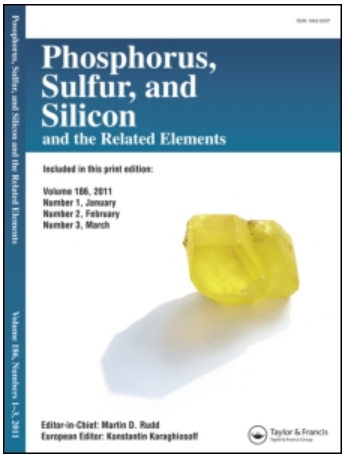

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NEW DIMETHYL(METHYLENEOXYARYL)-PHOSPHINE OXIDES

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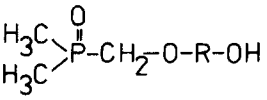
From dimethyl-chloromethyl-phosphine oxides and sodium phenolates of the corresponding mono-, di- and triphenols are prepared by the Williamson reaction new dimethyl(methyleneoxyaryl)phosphine oxides containing one, two or three phosphoryl groups.

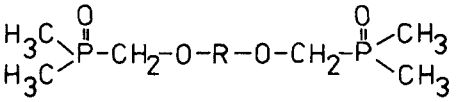
Key words: Tertiary phosphine oxides; preparation; Williamson reaction.

INTRODUCTION

The neutral organophosphorus compounds continue to be at the center of interest.[1–3]Of particular importance is their capability to form coordination compounds with metal ions. Among the organophosphorus compounds containing pentavalent phosphorus the best complexation properties have been shown by tertiary phosphine oxides.[4] Studies conducted about ten years ago have been devoted mainly to the complexing properties of tertiary phosphine oxides with the view to their use as metal extracting agents.[1,4] It has to be also said that compounds were prepared having more than one phosphine oxide group, trying in this manner to achieve a better efficiency and selectivity in complexation.[4,5] Tsvetkov and coworkers have reported lately the preparation of a series of new tertiary phosphine oxides containing one or more phosphine oxide functions.[6,7] Furthermore several compounds of this type have also been described previously in the literature.[8] These compounds can be viewed as acyclic analogues of the crown ethers and for some of them have been also investigated the complexation properties with alkaline metals.[9–12]

We recently reported about the preparation of α-(dimethylphosphinylmethylenoxy)-alkan-ω-ols and of α, ω-*bis*(dimethylphosphinylmethylenoxy)alkanes derivatives making use of the Williamson reaction and starting from dimethyl-chloromethylphosphine oxide and sodium glycolates[13]:





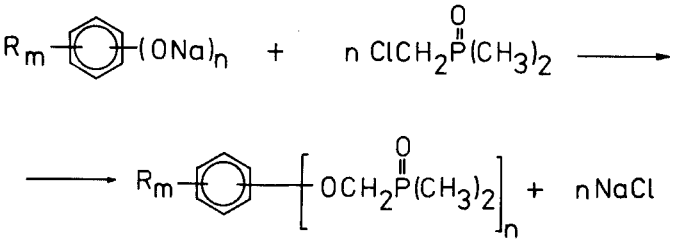
where $R = CH_2CH_2OCH_2CH_2$ or $(CH_2)_n$ $n = 2 \div 6$

† Author to whom all correspondence should be addressed.

We presently wish to report the results for the preparation of new tertiary phosphine oxides, which contain one, two or three dimethyl(methyleneoxyaryl)-phosphine oxide groups. The new products have been synthesized again via the Williamson reaction from dimethyl-chloromethyl-phosphine oxide and sodium phenolates.

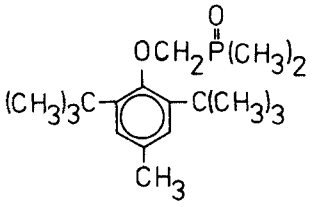
RESULTS AND DISCUSSION

The synthesis of the new dimethyl(methyleneoxyaryl)phosphine oxides (TPO) can be described by the scheme:



Scheme 1

It is well known that the nucleophilic substitution of the chlorine atoms of the chloromethyl groups in tertiary phosphine oxides, such as dimethyl-chloromethyl-phosphine oxide, proceeds smoothly mainly in aromatic hydrocarbons as solvents (benzene, toluene or xylene).[14–18] Lower nucleophilicities require the use of other solvents.[19,20] We succeeded in obtaining the TPO shown in Table I by refluxing the reagents in xylene the yields being in the major part above 80–85%. This



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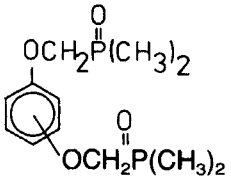
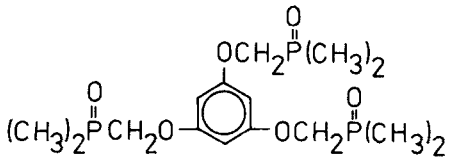


