



## One Pot Synthesis of 3,9-Bis-(2,4-di-*tert*-butyl phenoxy)-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane, their Chalcogenides and Metal Complexes

MANJU RANI, DAVENDER KUMAR SHUKLA and ARIF ALI KHAN\*

University School of Basic & Applied Sciences, Guru Gobind Singh Indraprastha University, Dwarka, Sector 16C, New Delhi-110 078, India

\*Corresponding author: E-mail: khanaarif@hotmail.com

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A simple method for the synthesis of 3,9-di[2,4-di-*tert*-butyl phenoxy]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane and its chalcogenides and metal complex are reported.

**Key Words:** Pentaerythritol, 2,4-Di-*tert*-butylphenol, Diphosphite, Chalcogenides.

### INTRODUCTION

Organophosphorus compounds are degradable containing carbon-phosphorus bonds, primarily used in pest control as an alternative to chlorinated hydrocarbons which persist in the environment. The importance of organic phosphites as stabilizers for polymers has led to the development of a variety of specialty organic phosphites that have enhanced effectiveness for stabilization<sup>1</sup>. Phosphorous based derivatives phosphites and phosphonites are well known to be effective as polymer stabilizers mainly during processing, acting as secondary antioxidants and are particularly effective in combination with phenols. In addition some phosphites and phosphonites can help in improving the discoloration of polymer articles when they are exposed to heat, UV light, nitrogen oxides and to  $\gamma$ -rays. However, phosphorous based stabilizers are sensitive to heat and moisture so that they can cause undesired side problems during processing and in the life time of polymer articles making their benefits<sup>2</sup> useless. Prevention of discoloration may require inhibiting reactions which yield new chromophores or colour bodies in the substrates or stabilizers<sup>3</sup>. An antioxidant is a molecule capable of inhibiting the oxidation of other molecules. In this paper, we report a simple, quick and cost effective synthesis of highly pure 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane and its chalcogenides and metal complexes under mild reaction conditions.

### EXPERIMENTAL

Starting materials and solvents were obtained from Merck and spectrochem and were used with further purification. Low

temperature chromatography columns were prepared from Merck silica gel powder. IR spectra were measured on a Shimadzu IR-460 spectrometer. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a Bruker AV-300 MHz spectrometer as CDCl<sub>3</sub> solution with TMS as internal and 85 % H<sub>3</sub>PO<sub>4</sub> as external solution. The methods were used to follow the reactions were TLC and NMR. TLC and NMR indicated that there is no side product. Mass spectra were recorded on PDL/ARD-062 mass spectrophotometer.

### Procedure for the preparation of compounds

**3,9-Bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (1):** To a precooled toluene solution of pentaerythritol (1 mmol) at 5 °C, a triethyl amine (5 mmol) was added, followed by phosphorus trichloride (2 mmol) and stirring was continued for 1 h. Then a solution of 2,4 di-*tert*-butyl phenol in toluene was added to it and refluxed for 5 h followed by stirring overnight at room temperature. The reaction solution was filtered and solvent was evaporated and the product was separated by column chromatography (SiO<sub>2</sub>, 5 °C, hexane:diethyl ether; 99.5:0.5). Evaporation of the solvents of the second fraction and recrystallization from diethyl ether at 5 °C yielded 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane as white crystalline solid, yield 22 %, m.p. 169-170 °C.

**3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (2):** To a precooled dichloromethane solution of 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (2 mmol) at -80 °C, a DMSO (3.0 mmol) solution in dichloromethane was added dropwise and stirring was continued for

TABLE-1  
 ELEMENTAL ANALYSIS OF COMPOUND (1-5)

Compound No.	m.f.	Elemental analysis (%) calcd. ( Found)		
		C	H	P
1	C <sub>33</sub> H <sub>50</sub> O <sub>6</sub> P <sub>2</sub>	65.49 (65.55)	8.29 (8.33)	10.12 (10.24)
2	C <sub>33</sub> H <sub>50</sub> O <sub>8</sub> P <sub>2</sub>	57.00 (62.25)	3.73 (7.92)	3.41 (9.73)
3	C <sub>33</sub> H <sub>50</sub> O <sub>6</sub> P <sub>2</sub> S <sub>2</sub>	54.36 (59.26)	3.73 (7.54)	3.38 (9.26)
4	C <sub>33</sub> H <sub>50</sub> O <sub>6</sub> P <sub>2</sub> Se <sub>2</sub>	49.16 (51.97)	3.23 (6.61)	3.01(8.12 )
5	C <sub>43</sub> H <sub>50</sub> O <sub>16</sub> P <sub>2</sub> W <sub>2</sub>	40.37 (41.24)	2.10 (4.02)	1.83 (4.95)

 TABLE-2  
<sup>1</sup>H NMR SPECTRUM OF COMPOUND (1-5)

