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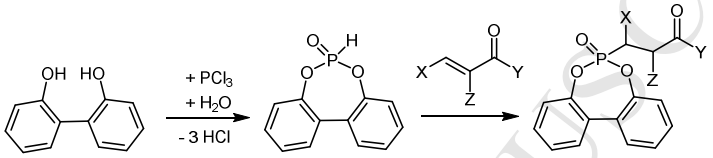

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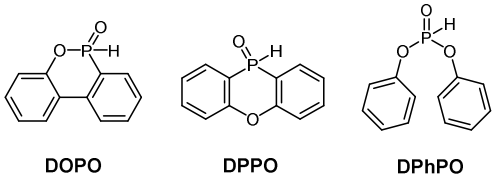
ABSTRACT

A series of phosphonate-containing compounds based on dibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide (BPPO) is presented. BPPO is synthesized by a three–component condensation and is added to activated alkenes with systematically varied structure via phospha-Michael addition. Acrylates, α,β-unsaturated carboxylic acid diesters and benzoquinone are used as activated alkenes. The new compounds are characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The as-prepared phosphonates are envisioned to have flame retardant properties.

1. Introduction

Phosphorus-containing, cyclic molecules like 9,10-dihydro-9-oxaphosphaphenanthrene-10-oxide (DOPO, Scheme 1) were developed in the 1970ies.[1] As soon as the high flame retardant potential of this compound was recognized, DOPO was employed to modify other organic molecules, for instance by phospha-Michael addition to benzoquinone.[2] The resulting 10-(2,5-dihydroxyphenyl)-10H-9-oxa-10-phospha-phenanthrene-10-oxide (DOPO-HQ) served as flame retardant additive as well. It was also employed as (co)monomer for aromatic poly(phosphonate)s,[3] poly(ether sulfone)s,[4] and aromatic polyesters.[5] Subsequent glycolization of DOPO-HQ yielded 10-[2,5-bis(2-hydroxyethoxy)-phenyl]-9,10-dihydro-9-oxa-10-pospha-phenanthrene-10-oxide (DOPO-HQ-GE, alternative name: 2,2‘-[[2-(6H-dibenz[c,e][1,2]-oxaphosphorin-6-yl)-1,4-phenylene]-bis(oxy)] bis[ethanol]), a bifunctional monomer with aliphatic OH-groups for synthesis of aliphatic-aromatic polyesters.[6–8] Since then, the versatility of phospa-Michael additions of DOPO to a wide number of unsaturated compounds has been demonstrated, among them addition to itaconic acid and dimethyl itaconate,[9,10] to double bonds in plant oils,[11] and to acrylates.[12] A recent review is given by Salmeia and Gaan.[13]

Additionally, electrophilic additions of DOPO to C=N bonds,[13] to ketones,[14,15] as well as reactions with secondary amines[16] have been described.



Scheme 1. Chemical structure of DOPO, DPPO and DPhPO.

The phospha-Michael reaction has also been applied for the synthesis of phosphorus-containing compounds with other structural features than DOPO, e.g. for compounds having 2,8-dimethyl-phenoxaphosphine-10-oxide (DPPO, Scheme 1) units.[17] yielding slightly higher condensed phase action,[18] and to diphenyl phosphine oxide[19] (DPhPO, Scheme 1) supporting gas phase action.[18]

While low molecular weight DOPO derivatives as flame retardant additives in polymer materials act mainly in the gas phase and interrupt radical reactions occurring there, polymers with DOPO substituents show often a combination of gas phase

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activity, condensed phase action, eventually combined with the formation of an intumescent layer.[20] The impact of the oxidation state of phosphorus in flame retardants for polyurethanes has already been studied by Modesti.[21]

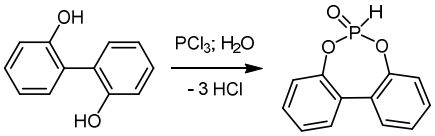
In this paper, the synthesis of compounds having a different phosphorus-containing ring system, dibenzo[d,f][1,3,2] dioxaphosphepine 6-oxide (BPPO, **1**), is presented. BPPO differs from DOPO by one additional oxygen atom between phosphorus and the biphenyl moiety. BPPO is therefore a phosphonate analogue to the phosphinate DOPO. BPPO has not been described yet as a subunit for flame retardants.

