

# One-Pot Synthesis of Phosphoramidates from dibenzo[1,3,2]dioxaphosphepine-6-oxide<sup>†</sup>

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**Abstract:** Flame retardants play a crucial role in mitigating the hazards associated with fires by impeding their ignition and spread. However, conventional halogen-based flame retardants have encountered environmental and health concerns due to their persistence, bioaccumulation, and potential toxicity. In light of these concerns, the present study aimed to develop innovative compounds with potential applications as a flame retardant system that mitigates the drawbacks associated with halogen-based compounds. Several phosphoramidates were synthesized in a single step under mild conditions from the *H*-phosphonate dibenzo[1,3,2]dioxaphosphepine-6-oxide (BPPO), following a method based on the oxidation of the reactant in the presence of a suitable aliphatic or aromatic amine. The compounds were isolated with high purity, and the formulations were confirmed by multinuclear NMR spectroscopy.

**Keywords:** BPPO; phosphoramidates; flame retardants; P-N bond formation

## 1. Introduction

Since the initial report in 1972, the organophosphorus compound 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have been known to be of noticeable industrial interest, being viable alternatives to halogenated flame retardants [1,2]. Being a *H*-phosphinate, DOPO shows two different tautomeric forms in equilibrium in solution, and it is thus able to behave both as a nucleophile and as an electrophile [3,4]. The reactivity of the P-H bond opens the possibility of formally replacing the hydrogen atom with several functional groups, allowing compounds to have specific properties but maintain flame-retardant activity both in the gas and condensed phases [5–9]. For instance, the P-H bond can be replaced with a P-C bond through reactions based on the nucleophilic attack on electron-poor carbon atoms [10–15], on the Michael addition [16–20], and on the Michaelis–Arbuzov rearrangement [21–23]. Phosphoramidates and phosphonates can be prepared from DOPO with the intermediate synthesis of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-chloride (DOPO-Cl). Such a compound is generally obtained on the basis of the Atherton–Todd reaction using CCl<sub>4</sub> as reactant [24–29], even if alternative chlorinating agents were considered, such as sulfuryl chloride, trichlorocyanuric acid, chlorine gas, and N-chlorosuccinimide [30–34].

Another cyclic phosphorus compound of growing interest in the field of flame reactants is the *H*-phosphonate dibenzo[1,3,2]dioxaphosphepine-6-oxide (BPPO) that can be isolated from a three-component reaction involving 2,2'-bisphenol, phosphorus trichloride, and water. The P-H bond revealed noticeable reactivity, and several organophosphorus BPPO derivatives can be prepared on the basis of phospho-Michael additions to unsaturated compounds [35–37]. It is worth noting that the different electron density on the phosphorus



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atom in BPPO with respect to DOPO alters the flame retardant behaviour since P-containing gases are preferentially released when low positive partial charges are present on the phosphorus atom. Hence, DOPO derivatives with low molecular weights mainly act in the gas phase, stopping the chain radical reaction, while the flame retardant action of BPPO-based compounds is more concentrated in the condensed phase, where the formation of a thermally stable char layer is promoted.

It is known that synergistic effects in the flame retardant behaviour can occur on mixing or reacting phosphorus- and nitrogen-based compounds [38–43]; therefore, the development of phosphoramidate (or amidophosphate) derivatives of BPPO appears as a promising approach to obtain flame retardants with tailored properties. Given our interest in cyclic organophosphorus compounds and phosphoramidates [44–48], some of us patented a straightforward approach for the preparation of BPPO derivatives with P-N bonds, working under mild conditions [49]. Herein, we report the synthesis and characterization of dibenzo[1,3,2]dioxaphosphepine-6-oxide phosphoramidates derived from butylamine, morpholine, 4-acetylpiperazine, aniline, and *p*-toluidine.

