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Synthesis of Chalcogenides and Metal Complex of 2-Phenyl-benzo[1,3,2]dioxophosphinin-4-one

MANJU RANI, DAVENDER KUMAR SHUKLA and ARIF ALI KHAN*

University School of Basic & Applied Sciences, Guru Gobind Singh Indraprastha University, Dwarka, Sector16-C, New Delhi-110 078, India

*Corresponding author: Email: khanaarif@hotmail.com

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The chalcogenides and the metal complexes of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one are prepared by single step reaction of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one (**1**) with DMSO, elemental S, Se and $W(CO)_5CH_3CN$.

Keywords: Salicylic acid, Phosphorous-chalcogenides, Triethylamine, P-heterocycles.

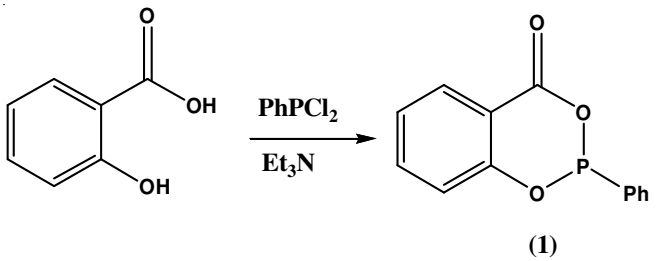
INTRODUCTION

Phosphorus heterocycles and their derivatives are of great interest as bioactive substances with various properties[1,2]. Organo-phosphorus compounds also constitute a family of flame retardants due to their unique combustion inhibition properties[3,4]. They have been known to act in both gas phase and condensed phase[5,6]. Synthesis of flame retardants with low flammability and melt dropping limits is in urgent need now-a-days and is gaining much attention[7]. In this paper, we report the synthesis of chalcogenides and metal complexes of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one (**1**). The parent compound **1** has been synthesized long back[8-10] but to best of our knowledge no chalcogenides and metal complexes of it has been reported so far.

EXPERIMENTAL

Starting materials and solvents were obtained from Merck and Spectrochem and were used with further purification. IR spectra were measured on a Shimadzu IR-460 spectrophotometer. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were measured ($CDCl_3$ solution) with a Bruker AV-300 spectrometer (300 MHz for ^{1}H; and 121.5 MHz for ^{31}P) using $CDCl_3$ as solvent and internal standard; shifts are given relative to ext. tetramethylsilane (^{1}H, ^{13}C) or 85 % H_3PO_4 (^{31}P). Chemical shifts are designated using the following abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet. Mass spectra were recorded on a Shimadzu GCMS QP2010 plus instrument and fragments having intensity more than 20 % has been given. Progress of reaction was monitored by TLC as well as ^{31}P NMR.

Procedure for preparation of compounds (1-5): Synthesis of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one (**1**), prepared according to literature[8] (**Scheme-I**).



(1)

Scheme-I

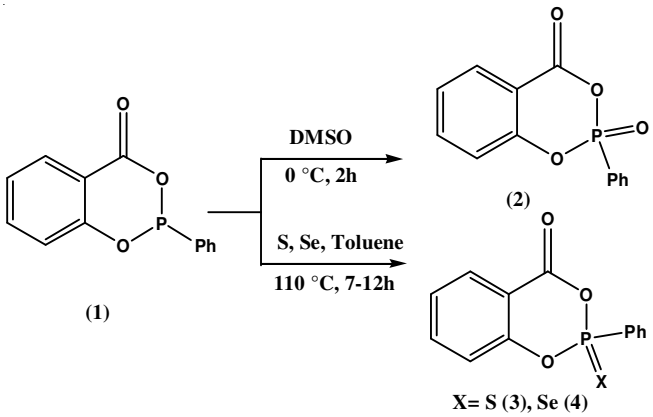
Synthesis of 2-oxo-2-phenyl-2λ^5-benzo[1,3,2] dioxophosphinin-4-one (2): To a pre-cooled dichloromethane solution of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one (2 mmol) at 0 °C, a DMSO (2 mmol) solution in dichloromethane was added dropwise and stirring was continued for 2 h at 0 °C then at room temperature overnight. The solvent was removed under reduced pressure and the product was isolated by recrystallization from diethyl ether at 5 °C as off white crystalline material, Yield 78 %; m.p. 91-92 °C. Elemental analysis calculated for $C_{13}H_9O_4P$: C, 60.01; H, 3.49. Found: C, 58.16; H, 3.32. FTIR (cm^{-1}) 1245.9 (P=O); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 20.422; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 6.840-7.931 (m, 9H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.70, 111.64, 117.71, 119.42, 128.63, 128.81,130.62, 130.88, 132.96, 136.61, 162.15, 173.92; GCMS *m/z*: 260.10, Mass Fragments: 92(35.07), 120(100.00), 260(37.90).

Synthesis of 2-phenyl-2-thioxo-2λ^5-benzo[1,3,2]-dioxaphosphinin-4-one (3): A solution of 2-phenyl-benzo-[1,3,2] dioxophosphinin-4-one (1 mmol) and elemental sulphur (5 mmol) in 25 mL toluene was heated at 108-110 °C for 12 h. The resulting dark brown solution was filtered hot under nitrogen and concentrated under reduced pressure. The crude product thus obtained was recrystallized from diethyl ether at 5 °C as

yellow crystalline material, Yield 29 %; m.p. 118-120 °C. Elemental analysis calculated for $C_{13}H_9O_3PS$: C, 48.32; H, 2.81. Found: C, 46.26; H, 2.51. FTIR (cm^{-1}) 692.4 (P=S); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 70.068; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.049-7.835 (m, 9H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 116.57, 119.58, 119.64, 124.75, 127.79, 129.01, 129.14, 131.75, 131.92, 137.13; GCMS *m/z*: 276.00, Mass Fragments: 28.10 (100.00), 120 (30.14), 276.00(7.20).