Here, it is used as educt for phospha-Michael additions to a series of unsaturated compounds. As the BPPO ring system represents a phosphonate structure, while DOPO is a phosphinate, a significant change in flame retardant action towards gas phase activity of the resulting compounds and polymeric materials is expected. The present report is, however, restricted to the synthesis of the respective BPPO-containing compounds resulting in non-reactive (without functional groups) as well as reactive flame retardant additives (with functional hydroxyl and amide groups).

2. Results and discussion

2.1. Synthesis of BPPO

The synthesis of BPPO via three-component condensation of 2,2´-biphenol, phosphorus trichloride and water was described for the first time by Natchev in 1988 (Scheme 2).[22]



Scheme 2. Synthesis of BPPO.

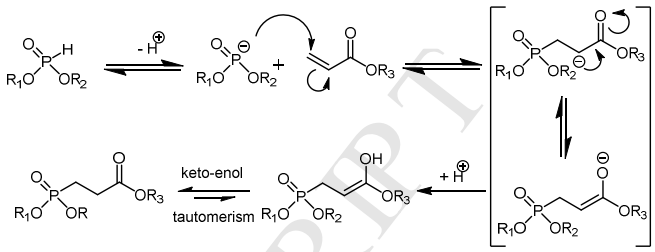
Another method describing the synthesis of different heterocyclic hydrogen phosphine oxides by using P_4O_6 was patented in 2016.[23] P_4O_6 is not commercially available. Its synthesis from white phosphorus requires very high reaction temperatures and specific atmospheric conditions (high pressure) and was not employed here.

Therefore, we worked with the procedure described by Natchev[22] and optimized the reaction conditions. So, the concentration of 2,2´-biphenol in the reaction mixture was raised from 0.1 M to 2.7 M. Additionally, the workup was modified. After evaporation of the solvent, Natchev treated the residue with sodium hydroxide solution. During this step, we observed a partial decomposition of BPPO and the expected product could not be isolated. Therefore, the workup was simplified by letting the residue crystallize and washing it with diethyl ether. Thus, the yield was raised to 84% compared to the Natchev procedure with a reported yield of 72% and comparable puirty.

2.2. The phospha-Michael addition of H-phosphonates to unsaturated compounds

The mechanism of the reaction of BPPO with unsaturated compounds follows a phospha-Michael addition. The Michael addition is a base-catalyzed 1,4-addition of a C-H-acidic compound to an α,β-unsaturated carbonyl compound.[24] The phospha-Michael addition proceeds similarly. Here, the phosphorus acts as nucleophile which is added to an alkene or alkyne. This reaction is an effective method for the formation of phosphorus-carbon bonds with several electrophiles[25] and is often applied to synthesize phosphorus-containing flame retardant additives.[13,16,26,27]

The reaction mechanism between a phosphinate and an acrylate is known from literature.[25] It is assumed that a similar mechanism applies for the reaction with a H-phosphonate, as shown in Scheme 3.[28]



Scheme 3. Phospha-Michael addition of H-phosphonate to acrylates.

In the first step, the phosphonate is deprotonated by the base (in this case triethyl amine) generating the phosphonate ion. Then, a nucleophilic attack on the β-C atom takes place, followed by delocalization of the anion. After protonation and tautomerization the product is formed.[25] If R_1 and R_2 are connected as in the case of BPPO, P-containing heterocyclic compounds result.