## 2. Materials and Methods

The reactants and solvents were Merck products and they were used as received. Dibenz[1,3,2]dioxaphosphepine-6-oxide (BPPO) was synthesized according to a reported procedure [37]. In a 100 mL three-necked round-bottom flask equipped with condenser, magnetic stirring bar, dropping funnel, and nitrogen inlet, 2,2'-biphenol (25.75 g, 13.8 mmol) was dissolved in 50 mL of 1,4-dioxane and 2.5 mL of water and heated to reflux. A minimum flow of nitrogen was continuously passed through the solution. Phosphorus trichloride (12.1 mL, 13.8 mmol) was added within 3 h to the boiling reaction mixture. The generated HCl gas was absorbed in a trap filled with water. The reaction mixture was heated to reflux for an additional hour, then the solvent was removed under reduced pressure to obtain a viscous oil that became solid overnight. The product was triturated with 50 mL of diethyl ether, filtered, washed with fresh diethyl ether (10 mL), and dried under vacuum. Yield 75%.

Elemental analyses (C, H, N) were carried out using an Elementar Unicube microanalyzer. Melting points were registered using a FALC 360 D instrument equipped with a camera. Infrared (IR) spectra were registered using a Perkin-Elmer SpectrumOne spectrophotometer between 4000 and 450  $\text{cm}^{-1}$  using KBr pellets. Mono- and bidimensional nuclear magnetic resonance (NMR) spectra were collected employing a Bruker Avance 400 instrument operating at 400.13 MHz of  $^1\text{H}$  resonance.  $^1\text{H}$  NMR spectra are referred to the partially non-deuterated fraction of the solvent, itself quoted with respect to tetramethylsilane.  $^{31}\text{P}\{^1\text{H}\}$  chemical shifts are reported with respect to 85%  $\text{H}_3\text{PO}_4$ , with downfield shifts considered positive.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are referred to the solvent signal, quoted with respect to tetramethylsilane.

### 2.1. Synthesis of BPPO Phosphoramidate Derivatives

6-(butylamino)dibenzo[1,3,2]dioxaphosphepine-6-oxide (**BPPO-N<sub>HB</sub>Butyl**), 6-morpholinodibenzo[1,3,2]dioxaphosphepine-6-oxide (**BPPO-N<sub>morph</sub>**), 6-(4-acetylpiperazino)dibenzo dioxaphosphepine-6-oxide (**BPPO-N<sub>AcPz</sub>**), 6-(phenylamino)dibenzo[1,3,2]dioxaphosphepine-6-oxide (**BPPO-N<sub>HPh</sub>**), and 6-(*p*-tolylamino)dibenzo[1,3,2]dioxaphosphepine-6-oxide (**BPPO-N<sub>HTol</sub>**) were all synthesized following the same general method. In a typical preparation, BPPO (1.15 g, 5.00 mmol) and 16.5 mmol of the proper amine (butylamine, 1.6 mL; morpholine, 1.4 mL; 1-acetylpiperazine, 2.13 g; aniline, 1.51 g; *p*-toluidine, 1.77 g) were dissolved in 30 mL of dichloromethane, then  $\text{I}_2$  (1.26 g, 5.00 mmol) was slowly added. The resulting reaction mixture was kept under vigorous stirring at room temperature for three hours. The solid by-product that separated with all the amines with the exception of butylamine was removed by filtration and washed with dichloromethane; then the organic solution was washed with brine ( $3 \times 100$  mL), dried with anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was removed by evaporation under reduced pressure. In the case

of the morpholine derivative, the raw product was purified by crystallization with cold ethanol (10 mL), followed by filtration. In the other cases, diethyl ether (10 mL) was added, and the solid formed was collected by filtration and washed with diethyl ether. All the products were finally dried under vacuum. Further product was collected from the diethyl ether solution in the case of the butylamine derivative after keeping the solution at  $-20\text{ }^{\circ}\text{C}$  overnight. Yields: 30% (**BPPO-N<sub>H</sub>Butyl**); 54% (**BPPO-N<sub>morph</sub>**); 12% (**BPPO-N<sub>AcPz</sub>**); 94% (**BPPO-N<sub>HPh</sub>**); 60% (**BPPO-N<sub>HTol</sub>**).

