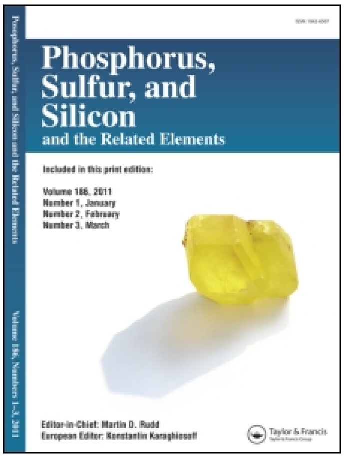

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF TERTIARY PHOSPHINE OXIDES CONTAINING PYRIDINE RINGS

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To cite this Article Tashev, E. , Varbanov, S. and Vassileva, V.(1996) 'SYNTHESIS OF TERTIARY PHOSPHINE OXIDES CONTAINING PYRIDINE RINGS', Phosphorus, Sulfur, and Silicon and the Related Elements, 108: 1, 189 — 195
To link to this Article: DOI: 10.1080/10426509608029650
URL: http://dx.doi.org/10.1080/10426509608029650

Phosphorus, Sulfur, and Silicon, 1996, Vol. 108, pp. 189–195
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SYNTHESIS OF TERTIARY PHOSPHINE OXIDES CONTAINING PYRIDINE RINGS

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(Received September 19, 1995)

Several (pyridyloxymethylene)dimethylphosphine oxides and (8-quinolyloxymethylene)dimethylphosphine oxide have been synthesized via the Williamson reaction from (chloromethyl)dimethylphosphine oxide and the sodium salts of hydroxypyridines and 8-hydroxyquinoline. The structure of these new compounds was confirmed by elemental analysis, IR-, ^{1}H- and ^{31}P-NMR spectroscopy.

Key words: Tertiary phosphine oxides, (chloromethyl)dimethylphosphine oxide, (pyridyloxymethylene)-dimethylphosphine oxides, (8-quinolyloxymethylene)dimethylphosphine oxide, Williamson reaction.

INTRODUCTION

The tertiary phosphine oxides (TPO) possess the highest complexing ability among the known organic phosphoryl compounds with four-coordinated phosphorus.[1-4] In fact, they interact with the majority of metal ions to form stable complexes.[1,3-6] The properties of TPO's and the possibilities to apply these complexes arose the interest of many authors.

The introduction of various functional groups into the TPO molecules provides an effective way to regulate their complexation ability and selectivity.[7-13] Among known substituents aromatic nitrogen containing heterocycles appeared to be the most advantageous. Several pyridine containing TPO's have been reported in the literature so far,[14-17] but the complexation of only one of them, namely 2-pyridyldiphenylphosphine oxide, with nickel (III) and cobalt (III) chlorides, iodides and thiocyanides has been investigated.[17]

In the present paper we report the preparation of some new TPO's containing pyridine- or quinoline rings in their molecules. It is supposed that these compounds will possess interesting complexing properties.

RESULTS AND DISCUSSION

The chloromethyl derivatives of TPO's are available compounds and they are known to possess a high reaction ability. They have been used for phosphorylation of organic compounds and polymers.[18-20]

One of the possible ways for phosphorylation of hydroxypyridines is interaction of (chloromethyl)dimethylphosphine oxide (CMPO) with the sodium salt of hydroxypyridine via the Williamson reaction according to the following scheme:

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$$2\,CH_3OH + 2\,Na \longrightarrow 2\,NaOCH_3 + H_2$$

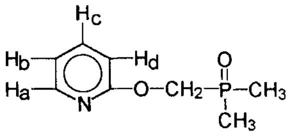
$$NaOCH_3 + HO\text{-}R \longrightarrow NaO\text{-}R + CH_3OH$$

$$NaO\text{-}R + ClCH_2P(O)(CH_3)_2 \longrightarrow R\text{-}OCH_2P(O)(CH_3)_2 + NaCl$$

where R is Pyridyl or Quinolyl.

It is well known that nucleophilic substitution of the chlorine atoms of the chloromethyl groups in TPO by highly active nucleophilic reagents proceeds smoothly in aromatic hydrocarbons—benzene, toluene, xylene.[21,22] That is why the synthesis of the products was carried out in xylene. The sodium salts of hydroxypyridines and 8-hydroxyquinoline were prepared by exchange reaction of sodium methoxide and hydroxyl containing cycles. The interaction between these salts and CMPO runs very vigorously as seen from the observed exothermic effect. The yield of the isolated sodium chloride in all cases was nearly 100% which was an indication for the high degree of substitution of the chlorine atoms.