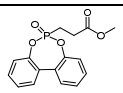
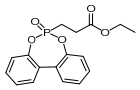
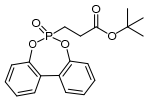
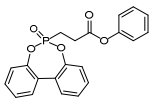
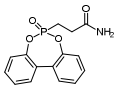
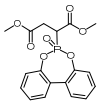
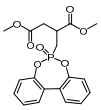
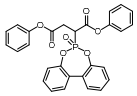
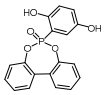
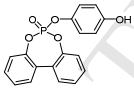
BPPO was subsequently reacted with a number of unsaturated molecules in order to prepare BPPO-containing compounds with systematically changed chemical structure. These unsaturated molecules were selected to obtain BPPO-derivatives with reactive groups (esters, amides and alcohols). Like DOPO, these BPPO-derivatives can be used as monomers for polycondensation and polyaddition reactions. Additionally, the ester group was varied (methyl, ethyl, tert.-butyl and phenyl) giving non-reactive compounds.

The detailed procedures of the addition of BPPO to acrylates (**2**-**6**), unsaturated diesters (**7**-**9**), and to p-benzoquinone (**10**, **11**) are described in the Experimental section. A summary of the compounds obtained is given in Table 1.

All reactions except **10** were performed in presence of the base triethyl amine. In most experiments, yields between 77 and 87% were reproducibly achieved. For compound **7** both educts, dimethyl fumarate and dimethyl maleate, provided similar yields of 77%. In case of the phenyl esters **5** and **9**, the yields were lower (between 57 and 71%) due to the lower reactivity of the double bond. In case of p-benzoquinone as educt and in the presence of triethyl amine Michael 1,4-addition did not take place, but BPPO is oxidized to the corresponding aromatic phosphate ester **11**. The mechanism could be envisioned as a 1,2-addition to the hydroquinone C=O bond. This oxidation has been described for the addition of DOPO to p-benzoquinone under comparable conditions, too.[29]

The chemical structure of compounds **1 – 11** was verified by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy (see Experimental section).

Table 1. Phospha-Michael addition of BPPO to unsaturated compounds studied here.

Compound	Educt	Product	Yield [%]
2	Methyl acrylate (MA)		83
3	Ethyl acrylate (EA)		87
4	tert.-Butyl acrylate (tBuA)		87
5	Phenyl acrylate (PA)		57
6	Acryl amide (AM)		85
7	Dimethyl fumarate / maleate (DMF / DMM)		77[a]
8	Dimethyl itaconate (DMI)		81
9	Diphenyl fumarate (DPF)		71
10	p-Benzoquinone		68
11	p-Benzoquinone		98

[a] Yield independent of educts (dimethyl fumarate or dimethyl maleate)

3. Conclusions

BPPO was synthesized based on the procedure reported by Natchev[22] and used as nucleophile in phospha-Michael additions to a series of unsaturated compounds. The reactions were successfully and reproducibly executed resulting in new BPPO-containing compounds. The procedures applied were relatively straightforward and performed under normal atmosphere. The solid compounds obtained (except oily **8**) could be purified easily by washing with diethyl ether.

Thus, a series of new BPPO-containing compounds was developed which are currently studied as flame retardants. The impact of the structural variations on the flame retarding properties is explored and will be published separately.

4. Experimental section

2,2-Biphenol (99.0%, Sigma-Aldrich), phosphorus trichloride (99.0%, Sigma-Aldrich), methyl acrylate (99.0%, stabilized with MEHQ, TCI), ethyl acrylate (99.0%, stabilized with MEHQ, TCI), tert.-butyl acrylate (99.0%), phenyl acrylate (98.0%, stabilized with MEHQ, TCI), acryl amide (99%), dimethyl maleate (97.0%, TCI), dimethyl fumarate (97.0%, Sigma-Aldrich), dimethyl itaconate (98.0%, TCI), and 1,4-benzoquinone (98.0%, TCI) were used as received. The solvents 1,4-dioxane (99%, stabilized with BHT, TCI), diethyl ether (99.0%, Sigma-Aldrich), toluene (99.0%, Sigma-Aldrich), and chloroform (99.0%, Sigma-Aldrich), were reagent grade and were also used without purification. Diphenyl fumarate was synthesized by reacting phenol (99.5%, Sigma-Aldrich) and fumaryl chloride (95%, Aldrich) according to a literature procedure.[30]