#### 2.1.1. Characterization of **BPPO-N<sub>H</sub>butyl**

Anal. calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}_3\text{P}$  ( $303.29\text{ g mol}^{-1}$ , %): C, 63.36; H, 5.98; N, 4.62. Found (%): C, 63.10; H, 6.00; N, 4.59. M.p. ( $^{\circ}\text{C}$ ): 101. IR (KBr,  $\text{cm}^{-1}$ ): 3355  $\nu_{\text{NH}}$ , 1243  $\nu_{\text{P=O}}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  7.53 (dd, 2H,  $J_{\text{HH}} = 7.6\text{ Hz}$ ,  $J_{\text{HH}} = 1.8\text{ Hz}$ , arom), 7.42 (t, 2H,  $J_{\text{HH}} = 7.6\text{ Hz}$ , arom), 7.33 (t, 2H,  $J_{\text{HH}} = 7.6\text{ Hz}$ , arom), 7.29 (d, 2H,  $J_{\text{HH}} = 7.6\text{ Hz}$ , arom), 3.05–2.90 (m, 3H,  $\text{NH}+\text{CH}_2$ ), 1.48 (m, 2H,  $\text{CH}_2$ ), 1.31 (m, 2H,  $\text{CH}_2$ ), 0.88 (t, 3H,  $J_{\text{HH}} = 7.3\text{ Hz}$ ,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  13.36 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K): 148.12 (d,  $J_{\text{PC}} = 9.4\text{ Hz}$ , arom- $\text{C}_{\text{ipso}}$ ), 129.90 (d,  $J_{\text{PC}} = 1.2\text{ Hz}$ , arom-CH), 129.78 (d,  $J_{\text{PC}} = 1.2\text{ Hz}$ , arom-CH), 128.59 (d,  $J_{\text{PC}} = 1.6\text{ Hz}$ , arom- $\text{C}_{\text{ipso}}$ ), 126.50 (d,  $J_{\text{PC}} = 1.8\text{ Hz}$ , arom-CH), 121.67 (d,  $J_{\text{PC}} = 4.2\text{ Hz}$ , arom-CH), 41.92 (s,  $\text{CH}_2$ ), 34.03 (d,  $J_{\text{PC}} = 5.5\text{ Hz}$ ,  $\text{CH}_2$ ), 19.58 (s,  $\text{CH}_2$ ), 13.63 (s,  $\text{CH}_3$ ).

#### 2.1.2. Characterization of **BPPO-N<sub>morph</sub>**

Anal. calcd for  $\text{C}_{16}\text{H}_{16}\text{NO}_4\text{P}$  ( $317.28\text{ g mol}^{-1}$ , %): C, 60.57; H, 5.08; N, 4.41. Found (%): C, 60.65; H, 5.10; N, 4.39. M.p. ( $^{\circ}\text{C}$ ): 171. IR (KBr,  $\text{cm}^{-1}$ ): 1251  $\nu_{\text{P=O}}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  7.53 (dd, 2H,  $J_{\text{HH}} = 7.7\text{ Hz}$ ,  $J_{\text{HH}} = 1.7\text{ Hz}$ , arom), 7.44 (tdd, 2H,  $J_{\text{HH}} = 7.7\text{ Hz}$ ,  $J_{\text{HH}} = 1.7\text{ Hz}$ ,  $J_{\text{PH}} = 0.9\text{ Hz}$ , arom), 7.35 (tt, 2H,  $J_{\text{HH}} = 7.7\text{ Hz}$ ,  $J_{\text{HH}} = J_{\text{PH}} = 1.2\text{ Hz}$ , arom), 7.32 (dt,  $J_{\text{HH}} = 7.7\text{ Hz}$ ,  $J_{\text{HH}} = 1.2\text{ Hz}$ ), 3.62 (m, 4H,  $\text{O}-\text{CH}_2$ ), 3.16 (m, 4H,  $\text{N}-\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  10.17 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  148.31 (d,  $J_{\text{PC}} = 9.6\text{ Hz}$ , arom- $\text{C}_{\text{ipso}}$ ), 130.04 (d,  $J_{\text{PC}} = 1.2\text{ Hz}$ , arom-CH), 139.97 (d,  $J_{\text{PC}} = 1.2\text{ Hz}$ , arom-CH), 128.23 (d,  $J_{\text{PC}} = 1.4\text{ Hz}$ , arom- $\text{C}_{\text{ipso}}$ ), 126.28 (d,  $J_{\text{PC}} = 1.8\text{ Hz}$ , arom-CH), 121.70 (d,  $J_{\text{PC}} = 4.4\text{ Hz}$ , arom-CH), 66.98 (d,  $J_{\text{PC}} = 5.0\text{ Hz}$ ,  $\text{O}-\text{C}$ ), 45.47 (d,  $J_{\text{PC}} = 1.0\text{ Hz}$ ,  $\text{N}-\text{C}$ ).

