Research Article

Rapid and Efficient Synthesis of ω -Alkylenediphosphoric Acids from Phosphorus Oxychloride

Dalila Meziane,¹ Abdelhamid Elias,¹ and Erwann Guénin²

¹Département de Chimie, Faculté des Sciences, Université Mouloud Mammeri, BP 17 RP, 15000 Tizi Ouzou, Algeria

²UFR SMBH, Université Paris 13, Sorbonne Paris Cité, 74 rue Marcel Cachin, 93017 Bobigny, France

Correspondence should be addressed to Erwann Guénin; guenin@univ-paris13.fr

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The aim of this investigation was to develop an efficient, rapid, and selective method for the synthesis of ω -alkylenediphosphoric acids $(\text{HO})_2(\text{O})\text{P}-\text{O}-(\text{CH}_2)_n-\text{O}-\text{P}(\text{O})(\text{OH})_2$ from reaction of several diols with phosphorus oxychloride. The reaction was investigated using three methodologies: (i) presence of a base, (ii) classical heating, and (iii) use of microwave irradiation. Influence of reaction temperature and molar ratio of reagents, as well as the nature of the solvent, was studied using these three different methods.

1. Introduction

Alkylphosphates, also called phosphate esters, have found numerous applications over the years mainly in various industrial processes, such as flame retardants, plasticizing agents, lubricants, surfactants, reagents in solvent extraction of heavy metal ions, and corrosion inhibitors [1–9].

Organic phosphates are generally synthesized from condensation of alcohol with several phosphorus substances: P_2O_5 , POCl_3 , PCl_3 , PCl_5 , and H_3PO_4 [10–14]. In general, the products are mixtures of mono-, di-, and triesters, together with some byproducts and unreacted alcohols [15]. This phenomenon is of course enhanced when reacting diols or polyols. Nevertheless, selective formation of monoesters could be obtained by reacting excess of the phosphorus species, but this involves more difficult purification steps.

Among the different phosphorus reactants, phosphorus oxychloride appears as a good compromise to obtain monoalkylphosphates as it is less reactive than phosphorus chlorides. The synthesis of alkylphosphoric acids through the reaction of phosphorus oxychloride with alcohols involves two steps. The first step consists in a nucleophilic attack of the alcohol at the P center of POCl_3 , in order to yield the formation of an intermediate compound: phosphorodichloridate by a bimolecular mechanism (termed SN_2P) [16]. The second

step is the hydrolysis of the phosphorodichloridate formed in the first step. By a similar way, the reaction of diols with POCl_3 may be represented as shown in Scheme 1. By the same mechanism, two molecules of POCl_3 may react with the same molecule of diol to form diphosphorotetrachloridate, which is then hydrolyzed in a second step, thus forming the desired alkylenediphosphoric acids: $(\text{HO})_2(\text{O})\text{P}-\text{O}-(\text{CH}_2)_n-\text{O}-\text{P}(\text{O})(\text{OH})_2$.

In fact, the reaction of a diol (as in case of an alcohol) with phosphorus oxychloride leads to a complex mixture of mono(di)alkylphosphoric acids, trialkylphosphate, and polyphosphoric acids. The proportion of each compound depends on the reaction conditions [17]. The lack of selectivity is a major inconvenience for this synthetic route, since the composition is hardly controlled giving generally low yields of the desired product which is difficult to separate from the crude mixture. Another problem of this reaction, mainly in case of alcohols or diols with long hydrocarbon chains, is their lower reactivity compared to the alcohols with shorter alkyl chain. At classical conditions, this low reactivity induces the need of long reaction times and high temperatures ($>100^\circ\text{C}$) [11, 18].

In this paper, we report reactions of phosphorus oxychloride with several diols with varying hydrocarbon chain length. In order to try to control the selectivity of the reaction,

SCHEME 1: General route for the formation of ω -alkylenediphosphoric acids from phosphorus oxychloride.

to obtain monoalkyl diphosphoric esters, and improve the synthetic process, we investigated three different approaches for this reaction: firstly the reactions were activated by classical heating and then by the use of triethylamine at low temperature and finally the reactions were run under microwave irradiation.