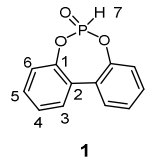
4.1. Instrumentation

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using a Bruker Avance III 500 NMR spectrometer operating at 500 MHz for ^{1}H, at 125 MHz for ^{13}C, and at 202 MHz for ^{31}P NMR, respectively. DMSO-d_6 was used as solvent and internal standard ($\delta(^{1}H)$ = 2.50 ppm, $\delta(^{13}C)$ = 39.6 ppm). The ^{31}P NMR spectra are referenced on external H_3PO_4.

4.2. Synthesis procedures

*4.2.1. Dibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide (**1**)*

In a 1000 mL three-necked round-bottom flask equipped with condenser, magnetic stirring bar, dropping funnel, and nitrogen inlet, 2,2´-biphenol (257.5 g, 1.38 mol) and water (24.9 mL, 1.38 mol) were dissolved in 1,4-dioxane (500 mL) and heated to reflux. A continuous flow of nitrogen was passed through the solution. The dropping funnel was charged with phosphorus trichloride (189.9 g, 1.38 mol). Within 3 hours, the PCl_3 was slowly added to the boiling reaction mixture. The generated HCl gas was absorbed in a beaker with concentrated NaOH solution. After complete addition of PCl_3, the mixture was heated to reflux for an additional hour. The solvent was removed under reduced pressure and a viscous oil was obtained. It crystallized after 24 hours. The solid product was washed three times with diethyl ether and dried under reduced pressure to give **1** (Yield: 84%), Scheme 4.



1

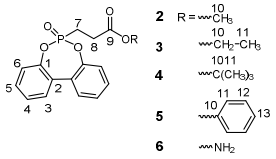
Scheme 4. Chemical structure of **1.**

^{1}H NMR (DMSO-d_6): δ 7.70 (d, J = 7.6 Hz, 2H, 3), 7.57 (d, $^{1}J_{PH}$ = 761 Hz, 7), 7.56 (t, J = 7.6 Hz, 2H, 5), 7.48 (t, J = 7.6 Hz, 2H, 4), 7.43 ppm (d, J = 8.0 Hz, 2H, 6). ^{13}C NMR (DMSO-d_6): δ 146.1 (d, $^{2}J_{PC}$ = 10.1 Hz, 1), 130.4 (3 and 5), 128.2 (2), 127.0 (4), 121.8 ppm (d, $^{3}J_{PC}$ = 3.2 Hz, 6). ^{31}P NMR (DMSO-d_6): δ 15.7 ppm.

4.2.2. General procedure of phospha-Michael addition of BPPO to acrylates (MA, EA, tBuA, AM, PA)

In a 1000 mL round-bottom flask equipped with condenser and magnetic stirring bar, **1** (210.0 g, 0.90 mol), the appropriate acrylate (0.90 mol) and triethyl amine (11.0 mL, 0.09 mol) were dissolved in chloroform (260 mL). The solution was heated to reflux and stirred at that temperature overnight. After cooling

down, water (200 mL) and conc. HCl (7.5 mL) were added to the solution and stirred for 30 minutes. The organic layer was separated and dried with sodium sulfate. After removing the solvent the product was dried under reduced pressure. The chemical structures are outlined in Scheme 5-10.



Scheme 5. Chemical structure of **2 - 6**.