#### 2.1.3. Characterization of **BPPO-N<sub>AcPz</sub>**

Anal. calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_4\text{P}$  ( $358.33\text{ g mol}^{-1}$ , %): C, 60.33; H, 5.34; N, 7.82. Found (%): C, 60.09; H, 5.37; N, 7.78. M.p. ( $^{\circ}\text{C}$ ): 141. IR (KBr,  $\text{cm}^{-1}$ ): 1646  $\nu_{\text{C=O}}$ , 1251  $\nu_{\text{P=O}}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  7.55 (dd, 2H,  $J_{\text{HH}} = 7.8\text{ Hz}$ ,  $J_{\text{HH}} = 1.2\text{ Hz}$ , arom), 7.44 (t, 2H,  $J_{\text{HH}} = 7.4\text{ Hz}$ , arom), 7.36 (t, 2H,  $J_{\text{HH}} = 7.4\text{ Hz}$ , arom), 7.30 (d, 2H,  $J_{\text{HH}} = 7.8\text{ Hz}$ , arom), 3.53 (s, br, 2H,  $\text{N}-\text{CH}_2$ ), 3.44 (s, br, 2H,  $\text{N}-\text{CH}_2$ ), 3.22 (s, br, 2H,  $\text{N}-\text{CH}_2$ ), 3.09 (s, br, 2H,  $\text{N}-\text{CH}_2$ ), 2.08 (s, 3H,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  9.54 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  169.17 (s,  $\text{C}=\text{O}$ ), 148.16 (d,  $J_{\text{PC}} = 9.6\text{ Hz}$ , arom- $\text{C}_{\text{ipso}}$ ), 130.12 (d,  $J_{\text{PC}} = 0.9\text{ Hz}$ , arom-CH), 130.05 (d,  $J_{\text{PC}} = 1.0\text{ Hz}$ , arom-CH), 128.15 (d,  $J_{\text{PC}} = 1.5\text{ Hz}$ , arom-CH), 126.42 (d,  $J_{\text{PC}} = 1.8\text{ Hz}$ , arom-CH), 121.59 (d,  $J_{\text{PC}} = 4.3\text{ Hz}$ , arom-CH), 46.73 (s,  $\text{N}-\text{C}$ ), 45.35 (s,  $\text{N}-\text{C}$ ), 41.66 (s,  $\text{N}-\text{C}$ ), 21.30 (s,  $\text{CH}_3$ ).