The following substances were obtained:



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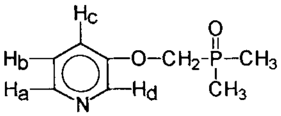

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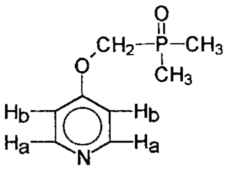

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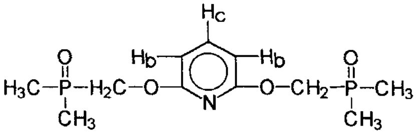

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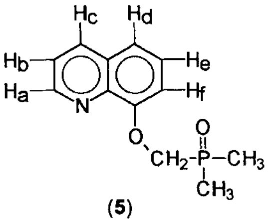

(5)

Some characteristics of the synthesized (pyridyloxymethylene)- and (8-quinolyloxymethylene)-dimethyl phosphine oxides are listed in Table I. The compounds are

TABLE I

Some data of tertiary phosphine oxides containing pyridine rings

No	Compound	Yield (%)	M.P., °C (Recryst. solvent)	Molecular formula	Phosphorus content, %	
					Calc.	Found
1	(2-Pyridyloxymethylene)dimethylphosphine oxide	95	131-132 (Toluene)	$C_8H_{12}NO_2P$	16.76	16.37
2	(3-Pyridyloxymethylene)dimethylphosphine oxide	88	65-70 (B.P.155-160, 0.8 mm Hg)	$C_8H_{12}NO_2P$	16.76 (15.27)[b]	15.12
3	(4-Pyridyloxymethylene)dimethylphosphine oxide	91	142-143 (130-135)[a] (Xylene)	$C_8H_{12}NO_2P$	16.76 (16.35)[c]	16.18
4	2,6-Pyridinediyl-bis(oxymethylenedimethylphosphine oxide)	83	172-174 (157-163)[a] (Toluene)	$C_{11}H_{19}NO_4P_2$	21.30 (20.67)[d]	19.97
5	(8-Quinolyloxymethylene)dimethylphosphine oxide	96	143-145 (85-90)[a] (Toluene)	$C_{12}H_{14}NO_2P$	13.19 (12.17)[e]	12.25

[a] Intermediate melting temperature; Calc. for crystal hydrate with: [b] 1 H_2O; [c] 0.25 H_2O; [d] 0.5 H_2O; [e] 0.5 H_2O.

TABLE II

Some characteristic infrared frequencies (ν cm^{-1}) of tertiary phosphine oxides containing pyridine rings

omp. No	P=O	CH_3-P	C-P-C	C-O-C	CH_2	Pyridine ring
1	1169(vs)	1296(s)	770(s)	1095(m)	2910(s), 2980(s)	1410(s), 1460(s), 1535(vs), 1580(vs)
2	1185(vs)	1285(s)	765(s)	1110(m)	2870(s), 2930(s)	1420(m), 1440(s), 1495(vs), 1590(vs)
3	1185(vs)	1285(s)	790(s)	1120(m)	2850(s), 2930(s)	1425(s), 1455(m), 1540(s), 1585(vs)
4	1180(vs)	1290(s)	790(s)	1080(m)	2850(s), 2920(s)	1420(s), 1455(s), 1540(s), 1585(vs)
5	1175(vs)	1290(s)	780(s)	1090(m)	2860(s), 3000(s)	1430(s), 1450(s), 1530(s), 1585(s)

TABLE III

^{1}H- and ^{31}P-NMR data of tertiary phosphine oxides containing pyridine rings (*δ* in ppm, *J* in Hz)

Comp. No	^{1}H - NMR data , protons								^{31}P{H}
	P-CH$_3$		P-CH$_2$		Pyridine ring				
	δ	^{2}H$_{HP}$	δ	^{2}J$_{HP}$	H$_a$	H$_b$	H$_c$	H$_d$	δ
1	1.58(d)	12.9	4.42(d)	6.6	$\delta=7.54$(dd) $^3J_{a,b}=6.8$ $^4J_{a,c}=1.9$	$\delta=6.23$(td) $^3J_{b,a}={}^3J_{c,b}=6.8$ $^4J_{b,d}=1.4$	$\delta=7.38$(td) $^3J_{c,b}={}^3J_{c,d}=6.8$ $^4J_{c,a}=2.1$	$\delta=6.6$(dd) $^3J_{d,c}=9.2$ $^4J_{d,b}=0.5$	+41.77
2	1.67(d)	13.3	4.29(d)	8.2	(H$_a$ + H$_c$)* $\delta=8.33$(m)	(H$_b$ + H$_d$)* $\delta=7.27$(m)			+42.06
3	1.67(d)	13.3	4.28(d)	8.3	$\delta=8.50$(dd) $^3J_{a,b}=4.8$ $^4J_{a,a}=1.5$	$\delta=6.88$(dd) $^3J_{b,a}=4.9$ $^4J_{b,b}=1.5$	-	-	+41.54
4	1.64(d)	13.2	4.62(d)	6.1	-	$\delta=6.46$(d) $^3J_{b,c}=8.0$	$\delta=7.58$(t) $^3J_{c,b}=7.9$	-	+41.72
5**	1.79(d)	13.3	4.58(d)	7.4	$\delta=8.81$(dd) $^3J_{a,b}=4.2$ $^4J_{a,c}=1.7$	$\delta=7.25$(m)	$\delta=8.15$(dd) $^3J_{c,b}=8.3$ $^4J_{c,a}=1,7$	-	+43.80

