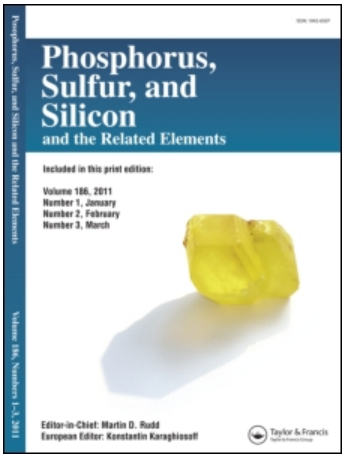

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SYNTHESIS OF TERTIARY PHOSPHINE OXIDES CONTAINING HALOGENATED PHENOXY GROUPS

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New tertiary phosphine oxides containing chlorinated or brominated phenoxy groups are prepared in high yields from methyl-bis(chloromethyl) phosphine oxide or tris(chloromethyl)phosphine oxide and sodium salts of chloro- or bromo-substituted phenols via Williamson reaction.

INTRODUCTION

Among the various types of unreactive flame-retardants used for reduction of combustibility of polymeric materials the halide-containing organophosphorus compounds are especially numerous,[1–4] notably few are, however, the halogenated tertiary phosphine oxides.

In the present communication we report the synthesis of new tertiary phosphine oxides **1–16** containing chlorinated or brominated phenoxy groups as a continuation of our studies on the preparation from tetrakis(hydroxymethyl)phosphonium chloride derivatives of phosphorus-containing monomers and polymers with reduced combustibility.[5–7]. It is to be expected that some of these organophosphorus compounds will be efficient flame-retardants for various types of polymeric materials.

RESULTS AND DISCUSSION

The tertiary phosphine oxides (TPO) were prepared by the Williamson reaction from methyl-bis(chloromethyl)phosphine oxide (MBPO) or tris(chloromethyl)phosphine oxide (TCPO) and sodium chloro- or bromo-phenoxides according to the scheme 1.

It is well known that nucleophilic substitution of the chlorine atoms in MBPO and TCPO proceeds smoothly on refluxing in benzene, toluene or xylene[8–10]. We found that even the highest boiling from these solvents i.e. xylene is not always suitable for carrying out this interaction between MBPO and TCPO and chloro- and bromo-substituted sodium phenoxides, probably because of the poor nucleophilicity of the halogen-substituted phenoxide ions. Because of this reason other authors[10] following

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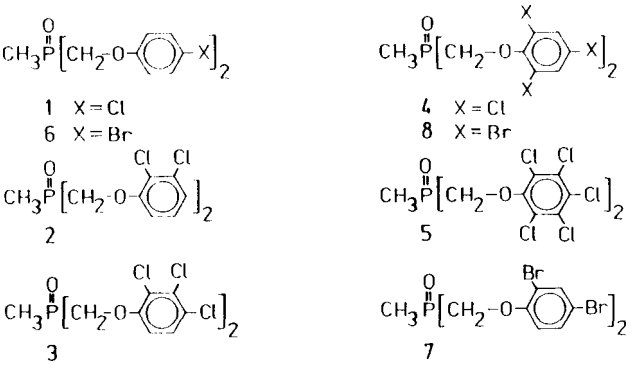


1 X = Cl
6 X = Br

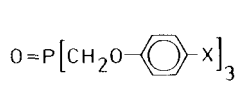
2

3

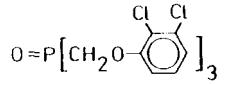
4 X = Cl
8 X = Br

5

7



9 X = Cl
13 X = Br



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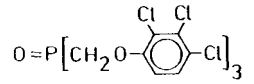

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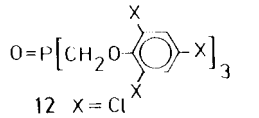

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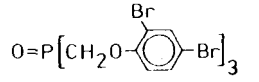
16 X = Br



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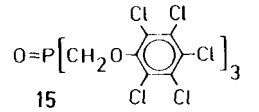

