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Proceeding Paper

Alternative Synthesis of Phosphonate Derivatives of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide [†]

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Abstract: The phosphonates 6-methoxy-6*H*-dibenzo[1,2]oxaphosphinine-6-oxide and 6-(allyloxy)-6*H*-dibenzo[1,2]oxaphosphinine 6-oxide were synthesized in a single step under mild conditions from the *H*-phosphinate 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), following a method based on the oxidation with I_2 of the reactant in the presence of the reactant alcohol as solvent and triethylamine as base. The compounds, of potential interest in the field of non-halogenated flame retardants, were isolated with high purity and the formulations were confirmed by multinuclear NMR spectroscopy.

Keywords: DOPO; phosphonates; flame retardants; P-O bond formation

1. Introduction

The organophosphorus *H*-phosphinate 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a molecule of great interest in the field of non-halogenated flame retardants for plastics, and the peculiar reactivity of the P-H bond opens the possibility of different types of functionalization while maintaining the flame retardant activity both in gas and condensed phase [1–9]. Related phosphinates where the P-H bond is formally replaced with a P-C bond can be obtained following approaches such as the nucleophilic attack of the conjugate base of DOPO on electron-poor carbon atoms [10–15], the phospha-Michael addition [16–20] and the Michaelis-Arbuzov rearrangement of related phosphonites [21–23]. On the other hand, the formation of a P-N or a P-O bond in place of the P-H one, with consequent isolation of phosphonamidates and phosphonates from DOPO, is commonly carried out through the intermediate synthesis of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-chloride (DOPO-Cl). Such a species can be obtained on the basis of the Atherton-Todd reaction using CCl_4 as reactant in combination with a suitable base [24–29], even if alternative chlorinating agents such as sulfuryl chloride, trichlorocyanuric acid, chlorine gas and N-chlorosuccinimide revealed to be suitable [30–34]. For what concerns the preparation of DOPO-based aliphatic phosphonates, examples of other synthetic approaches are the esterification of the phosphonic acid 6-hydroxydibenzo[1,2]oxaphosphinine-6-oxide [35] and the electrochemical dehydrogenative coupling of the *H*-phosphinate with alcohols [36].

In recent years, our research group investigated the coordinating behaviour as oxygen-donors towards metal centres such as manganese(II) and zinc(II) of the simple phosphonate $O=P(OPh)_2Ph$ (diphenyl phenylphosphonate) and of the *H*-phosphinate DOPO, with the aim of obtaining multifunctional compounds thanks to the luminescence exhibited by the resulting complexes [37,38]. These studied prompted the investigation of

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alternative approaches for the conversion of DOPO in related phosphonates, and we recently patented a one-pot approach for the formal replacement of the P-H bond of DOPO with P-OR bonds, working under mild conditions [39]. Herein we report as examples of this research the syntheses and characterization data of the compounds 6-methoxy-6*H*-dibenzo[1,2]oxaphosphinine-6-oxide (**DOPO-O$_{Me}$**) and 6-(allyloxy)-6H-dibenzo[c,e][1,2]oxaphosphinine-6-oxide (**DOPO-O$_{Allyl}$**)

2. Materials and Methods

The reactants and solvents were Merck products with the exception of DOPO, purchased from Fluorochem, and they were used as received. Elemental analyses were carried out using an Elementar Unicube microanalyzer Infrared (IR) spectra were registered using a Perkin-Elmer SpectrumOne spectrophotometer between 4000 and 450 cm^{-1}. The products were dispersed between KBr windows. Absorption spectra in dichloromethane were recorded with a Yoke 6000Plus double-beam spectrophotometer. Mono- and bidimensional nuclear magnetic resonance (NMR) spectra were collected employing a Bruker Avance 400 instrument operating at 400.13 MHz of ^{1}H resonance. ^{1}H NMR spectra are referred to the partially non-deuterated fraction of the solvent, itself quoted with respect to tetramethylsilane. ^{31}P{^{1}H} chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. ^{13}C{^{1}H} NMR spectra are referred to the solvent signal, quoted with respect to tetramethylsilane.

