respect to **2**, owing to the stronger nucleophilicity of $Ph_2P(O)O^-$ with respect to $(PhO)_2P(O)O^-$.

However, our attempts to further support this hypothesis by isolating the mixed anhydride (**G**) from the reaction mixture were not successful in the reaction conditions. Lowering the temperature to 293 K caused slowing down of reaction 6 (R = Me, Ph; P-acid = $Ph_2P(O)OH$) at such an extent that even after several days, the formation of organic carbamate was not observed.

In order to prove our hypothesis we went another way around and prepared the mixed anhydride $Ph_2P(O)OC(O)OMe$ (**4**) by reaction of NaO(O)COMe with $Ph_2P(O)Cl$ in THF at 253 K. **4**, a viscous colorless liquid, has been fully characterized using spectroscopic techniques (NMR, IR) and elemental analyses. At 293 K, both in the pure state and in solution (THF, $CHCl_3$), **4** slowly decarboxylates and converts into $Ph_2P(O)OMe$ according to reaction 11 that is much faster at 373 K. At this temperature, the decarboxylation process is practically complete within a few minutes.

$$Ph_2P(O)OC(O)OMe \text{ -----> } Ph_2P(O)OMe + CO_2 \qquad (11)$$

The reaction of **4** with aniline at 293 K has been monitored by means of NMR spectroscopy. Upon addition of the amine to a $CDCl_3$ solution of **4**, the ^{31}P spectrum of the solution shows the immediate disappearance of the signal at 31.65 ppm due to **4**. In the ^{13}C spectrum, the doublet at 149.3 ppm (J = 5.7 Hz) due to the carboxylic carbon of **4** disappears and a new signal rises at 154.2 ppm revealing the formation of PhNHC(O)OMe. The carbamate was further confirmed by the GC-MS analysis of the solution that confirmed that decarboxylation products of the mixed anhydride were not formed. The same features were found at 363 K.

These data are consistent with previous findings by Tarbell who reported the formation of carbamate esters from ammonia and *tert*-butylcarbonic diethyl phosphoric anhydride.[31] Therefore, the assumption of mixed anhydrides $X_2P(O)OC(O)OR$ as intermediates in reaction 6 seems to be correct and the fact that it is not found in the reaction medium is justified by its high reactivity with aniline.

$$Ph_2P(O)OC(O)OMe + PhNH_2 \text{ ----> } Ph_2P(O)OH + PhNHC(O)OMe \qquad (12)$$

The absence of $Ph_2P(O)OMe$ in this reaction shows that mixed anhydride aminolysis occurs much faster than the decarboxylation reaction. These findings agree with the fact that under the working conditions used for reaction 6 we neither detected the mixed anhydride nor observed the formation of $X_2P(O)OR$ species (X = Ph, PhO; R = Me, Ph) involving $X_2P(O)OC(O)OR$ decarboxylation. This feature is of interest as formation of $X_2P(O)OR$ would bring about $X_2P(O)OH$ catalyst deactivation.

CONCLUSIONS

We have shown that the reaction of aromatic amines with DMC or DPC to give organic carbamates ArNHC(O)OR (R = Me, Ph) can be efficiently promoted by several organo-phosphorus acids [$Ph_2P(O)OH$; $(PhO)_2P(O)OH$; $(BuO)_2P(O)OH$/$(BuO)P(O)(OH)_2$ equimolar mixture].

Among the acids investigated the best catalytic activity was shown by $Ph_2P(O)OH$. The reaction of aromatic amines with DPC in the presence of $Ph_2P(O)OH$ affords ArNHC(O)OPh in fairly good to excellent yields, depending on the working conditions and the reactivity of the aromatic amine, and with excellent selectivity (100 %). The latter feature is quite important from the synthetic point of view.

The organo-phosphorus acids (**1-3**) have been compared with other Brœnsted acids (HCl, CF_3SO_3H, $CF_3C(O)OH$, $CH_3CH_2C(O)OH$) that exhibit a markedly lower or no catalytic activity. In all cases the selectivity is completely lost.

The results obtained suggest that the formation of carbamate esters from aromatic amines and organic carbonates in the presence of organo-phosphorus acids takes place through a mechanism that mimics the formation of carbamate ions in living systems by CPS enzyme.