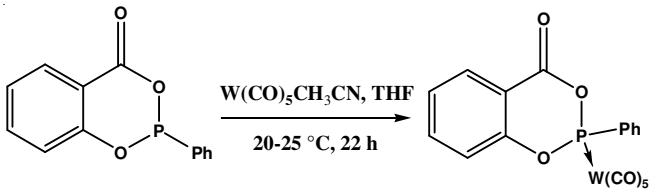
Synthesis of 2-phenyl-2-selenoxo-2λ^5-benzo[1,3,2] dioxophosphinin-4-one (4) (Scheme-II): A solution of phenyldichlorophosphene (1 mmol) and elemental selenium powder (5 mmol) in 15 mL toluene was heated at 108-110 °C for 7 h. The resulting solution was filtered under nitrogen and cool then it was added drop wise to a solution of salicylic acid in toluene followed by addition of triethylamine at 0 °C stirred at room temperature overnight. The crude product thus obtained was separated by recrystallization from diethyl ether at 5 °C as orange crystalline solid, Yield 38 %; m.p. 88-90 °C. Elemental analysis calculated for $C_{13}H_9O_3PSe$: C, 56.52; H, 3.28. Found: C, 56.54; H, 3.12. FTIR (cm^{-1}) 596.2 (P=Se); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 91.826 ($^1J_{P\text{-}Se}$ 959.6 Hz); ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.129-8.057 (m, 9H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.88, 119.31, 119.98, 125.45, 128.60, 128.91, 129.13, 130.34, 131.59, 132.01, 134.38, 134.62, 137.89; GCMS *m/z*: 324.00, Mass Fragments: 64(18.90), 92 (68.23), 120(100), 183.90 (22.93), 323.90 (41.29).

(**Note:** 2-Phenyl-2-selenoxo-2λ^5-benzo[1,3,2]dioxophosphinin-4-one can be prepared by this method but the yield was low. A solution of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one (1 mmol) and selenium powder (5 mmol) in 15 mL toluene was heated at 110 °C for 7 h. The resulting dark brown solution was filtered hot under nitrogen and concentrated under reduced pressure. The crude product was recrystallized from diethyl ether at 5 °C (yield 60 %).



Scheme-II

Synthesis of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one-W(CO)$_5$ complex (5) (Scheme-III): A solution of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one (1 mmol) and $W(CO)_5CH_3CN$ (1.1 mmol) in 15 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 recrystallization from diethyl ether at 5 °C as off white crystalline solid, Yield 62 %; m.p. 97-98 °C. Elemental analysis calculated for $C_{18}H_9O_8PW$: C, 38.06; H, 1.60. Found: C, 36.13; H, 1.41. FTIR (cm^{-1}) 1753.2, 1932.5 and 2081.0 (CO); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 128.015 ($^1J_{P\text{-}W}$ 180.3 Hz); ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.032-7.853 (m, 9H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 116.42, 116.55, 119.56, 124.73, 127.78, 127.95, 128.99, 129.11, 131.70, 137.13, 139.36, 139.88, 155.18, 156.60, 193.76, 193.88, 197.25 197.75.



Scheme-III

RESULTS AND DISCUSSION

Herein, we report synthesis of chalcogenides and metal complex of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one (**1**). The compound **1** was obtained from cyclo-condensation of salicylic acid with phenyldichlorophosphene in equimolar quantities, in presence of triethylamine in dry toluene at room temperature overnight[8]. The P-oxide derivative **2** was selectively prepared by reacting compound **1** with DMSO in dry dichloromethane at 0 ºC. The P-chalcogenides (**3**) and (**4**) were prepared by reacting 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one (**1**) with elemental sulphur and selenium powder in dry toluene at 110 ºC[11,12]. Tungsten pentacarbonyl complex (**5**) was prepared by reacting **1** with $W(CO)_5CH_3CN$ in THF and purified by recrystallization with diethyl ether. The compounds were characterized by IR, ^1H, ^{13}C, ^{31}P and GC-MS spectroscopic data.

All the compounds exhibited characteristic absorption bands for P=O, P=S and P=Se functional groups in the normal region 1246, 692 and 596 cm^{-1} showing that they are not involved in hydrogen bonding. Tungsten pentacarbonyl complex shows characteristic absorption bands for -CO stretching vibrations in the region 1753, 1932 and 2081 cm^{-1}.

In the ^1H NMR spectra, the aromatic protons resonated as multiplets in the region 6.84-8.06. The ^{13}C NMR chemical shifts were interpreted based on comparison with carbon chemical shifts, additivity rules and intensity of the signals and coupling with phosphorus. Carbon bonded to endocyclic oxygen gave signals at 130.9-137.9. The carbonyl carbons of $W(CO)_5$ were appears in the region 193.8-197.7. The remaining carbon shifts were observed in the expected regions.

Phosphorous resonance signals, P=O, P=S and P=Se were observed at 20.422, 70.068 and 91.826, respectively. Phosphorous selenium resonance occurs as triplet with coupling constant 959.6 Hz due to the phosphorous selenium coupling, whereas the P-$W(CO)_5$ resonance occurs at 128.01 as triplet with coupling constant 180.3 Hz due to phosphorous tungsten coupling. GC-MS of all the compounds exhibited molecular (M^+) and characteristic daughter ion peaks at their respective expected *m/z* values.

Conclusion

In conclusion, we have reported a simple route for the synthesis of chalcogenides and metal complex of 2-phenyl-benzo[1,3,2]dioxophosphinin-4-one in good to excellent yields.

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