Synthesis of 6-methoxy-6H-dibenzo[1,2]oxaphosphinine-6-oxide (DOPO-O$_{Me}$) and 6-(allyloxy)-6H-dibenzo[c,e][1,2]oxaphosphinine-6-oxide (DOPO-O$_{Allyl}$)

In a typical preparation, DOPO (1.08 g, 5.0 mmol) was dissolved in 15 mL of methanol or allyl alcohol. Triethylamine (1.4 mL, 10.0 mmol) was added to the solution, then solid iodine (1.26 g, 5.0 mmol) was slowly added to the stirred solution. The reaction mixture was kept under stirring at room temperature for 5 h. The solvent was then evaporated and dichloromethane (20 mL) was added. Triethylammonium iodide and other by-products were removed by extraction with water (2 × 20 mL). The organic phase was dried with anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the product was selectively dissolved with hot aliquots (3 × 20 mL) of cyclohexane. After rapid filtration of the hot solutions, the solvent was removed under reduced pressure and the products were isolated in oily form. Yields: 30% (0.369 g) for **DOPO-O$_{Me}$**; 33% (0.449 g) for **DOPO-O$_{Allyl}$**.

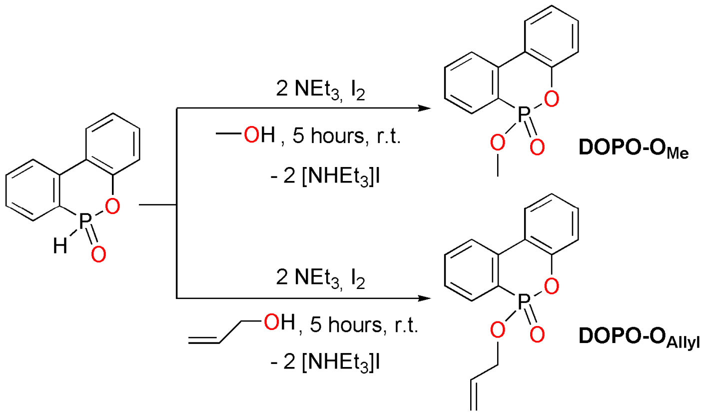
Characterization of **DOPO-O$_{Me}$**: Anal. calcd for $C_{13}H_{11}O_3P$ (246.2 g mol^{-1},%): C, 63.42; H, 4.50. Found (%): C, 63.17; H, 4.52. IR (KBr, cm^{-1}): 1273 $\nu_{P=O}$, 1035 $\nu_{P=O}$. UV-Vis (CH_2Cl_2, r.t., nm): <330, 300 sh, 290, 267, 260. ^{1}H NMR ($CDCl_3$, 300 K): δ 7.98 (ddd, 1H, J_{HH} = 7.4 Hz, J_{HH} = 1.6 Hz, J_{PH} = 14.4 Hz, arom), 7.97 (dd, 1H, J_{HH} = 8.1 Hz, J_{PH} = 6.4 Hz, arom), 7.94 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.7 Hz, arom), 7.73 (tdd, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.5 Hz, J_{PH} = 1.1 Hz, arom), 7.52 (tdd, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.1 Hz, J_{PH} = 3.7 Hz, arom), 7.40 (tdd, 1H, J_{HH} = 7.7 Hz, J_{HH} = 1.5 Hz, J_{PH} = 1.3 Hz, arom), 7.30–7.24 (m, 2H, arom), 3.80 (d, 3H, J_{PH} = 11.5 Hz, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 300 K): δ 11.36 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 300 K): δ 149.92 (d, J_{PC} = 7.9 Hz, arom-C_{ipso}), 137.07 (d, J_{PC} = 7.0 Hz, arom-C_{ipso}), 133.57 (d, J_{PC} = 2.5 Hz, arom-CH), 130.54 (s, arom-CH), 130.26 (d, J_{PC} = 9.2 Hz, arom-CH), 128.29 (d, J_{PC} = 15.4 Hz, arom-CH), 125.25 (d, J_{PC} = 1.1 Hz, arom-CH), 124.77 (s, arom-CH), 124.08 (d, J_{PC} = 12.1 Hz, arom-CH), 122.57 (d, J_{PC} = 12.0 Hz, arom-C_{ipso}), 121.85 (d, J_{PC} = 181.1 Hz, arom-C_{ipso}), 120.17 (d, J_{PC} = 6.7 Hz, arom-CH), 52.93 (d, J_{PC} = 6.6 Hz, CH_3).