*4.2.2.1. Methyl 3-(6-oxidodibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)propanoate (R = CH_3) (**2**)*

^{1}H NMR (DMSO-d_6): δ 7.68 (d, J = 7.6 Hz, 2H, 3), 7.55 (t, J = 7.6 Hz, 2H, 5), 7.46 (t, J = 7.6 Hz, 2H, 4), 7.41 (d, J = 8.0 Hz, 2H, 6), 3.63 (s, 3H, 10), 2.72 (m, 2H, 8), 2.35 ppm (m, 2H, 7). ^{13}C NMR (DMSO-d_6): δ 171.6 (d, $^3J_{PC}$ = 16.8 Hz, 9), 147.3 (d, $^2J_{PC}$ = 10.0 Hz, 1), 130.5 (5), 130.4 (3), 128.2 (2), 126.8 (4), 121.5 (d, $^3J_{PC}$ = 3.2 Hz, 6), 51.9 (10), 26.4 (d, $^2J_{PC}$ = 3.2 Hz, 8), 18.4 ppm (d, $^1J_{PC}$ = 137 Hz, 7). ^{31}P NMR (DMSO-d_6): δ 40.1 ppm (s). Yield 83%.

*4.2.2.2. Ethyl 3-(6-oxidodibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)propanoate (R = CH_2CH_3) (**3**)*

^{1}H NMR (DMSO-d_6): δ 7.69 (d, J = 7.6 Hz, 2H, 3), 7.56 (t, J = 7.6 Hz, 2H, 5), 7.47 (t, J = 7.6 Hz, 2H, 4), 7.41 (d, J = 8.0 Hz, 2H, 6), 4.10 (q, J = 7.1 Hz, 2H, 10), 2.71 (m, 2H, 8), 2.35 (m, 2H, 7), 1.19 ppm (t, J = 7.1 Hz, 3H, 11). ^{13}C NMR (DMSO-d_6): δ 171.1 (d, $^3J_{PC}$ = 16.2 Hz, 9), 147.3 (d, $^2J_{PC}$ = 10.0 Hz, 1), 130.5 (5), 130.4 (3), 128.2 (d, $^3J_{PC}$ = 1.9 Hz, 2), 126.7 (4), 121.5 (d, $^3J_{PC}$ = 3.6 Hz, 6), 60.5 (10), 26.6 (d, $^2J_{PC}$ = 3.5 Hz, 8), 19.4 (d, $^1J_{PC}$ = 137 Hz, 7), 14.0 ppm (11). ^{31}P NMR (DMSO-d_6): δ 40.2 ppm. Yield 87%.

*4.2.2.3. tert.-Butyl 3-(6-oxidodibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)propanoate (R = $C(CH_3)_3$) (**4**)*

^{1}H NMR (DMSO-d_6): δ 7.68 (d, J = 7.6 Hz, 2H, 3), 7.55 (t, J = 7.6 Hz, 2H, 5), 7.46 (t, J = 7.6 Hz, 2H, 4), 7.40 (d, J = 8.0 Hz, 2H, 6), 2.60 (m, 2H, 8), 2.31 (m, 2H, 7), 1.38 ppm (s, 9H, 11). ^{13}C NMR (DMSO-d_6): δ 170.2 (d, $^3J_{PC}$ = 15.1 Hz, 9), 147.3 (d, $^2J_{PC}$ = 10.0 Hz, 1), 130.4 (5), 130.3 (3), 128.2 (2), 126.7 (4), 121.5 (d, $^3J_{PC}$ = 3.3 Hz, 6), 80.5 (10), 27.7 (11), 27.6 (d, $^2J_{PC}$ = 3.5 Hz, 8), 18.6 ppm (d, $^1J_{PC}$ = 137 Hz, 7). ^{31}P NMR (DMSO-d_6): δ 40.3 ppm. Yield: 87%.

*4.2.2.4. Phenyl 3-(6-oxidodibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)propanoate (R = Ph) (**5**)*