Compound No.	<sup>1</sup> H NMR data
1	δ 1.311(s, 18H, <i>t</i> -Bu), 1.437 (s, 18H, <i>t</i> -Bu), 3.457-4.535 (m, 8H, -CH <sub>2</sub> ), 6.977-7.401 (m, 6H, aromatic)
2	δ 1.300 (s, 18H, <i>t</i> -Bu), 1.428 (s, 18H, <i>t</i> -Bu), 4.228-4.865 (m, 8H, -CH <sub>2</sub> ), 7.194-7.394 (m, 6H, aromatic)
3	δ 1.272(s, 18H, <i>t</i> -Bu), 1.390 (s, 18H, <i>t</i> -Bu), 3.586-4.569 (m, 8H, -CH <sub>2</sub> ), 7.082-7.332 (m, 6H, aromatic)
4	δ 1.315(s, 18H, <i>t</i> -Bu), 1.421 (s, 18H, <i>t</i> -Bu), 4.303-4.558 (m, 8H, -CH <sub>2</sub> ), 7.141-7.414 (m, 6H, aromatic)
5	δ 1.242(s, 18H, <i>t</i> -Bu), 1.466 (s, 18H, <i>t</i> -Bu), 3.627-4.621 (m, 8H, -CH <sub>2</sub> ), 6.979-7.338 (m, 6H, aromatic)

2 h at -80 °C. The solvent was removed under reduced pressure and the product was separated by low-temperature column chromatography (SiO<sub>2</sub>, 5 °C, hexane:diethyl ether; 98:2). Evaporation of the solvents of the second fraction and recrystallization from diethyl ether at 5 °C yielded 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane-3,9-dioxide as creamish crystalline material, yield 63.0 %, m.p. 229-230 °C.

**3,9-Bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane-3,9-disulfide (3):** A solution of 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane (1 mmol) and elemental sulphur (10 mmol) in 20 mL toluene was heated at 108-110 °C for 24 h. The resulting dark brown solution was filtered hot under nitrogen and concentrated under reduced pressure. The crude product thus obtained was separated by low-temperature column chromatography (SiO<sub>2</sub>, 5 °C, hexane:diethyl ether; 98:2). Evaporation of the solvents of the second fraction and recrystallization from diethyl ether at 5 °C yielded 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane-3,9-disulfide as yellow crystalline powder, yield 54.0 %, m.p. 161-162 °C.

**3,9-Bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane-3,9-diselone (4):** A solution of 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane (1 mmol) and elemental selenium powder (10 mmol) in 20 mL toluene was heated at 108-110 °C for 14 h. The resulting dark brown solution was filtered hot under nitrogen and concentrated under reduced pressure. The crude product thus obtained was separated by low-temperature column chromatography (SiO<sub>2</sub>, 5 °C, hexane:diethyl ether; 98:2). Evaporation of the solvents of the second fraction and recrystallization from diethyl ether at 5 °C yielded 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane-3,9-diselone as orange colour crystalline solid, yield 49.0 %, m.p. 220-221 °C.

**Preparation of 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane-3,9-ditungstonpentacarbonyl (5):** A solution of 3,9-bis[2,4-di(*tert*-butyl)phenoxy]-2,4,8,10-tetraoxa-3,9-diphospha-

spiro[5.5]undecane (1 mmol) and W(CO)<sub>5</sub>CH<sub>3</sub>CN (1.1 mmol) in 20 mL THF was stirred at 25-30 °C for 22 h. The resulting dark brown solution was filtered under nitrogen and concentrated under reduced pressure. The crude product thus obtained was separated by low-temperature column chromatography (SiO<sub>2</sub>, 5 °C, hexane:diethyl ether; 98:2). Evaporation of the solvents of the second fraction and recrystallization from diethyl ether at 5 °C yielded 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro [5.5]undecane-3,9-ditungstonpentacarbonyl as off white crystalline solid, yield 78.0 %, m.p. 129-130 °C.

The analytical, <sup>1</sup>H NMR, <sup>31</sup>P NMR and <sup>13</sup>C NMR spectral data of all the synthesized compounds **1-4** are given in Tables 1-4, respectively.

 TABLE-3  
<sup>31</sup>P NMR SPECTRUM OF COMPOUND (1-5)

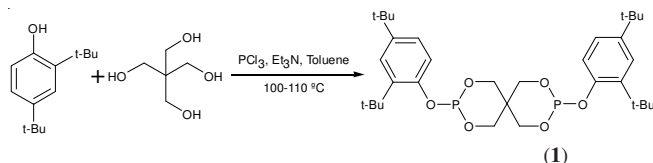
Compound No.	<sup>31</sup> P NMR	Coupling constant
1	δ 116.480	–
2	δ 13.483	–
3	δ 55.56	–
4	δ 60.422	(Triplet, <sup>1</sup> J <sub>P,Se</sub> = 517.061 Hz)
5	δ 130.84	(Triplet, <sup>1</sup> J <sub>P,W</sub> = 204.832 Hz)