The intermediacy of a phosphocarbonate $X_2P(O)OC(O)OR$ is very likely, that, in a following step, reacts with the aromatic amine to give the carbamate ester. This reaction pathway has been demonstrated starting from the phosphocarbonate synthesized by an independent route.

EXPERIMENTAL SECTION

All reactions and manipulations were carried out under a dinitrogen atmosphere with rigorous exclusion of both air and atmospheric moisture, by using vacuum line techniques. All solvents were dried as described in the literature[32] and stored under dinitrogen. Aniline (from Riedel De Haen AG Seelze) was dried and then distilled before use;[32] 1-aminonaphthalene, $Ph_2P(O)OH$, $(PhO)_2P(O)OH$, $(BuO)_2P(O)OH$/$(BuO)P(O)(OH)_2$ (1:1 mol/mol) and $Ph_2P(O)Cl$ (all from Aldrich) were used as received. DMC and DPC were a gift from EniChem Synthesis.

IR spectra were obtained with a Perkin Elmer 883 spectrophotometer. ^1H, ^{31}P and ^{13}C NMR spectra were recorded with a Varian XL 200 or a Bruker AM 500. Proton and carbon chemical shifts are in ppm *vs* TMS and have been referenced to the solvent peak. ^{31}P shifts were referenced to the peak of H_3PO_4 (85 %, ext. ref). GC-MS analyses were carried out with a HP 5890 gas-chromatograph linked to a HP 5970 selective mass detector (capillary column: 30 m SE-30, 0.25 mm film thickness). HPLC analyses were performed with a Perkin Elmer Series 4 LC (column: Erbasil C18/M, 10 μm, 250 x 4,6 mm) connected with a LC 290 UV/Vis spectrophotometer detector. GC analyses were made with a DANI HR 3800 gas-chromatograph equipped with a SE-30 packed column.

Reaction of DPC with aniline in the presence of ***1***

A) At 363 K: synthesis and isolation of N-phenyl phenyl carbamate. To a THF (20 mL) solution of aniline (1.05 mL, 11.4 mmol) and DPC (2.335 g, 10.9 mmol) 0.118 g (0.54 mmol) of **1** were added. The reaction mixture was stirred at 363 K for 20 h, then cooled to room temperature (293 K) and concentrated *in vacuo*. Upon addition of hexane (40 mL) the white solid obtained (contaminated by anilinium

diphenylphosphinate) was extracted with diethylether to give pure *N*-phenyl phenyl carbamate (0.750 g). Addition of more hexane to the THF/hexane mother solution and cooling to 253 K caused the precipitation of more pure carbamate that was isolated by filtration. Overall yield: 1.260 g, 50 %. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.52; H, 5.24; N, 6.40. IR (Nujol, KBr disks, cm^{-1}): 3321 (m-s, br, ν_{NH}), 1715 (s, ν_{CO}), 1597 (m-s), 1590 (m), 1530 (s), 1488 (m-s), 1443 (s), 1317 (m-s), 1260 (m), 1223 (s), 1201 (s), 790 (m-s), 755 (s), 724 (m), 694 (s). ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 7.46 (m), 7.42 (m), 7.38 (m), 7.34 (m), 7.29 (m), 7.26 (m), 7.21 (m), 7.18 (m), 7.15 (tt). Addition of D_2O reveals that the NH proton resonates around 7.1 ppm. ^{13}C APT NMR ($CDCl_3$, 50.3 MHz, 293 K): δ 151.79 (br, *C*(O)O), 150.53 (C_{ipso}, OPh), 137.36 (br, C_{ipso}, NHPh), 129.43 and 129.15 (C_{meta}, OPh and C_{meta}, NHPh), 125.74 (C_{para}, OPh), 123.91 (br, C_{para}, NHPh), 121.68 (C_{ortho}, OPh), 118.78 (br, C_{ortho}, NHPh).

B) The reaction of DPC with aniline in the presence of **1** was carried out at various temperatures (see Table 1) and monitored by HPLC using toluene as internal standard. The isolation of the products was performed as described above. The procedure used for kinetic measurements (Figures 1 and 2) is reported below.