#### 2.1.4. Characterization of **BPPO-N<sub>HPh</sub>**

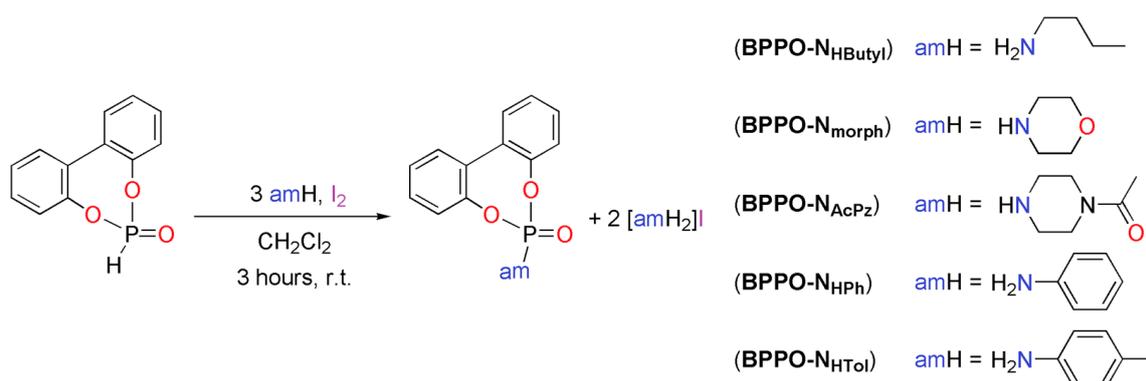
Anal. calcd for  $\text{C}_{18}\text{H}_{14}\text{NO}_3\text{P}$  ( $323.28\text{ g mol}^{-1}$ , %): C, 66.87; H, 4.36; N, 4.33. Found (%): C, 66.60; H, 4.38; N, 4.35. M.p. ( $^{\circ}\text{C}$ ): 155. IR (KBr,  $\text{cm}^{-1}$ ): 3378  $\nu_{\text{NH}}$ , 1197  $\nu_{\text{P=O}}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  7.55 (dd, 2H,  $J_{\text{HH}} = 7.4\text{ Hz}$ ,  $J_{\text{HH}} = 2.1\text{ Hz}$ , arom), 7.42–7.33 (m, 4H, arom), 7.24–7.16 (m, 4H, arom), 7.07 (d, 2H,  $J_{\text{HH}} = 7.9\text{ Hz}$ , arom), 7.01 (t, 1H,  $J_{\text{HH}} = 7.4\text{ Hz}$ , arom), 5.44 (d, 1H,  $J_{\text{PH}} = 8.0\text{ Hz}$ , NH).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  6.28 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  147.84 (d,  $J_{\text{PC}} = 9.3\text{ Hz}$ , arom- $\text{C}_{\text{ipso}}$ ), 137.98 (d,  $J_{\text{PC}} = 2.2\text{ Hz}$ , arom- $\text{C}_{\text{ipso}}$ ), 130.12 (d,  $J_{\text{PC}} = 1.4\text{ Hz}$ , arom-CH), 129.92 (d,  $J_{\text{PC}} = 1.4\text{ Hz}$ , arom-CH), 129.33 (s, arom-CH), 128.41 (d,  $J_{\text{PC}} = 1.7\text{ Hz}$ , arom- $\text{C}_{\text{ipso}}$ ), 126.50 (d,  $J_{\text{PC}} = 1.9\text{ Hz}$ , arom-CH), 123.20 (s, arom-CH), 121.80 (d,  $J_{\text{PC}} = 4.4\text{ Hz}$ , arom-CH), 119.56 (d,  $J_{\text{PC}} = 6.6\text{ Hz}$ , arom-CH).