*The signals of the shown protons overlapped.

**The signals of the three benzene protons overlapped, $\delta=7.40$ - 7.50

white crystalline odourless substances and only product **2** is hygroscopic. They are soluble in water and common organic solvents—alcohols, chloroform, methylene chloride, dioxane, dimethylformamide, toluene, xylene and insoluble in aliphatic hydrocarbons, tetrachlormethan, diethyl ether.

The structure of the prepared compounds was confirmed by elemental analysis of phosphorus, IR-, ^{1}H- and ^{31}P-NMR spectroscopy.

The IR spectra (Table II) showed characteristic bands for the main groups: phosphoryl group (P=O) at 1169–1185 cm^{-1}, methyl group bound to phosphorus atom at 1285–1296 cm^{-1}, pyridine ring at 1410–1580 cm^{-1}. A band at 1090–1120 cm^{-1} confirms the presence of an ether bond.

^{1}H-NMR spectra of the substances (Table III) showed characteristic doublets for the protons of methyl and methylene groups [$(CH_3)_2P{=}O$ and $—CH_2—P{=}O$] at 1.58–1.79 ppm and 4.28–4.62 ppm respectively. The signals for the pyridine ring protons were observed at 6.26–9.08 ppm.

The signals of the benzene ring protons in (8-quinolyloxymethylene)-dimethylphosphine oxide overlap and a multiplet at 7.40–7.50 ppm is observed. The constants of spin-spin interactions are listed in the table. The integral intensities correspond to the number of protons.

The ^{31}P-NMR spectra taken with decoupling showed singlets with a chemical shift at 41.5–43.8 ppm, which is characteristic[23] of TPO's with a similar surrounding $(CH_3)_2P(O)CH_2—$ group. No other signals were observed.

The phosphorus content found for the majority of products was lower than the theoretical value. Probably that is due to the ability of the substances to crystallize with some quantity of water in the process of their isolation. That assumption can explain as well the observed intermediate melting range and rearrangement of the crystals (products **3**, **4** and **5**) provoked by the presence of crystal hydrates. There are bands at 1620–1650 cm^{-1} and 3300–3400 cm^{-1} in the IR spectra due to the presence of hydrates. In addition, in the ^{1}H-NMR spectra were observed singlets at 2–3 ppm, characteristic of the water of crystallization. These signals disappear after D_2O exchange. From the ratio between the integral intensities of the H_2O proton signals and the signals of $CH_3—P$ or $CH_2—P$ protons it is possible to estimate the approximate quantity of the water of crystallization. For substance **2** it is one molecule, for products **4** and **5**—half a molecule and for product **3**—a quarter molecule of water.

No intermediate melting was observed with **1** and no water proton signal was present in its ^{1}H-NMR spectrum, respectively.

EXPERIMENTAL

Starting Materials

(CMPO), 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, 2,6-dihydroxypyridine, 8-hydroxyquinoline were commercially available. The solvents were dried by standard procedures.

Characterization of the Synthesized Products

The phosphorus content was determined as described.[24] The melting points of substances were obtained on a Boetius apparatus and were not corrected. The IR spectra (400–4000 cm^{-1}) were recorded in KBr tablets on a UR-20 spectrophotometer. ^{1}H-NMR spectra were obtained in $CDCl_3$ using a Bruker WM

(250.13 Mhz). Internal TMS was used as a reference. The ^{31}P-NMR spectra were taken also in $CDCl_3$ on a Varian XL 200q spectrometer. External 85% H_3PO_4 was used as a reference.