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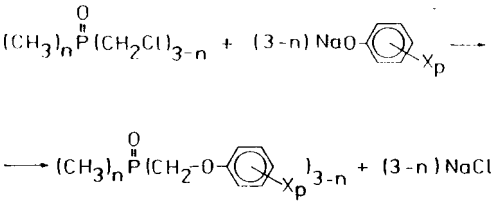

where n = 0 or 1 ; X = Cl or Br

SCHEME 1

the scheme above synthesized earlier tris(4-bromophenoxymethyl)phosphine oxide (**13**) in very poor yield. As can be seen from Table I we prepared the main part of the TPO in anisole. They were all isolated and purified comparatively easily. They are white, odorless solids with comparatively high initial decomposition temperatures, with limited solubility in chloroform, benzene and dimethylformamide; they are insoluble in water. Their structures are confirmed by infrared and ^{1}H NMR spectra.

TABLE I

Tertiary phosphine oxides containing halogenated phenoxy groups

Compound	Preparation procedure	Yield %	M.P. °C	% Phosphorus		Initial temperature of decomposition °C	^{1}H NMR data—δ in ppm ($^2J_{H-P}$ or $^2J_{H-H}$ in Hz)			
				Calc.	Found		Solvent and temperature[a]	CH_3P	OCH_2P	Ar—H
1	2	3	4	5	6	7	8	9	10	11
1	A[b]	88	125–127[c]	8.98	9.00	260	$CDCl_3$	1.8 (J 14.0)	4.4 (J 6.0; 6.0)	6.8–7.3 m
2	A[d]	77	135–136.5[c]	7.49	7.57	260	$CDCl_3$	1.9 (J 14.0)	4.6 (J 6.0; 8.0)	7.0 m
3	A[d]	70	157–158[c]	6.41	6.45	300	$CDCl_3$	1.9 (J 13.0)	4.6 (J 6.0; 8.0)	6.9 (J 9.0) 7.3 (J 9.0)
4	A[d]	84	169–170[c]	6.41	6.42	280	$CDCl_3$	2.1 (J 13.0)	4.6 (J 8.0; 6.0)	7.4
5	A[d]	84	235.5–236.5[e]	4.99	4.94	250 140	DMSO-D_6[f]	2.0 (J 13.0)	4.8 (J 6.0)	—
6	A[d]	93	139–140[e]	7.13	7.11	290	$CDCl_3$	1.8 (J 13.0)	4.4 (J 6.0; 7.0)	7.0 m
7	A[d]	87	96–98[e]	5.23	5.23	290	$CDCl_3$	1.9 (J 14.0)	4.6 (J 6.0; 7.0)	6.8–8.0 m
8	A[d]	97	203–205[c]	4.13	4.08	300	$CDCl_3$	2.1 (J 14.0)	4.5 (8.0; 6.0)	7.6
9	A[b]	71	136.5–137[e]	6.57	6.68	340	$CDCl_3$	—	4.6 (J 6.0)	6.8–7.3 m
10	B[d]	90	240–240.5[g]	5.44	5.44	330 120	DMSO-D_6	—	4.9 (J 6.0)	7.0 m
11	B[d]	95	229.5–230[g]	4.53	4.53	320 120	DMSO-D_6	—	5.0 (J 6.0)	7.2 (J 9.0) 7.5 (J 9.0)
12	B[d]	99	247–248[g]	4.53	4.57	305 140	DMSO-D_6	—	4.9 (J 5.0)	7.4
13	A[d]	88	162–163[g]	5.12	5.22	310	$CDCl_3$	—	4.6 (J 6.0)	6.8–7.4 m
14	A[d]	88	128–130[g]	3.68	3.68	310	$CDCl_3$	—	4.8 (J 6.0)	6.9–7.6 m
15	B[d]	95	—[h]	3.50	3.36	290	—	—	—	—
16	B[d]	75	318–320[g]	2.87	2.80	320	—	—	—	—

[a] At different from room temperature.
[b] In xylene.
[c] From benzene–petroleum ether.
[d] In anizole.
[e] From benzene.
[f] Dimethylsulfoxyde.
[g] From dimethylformamide.
[h] The analytical sample didn't melt till 360°C and was isolated by extraction with dimethylformamide.