Characterization of **DOPO-O$_{Allyl}$**: Anal. calcd for $C_{15}H_{13}O_3P$ (272.24 g mol^{-1},%): C, 66.18; H, 4.81. Found (%): C, 65.95; H, 4.79. IR (KBr, cm^{-1}): 1271 $\nu_{P=O}$, 1009 $\nu_{P=O}$. UV-Vis (CH_2Cl_2, r.t., nm): <330, 300 sh, 290, 267, 260. ^{1}H NMR ($CDCl_3$, 300 K): δ 7.94 (ddd, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.6 Hz, J_{PH} = 14.4 Hz, arom), 7.91 (dd, 1H, J_{HH} = 8.2 Hz, J_{PH} = 6.6 Hz, arom), 7.88 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.6 Hz, arom), 7.66 (tdd, 1H, J_{HH} = 7.7 Hz, J_{HH} = 1.4 Hz, J_{PH} = 1.4 Hz, arom), 7.46 (tdd, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.0 Hz, J_{PH} = 3.7 Hz, arom), 7.34 (tdd, 1H, J_{HH} = 7.8

Hz, J_{HH} = 1.5 Hz, J_{PH} = 1.4 Hz, arom), 7.24–7.17 (m, 2H, arom), 5.82 (ddt, 1H, J_{HH} = 17.2 Hz, J_{HH} = 10.4 Hz, J_{HH} = 5.5 Hz, CH_2-C<u>H</u>), 5.20 (dq, 1H, J_{HH} = 17.2 Hz, J_{HH} = 1.6 Hz, =CH_2), 5.13 (dq, 1H, J_{HH} = 10.4 Hz, J_{HH} = 1.2 Hz, =CH_2), 4.61 (ddt, 2H, J_{HH} = 5.5 Hz, J_{PH} = 9.5 Hz, J_{HH} = 1.4 Hz, C<u>H</u>$_2$-CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 300 K): δ 10.50 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K): δ 149.84 (d, J_{PC} = 8.0 Hz, arom-C_{ipso}), 136.98 (d, J_{PC} = 7.0 Hz, arom-C_{ipso}), 133.54 (d, J_{PC} = 2.6 Hz, arom-CH), 132.27 (d, J_{PC} = 6.0 Hz, CH_2-<u>C</u>H), 130.46 (s, arom-CH), 130.16 (d, J_{PC} = 9.3 Hz, arom-CH), 128.26 (d, J_{PC} = 15.5 Hz, arom-CH), 125.23 (d, J_{PC} = 1.0 Hz, arom-CH), 124.74 (s, arom-CH), 124.04 (d, J_{PC} = 12.2 Hz, arom-CH), 122.49 (d, J_{PC} = 11.8 Hz, arom-C_{ipso}), 122.02 (d, J_{PC} = 181.5 Hz, arom-C_{ipso}), 120.16 (d, J_{PC} = 6.7 Hz, arom-CH), 118.52 (s, =CH_2), 67.02 (d, J_{PC} = 6.3 Hz, <u>C</u>H$_2$-CH).