^{1}H NMR (DMSO-d_6): δ 7.70 (d, J = 7.6 Hz, 2H, 3), 7.56 (t, J = 7.6 Hz, 2H, 5), 7.48 (t, J = 7.6 Hz, 2H, 4), 7.45 (d, J = 8.0 Hz, 2H, 6), 7.43 (t, J = 7.7 Hz, 2H, 12), 7.26 (t, J = 7.4 Hz, 1H, 13), 7.14 (d, J = 7.7 Hz, 2H, 11), 3.01 (m, 2H, 8), 2.47 ppm (m, 2H, 7). ^{13}C NMR (DMSO-d_6): δ .170.1 (d, $^3J_{PC}$ = 16.4 Hz, 9), 150.5 (10), 147.2 (d, $^2J_{PC}$ = 10.0 Hz, 1), 130.5 (5), 130.4 (3), 129.5 (12), 128.2 (2), 126.8 (4), 125.9 (13), 121.7 (11), 121.6 (d, $^3J_{PC}$ = 3.5 Hz, 6), 26.9 (d, $^2J_{PC}$ = 3.3 Hz, 8), 18.4 ppm (d, $^1J_{PC}$ = 137 Hz, 7). ^{31}P NMR (DMSO-d_6): δ 39.9 ppm. Yield: 57%.

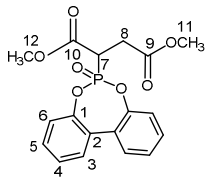
*4.2.2.5. 3-(6-Oxidodibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)propanamide (R = NH_2) (**6**)*

^{1}H NMR (DMSO-d_6): δ 7.68 (d, J = 7.6 Hz, 2H, 3), 7.55 (t, J = 7.6 Hz, 2H, 5), 7.45 (t, J = 7.6 Hz, 2H, 4), 7.44 (br s, 1H, NH), 7.39 (d, J = 8.0 Hz, 2H, 6), 6.95 (br s, 1H, NH), 2.49 (m, 2H, 8), 2.25 ppm (m, 2H, 7). ^{13}C NMR (DMSO-d_6): δ 171.7 (d, $^3J_{PC}$ = 16.9 Hz, 9), 147.3 (d, $^2J_{PC}$ = 9.9 Hz, 1), 130.4 (5), 130.3 (3), 128.3 (2), 126.7 (4), 121.5 (d, $^3J_{PC}$ = 3.0 Hz, 6), 27.2 (d, $^2J_{PC}$ = 3.1 Hz, 8), 18.5 ppm (d, $^1J_{PC}$ = 136 Hz, 7). ^{31}P NMR (DMSO-d_6): δ 41.8 ppm. Yield: 84%.

4.2.2.6. Phospha-Michael addition to unsaturated diesters (DMF, DMM, DMI, DPF)

In a 1000 mL round-bottom flask equipped with condenser and magnetic stirring bar, **1** (210.0 g, 0.90 mol), the appropriate diester (0.90 mol) and triethyl amine (11.0 mL, 0.09 mol) were dissolved in chloroform (260 mL). The solution was heated to reflux and stirred at that temperature overnight. After cooling down, water (200 mL) and 7.5 mL conc. HCl were added to the solution and stirred for 30 minutes. The organic layer was separated and dried with sodium sulfate. After filtration and removing the solvent the solid product was dried under reduced pressure. The workup for compound **8** was identical but yielded a highly viscous oil.

*4.2.2.7. Dimethyl 2-(6-oxidodibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)succinate (**7**)*

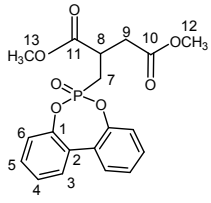


7

Scheme 6. Chemical structure of **7.**

^{1}H NMR (DMSO-d_6): δ 7.71 (d, J = 7.6 Hz, 2H, 3), 7.59 (t, J = 7.6 Hz, 2H, 5), 7.50 (t, J = 7.6 Hz, 2H, 4), 7.44 and 7.42 (two d, J = 8.0 Hz, 2H, 6), 3.85 (m, 1H, 7), 3.62 (s, 3H, 11), 3.58 (s, 3H, 12), 3.06 ppm (m, 2H, 8). ^{13}C NMR (DMSO-d_6): δ 170.5 (d, $^3J_{PC}$ = 19.8 Hz, 9), 167.0 (d, $^2J_{PC}$ = 4.8 Hz, 10), 147.1 and 147.0 (two d, $^2J_{PC}$ = 10.4 Hz, 1), 130.6 (3 and 5), 127.8 and 127.7 (2), 127.1 (4), 121.7 and 121.6 (two d, $^3J_{PC}$ = 3.9 Hz, 6), 52.9 (12), 52.1 (11), 39.1 (d, $^1J_{PC}$ ~ 130 Hz, 7), 30.6 ppm (8). ^{31}P NMR (DMSO-d_6): δ 28.5 ppm. Yield: 71%.