Kinetic measurements

Into a 10 mL vial, containing a THF solution of DPC, aniline and the internal standard (toluene), the acid catalyst (if used) was added. After sealing the vial by means of a Mininert Valve (Alltech), the reaction mixture was heated to the given temperature (±1 K). At measured times the reaction mixture was cooled to room temperature (293 K) and the liquid phase analyzed by HPLC.

Reaction of DPC with 1-aminonaphthalene in the presence of 1

A) At 363 K: synthesis and isolation of N-1-naphthyl phenyl carbamate. To a THF (20 mL) solution of 1-aminonaphthalene (1.704 g, 11.9 mmol) and DPC (2.332 g, 10.9 mmol), 0.118 g (0.54 mmol) of **1** were added. The reaction mixture was stirred at 363 K for 23 h and then cooled to room temperature (293 K). The solid precipitated upon addition of pentane (15 mL) was filtered out, washed with pentane-THF (2:1 v/v) and dried *in vacuo*. The mother liquor and washing solutions were collected, evaporated *in vacuo* to dryness and the residue crystallized from THF/hexane to afford two fractions which showed (by HPLC) slight contamination by the arylamine. After further recrystallization from THF (5 mL)/diethylether (50 mL) 0.661 g of pure violet *N*-1-naphthyl phenyl carbamate were isolated. More carbamate (0.200 g) could be recovered from the mother solution upon addition of hexane (30 mL) and cooling to 253 K. Overall yield: 30 %. Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.54; H, 4.98; N, 5.32. Found: C, 77.66; H, 5.12; N, 5.22. IR (Nujol, KBr disks, cm^{-1}): 3210 (m-s, br, ν_{NH}), 1722 (m-s, ν_{CO}), 1698 (s, ν_{CO}), 1595 (m-w), 1540 (s), 1490 (m-s), 1262 (m-s), 1238 (s, sh), 1208 (s, sh), 780 (m-s), 745 (m), 685 (m). The presence of two C=O bands at 1722 and 1698 cm^{-1} suggests the presence of two different rotamers as confirmed by ^{13}C NMR. ^1H NMR ($CDCl_3$, 200 MHz, 293 K): δ 7.93 (m, 3 H), 7.71 (d, 1 H, J = 8.06 Hz), 7.57-7.38 (m, 6 H), 7.27 (d, 3 H). ^{13}C NMR ($CDCl_3$, 125.76 MHz, 293 K): δ 152.55 (br, *C*(O)O); 150.88 and 150.85 (C_{ipso}, OPh); 129.36 and 129.32 (C_{meta}, OPh); 125.60 and 125.56 (C_{para}, OPh); 121.59 and 121.54 (C_{ortho}, OPh); 134.14 and 134.10 (quaternary C atom of naphthyl group); 132.06 (quaternary C atom of naphthyl group), 128.72, 126.33, 126.03, 125.71, 125.46 (br), 120.43 (br) (primary C atoms of naphthyl group); 127.77 (v br), 119.34 (v br)

(C atoms of naphthyl group). The reported assignement was supported by ^{13}C APT NMR ($CDCl_3$, 293 K) measurements at 50.3 MHz: δ 152.55 (br, -*C*(O)O-), 150.75 (C_{ipso}, OPh), 129.43 (C_{meta}, OPh), 125.70 (C_{para}, OPh), 121.64 (C_{ortho}, OPh), 134.08, 132.02 (quaternary C atoms of naphthyl group), 128.81, 126.43, 126.13, 125.81, 125.41 (br), 120.38 (br) (primary C atoms of naphthyl group). The inspection of the ^{13}C spectrum measured at 125.76 MHz shows doubling of the resonance of several carbon atoms (each carbon atom of phenoxy group, for instance). This behaviour, indicative of the presence of two rotamers,[33] is currently under investigation.

B) At 393 K. To a THF (5 mL) solution containing DPC (3.28 mmol), 1-aminonaphthalene (1.0 mmol) and toluene (0.5 mL, internal standard), **1** (0.069 mmol) was added, and the reaction mixture heated to 393 K. After 15 h, it was cooled to room temperature (293 K) and analyzed by HPLC. Carbamate HPLC yield: 40 %.