The infrared spectra show absorption bands due to a phosphoryl group (P=O) at 1175–1200 cm^{-1}, to methyl group attached to a phosphorus atom at 1295–1300 cm^{-1} for compounds **1–8**; also due to ether linkage to aromatic rings at 1040–1050 cm^{-1} and at 1220–1275 cm^{-1}. A band at 830 cm^{-1} characteristic for a 1,4-substituted aromatic ring is observed in the spectra of compounds **1**, **6**, **9** and **13**; at 805 cm^{-1} due to a 1,2,3,4-substituted aromatic nucleus in the spectra of compounds **3** and **11**; at 710–730 and 760–780 cm^{-1} characteristic for 1,2,3-substituted aromatic rings in the spectra of compounds **2** and **10**; at 810 cm^{-1} characteristic for 1,2,4-substituted aromatic nuclei in compounds **7** and **14**.

The ^1H NMR spectra (Table I) of compounds **1–8** show for the methyl group protons attached to the phosphorus atom doublets at δ = 1.8–2.1 ppm with coupling constants $^2J_{H,P}$ = 13.0–14.0 Hz in agreement with literature data.[11] The chemical shifts of the methylene protons attached to phosphorus are at δ = 4.4–5.0 ppm. In the case of compounds 5.9–14 these signals appear as doublets with $^2J_{H,P}$ = 5–6 Hz, while in the spectra of compounds **1–4**, **6–8** are observed eight peaks representing the AB portion of the ABX system due to the lack of equivalence of the protons attached to the same carbon atom. The difference in the chemical shifts of the separate portions of the CH_2-signals ($^2J_{H,H}$) is about 0.1 ppm. The $^2J_{H,P}$ of the same protons are in the interval of 5 to 8 Hz in agreement with the literature data.[11] The aromatic ring protons resonate in the normal interval of δ = 6.8 to 7.6 ppm.[12] From the data listed in Table I it can be seen that generally speaking the increase in halogen atoms attached to the aromatic nuclei is reflected in a deshielding effect observed in the spectra of the methyl and methylene protons.

EXPERIMENTAL

The starting chloro- and bromo-substituted phenols were commercial products. MBPO and TCPO were synthesised according to literature data;[8,13] their constants agreed with the described ones.[14] The melting points were determined on a Kofler microscope. The infrared spectra were obtained in KBr tablets using a UR-20 instrument. The ^1H NMR spectra were recorded on a Tesla BS487C/80 MHz apparatus using $CDCl_3$ solutions against TMS as standard at room temperature or DMSO-D_6 solutions against hexamethyldisiloxane at higher temperatures. The thermal analyses were conducted in an atmosphere of air with a "Paulik-Paulik-Erdey" (MOM, Hungary) derivatograph at a rate of temperature rise of 5°C/min.

Synthesis of TPO. All TPO listed in Table I were prepared using one of the following two procedures:

Procedure A: *Methyl-bis(4-chlorophenoxymethyl) phosphine oxide* (**1**). A solution of MBPO (2.4 g, 0.015 mole) in xylene (10 ml) was added portionwise to the refluxing suspension of sodium phenoxide in xylene prepared by the subsequent addition of 4-chlorophenol (4.2 g, 0.033 mole) and sodium (0.8 g, 0.033 g-at) to a mixture of xylene (80 ml) and methanol (15 ml) followed by the latter's distillation. The reaction mixture was refluxed under argon for 7 hours and then the xylene was distilled off. The residue was dissolved in chloroform, the chloroform extract was washed with 5% aqueous sodium carbonate, water and then dried (sodium sulphate) to afford after removal of the solvent a white solid (4.5 g, 88%) which was recrystallized from benzene–petroleum ether.

Procedure B: *Tris(2,3-dichlorophenoxymethyl) phosphine oxide* (**10**). The synthesis was conducted as described in Procedure A by using methanol (20 ml), anisole (60 ml), 2,3-dichlorophenol (5.4 g, 0.033 mole), sodium (0.8 g, 0.033 g-at) and TCPO (1.9 g, 0.01 mole). After removing the anisole the product was washed subsequently with chloroform, 5% aqueous sodium carbonate and water to give 5.1 g (90%) of product which was recrystallized from dimethylformamide.

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