### 2.1.5. Characterization of **BPPO-N<sub>H</sub>Tol**

Anal. calcd for C<sub>19</sub>H<sub>16</sub>NO<sub>3</sub>P (337.31 g mol<sup>-1</sup>, %): C, 67.65; H, 4.78; N, 4.15. Found (%): C, 67.40; H, 4.80; N, 4.12. M.p. (°C): 189. IR (KBr, cm<sup>-1</sup>): 3379 ν<sub>NH</sub>, 1198 ν<sub>P=O</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 7.54 (dd, 2H, J<sub>HH</sub> = 7.1 Hz, J<sub>HH</sub> = 1.8 Hz, arom), 7.42–7.31 (m, 4H, arom), 7.23 (d, 2H, J<sub>HH</sub> = 7.4 Hz, arom), 7.04–6.95 (m, 4H, arom), 5.45 (d, 1H, J<sub>PH</sub> = 7.6 Hz, NH), 2.27 (s, 3H, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K): δ 6.16 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K): δ 147.95 (d, J<sub>PC</sub> = 9.5 Hz, arom-C<sub>ipso</sub>), 135.34 (d, J<sub>PC</sub> = 1.9 Hz, arom-C<sub>ipso</sub>), 132.74 (s, arom-C<sub>ipso</sub>), 130.05 (d, J<sub>PC</sub> = 0.8 Hz, arom-CH), 129.86 (d, J<sub>PC</sub> = 0.9 Hz, arom-CH), 129.78 (s, arom-CH), 128.46 (d, J<sub>PC</sub> = 1.5 Hz, arom-C<sub>ipso</sub>), 126.38 (d, J<sub>PC</sub> = 1.7 Hz, arom-CH), 121.83 (d, J<sub>PC</sub> = 4.4 Hz, arom-CH), 119.85 (d, J<sub>PC</sub> = 6.4 Hz, arom-CH), 20.66 (s, CH<sub>3</sub>).

## 3. Results and Discussion

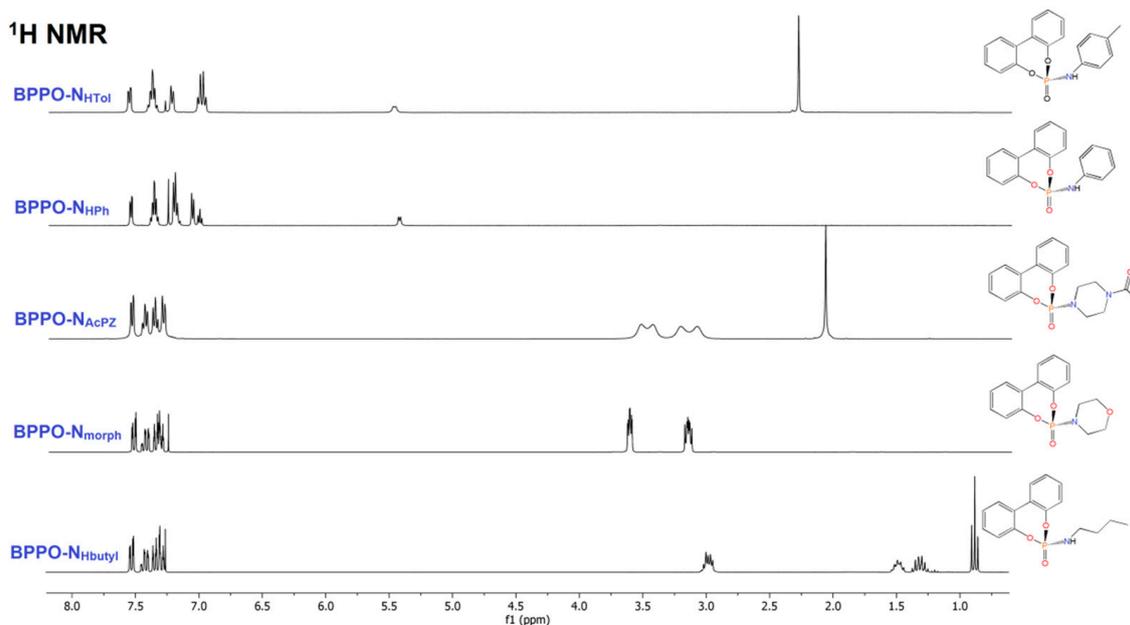
According to the recently published patent [49], the conversion of BPPO is related phosphoramidates can be carried out in a single step by reacting the precursor with I<sub>2</sub> in the presence of a suitable aliphatic or aromatic amine (amH), as depicted in Scheme 1. The compounds **BPPO-N<sub>H</sub>Butyl**, **BPPO-N<sub>morph</sub>**, **BPPO-N<sub>AcPz</sub>**, **BPPO-N<sub>HPh</sub>**, and **BPPO-N<sub>H</sub>Tol** were isolated with yields comprised between 12% and 94% and had a high degree of purity. The low yields obtained in some cases are mainly attributable to work-up issues. With the exception of butylammonium iodide, the by-product [amH<sub>2</sub>]I was always recovered by filtration from the reaction mixture. It is worth noting that an alternative synthetic approach for the preparation of **BPPO-N<sub>morph</sub>** is already present in the literature [50].