Reaction of DMC with aniline in the presence of P-acids

A) At 363 K in the presence of 3: synthesis and isolation of N-phenyl methyl carbamate. To a DMC (20 mL) solution of aniline (2 mL, 21.8 mmol), 0.35 g of equimolar mixture of $(BuO)_2P(O)OH$ and $(BuO)P(O)(OH)_2$ (**3**), previously dissolved in 2 mL of DMC, were added. The reaction mixture was stirred at 363 K for 4 days, then cooled to room temperature. The white solid precipitated was filtered, washed with diethyl ether and dried *in vacuo*. It was identified as a mixture of anilinium salts of **3** and was identical with an authentic sample obtained from the reaction of **3** with a DMC solution of aniline at 293 K. The mother liquor and washing solutions were collected, evaporated to dryness *in vacuo* and the residue was separated by chromatography on a silica gel column using diethylether/hexane (1:2 v/v) as eluent to give 0.46 g of pure carbamate (yield: 14 %). Anal. Calcd for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.26. Found: C, 63.50; H, 6.05; N, 9.30. MS (*m/z*): 151, 119, 106, 92, 77. IR (Nujol , KBr disks, cm^{-1}): 3305 (s, v br, ν_{NH}), 3200 (m, sh) 3140 (m, sh), 1725 and 1705 (vs, br, ν_{CO}), 1615 (s), 1600 (s), 1545 (s), 1500 and 1490 (m-s), 1450 (s), 1320 (m-s), 1240 (s, br), 1085 (m-s), 1070 (s), 1035 (m-s), 845 (m-s), 770 and 755 (s), 730 and 690 (s). The presence of two C=O bands at 1725 and 1703 cm^{-1} suggests the presence of two rotamers.[33] To confirm this, the IR spectrum of the aged solid carbamate (stored at 293 K for 20 days in a sealed tube under dinitrogen) shows only one ν_{CO} band and is identical with the spectrum of a sample of *N*-phenyl methyl carbamate prepared from aniline (2 mol) and MeOC(O)Cl (1 mol) in diethyl ether and recrystallized from diethyl ether/hexane (1:7 v/v). IR (Nujol , KBr disks, cm^{-1}): 3360 (m, sh), 3303 (m-s), 1705 (s), 1600 (m-s), 1545 (s), 1505 (m-s), 1445 (s), 1335 (m), 1320 (m-s), 1305 (m) 1240 (s), 1070 (m-s), 905 (m), 770(m), 762 (m), 755 (m), 728 (m-s), 692(m-s). Attempts to isolate the two rotamers are in course.

The NMR spectra of the product carried out on aged samples (see above) were identical to those of *N*-phenyl methyl carbamate prepared from aniline and MeOC(O)Cl. ^1H NMR ($CDCl_3$, 200 MHz, 293 K): δ 7.40-7.26 (m, 4 H, H_{ortho} and H_{meta}), 7.06 (t, 1 H, H_{para}, J = 7.04 Hz), 6.68 (s, 1 H, br, N*H*), 3.77 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$, 200 MHz, 293 K): δ 154.10 (*C*(O)O), 137.85 (C_{ipso}), 129.04 (C_{meta}), 123.45 (C_{para}), 118.74 (C_{ortho}), 55.33 (CH_3).

B) The reaction of DMC with aniline was carried in several other conditions (see Table 2). The carbamate yield was determined by GC, using either 1-bromonaphthalene or $C_{20}H_{42}$ (eicosane) as internal standard. The product isolation procedure was identical with that described above.

Synthesis of $Ph_2P(O)OC(O)OMe$

To a dispersion of NaO(O)COMe (0.201 g, 2.05 mmol) in THF (20 mL) $Ph_2P(O)Cl$ (0.39 mL, 2.05 mmol), previously dissolved in 10 mL of THF, was added. The reaction solution was stirred at 253 K for 24 h, then concentrated to half volume, filtered at 273 K and the solvent evaporated *in vacuo* at 293 K. The residual colorless oil was identified as $Ph_2P(O)OC(O)OMe$. Yield: 70 % Anal. Calcd for $C_{14}H_{13}PO_4$: C, 60.86; H, 4.74; P, 11.22. Found: C, 60.76; H, 4.66; P, 11.15 IR (Nujol, KBr disks, cm^{-1}): 1770 (s, br, ν_{CO}), 1591 (m), 1440 (s), 1250 (s, br). ^1H NMR ($CDCl_3$, 200 MHz, 293 K): δ 3.76 (s, 3 H, methyl protons), 7.3-7.9 (10 H, aromatic protons). ^{13}C NMR ($CDCl_3$, 50.3 MHz, 293 K): δ 149.27 (d, br, *O*C(O)O, $^2J_{COP}$ = 5.6 Hz), 132.99 (d, C_{para}, J_{CP} = 2.8 Hz), 131.59 (C_{ortho}, J_{CP} = 10.8 Hz), 128.71 (C_{meta}, J_{CP} = 14.2 Hz), 56.03 (s, *C*H_3). ^{31}P NMR ($CDCl_3$, 50.3 MHz, 293 K): δ 31.7.