2. Results and Discussion

2.1. Method 1: Conventional Thermal Activation. Using conventional heating, the reactions were carried out according to a slightly modified procedure with respect to the one reported for similar products [18]. A large excess of POCl_3 versus diol was used ($R = 4$) and refluxed with the diol for several hours in toluene. The evolution of the reaction was followed by NMR; the ^{31}P $\{^1\text{H}\}$ spectrum showed the appearance of a new peak around 5-6 ppm which corresponds to the monoalkyl phosphorodichloridate intermediates (POCl_3 signal appears around 4.5 ppm (Figure 1(a))). During the hydrolysis step, we noted some progressive decrease of the peak area, at 6 ppm, in favor of a new one, around 0 ppm, corresponding to the desired products. The other peaks, observed with a little contribution, correspond to byproducts due to a partial hydrolysis of POCl_3 and formation of anhydride (Figure 1(b)). The desired product was then isolated by means of precipitation

from methanol/ethyl acetate (1/4). The final product corresponds to the monoesterified phosphoric acids. However, it is worth mentioning that under whatever conditions used it was never obtained in pure form. The maximum purity (calculated by ^{31}P NMR) that corresponds to optimized conditions was 95%. The remaining 5% impurities were attributed to the formation of at least one dialkyl phosphoric acid. Attempts to realize the reaction with a decreased or stoichiometric ratio of $\text{POCl}_3/\text{Diol}$ ($R = 2$ or $R = 3$) were unsuccessful; it resulted in product mixtures only, which were quite difficult to separate or even to identify. Using the optimized conditions, pure products were obtained, yields ranging from 65% to 85%, depending on the diols nature (Table 1). Although appreciable yields and purity are obtained, this method presents some drawback, such as length of reaction (several hours) and need of high reaction temperatures and excess of POCl_3 .

2.2. Method 2: Activation by a Base (NEt_3). Due to the low nucleophilicity of diols their reaction with POCl_3 is slow. In the literature, bases are frequently used to activate the reaction of hydroxyl compounds with phosphorus oxychloride [17]. In this study, we tested the activating role of triethylamine (NEt_3) in the reaction of diols with POCl_3 . NEt_3 has a double character: nucleophilic and basic, so it can readily react with POCl_3 to form an activated product

FIGURE 1: ^{31}P NMR spectra of the reaction mixtures, obtained during the two-step synthesis. (a) Step 1, (b) step 2 (Method 1).

SCHEME 2: General route to the formation of ω -alkylenediphosphoric acids from phosphorus oxychloride, using triethylamine.

(Scheme 2). This positively charged intermediate is more reactive than the POCl_3 . It is then easily attacked by the hydroxyl group of the diols. The reaction is even exothermic and was conducted at low temperature (-15°C), implying some handling caution. In this reaction, the amine plays a second role which consists in the fixation of the formed HCl and provides the corresponding chlorhydrate (NEt_3 , HCl). The precipitation of the chlorhydrate, in an adequate solvent, displaces the reaction-equilibrium towards the formation of the phosphonic ester (Scheme 2).

The reactions of POCl_3 with diols, according to this pathway, were followed by NMR. The ^{31}P $\{^1\text{H}\}$ NMR spectra showed the formation of different intermediates, but at the

end of the process, the major product showed a signal around 5-6 ppm (Figure 2(a)). After a hydrolysis step, these intermediates mainly afford the desired product and other unidentified byproducts, probably resulting from polyesterification. In this procedure, an excess of POCl_3 was also necessary to lessen double or even triple attack of the diols, on the same POCl_3 molecule, allowing for the formation of di- or trialkylphosphates compounds. Nevertheless use of 4 equivalents of POCl_3 did not completely avoid the formation of these byproducts, since the desired product was never obtained in pure form (maximum purity obtained was 90%). One must also note that an increase in POCl_3 did not result in any increase of purity either.

TABLE 1: Reaction conditions and results of the synthesized products with the different methods.

Diols $\rightarrow$	Yield η (%)		
	C_6	C_9	C_{12}
<i>Method 1</i>			
$T = 110^\circ\text{C}$, $R = 4$, $t_r = 8\text{--}10\text{ h}$, solvent: toluene	70 ^a	65 ^a	85 ^a
<i>Method 2</i>			
$T = -15^\circ\text{C} \rightarrow 20^\circ\text{C}$, $R = 4$, $R' = 4$, $t_r = 2\text{ h}$, solvents: THF (C_{12}) or diethyl ether (C_6 and C_9)	65 ^b	62 ^b	75 ^b
<i>Method 3</i>			
$T_{\text{Max}} = 85^\circ\text{C}$, $R = 2$, $t_r = 2\text{ min}$, $W = 100\text{ W}$, solvent: acetonitrile	65	68	72

t_r : reaction time (step 1), R : molar ratio POCl_3 /diol, R' : molar ratio triethylamine/diol, C_6 : hexane-1,6-diol, C_9 : nonane-1,9-diol, and C_{12} : dodecane-1,12-diol.

^{a,b}Products were not obtained in pure form (maximum purity a: 95%, b: 90%).