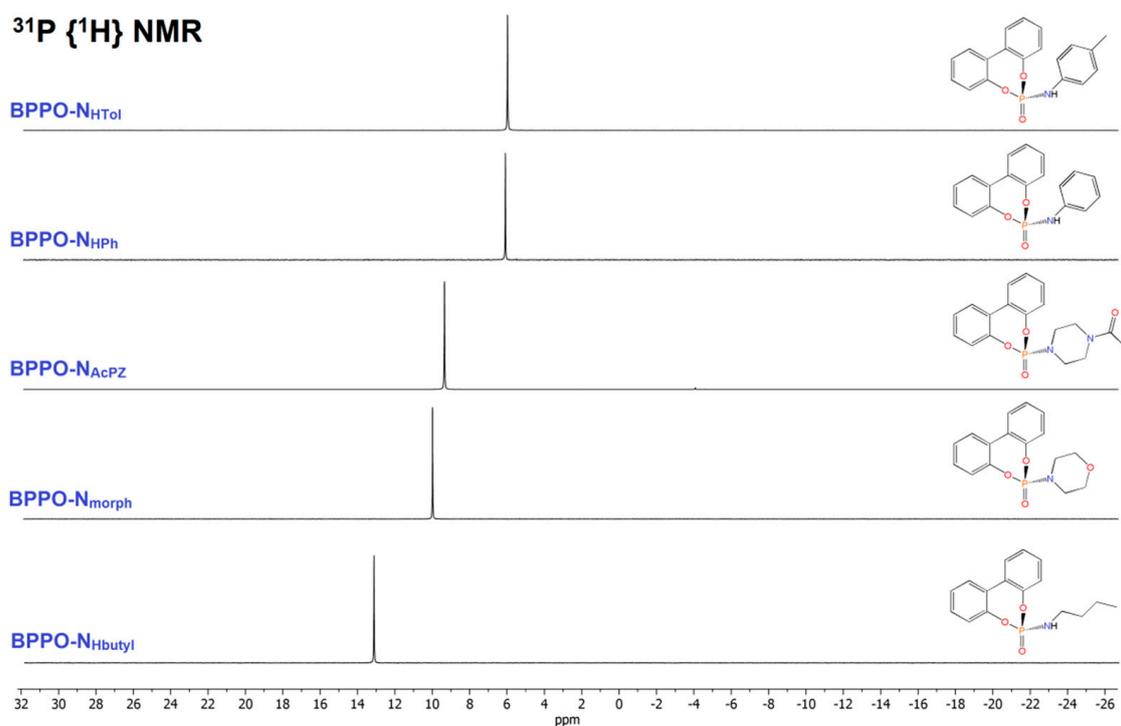
**Scheme 1.** Synthesis of phosphoramidates from BPPO.