Reaction of $Ph_2P(O)OC(O)OMe$ with aniline

A) *At 293 K.* A $CDCl_3$ (4 mL) solution of **4** (0.5 mmol) was introduced into a NMR tube and the NMR (^{31}P, ^{13}C) spectrum recorded. The spectra (^{31}P, ^{13}C) were repeated soon after the addition of an excess of aniline and showed the complete disappearance of the signals due to **4** and the presence of new signals due to PhNHC(O)OMe and $Ph_2P(O)OP(O)Ph_2$ [δ (^{31}P) 29.2 ppm][34] identified as the only products in solution on the basis of the comparison of the ^{13}C and ^{31}P spectra with those of an authentic sample. The acid **1** was found as anilinium salt, that separated from the solution. The reaction was repeated in batch and PhNHC(O)OMe isolated in quantitative yield by chromatography, as described above.

B) *At 363 K.* A THF (5 mL) solution of **4** was introduced into a 10 mL tube (equipped with a magnetic rod) and freezed in a liquid nitrogen bath. An excess of aniline, that rapidly freezed, was added and the tube was dipped into an oil bath at 363 K. The resulting solution was stirred at 363 K for 10 min. The reaction mixture was then cooled to 293 K and analyzed by GC-MS. PhNHC(O)OMe was determined in quantitative yield. $Ph_2P(O)OMe$ was practically absent in the reaction mixture.

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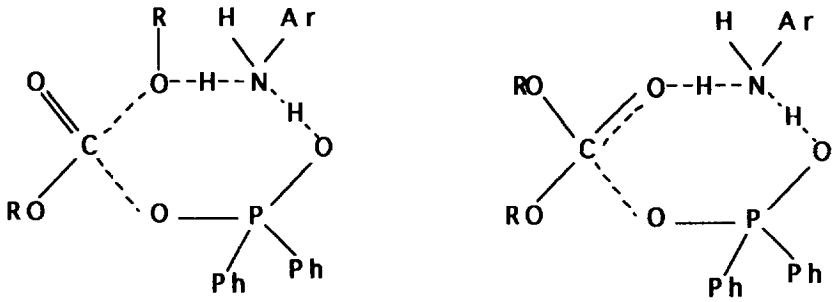
REFERENCES AND NOTES

1. Adams, P.; Baron F.A. *Chem. Rev.* **1965**, *65*, 567 and references therein.
2. (a) Barthelemy, J. *Lyon Pharm.* **1986**, *37(6)*, 297. (b) Tai-Teh Wu; Huang, J.; Arrington, N.D.; Dill, G.M. *J. Agric. Food Chem.* **1987**, *35*, 817. (c) Kato, T.; Suzuki, K.; Takahashi, J.; Kamoshita, K. *J. Pesticide Sci.* **1984**, *9*, 489. (d) Picardi, P. *La Chimica e l'Industria* **1986**, *68 (11)*, 108. (e) Rivetti, F.; Romano, U.; Sasselli, M. *U.S. Pat.* 4514339, 1985.
3. Babad, H.; Zeiler, A.G. *Chem. Rev.* **1973**, *73*, 75.
4. Ragaini, F.; Cenini, S.; De Martin, F. *J. Chem. Soc., Chem. Commun.* **1992**, 1467 and references therein.