During the reaction, an excess of NEt_3 was also needed in order to scavenge the totality of the formed HCl and thus avoid the formation of chloroalkanes as byproducts. Use of low molar ratios (2-3 equivalents) of POCl_3 and/or NEt_3 gave quite complex mixtures. Only small quantities of the desired product were formed and isolated in this case. Different solvents were evaluated for the reaction (dichloromethane, tetrahydrofuran, and diethyl ether). The best results were obtained with diethyl ether in case of C_6 and C_9 diols, while in case of C_{12} the best results were obtained with THF. The success of the reactions with these solvents is probably due to the precipitation of the chlorhydrate salt (NEt_3 , HCl). When dichloromethane, in which triethylammonium salt is known to be partially soluble, was used, only low quantity of product was extracted. Using the optimized conditions, yields lie in the range 62%–75%. These are comparable to those obtained with the first method yet the products exhibit less purity (reaching its maximum at 90%). However, this second method presents two advantages as compared to thermal activation: that is a decrease of the reaction time (2 h versus 10 h) and the absence of any heating, since everything works at ambient temperature, as compared to the usual 110°C . The major inconvenience of this procedure lies in the need of reagents, POCl_3 ($R = 4$) and amine ($R' = 4$), in excess.

2.3. Method 3: Activation by Microwave Irradiation. Microwave offers a number of advantages over conventional heating, such as fast-and-homogeneous noncontact heating [19]. Moreover, use of microwaves offers drastically reduced processing time. That could, in fact, account for its spreading during the last three decades, in several areas of chemistry [20]. In particular, this methodology had a positive impact on phosphorus chemistry as well as on several organophosphorus reactions that has benefited from the use of microwaves [21, 22]. We thus apply it to the synthesis of ω -alkylenediphosphoric acids. The reaction was conducted in open

vessel by controlling power delivery during the reaction. Under microwave irradiation, the final and intermediate products emerging from the reaction of diols with POCl_3 were identical to those which were formed using conventional heating. These products essentially consist in the diphosphorotetrachloridate formed in the first step (Scheme 2) and the alkylenediphosphoric acids $(\text{HO})_2(\text{O})\text{P}-\text{O}(\text{CH}_2)_n-\text{O}-\text{P}(\text{O})-(\text{OH})_2$ obtained after the hydrolysis step (Figure 3).

The results are satisfactory (65–72%) and comparable to those obtained with the previous methods (1 and 2) (Table 1). However, this time the purity was better as no traces of di- or polyalkylphosphate were observed. Another asset of this methodology was that the amount of phosphorus oxychloride was reduced by a factor 2, from 4 to 2 equiv., and the reaction time of the diphosphorotetrachloridate formation was shortened to 2 minutes, instead of more than 8 hours when using thermal heating. This method, compared to method 2, has also the advantage of being catalyst-free.

Polar solvents like acetonitrile seem to be useful for the reaction under microwave irradiation. When toluene was used, only traces of products are detected even under much harsher conditions ($P = 150\text{ W}$, $t = 30\text{ min}$, and $R = 4$). This is due to the nonpolar nature of toluene, as only polar molecules selectively absorb microwaves while nonpolar molecules are known to be inert to microwave dielectric losses [20, 23]. Indeed, the heat generated by the reactants rotating molecules, when submitted to microwave irradiation, dissipated in this solvent through convection mechanisms. Using the conditions cited above, the resulting temperature ($T_{\text{max}} = 40^\circ\text{C}$) is too low to activate the reaction. Tests, carried out without solvent, generated a rapid and uncontrollable increase of the temperature in the reaction mixture, especially when no excess of POCl_3 ($R = 2$) was used. Yields in solvent-free conditions did not exceed 50%, even under the use of a large excess of the reagent ($R = 4$).

The optimal conditions and the corresponding yields for the 3 methodologies are summarized in Table 1.

3. Experimental Section

3.1. Reagents and Solvents. Phosphorus oxychloride (99%), triethylamine (>99%), and diols hexane-1,6-diol (99%), nonane-1,9-diol (98%), and dodecane-1,12-diol (99%) were purchased from Sigma-Aldrich. Diols were used without further purification. Phosphorus oxychloride and triethylamine were distilled before use. All solvents were purchased from Carlo Erba-SDS and also distilled before use. Dichloromethane, acetonitrile, and ethyl acetate were distilled over P_2O_5 . Methanol, ethanol, diethyl ether, and toluene were distilled over sodium. The THF was likewise distilled over sodium in presence of benzophenone.