The <sup>1</sup>H NMR spectra of all the compounds showed the disappearance of the P-H resonance of BPPO, while the four multiplets due to the equivalent aromatic rings of the biphenyl moiety were maintained. Besides the aromatic resonances, the <sup>1</sup>H NMR spectrum of **BPPO-N<sub>H</sub>Butyl** in CDCl<sub>3</sub> shows the superposition of multiplets between 3.05 and 2.90 ppm assigned to the N-bonded hydrogen atom and the CH<sub>2</sub> fragment. The other aliphatic resonances fall at 1.48, 1.31, and 0.88 ppm. The <sup>13</sup>C{<sup>1</sup>H} NMR signals of the butyl chain fall in the 42–13 ppm range, and the one at 34.03 ppm exhibits a coupling constant of 5.5 Hz with the <sup>31</sup>P nucleus, in agreement with the formation of the P-N bond. The presence of P-bonded morpholine in **BPPO-N<sub>morph</sub>** was highlighted by two multiplets at 3.62 and 3.16 ppm, correlated to resonances in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at 66.98 and 45.47 ppm. The <sup>13</sup>C{<sup>1</sup>H} NMR signals are doublets thanks to the coupling with <sup>31</sup>P. In the <sup>1</sup>H NMR spectrum of the comparable **BPPO-N<sub>AcPz</sub>** compound, the four CH<sub>2</sub> fragments of the piperazine heterocycle are all non-equivalent because of the different substituents at the nitrogen atoms and because of the lack of free rotation of the acetyl group around the N-C bond, that removes the equivalence of the two halves of the piperazine ring. The CH<sub>2</sub> <sup>1</sup>H NMR chemical shift values are 3.53, 3.44, 3.22, and 3.09 ppm, correlated to <sup>13</sup>C{<sup>1</sup>H} NMR resonances in the 47–41 ppm range. The acetyl substituent resonates at 2.08 ppm in the <sup>1</sup>H NMR spectrum and at 169.17 and 21.30 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. The

NMR spectra of **BPPO-N<sub>HPh</sub>** and **BPPO-N<sub>HTol</sub>** are similar, with obvious differences related to the presence in the second case of the methyl substituent. The NH resonance is clearly observable in the <sup>1</sup>H NMR spectrum at about 5.45 ppm, with *J*<sub>PH</sub> coupling constant close to 8 Hz. The <sup>1</sup>H NMR spectra are shown in Figure 1. A single sharp resonance was observed in all the <sup>31</sup>P{<sup>1</sup>H} NMR spectra between 13.5 and 9.5 ppm for the derivatives of aliphatic amines and around 6.2 ppm for **BPPO-N<sub>HPh</sub>** and **BPPO-N<sub>HTol</sub>** (Figure 2).



**Figure 1.** <sup>1</sup>H NMR spectra of the phosoramidate derivatives (CDCl<sub>3</sub>, 298 K).



**Figure 2.** <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the phosoramidate derivatives (CDCl<sub>3</sub>, 298 K).

The IR spectra show, in all the cases, the P=O stretching around 1200 cm<sup>-1</sup>. In some cases, further diagnostic signals were detected, such as the ν<sub>NH</sub> stretching above 3300 cm<sup>-1</sup>

for **BPPO-N<sub>H</sub>butyl**, **BPPO-N<sub>H</sub>Ph**, and **BPPO-N<sub>H</sub>Tol**, or the  $\nu_{\text{CO}}$  stretching band at  $1646\text{ cm}^{-1}$  for **BPPO-N<sub>Ac</sub>Pz**.

To conclude, in this article, we reported the straightforward synthesis of five phosphoramidates starting from BPPO, operating under mild conditions and avoiding the use of aggressive reactants. Most of the compounds described here are reported for the first time, and they are currently under investigation as flame retardants in combination with various plastics.

#### 4. Patents

The data provided in this work were obtained on the basis of the 2023 patent WO2023094526A1, entitled “Preparation process of P(=O)-heteroatom derivatives of dibenzooxaphosphacycles”, presented by our research group.

**Author Contributions:** Conceptualization, M.B. and L.A.; methodology, M.B.; validation, M.B., G.M. and L.A.; formal analysis, M.B. and G.M.; investigation, G.M. and M.B.; resources, L.A.; data curation, M.B. and G.M.; writing—original draft preparation, M.B.; writing—review and editing, G.M. and L.A.; visualization, M.B. and G.M.; project administration, L.A.; funding acquisition, L.A. All authors have read and agreed to the published version of the manuscript.

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**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data are available upon request due to restrictions related to the patent above reported.

**Conflicts of Interest:** The authors declare no conflict of interest.

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