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Reaction of Chlorides of Phosphoric, Sulfonic, and Carboxylic Acids on Solid Potassium Carbonate Surface under PTC Circumstances

Zsuzsa M. Jászay,[1] Imre Petneházy,[2] and László Tőke[1]

[1]*Organic Chemical Technology Research Group of the Hungarian Academy of Sciences, H-1521, Budapest, Hungary*

[2]*Department of Organic Chemical Technology, Budapest University of Technology and Economics, H-1521, Budapest, Hungary*

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ABSTRACT: *Simple syntheses of phosphoric (***4***) and carboxylic (***6***) acid anhydrides have been elaborated by means of solid potassium carbonate in phase-transfer catalytic acylation. Behavior of various acid chlorides, phosphoric (***1***), sulfonic (***2***), and carboxylic (***8***), have also been studied toward potassium carbonate in the presence of lipophilic quaternary ammonium salt.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:447–450, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20039

INTRODUCTION

Solid potassium carbonate has become a popular reagent in phase-transfer catalytic reactions and applied as dry material, in the absence of water, when water sensitive substrates are involved. It also has the advantage of being milder, promoting fewer hydrolytic reactions than, e.g., solid potassium hydroxide or potassium *tert*-butoxide does. Among the examples in which solid potassium carbonate has been applied as a base are Michael reaction [1], C- and N-alkylations [2], preparation of amino acids [1a,2c], Wittig–Horner syntheses [3] as well as N-acylation of ureas in the synthesis of carbodiimides [4].

Earlier, we published our results on the preparation of carboxylic esters and amides from free carboxylic acids using dialkylphosphoric acid chloride **1** ($R^1 = $ Me, Et) generated “in situ” from dialkyl phosphite **2** ($R^1 = $ Me, Et) and carbon tetrachloride [5], or *p*-toluenesulfonic acid chloride **3** ($R^3 = 4\text{-MeC}_6H_4$) [6], respectively, with the combination of solid, dry potassium carbonate, and lipophilic quaternary ammonium salt, such as benzyltriethylammonium chloride (TEBAC).

We found that in both methods a side product, tetraalkylpyrophosphate **4** ($R^1 = $ Me, Et) and the potassium salt of sulfonic acid **5** ($R^3 = 4\text{-MeC}_6H_4$), respectively, were formed.

To find the reason for the formation of these “side products” we continued the research work, and as a result of this effort we succeeded in developing a simple way to make available the tetraalkyl (aryl) pyrophosphates **4,** as well as a new method for the preparation of carboxylic acid anhydrides **6**. The present article gives an account of this research.

RESULTS AND DISCUSSIONS

Preparation of Pyrophosphates 4

In the first set of experiments, we put together diethyl chlorophosphate **1** ($R^1 = $ Et), solid potassium

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Correspondence to: Z. M. Jászay; e-mail: Zjaszay@mail.bme.hu.

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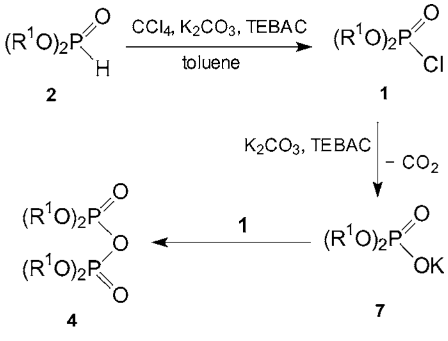
carbonate, and TEBAC in dry toluene, and found that the total amount of **1** was transformed to tetraethyl pyrophosphate **4** ($R^1 = Et$). As the reaction was accompanied by carbon dioxide evolution, we had to suppose that a part of **1** underwent a transformation with potassium carbonate providing diethyl phosphoric acid potassium salt **7** ($R^1 = Et$), which was acylated in a fast reaction by **1** ($R^1 = Et$) still present. It is important to mention that this transformation cannot be originated from the hydrolysis of **1**($R^1 = Et$) caused by the adherent water being always present even on the freshly dried potassium carbonate surface. A number of experiments were carried out with potassium carbonate adherent different amount of water to the surface of the solid, and it was found that the influence of the water content on the phosphoryl chloride hydrolysis was almost negligible.

In the next set of experiments, we used diethyl phosphite **2** ($R^1 = Et$) and carbon tetrachloride generating **1** ($R^1 = Et$) "in situ" in Atherton–Todd oxidative chlorination, and found that the formation of **4** ($R^1 = Et$) is also nearly quantitative. The pyrophosphate forming reaction proved to be general, all the examined phosphites **2** ($R^1 =$ alkyl, aralkyl, phenyl) provided the desired **4** in clean form and in good yield (Scheme 1, Table 1).