*4.2.2.8. Dimethyl 2-((6-oxidodibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)methyl)succinate (**8**)*

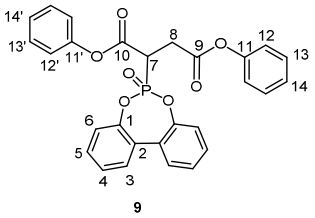


8

Scheme 7. Chemical structure of **8**.

^{1}H NMR (DMSO-d6): δ 7.69 (d, J = 7.6 Hz, 2H, 3), 7.57 and 7.55 (two t, J = 7.6 Hz, 2H, 5), 7.47 (t, J = 7.6 Hz, 2H, 4), 7.38 and 7.36 (two d, J = 8.0 Hz, 2H, 6), 3.64 (s, 3H, 13), 3.61 (s, 3H, 12), 3.27 (m, 1H, 8), 2.85 (d, J = 6.6 Hz, 2H, 9), 2.46 ppm (m, 2H, 7). ^{13}C NMR (DMSO-d_6): δ 172.8 (d, $^{3}J_{PC}$ = 11.9 Hz, 11), 171.3 (10), 147.1 and 147.0 (two d, $^{2}J_{PC}$ = 10.3 Hz, 1), 130.5 (5), 130.4 (3), 127.2 (2), 126.8 (4), 121.6 and 121.5 (two d, $^{3}J_{PC}$ = 3.2 Hz, 6), 52.2 (13), 51.7 (12), 35.4 (d, $^{3}J_{PC}$ = 9.0 Hz, 9), 35.3 (8), 24.3 ppm (d, $^{1}J_{PC}$ = 135.5 Hz, 7). ^{31}P NMR (DMSO-d_6): δ 38.3 ppm. Yield: 81%.

*4.2.2.9. Diphenyl 2-(6-oxidodibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)succinate (**9**)*



9

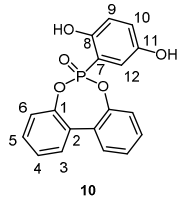
Scheme 8. Chemical structure of **9**.

^{1}H NMR (DMSO-d6): δ 7.75 (m, 2H, 3), 7.58 (m, 2H, 5), 7.55-7.45 (4H, 4 and 6), 7.43 and 7.38 (two t, J = 8.2 Hz, 2 x 2H, 13, 13'), 7.28 and 7.26 (two t, J = 8.2 Hz, 2H, 14, 14'), 7.13 and 6.85 (two d, J = 8.2 Hz, 2 x 2H, 12, 12'), 4.34 (m, 1H, 7), 3.52 and 3.41 ppm (two m, 2H, 8). ^{13}C NMR (DMSO-d_6): δ 169.1 (d, $^{3}J_{PC}$ = 19.1 Hz, 9), 165.7 (d, $^{2}J_{PC}$ = 4.9 Hz, 10), 150.3 and 150.0 (11, 11'), 147.1 and 147.0 (two d, $^{2}J_{PC}$ = 10.5 Hz, 1), 130.7 (3 and 5), 129.7 and 129.6 (13, 13'), 127.8 and 127.7 (2), 127.2 (4), 126.4 and 126.1 (14, 14'), 121.8 and 121.7 (two d, $^{3}J_{PC}$ = 4.0 Hz, 6), 121.6 and 121.0 (12, 12'), 39.7 (d, $^{1}J_{PC}$ ~ 125 Hz, 7), 31.3 ppm (8). ^{31}P NMR (DMSO-d_6): δ 27.5 ppm. Yield: 71 %.