3. Results and Discussion

According to the recently published patent [39], the iodine-based functionalization of DOPO allowed to isolate related phosphonates such as **DOPO-O$_{Me}$** and **DOPO-O$_{Allyl}$** under mild conditions, as depicted in Scheme 1. A supporting base is required for the reaction, and triethylamine was used because of its inability to behave as nucleophile. The alcohols considered in this communication are methanol and allyl alcohol, that were used as solvents.



Scheme 1. Synthesis of **DOPO-O$_{Me}$** and **DOPO-O$_{Allyl}$.**

The proposed formulations, corroborated by the elemental analysis data, were confirmed by the NMR spectra (see Figures 1–4), that showed, besides the aromatic signals of the phenyl rings in the aromatic regions of ^1H and $^{13}C\{^1H\}$ NMR spectra, resonances attributable to the O-containing substituents. In particular, a doublet at 3.80 ppm with $^3J_{PH}$ coupling constant of 11.5 ppm was observed for **DOPO-O$_{Me}$**, correlated to a doublet ($^2J_{PC}$ = 6.6 Hz) at 52.93 ppm in the $^{13}C\{^1H\}$ NMR spectrum. **DOPO-O$_{Allyl}$** showed signals at 5.82, 5.20 and 5.13 ppm for the vinylic protons and a multiplet at 4.61 ppm corresponding to the O-bonded CH_2, with $^3J_{PH}$ coupling constant of 9.5 Hz. The assignment was confirmed by the $^{13}C\{^1H\}$ and HSQC spectra, with three $^{13}C\{^1H\}$ NMR resonances for the allyl fragment, those involving the C=C bond at 132.27 and 118.57 ppm, while that corresponding to O-CH_2 at 67.02 ppm. The signals of two carbon atoms closer to the phosphorus centre are doublets because of the coupling with ^{31}P. Both the compounds showed only one $^{31}P\{^1H\}$ NMR sharp singlet in the 11.5–10.5 ppm range.

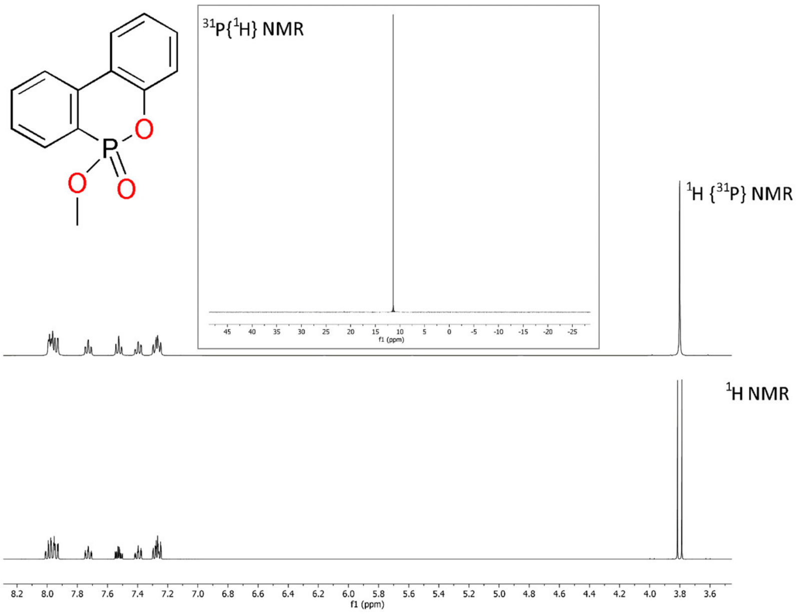


Figure 1. ^{1}H, ^{31}P{^{1}H} and ^{1}H{^{31}P} NMR spectra of **DOPO-O$_{Me}$** (CDCl$_3$, 300 K).