5. (a) Mulla, S.A.R.; Gupte, S.P.; Chaudari, R.V. *J. Mol. Catal.* **1991**, *6*, L7. (b) Aresta, M.; Giannoccaro, P.; Ravasio, N. *J. Organomet. Chem.* **1993**, *451*, 243. (c) Aresta, M.; Giannoccaro, P.; Tommasi, I. *J. Organomet. Chem.* **1994**, *476*, 13.
6. Aresta, M.; Quaranta, E. Synthesis of carbamates from CO_2, amines and alkylating agents. In *Proceedings*, International Conference on Carbon Dioxide Utilisation, University of Bari, Bari, Italy, September 1993; p. 63, and references therein.
7. (a) Aresta, M.; Quaranta, E. *J. Org. Chem.* **1988**, *53*, 4153. (b) Aresta, M.; Quaranta, E. *Ital. Pat.* 1198206, 1988. (c) Aresta, M.; Quaranta, E. *J. Chem. Soc., Dalton Trans.* **1992**, 1893. (d) Aresta, M.; Quaranta, E. *Tetrahedron* **1992**, *48*, 1515. (e) Aresta, M.; Quaranta, E. *Ital. Pat.* 1237208, 1993.
8. (a) Cahours, A. *Ann.* **1845**, *56*, 266. (b) Bortnick, N.; Luskin, L. S.; Hurwitz, M.D.; Rytina, A.W. *J. Am. Chem. Soc.* **1956**, *78*, 4358. (c) Hagemann, C. Kohlensaure derivate. In *Methoden der Organischen Chemie*; Houben-Weil, Eds.; Georg Thieme Verlag: Stuttgart. 1983, 4th ed., Band E4, p. 159.
9. Massi Mauri, M.; Romano, U.; Rivetti, F. *Ing. Chim. Ital.* **1985**, *21*, 6 and references therein.
10. Romano, U.; Tesei, R. *US Pat.* 4045464, 1977.
11. Kock, P.; Romano, U. *Ital. Pat. Appl.* 20264 A/82.
12. Porta, F.; Cenini, S.; Pizzotti, M.; Crotti, C. *Gazz. Chim. Ital.* **1985**, *115*, 275.
13. (a) Aresta, M.; Quaranta, E. *Tetrahedron* **1991**, *47*, 9489. (b) Aresta, M.; Quaranta, E. *Ital. Pat.* 1237207, 1993.
14. (a) Frulla, F.F.; Stuber, A.F.; Whitman, J.P. *U.S. Pat.* 4550188, 1985; *Chem. Abstr.* **1986**, *104*, 224725u. (b) Giurgiolo, A.E. *U.S. Pat.* 4268684, 1981; *Chem. Abstr.* **1981**, *96*, 97407k. (c) Giurgiolo, A.E. *U.S. Pat.* 4268683, 1981; *Chem. Abstr.* **1981**, *95*, 168832h. (d) Romano, U.; Tesei, R. *Ger. Offen.* 2716540, 1977; *Chem. Abstr.* **1978**, *88*, 37459. (e) Onoda, T.; Tano, K.; Hara, Y. *Jap. Pat. Appl.* 04316, 1980. (f) Buysch, H.J.; Krimm, H.; Richter, W. *Eur. Pat. Appl.* 48371, 1982. (g) Romano, U.; Fornasari, G.; Sgambato, U. *Ital. Pat. Appl.* 22967 A/82.
15. (a) Anon., *Res. Discl.* **1987**, *275*, 162; *Chem. Abstr.* **1988**, *108*, 167429g. (b) Romano, U.; Fornasari, G.; Di Gioacchino, S. *Ger. Offen.* DE 3202690, 1982; *Chem. Abstr.* **1982**, *97*, 144607d. (c) Mukai, T.; Suenobu, K.; Masago, M. *Japan Kokai* 77 14745, 1977; *Chem. Abstr.* **1977**, *87*, 52961e.
16. Knight W.B. Carboxyphosphate: Predicted Chemical Properties, Synthesis and Role as an Intermediate in Enzymic Reactions. In *Enzymatic and Model Carboxylation and Reduction Reactions for Carbon Dioxide Utilization*; Aresta, M.; Schloss, J.V. Eds.; Kluwer Academic Publishers: Dordrecht. 1990, NATO-ASI Series C, Vol. 314, p. 239.
17. Rubio, V. *Biochem. Soc. Trans.* **1993**, *21*, 198.
18. In a typical run, a THF (15 mL) solution of DPC (1.050 g, 4.90 mmol) and benzylamine (0.5 mL, 4.60 mmol) was stirred for 3 h at 293 K. The solvent was evaporated *in vacuo* to dryness and the residue recrystallized from diethylether/hexane to afford pure *N*-benzyl phenyl carbamate (0.84 g, 80 %). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.02; H, 5.80; N, 6.13. IR (Nujol, KBr disks, cm^{-1}): 3295 (m-s, br, ν_{NH}), 1705 (s,ν_{CO}), 1595 (m), 1590 (m), 1535 (s), 1245 (m-s), 1205 (s). ^1H NMR ($CDCl_3$, 200 MHz, 293 K): δ 4.47 (d, br, CH_2, $^3J_{HH}$