4.2.3. Phospha-Michael addition to p-benzoquinone

*4.2.3.1. 6-(2,5-Dihydroxyphenyl)dibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide (**10**)*

In a 250 mL round-bottom flask equipped with condenser and magnetic stirring bar, **1** (70.0 g, 0.30 mol) and 1,4-benzoquinone (32.6 g, 0.30 mol) were dissolved in toluene (150 mL). No base was added. The solution was heated to 80 °C and stirred at that temperature overnight. The precipitate formed upon cooling was collected and washed with diethyl ether. After drying under reduced pressure, the product (**10**, Scheme 8) was obtained as light brownish solid. Yield: 68%.



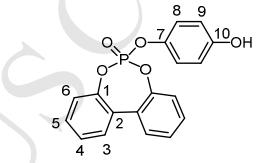
10

Scheme 9. Chemical structure of **10**.

^{1}H NMR (DMSO-d_6): 9.82 (br s, 1H, OH), 9.05 (br s, 1H, OH), 7.68 (d, J = 7.6 Hz, 2H, 3), 7.48 (t, J = 7.6 Hz, 2H, 5), 7.42 (t, J = 7.5 Hz, 2H, 4), 7.25 (d, J = 8.0 Hz, 2H, 6), 6.91 (m, 1H, 12), 6.89 (m, 1H, 10), 6.83 ppm (m, 1H, 9). ^{13}C NMR (DMSO-d_6): δ 152.8 (d, $^{2}J_{PC}$ = 3.0 Hz, 8), 149.4 (d, $3J_{PC}$ = 18.2 Hz, 11), 147.7 (d, $^{2}J_{PC}$ = 9.6 Hz, 1), 130.2 (3 and 5), 128.3 (d, $^{3}J_{PC}$ = 1.0 Hz, 2), 126.4 (4), 122.7 (d, $^{4}J_{PC}$ = 2.7 Hz, 10), 121.6 (d, $^{3}J_{PC}$ = 3.7 Hz, 6), 118.2 (d, $^{2}J_{PC}$ = 7.3 Hz, 12), 117.7 (d, $^{3}J_{PC}$ = 13.4 Hz, 9), 110.5 ppm (d, $^{1}J_{PC}$ = 186 Hz, 7). ^{31}P NMR (DMSO-d_6): δ 27.0 ppm.

*4.2.3.2. 6-(4-Hydroxyphenoxy)dibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide (**11**)*

In a 250 mL round-bottom flask equipped with condenser and magnetic stirring bar, **1** (20.0 g, 86.1 mmol) and 1,4-benzoquinone (9.31 g, 86.1 mmol) were dissolved in chloroform (50 mL). Within 30 minutes, triethyl amine (1.1 mL, 8.6 mmol) was added portion wise (strong exothermic reaction). Then, the reaction mixture was heated to reflux for 2 hours. After cooling, the precipitate was collected by filtration, washed with n-pentane and dried under reduced pressure (Scheme 10).



11

Scheme 10. Chemical structure of **11**.

^{1}H NMR (DMSO-d_6): 9.56 (br s, 1H, OH), 7.73 (d, J = 7.5 Hz, 2H, 3), 7.58 (t, J = 7.7 Hz, 2H, 5), 7.50 (t, J = 7.5 Hz, 2H, 4), 7.44 (two d, J = 8.0 Hz, 2H, 6), 7.13 (d, J = 8.8 Hz, 2H, 8), 6.79 ppm (d, J = 8.8 Hz, 2H, 9). ^{13}C NMR (DMSO-d_6): δ 155.2 (10), 147.0 (d, ^{2}J PC = 9.3 Hz, 1), 142.0 (d, ^{2}JPC = 6.6 Hz, 7), 130.8 (5), 130.4 (3), 127.5 (2), 127.2 (4), 121.3 (d, $^{3}J_{PC}$ = 4.4 Hz, 6), 121.0 (d, $^{3}J_{PC}$ = 4.4 Hz, 8), 116.2 ppm (9). ^{31}P NMR (DMSO-d_6): δ -3.2 ppm. Yield: 98%.

5. Acknowledgments

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6. References and notes

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