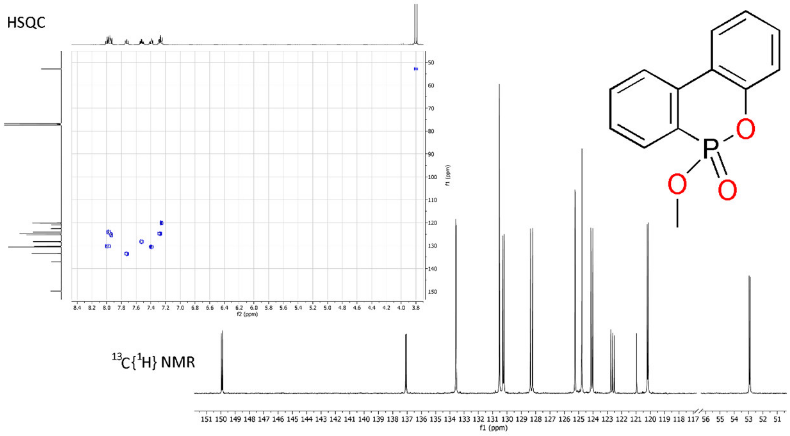


Figure 2. ^{13}C{^{1}H} and ^{1}H-^{13}C HSQC NMR spectra of of **DOPO-O$_{Me}$** (CDCl$_3$, 300 K).

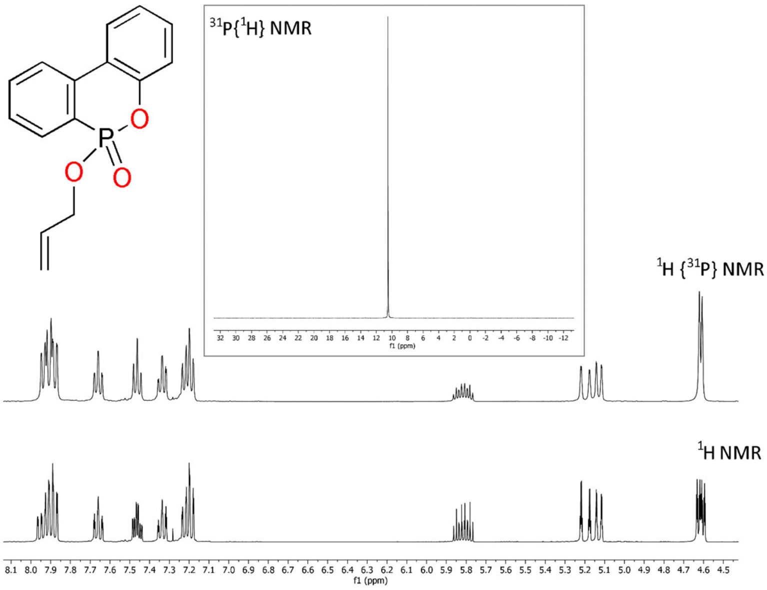


Figure 3. ^{1}H, ^{31}P{^{1}H} and ^{1}H{^{31}P} NMR spectra of **DOPO-O$_{Allyl}$** (CDCl$_3$, 300 K).