It must be noted that in contrast with our method none of the numerous procedures available in the literature are generally applicable for the preparation of phosphoric acid anhydrides. The known method resulting in tetramethyl pyrophosphate gives this product only in poor yield, because of its tendency toward decomposition [7]. Though, several methods are known for the preparation of the stable pyrophosphates, which involve the controlled partial hydrolysis of dialkyl phosphoryl chloride prepared in the previous step [7], or generated "in situ" [8,9] in the presence of water and organic or inorganic base. These methods give poor yields in the preparation of the more sensitive tetramethyl pyrophosphate **4** ($R^1 = Me$) [7], and cannot be used for the preparation of tetraphenyl pyrophosphate **4** ($R^1 = Ph$). The usual way of its preparation involves the reaction of diphenyl chlorophosphate and phosphoric acid diphenyl ester in the presence of pyridine [10].



SCHEME 1

It is also known from the literature that formation of tetraethyl pyrophosphate can be observed from diethyl phosphoryl chloride without adding water by means of solid potassium hydroxide [11] or by using an acetic acid pyridine mixture [12]. In [11] the hydroxyl anion serves as nucleophile, in [12] water is formed from one molecule of acetate anion and one molecule of acetic acid, while in our PTC experiments the formation of the pyrophosphates proceeds on the surface of the potassium carbonate producing potassium chloride and carbon dioxide.

Preparation of Carboxylic Anhydrides **6**

As a consequence of the experiments presented above, it was imperative to check the behavior of the mixture of carboxylic acid chlorides **8** with dry potassium carbonate and lipophilic quaternary salt in toluene. We found that a fast reaction proceeded with benzoyl chloride **8** ($R^2 = Ph$) in hot toluene solution giving benzoic acid anhydride **6** in practically quantitative yield. The reaction proved to be general also for the preparation of various types of anhydrides (Scheme 2, Table 2).

Because of the simplicity, our method seems to be superior to other PTC methods starting from acid chlorides, such as that of Plusquellec [18], which uses aqueous sodium hydroxide as a base, and that of Wang, which applies solid sodium or potassium hydrocarbonate and either Co/Pd complex catalyst [13], or ultrasound [19].

Formation of Sulfonic Acid Potassium salt on Solid Potassium Carbonate

It was also noticed that *p*-toluenesulfonic acid chloride **3** ($R^3 = 4\text{-}MeC_6H_4$) was consumed in the presence of solid potassium carbonate and TEBAC in hot toluene resulting in the formation of the potassium salt of *p*-toluenesulfonic acid **5** ($R^3 = 4\text{-}MeC_6H_4$) (Scheme 3). As one can expect, the same result was obtained when benzenesulfonyl chloride **3** ($R^3 = Ph$), or *p*-bromobenzenesulfonyl chloride **3** ($R^3 = 4\text{-}BrC_6H_4$) was used instead of *p*-toluenesulfonyl chloride in the reaction mixture. It is important to note that methanesulfonyl chloride **3** ($R^3 = Me$) also gives the appropriate potassium salt, but in a much faster reaction.

The main difference, as the side product quality is concerned using sulfonic acid chloride instead of

TABLE 1 Conditions for the Preparation of Pyrophosphates **4**

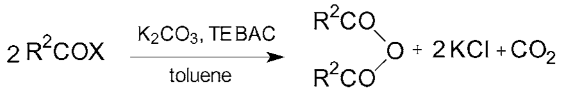
R^1	*Yield (%) Time (h) (Temp.)*	*^{31}PNMR δ(ppm)*	*Bp(°C/mm) or mp(°C)*	*Lit. bp(°C/mm) or mp (°C)*
Me	86 1(Rt)	−10.5	92–94/0.3	114–116/0.5 [7]
Et	82 1(80)	−13.1	102–106/0.02	105–109/0.03 [8]
i-Pr	92 3(80)	−15.0	99–102/0.05	94–99/0.02 [8]
$PhCH_2$	88 0.5(60)	−13.0	59–61	59–61 [9]
Ph	73 1(Rt)	−25.6	165–170/0.05	150–155/10^{-4} [10]

phosphoric acid chloride, is that the sulfonic acid anion being "harder" and less nucleophilic than the phosphate anion that cannot be acylated, while the phosphate anion is converted to pyrophosphate.