Preparation of (2-pyridyloxymethylene)dimethylphosphine Oxide (**1**)

To a solution of 1.003 g (10.5 mmol) 2-hydroxypyridine in 10 ml dry methanol was slowly added in small pieces 0.242 g (10.5 mg-at) sodium. After the reaction of sodium was completed 25 ml xylene was added to the reaction mixture and methanol was removed by distillation. A solution of 1.34 g (10.5 mmol) (CMPO) in 15 ml xylene was added dropwise slowly to the boiling reaction mixture. It was refluxed for 12 hrs and after that the xylene was removed by distillation. The residue was dissolved in chloroform and after filtration of the sodium chloride the solvent was evaporated. The resulting crude product **1** (1.82 g, 94%) was recrystallized from toluene to constant melting point 131–132°C.

All other products were prepared analogously but the product **2** was isolated by distillation under reduced pressure.

ACKNOWLEDGEMENTS

This investigation was supported by the National Science Foundation of Bulgaria (Project X-261).

REFERENCES

1. E. I. Sinyavskaya, in K. B. Yatsimirskii (ed.), "Uspekhi Khimii Koordinatsionnykh Soedinenii (Advances in the Chemistry of Coordination Compounds)," Naukova Dumka, Kiev, 1975, Chap. III, pp. 113–214; CA **85**, 136493a (1976).
2. A. G. Cook and G. W. Mason, *J. Inorg. Nucl. Chem.*, **35**, 2090 (1973).
3. T. S. Lobana, in F. R. Hartley (ed.), "Chemistry of Organophosphorus Compounds," John Wiley & Sons Ltd., 1992, Vol. 2, pp. 409–566.
4. T. Ya. Medved, Yu. M. Polikarpov, L. E. Bertina, V. G. Kossykh, K. S. Yudina and M. I. Kabachnik, *Uspekhi Khimii*, **44**, 1003 (1975); CA **83**, 147527z (1975).
5. W. G. de Bolster, in E. J. Griffith and M. Grayson (eds.), "Topics in Phosphorus Chemistry," Wiley Interscience, New York, 1983, Vol. 11, pp. 69–295.
6. N. M. Karayannis, C. M. Mikulski and L. L. Pytlewski, *Inorg. Chim. Acta Rev.*, 69 (1971).
7. G. V. Bodrin, M. I. Kabachnik, N. E. Kochetkova, T. Ya. Medved, B. F. Miasoedov, Yu. M. Polikarpov and M. K. Chmutova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2572 (1979).
8. T. E. Kron, N. A. Novikov, E. I. Sinyavskaya and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 810 (1986).
9. M. I. Kabachnik, N. M. Dyatlova, T. Ya. Medved, V. V. Medintzev, Yu. M. Polikarpov and Z. I. Tsareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2058 (1968).
10. T. Ya. Medved, Yu. M. Polikarpov, S. A. Pisareva, E. N. Matrosov and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2062 (1968).
11. L. Maier, *Helv. Chim. Acta*, **52**, 858 (1969).
12. S. Varbanov, G. Agopian and G. Borisov, *Eur. Polym. J.*, 639 (1987).
13. S. Varbanov, E. N. Tsvetkov and G. Borisov, *Phosphorus and Sulfur*, **19**, 305 (1984).
14. G. V. Bodrin, A. G. Matveeva, M. I. Terehova, E. I. Matrosov, E. S. Petrov, Yu. M. Polikarpov and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim*, 912 (1991).
15. E. Maruszewska-Wieczorkowska and J. Michalski, *Roczn. Chem.*, **38**, 625 (1964).
16. A. R. Katrizky and B. Ternai, *J. Chem. Soc., B*, 631 (1966).
17. E. Uhlig and M. Schaefer, *J. Inorg. Nucl. Chem.*, **30**, 3109 (1968).
18. E. N. Tsvetkov, T. E. Kron, E. S. Petrov and A. I. Shatenstein, *Zh. Obshch. Khim.*, **54**, 2338 (1984).
19. A. N. Yarkevich, S. E. Tkachenko and E. N. Tsvetkov, *Zh. Obshch. Khim.*, **60**, 1511 (1990).
20. S. Varbanov and G. Borisov, *Acta Polymerica*, **39**, 507 (1988).
21. M. Anteunis, M. Verzele and G. Dacremont, *Bull. Soc. Chim. Belges*, **74**, 622 (1965).
22. E. N. Tsvetkov, G. Borisov, H. Sivriev, R. A. Malevannaya and M. I. Kabachnik, *Zh. Obshch. Khim.*, **40**, 285 (1970).
23. E. N. Tsvetkov, T. E. Kron and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 669 (1980).
24. S. Varbanov, E. Russeva and N. Nikolov, *Bulg. Chem. Commun*, **26**, 91 (1993).