3.2. Instruments. NMR spectra were recorded with a VARIAN Unity Inova 500 MHz (^{13}C : 125.9, ^1H : 500.6 MHz) or a VARIAN Gemini 200 MHz (^{31}P : 80.9 MHz) spectrometer in CD_3OD . Chemical shifts are reported in parts per million (ppm) on the δ scale. The residual solvent peak (CD_3OH) was used as a reference for ^1H NMR (3.31 ppm) and ^{13}C

FIGURE 2: ^{31}P NMR spectra of the reaction mixtures obtained during the two-step synthesis. (a) Before the hydrolysis (step 1). (b) During hydrolysis step 2 (Method 2).

FIGURE 3: ^{31}P NMR spectra of 1,12-Bis[(dihydroxyphosphinyl)oxy]dodecane obtained with method 3. (a) Crude mixture obtained during step 1. (b) Crude mixture obtained after hydrolysis step 2 and before purification.

NMR (49.0 ppm). ^{31}P NMR spectra were recorded using phosphoric acid (85%) as the external reference. Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplet, and m = multiplet. Coupling constants are given in Hz. The FTIR spectra were recorded using a Nicolet FTIR 380 spectrophotometer and measured in wavenumbers (cm^{-1}). The mass spectra were run on a MALDI-TOF mass spectrometer (Biflex IV, Bruker Daltonique) with 2,5-dihydroxybenzoic acid as matrix.

All melting points are recorded using a Stuart SMP3 melting point apparatus and are uncorrected.

All experiments under microwave irradiations were run in open vessel, using a CEM-Discover microwave apparatus.

3.3. General Procedure for the Conventional Heating Synthesis (Method 1). The following procedure was adapted from synthesis reported for similar compounds [18]. Phosphorus oxychloride (30.66 g; 200 mmol) and the diol (5.9; 8.01; 10.11 g (resp., for $n = 6, 9$, or 12); 50 mmol) were added under argon successively to a round bottom flask containing 120 mL of toluene. The mixture was refluxed for 8 to 10 h under magnetic stirring. The solution was then concentrated with a rotary evaporator and the viscous residue was coevaporated twice with 100 mL of toluene.

In the second step the obtained residue was hydrolyzed by 100 mL of cold water. Distilled water was added carefully to the residue, previously cooled ($5\text{--}10^\circ\text{C}$). Then the

solution was warmed down to 90°C and stirred for 2 to 3 hours. During the hydrolysis, a white precipitate appeared and was isolated after water filtration. The obtained white solid was dissolved in 100 mL of ethanol which was then evaporated. This operation was repeated twice in order to remove the remaining HCl. The residue was finally dissolved in methanol/ethyl acetate (1/4) (v/v) and the solution was left to precipitate overnight (in a freezer for compounds I and II, at r.t for compound III). The white powder was filtered, washed with diethyl ether, and dried in desiccators.

3.4. General Procedure for the Synthesis Using Triethylamine (Method 2). In a 150 mL tricol flask equipped with a reflux condenser, a thermometer, and an addition funnel a solution of phosphorus oxychloride (9.2 g; 60 mmol) was mixed with 30 mL of solvent (diethyl ether, dichloromethane, or tetrahydrofuran (THF)). A solution of diol (15 mmol) and triethylamine (6.08 g; 60 mmol) was then introduced dropwise. The reaction being very exothermic, the flask was placed in a mixture of liquid nitrogen and ethanol to keep the temperature at approximately -15°C, during the reagent addition. After completion of the addition, the mixture was stirred at room temperature (20°C) for 2 hours. 20 mL of distilled water was then added to the reaction mixture and left under magnetic stirring, at room temperature, overnight. The mixture was then concentrated with a rotary evaporator before 20 mL of cold water was finally added to the viscous residue and the yellow organic layer removed from the aqueous phase. The desired product was isolated by recrystallization from methanol/ethyl acetate (1/4) (v/v).

3.5. General Procedure for the Synthesis under Microwave Irradiation (Method 3). Phosphorus oxychloride (3.36 g; 22 mmol) was placed in a 100 mL flask, equipped with a reflux condenser and closed by a calcium chloride tube with a diol (10 mmol) and acetonitrile (15 mL) as solvent. The mixture was then irradiated at 100 W for 2 min, under vigorous stirring. The mixture initially heterogeneous became homogenous within a few seconds of irradiation. At the end of the irradiation process, the mixture is poured into a flask containing 30 mL of cold distilled water. The hydrolysis and the purification procedures are similar to those described in method 1.