Conclusion

Contrary to the above-mentioned phosphoric [11,12] and carboxylic [13,18] anhydride-forming methods in our PTC experiments, neither potassium hydroxide nor acetate nucleophile was present in the reaction mixture. Therefore to interpret the reaction of dialkylphosphoric **1**, carboxylic **8**, and sulfonic **3** acid chlorides with solid potassium carbonate given in Schemes 1, 2, and 3, we have to suppose that it is the nucleophilic character of the carbonate anion, which is responsible for the formation of the intermediate of carbonic acid and sulfonic (**9**), phosphoric (**10**), and carboxylic acid (**11**), respectively (Scheme 4).

The structure of the intermediate has to involve a pentacoordinated sulfur (**9**) and phosphorus atom (**10**) in the case of sulfonyl chloride and phosphoryl chloride, respectively, while a tetrahedral carbon (**11**) in the case of carboxylic acid chlorides. Stabilization of the intermediates can occur by the anhydride C—O bond fission to afford potassium salt of the appropriate sulfonic, phosphoric, and carboxylic acid, carbon dioxide and potassium chloride. The phosphoric and carboxylic acid salts are acylated in the bulk to furnish products **4** and **6**, respectively. Based on the results collected by Makosza [20] and subsequently for solid potassium carbonate and quaternary onium salt in PTC systems by Sasson [21], we suppose that it is the interface where the formation of **9**, **10**, and **11** might proceed.



$$2\,R^2COX \xrightarrow[\text{toluene}]{K_2CO_3,\ TEBAC} (R^2CO)_2O + 2\,KCl + CO_2$$

8 **6**

SCHEME 2

EXPERIMENTAL

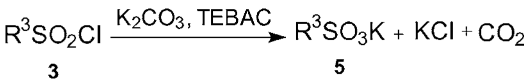
^{31}P NMR spectra were taken by a Bruker DRX-500 spectrometer using 85% H_3PO_4 as external standard, all in $CDCl_3$ solution. The GC measurements were performed on a Packerd-802 chromatograph using a silylated glass column packed with Chromosorb G impregnated with 5% QF_1 silicon oil. A column temperature of 210°C was used with hydrogen as a carrier gas and a thermal conductivity detector. The aromatic sulfonyl chlorides were freshly recrystallized. The toluene was dried on sodium. The potassium carbonate was powdered and dried at 350°C prior to use.

General Procedure for the Preparation of Pyrophosphates **4**

The toluene solution (10 mL) of dialkyl or diphenyl phosphite 2 (20 mmol) was added to a stirred mixture of solid potassium carbonate (5.53 g, 40 mmol), TEBAC (0.22 g, 1.0 mmol), CCl_4 (20 mL, 200 mmol), and toluene (20 mL), and the reaction mixture maintained at the given temperature and for the given time (see Table 1). The solid was filtered off and washed with toluene (5 mL). The solvent was evaporated and the residue was distilled, or crystallized

TABLE 2 Conditions for the Preparation of Carboxylic Acid Anhydrides **6**

R^2	*X*	*Yield (%) Time (h)*	*Mp. (°C) or bp. (°C/mm)*	*Lit.mp.(°C) or Lit.bp. (°C/mm)*
Ph	Cl	99 3	42–44	42–43 [13]
3,4,5$(MeO)_3C_6H_2$	Cl	60 0.75	138–142	159–161 [14]
2-thienyl-	Cl	99 3	52–56	62 [15]
tBu	Cl	80 7	82–84/32	106/50 [16]
$CH_3(Br)CH$	Br	89 6	115/3	120/5 [17]



$$\underset{\mathbf{3}}{R^3SO_2Cl} \xrightarrow{K_2CO_3,\ TEBAC} \underset{\mathbf{5}}{R^3SO_3K} + KCl + CO_2$$

SCHEME 3

from the solvent given in Table 1. All compounds are known from the literature. The details can be seen in Table 1.

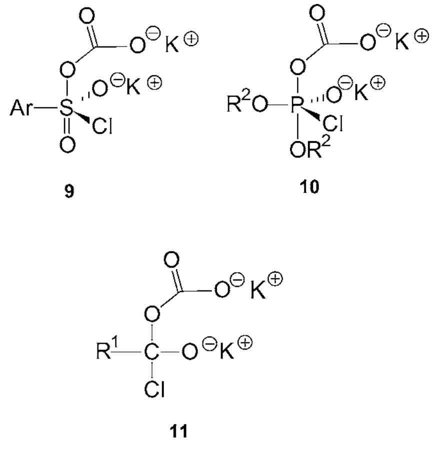
General Procedure for the Preparation of Carboxylic Anhydrides **6**

A mixture of carboxylic acid chloride 8 (10 mmol), dry K_2CO_3 (5.53 g, 40 mmol), TEBAC (0.22 g, 1.0 mmol), and toluene (20 mL), was stirred at reflux temperature for the time given in Table 2. The solid was filtered off and washed with toluene (5 mL). The solvent was evaporated and the residue crystallized or distilled. All compounds are known from the literature. The details can be seen in Table 2.