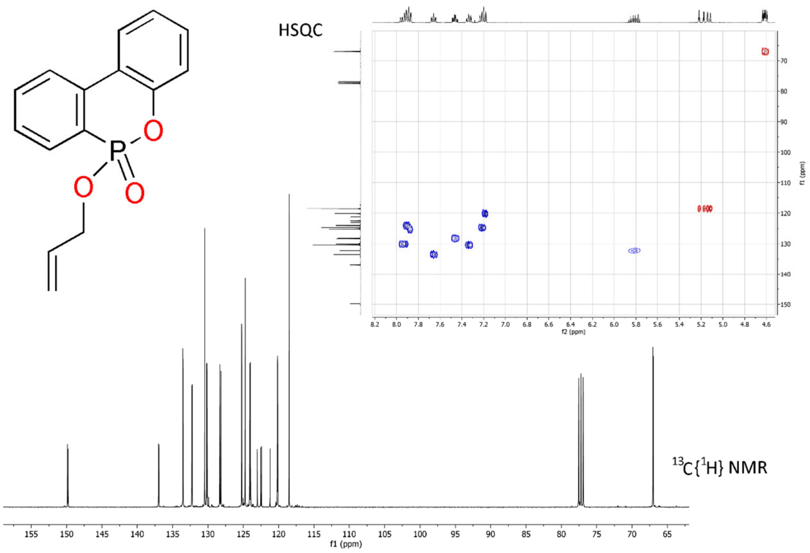


Figure 4. ^{13}C{^{1}H} and ^{1}H-^{13}C HSQC NMR spectra of of **DOPO-O$_{\text{Allyl}}$** ($CDCl_3$, 300 K).

The IR spectra of **DOPO-O$_{\text{Me}}$** and **DOPO-O$_{\text{Allyl}}$** showed $\nu_{P=O}$ stretchings around 1272 cm^{-1}, shifted by more than 30 cm^{-1} towards higher wavenumbers with respect to DOPO, as highlighted in Figure 5. The electron-withdrawing behaviour of the oxygen-containing substituents probably increases the electrophilicity of the phosphorous atom, causing an enforcement of the P=O double bonds. On the other hand, the UV-VIS spectra did not show any meaningful variation with respect to DOPO, with absorptions below 330 nm composed by two groups of bands respectively centred around 290 and 265 nm. Such an outcome indicates that the π-delocalized electronic structure of the aromatic moiety is scarcely affected by the substitution at the phosphorus atom.

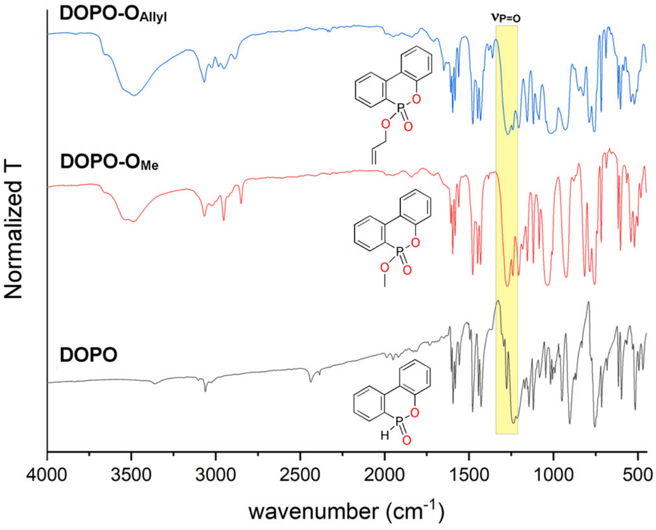


Figure 5. IR spectra of **DOPO-O$_{\text{Me}}$** and **DOPO-O$_{\text{Allyl}}$** and comparison with DOPO.

To conclude, in this communication we reported the straightforward synthesis of two phosphonates starting from DOPO, operating under mild conditions and avoiding the use of aggressive reactants. The changes on the {P=O} moiety with respect to DOPO revealed by the IR spectra make **DOPO-O$_{\text{Me}}$** of interest as ligand for hard transition metal centres, with the aim of developing luminescent coordination compounds suitable as multifunctional materials. On the other hand, **DOPO-O$_{\text{Allyl}}$** is a potentially reactive flame retardant thanks to the presence of the terminal double bond [40], that opens the possibility of co-polymerization with suitable monomers and the development of plastics with intrinsic flame retardant features.

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.; methodology, M.B.; validation, M.B., S.G. and L.A.; formal analysis, M.B. and S.G.; investigation, S.G. and M.B.; resources, L.A.; data curation, M.B and S.G.; writing—original draft preparation, M.B.; writing—review and editing, S.G. and L.A.; visualization, M.B. and S.G.; 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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