3.6. 1,6-Bis[(dihydroxyphosphinyl)oxy]hexane (Compound I). mp = 96°C. ^{31}P { ^1H } NMR δ : 0.2. ^1H NMR δ : 3.97 (dt, 4H, $^3J_{\text{H-H}} = ^3J_{\text{P-H}} = 6.5$ Hz, POCH_2); 1.68 (m, 4H, POCH_2CH_2); 1.45 (m, 4H, $\text{POCH}_2\text{CH}_2\text{CH}_2$). ^{13}C { ^1H } NMR δ : 67.7 (d, $^2J_{\text{P-C}} = 5.8$ Hz, POCH_2); 31.4 (d, $^3J_{\text{P-C}} = 5.8$ Hz, POCH_2CH_2); 26.3 ($\text{POCH}_2\text{CH}_2\text{CH}_2$). Elementary Analysis $\text{C}_6\text{H}_{16}\text{O}_8\text{P}_2$ calcd C: 25.9; H: 5.8; O: 46.0; P: 22.3 found C: 26.2; H: 5.7; O: 46.4; P: 21.7.

3.7. 1,9-Bis[(dihydroxyphosphinyl)oxy]nonane (Compound II). mp = 109°C. ^{31}P { ^1H } NMR δ : 0.6. ^1H NMR δ : 3.96 (dt, 4H, $^3J_{\text{H-H}} = ^3J_{\text{P-H}} = 6.7$ Hz, POCH_2); 1.67 (m, 4H, POCH_2CH_2); 1.41 (m, 4H, $\text{POCH}_2\text{CH}_2\text{CH}_2$); 1.32 (m, 8H, $\text{POCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$). ^{13}C { ^1H } NMR δ : 67.9 (d, $^2J_{\text{P-C}}$

= 5.8 Hz, POCH_2); 31.6 (d, $^3J_{\text{P-C}} = 5.8$ Hz, POCH_2CH_2); 30.3 ($\text{POCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$); 30.6 ($\text{POCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$); 26.7 ($\text{POCH}_2\text{CH}_2\text{CH}_2$). Elementary Analysis $\text{C}_9\text{H}_{22}\text{O}_8\text{P}_2$ calcd C: 33.8; H: 6.9; O: 40.0; P: 19.3 found C: 33.2; H: 7.2; O: 39.9; P: 19.7.

3.8. 1,12-Bis[(dihydroxyphosphinyl)oxy]dodecane (Compound III). mp = 114°C. ^{31}P { ^1H } NMR δ : 0.9. ^1H NMR δ : 3.96 (dt, 4H, $^3J_{\text{H-H}} = ^3J_{\text{P-H}} = 6.7$ Hz, POCH_2); 1.66 (m, 4H, POCH_2CH_2); 1.40 (m, 4H, $\text{POCH}_2\text{CH}_2\text{CH}_2$); 1.32 (m, 12H, $\text{POCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$). ^{13}C { ^1H } NMR δ : 67.9 (d, $^2J_{\text{P-C}} = 5.8$ Hz, POCH_2); 31.6 (d, $^3J_{\text{P-C}} = 5.9$ Hz, POCH_2CH_2); 30.4 ($\text{POCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$); 30.7 ($\text{POCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$); 26.3 ($\text{POCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$). IR (KBr), (cm^{-1}): 2919, 2852, 1474 (C-H), 2360 (P-O-H), 1234, 1095, 1038 (P=O) and (C-O), 1012, 937 (P-O). M/z (MH^+): 363.25; calcd: 363.13. Elementary Analysis $\text{C}_{12}\text{H}_{28}\text{O}_8\text{P}_2$ calcd C: 39.8; H: 7.8; O: 35.3; P: 17.1 found C: 39.7; H: 8.0; O: 35.0; P: 16.9.

4. Conclusion

In this work we evaluated three different methodologies to obtain various ω -alkylenediphosphoric acids from condensation of phosphorus oxychloride onto diols with varying chain length. Three methodologies were studied: (i) the conventional heating of both reactants in organic solvent, (ii) the reaction under basic activation at low temperature, and (iii) the use of short microwave heating. After optimization, all methodologies permit obtaining the desired alkylenediphosphoric acids $(\text{HO})_2(\text{O})\text{P-O}-(\text{CH}_2)_n\text{-O-P}(\text{O})-(\text{OH})_2$ as main product, but only the microwave assisted one allows for the obtaining of pure products without presence of any traces of polyalkylation byproducts. Moreover, this later methodology permits drastically decreasing the reaction time without using excess of either reactant or any catalyst. It thus appears as an interesting way of synthesizing selectively monoalkylphosphate. In addition, due to relatively friendly conditions, it could be further applied to more sensible substrates.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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