## RESULTS AND DISCUSSION

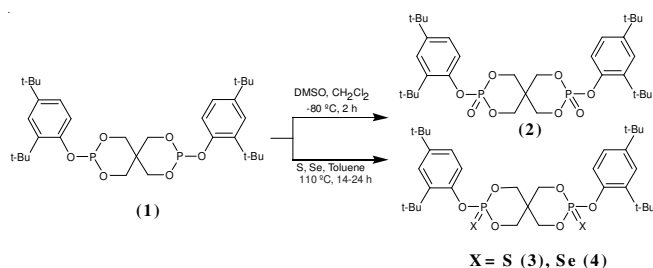
In the last few years, several synthetic methods have been reported for the preparation of 3,9-bis[2,4-di(*tert*-butyl)phenoxy]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane (**1**). There are several reports for the use of **1** in the antioxidation property. Even the process of this invention utilise a single pot, one step procedure and does not require recovery of PCl<sub>3</sub> from the reaction mass (**Scheme-I**). And the synthesis of its chalcogenides by reacting 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane with elemental sulphur, selenium in toluene (**Scheme-II**)<sup>4,5</sup>. Tungsten pentacarbonyl complex (**5**) was prepared by reacting (**2**) with W(CO)<sub>5</sub>CH<sub>3</sub>CN in THF at 20-25 °C (**Scheme-III**) and purified by recrystallisation with diethylether. The structure of the products **1-5** were deduced from their IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra. The mass spectra of these compounds (Table-5)

TABLE-4  
<sup>13</sup>C NMR SPECTRUM OF COMPOUND (1-5)

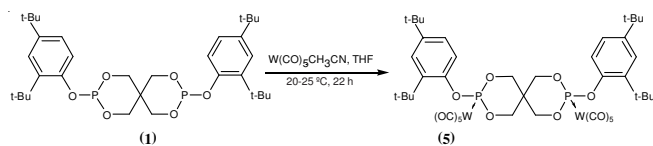
Compound No.	<sup>13</sup> C NMR data
1	δ 30.16, 31.61, 34.91, 37.04, 62.71, 118.61, 124.42, 139.13, 149.14.
2	δ 31.39, 34.83, 36.35, 69.79, 118.64, 124.80, 138.50, 146.98, 147.83.
3	δ 30.46, 31.59, 34.89, 36.71, 61.51, 119.54, 124.70, 139.24, 146.37, 148.89.
4	δ 31.42, 34.77, 36.89, 69.13, 119.96, 124.81, 139.34, 147.93.
5	δ 31.38, 34.93, 36.09, 65.94, 119.79, 123.81, 125.29, 139.48, 147.96, 194.01.



**Scheme-I:** Synthesis of 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-teraoxa-3,9-diphosphaspiro[5.5]undecane



**Scheme-II:** Synthesis of calcogenides of 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-teraoxa-3,9-diphosphaspiro[5.5]undecane



**Scheme-III:** Synthesis of tungsten complex of 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-teraoxa-3,9-diphosphaspiro[5.5]undecane

TABLE-5  
 MASS OF COMPOUND (1-5)

S. No.	(M + 1)	S. No.	(M + 1)
1	605	4	763
2	637	5	1251
3	669	—	—

TABLE-6  
 INFRARED SPECTRUM OF COMPOUND (1-5)

Compound No.	Absorption peaks (cm <sup>-1</sup> )
1	968, 1145.6 (P-O-C <sub>aromatic</sub> )
2	1251.1 (P=O)
3	671.2 (P=S)
4	588.2 (P=Se)
5	1718.5, 1944.1 and 2083.0 (CO)

displayed molecular ion peaks at the appropriate *m/z* values. The infrared spectra (Table-6) of 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-teraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-diselone (4) shows a strong and sharp absorption band at 588.2 cm<sup>-1</sup> which has been assigned to -P=Se stretching absorption vibrations. The proton magnetic resonance spectrum of compound (4) shows two multiplets at δ 4.303 and 4.558 for eight methylene protons, two singlets for *tert*. butyl protons at δ 1.315, 1.421 and all the aromatic protons in position at δ 7.141-7.414 as multiplet for 6H. The phosphorus magnetic resonance spectrum of compound (4) shows a doublet at δ 60.422 with a coupling constant of 1034.122 Hz due to phosphorous selenium coupling. In the <sup>13</sup>C NMR spectrum of compound (4) shows eight carbon, which are well in accordance to the proposed structure. and the peaks at δ 31.42, 34.77, 36.89, 69.13, 119.96, 124.81, 139.34, 147.93. Mass spectra of compound (4) shows molecular ion peak 763 (M + 1) that is in agreement with the formula and structure of (4).

## Conclusion

In summary, a simple and cost effective method is developed for the preparation of 3,9-bis[2,4-di(*tert*-butyl phenoxy)]-2,4,8,10-teraoxa-3,9-diphosphaspiro[5.5]undecane, which is used as stabilizer and antioxidant in polymers. And its chalcogenides having a great stability and antioxidant property have been prepared in good to excellent yields.

## ACKNOWLEDGEMENTS

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