Monitoring the Transformation of the Sulfonyl Chlorides **2**

To a solution of the sulfonyl chloride **2** (10 mmol) in dry toluene (20 mL), K_2CO_3 (5.53 g, 40 mmol) and TEBAC (0.22 g, 1.0 mmol) were added, and the reaction mixture was stirred at reflux temperature. The decrease in the amount of **2** was monitored by GC.

$t_{1/2}$ for: R^3: 4-MeC_6H_4: 60 min; 4-BrC_6H_4: 50 min; Ph: 55 min; Me: 8 min.



SCHEME 4

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REFERENCES

[1] (a) Chagyou, Z.; Daimo, C.; Yaozhong, J. Synth Commun 1987, 17, 1377–1382; (b) Cossentini, M.; Strazalko, T.; Seyden-Penne, J. Bull Soc Chim Fr 1987, 531–534.

[2] (a) Szabó, G. T.; Aranyosi, K.; Csiba, M.; Tőke, L. Synthesis 1987, 565–566; (b) Jawdosiuk, M.; Jonczyk, A.; Kwast, A.; Makosza, M.; Kmiotek-Skarzynska, I.; Wojciechowski, K. Pol J Chem 1979, 53, 191–200; (c) Kolodziejczik, A. M.; Arendt, A. Pol J Chem 1980, 54, 1327–1329; (c) Albanese, D.; Landini, D.; Penso, M. J Org Chem 1992, 57, 1603–1605; (d) Gesson, J. P.; Jacquesy, J. C.; Rambaud, D. Bull Soc Chim Fr 1992, 227–231.

[3] (a) Mouloungui, Z.; Delmas, M.; Gaset, A. Synth Commun 1985, 15, 491–494; (b) Mouloungui, Z.; Delmas, M.; Gaset, J Org Chem 1989, 54, 3936–3941; (c) Ben Attra, T.; Le Bigot, Y.; El Gharbi, R.; Delmas, M.; Gaset, A. Synth Commun 1992, 22, 1421–1425; (d) Trigo, G. G.; Llama, E. F. Heterocycles 1985, 23, 2999–3007.

[4] Jászay, M. Zs.; Petneházy, I.; Tőke L.; Szajáni, B. Synthesis 1987, 520–523.

[5] Jászay, M. Zs.; Petneházy, I.; Tőke L. Synth Commun 1998, 28, 2761–2767.

[6] Jászay, M. Zs.; Petneházy, I.; Tőke L. Synthesis 1989, 745–747.

[7] Toy, D. F. J Am Chem Soc 1948, 70, 3882–3886.

[8] Steinberg, G. M. J Org Chem 1950, 15, 637–647.

[9] Atherton, F. R.; Todd, A. R. J Chem Soc 1947, 674–678.

[10] Corby, N. S.; Kenner, G. W.; Todd, A. R. J Chem Soc 1952, 1234.

[11] Pianka, M. J Appl Chem 1955, 5, 109.

[12] Michalski, J.; Modro, T. Chem Ber 1962, 95, 1629–1636.

[13] Jin-Xian Wang; Yulai Hu; Wenfeng Cui. Synth Commun 1994, 24, 3261–3268.

[14] Heap, T.; Robinson, R. J Chem Soc 1929, 67–73.

[15] Steinkopf, W.; Ohse, W. Ann Chem 1924, 14–22.

[16] Braude, E. A.; Timmons, C. J. J Chem Soc 1955, 3766–3772.

[17] Bischoff, A.; Walden, P. Chem Ber 1894, 27, 2939–2952.

[18] Plusquellec, D.; Roulleau, F.; Lefeuvre, M.; Brown, E. Tetrahedron 1988, 44, 2471–2476.

[19] Yulai, Hu; Jin-Xian, Wang; Shihua, Li. Synth Commun 1997, 27, 243–248.

[20] Makosza, M. Pure Appl Chem 1975, 43, 439–462.

[21] (a) Arrad, O.; Sasson, Y. J Am Chem Soc 1988, 110, 185; (b) Sasson, Y.; Bilman, N. J Chem Soc, Perkin Trans 2. 1989, 2029; (c) Mason, D.; Magdassi, S.; Sasson, Y. J Org Chem 1990, 55, 2714.