= 5.86 Hz), 5.41 (br, N*H*), 7.1-7.5 (m, aromatic protons). ^{13}C NMR ($CDCl_3$, 50.3 MHz, 293 K): δ 154.68 (br, -*C*(O)O-), 150.99 (br, C_{ipso}, OPh), 138.00 (br, C_{ipso}, $PhCH_2$), 129.30 (C_{meta}, OPh), 128.77 and 127.71 ($PhCH_2$), 125.35 (C_{para}, OPh), 121.58 (C_{ortho},OPh), 45.30 ($PhCH_2$).

19. Yamazaki, N.; Higashi, F. *Int. Prog. Urethanes* **1980**, *2*, 61.
20. Menger, F.M.; Smith, J.H. *J. Am. Chem. Soc.* **1972**, *94*, 3824.
21. Weast, R.C. *Handbook of Chemistry and Physics;* Chemical Rubber Publishing Co.: Cleveland, Ohio. 1962; p. D90
22. Conversion of trifluoroacetic acid into trifluoroacetanilide took place under the working conditions. Formation of the amide occurred even when a toluene solution containing trifluoroacetic acid (1 mol) and aniline (excess) was heated at 363 K in the absence of $(RO)_2C(O)$ (R = Me, Ph).
23. Lum, R.C.; Grabowski, J.J. *J. Am. Chem. Soc.* **1992**, *114*, 8621.
24. (a) Nakamizo, N. *Bull. Chem Soc. Jpn.* **1969**, *42*, 1071. (b) Nakamizo, N. *Bull. Chem Soc. Jpn.* **1969**, *42*, 1078. (c) Satchell, D.P.N.; Secemski, I.I. *J. Chem. Soc. (B)* **1969**, 130.
25. The pKa (in water) for **1** is 1.74 +1.76.[26] The pKa (in water) for **2** can be estimated to be close to 0.76, that is the value measured for dimethylphosphoric acid, $(MeO)_2P(O)OH$.[27a] The pKa for **1** in 75 and 95 % ethanol (ethanol/water mixtures) is, respectively, 4.10 and 4.70. In the same media, the pKa for **2** is, respectively, 2.28 and 1.91.[27b] These values further confirm that **2** is a stronger acid than **1**.
26. Juillard, J.; Simonet, N. *Bull. Soc. Chim. Fr.* **1968**, 1883.
27. (a) Bunton, C.A.; Mhala, M.M.; Oldham, K.G.; Vernon, C.A. *J. Chem. Soc.* **1960**, 3293. (b) Peppard, D.F.; Mason, G.W.; Andreajasich, C.M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 697.
28. The formation of the mixed-anhydride might involve a H-bonded cyclic transition state (**E**) or (**F**). The ability of **1** and **2** to give self-association through inter-molecular hydrogen bonds is well documented in the literature.[29,30] The reaction of phosphorus acids (for instance, **2**) with nitrogen bases, such as imidazoles, can lead to the formation of hydrogen-bonded salts.[30]



(E) R = Me, Ph (F)

29. Walmsley, J.A. *J. Phys. Chem.* **1984**, *88*, 1226.
30. Holmes, R.R.; Day, R.O.; Yoshida, Y.; Holmes, J.M. *J. Am. Chem. Soc.* **1992**, *114*, 1771.
31. Tarbell, D.S.; Insalaco, M.A. *Proc. Nat. Acad.Sc. USA* **1967**, *57*, 233.

32. Perrin, D.D.; Armarego, W.L.F.; Perrin, D.R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, England. 1986.
33. Oki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3148.
34. Korth, H.-G.; Lusztyk, J.; Ingold, K.U. *J. Org. Chem.* **1990**, *55*, 624.

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