2: "o" isomer
3: "m" isomer
4: "p" isomer



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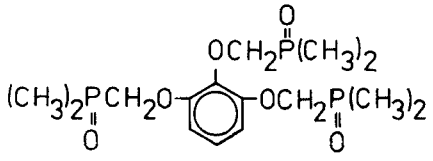

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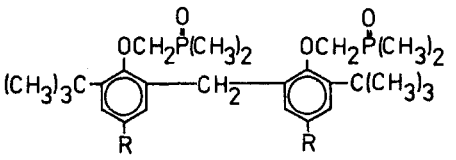

7: R = CH_3
8: R = C_2H_5

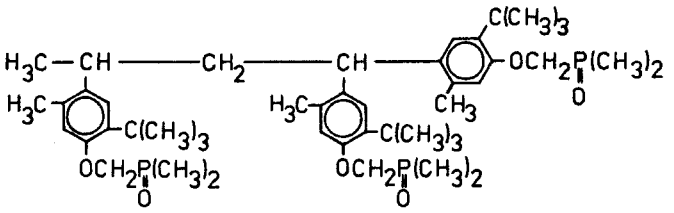

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TABLE I

Some data of the synthesized dimethyl(methyleneoxyaryl)phosphine oxides

No	Compound	Preparation procedure	Yield %	M.P.,°C (Recrystallization solvent)	Phosphorus content, %	
					Found	Calculated
1	2	3	4	5	6	7
1	2,6-Di-*tert*-butyl-1-dimethylphosphinylmethyleneoxy-4-methylbenzene	A	81	133–137 (Heptane)	9.88	9.98
2*	1,2-*Bis*(dimethylphosphinylmethyleneoxy)benzene	A	81	145–148 (Xylene)	21.32	21.35
3	1,3-*Bis*(dimethylphosphinylmethyleneoxy)benzene	A	91	98–101 (Diethyl ether Acetone)	21.20	21.35
4	1,4-*Bis*(dimethylphosphinylmethyleneoxy)benzene	B	95	196–197 (Xylene)	21.14	21.35
5	1,3,5-*Tris*(dimethylphosphinylmethyleneoxy)benzene	B	84	169–172 (Acetonitryl)	23.72	23.45
6	1,2,3-*Tris*(dimethylphosphinylmethyleneoxy)benzene	B	93	165–168 (Dichloromethane)	23.59	23.45
7	2,2-Methylene-*bis*(6-*tert*-butyl-4-methyl-1-dimethylphosphinylmethyleneoxybenzene)	A	99	193–197 (Heptane)	12.10	11.91
8	2,2-Methylene-*bis*(6-*tert*-butyl-4-ethyl-1-dimethylphosphinylmethyleneoxybenzene)	A	76	181–183 (Heptane)	11.46	11.31
9	1,1,3-*Tris*(5′-*tert*-butyl-2′-methyl-4′-dimethylphosphinylmethyleneoxy-benzene)butane	A	98	225–230 (Heptane)	11.39	11.41

* The synthesis of this product was first described in Reference 6.

TABLE II

^{1}H-NMR and ^{31}P-NMR data of dimethyl(methyleneoxyaryl)phosphine oxides (δ in ppm, J in Hz)

	^{1}H NMR data, types of protons								
	$P(O)(CH_3)_2$		$OCH_2P(O)$		Ar—H	CH_3—Ar	—C—$(CH_3)_3$	Ar—CH_2—Ar	^{31}P NMR
No	δ	$^2J_{H,P}$	δ	$^2J_{H,P}$	δ	δ	δ	δ	data δ
1	1.55 (d)	13	4.04 (d)	7	6.9–7.0(m)	2.22(s)	1.40 (s)	—	+40.91
2	1.65 (d)	13	4.25 (d)	8	6.97 (s)	—	—	—	+42.95
3	1.66 (d)	12	4.22 (d)	8	6.5–6.8 (m)	—	—	—	+43.83
4	1.65 (d)	13	4.22 (d)	8	6.87 (s)	—	—	—	+43.49
5	1.62 (d)	12	4.20 (d)	8	6.25 (s)	—	—	—	+42.83
6	1.71 (d)	13	4.34 (d)	7	6.6–7.3 (m)	—	—	—	+41.97
7	1.51 (d)	13	4.29 (d)*	7	6.5–6.9 (m)	2.14 (s)	1.39 (s)	4.20*	+41.57
8[a]	1.53 (d)	14	4.1–4.5*	7	6.5–6.9 (m)	—	1.40 (s)	4.1–4.5*	+41.52
9[b]	1.60 (d)	12	4.25 (d)	7	6.6–7.3 (m)	2.08 (s)	1.38 (s)	—	+43.40

* The indicated signals overlap. [a] The signals of CH_3CH_2—Ar protons of this compound are as follows: for CH_3 protons at 1.09 (t), $J_{H,H} = 6$; for CH_2 protons at 2.44 (k), $J_{H,H} = 9$. [b] The signal of the methyl protons in CH_3CH—Ar group of this compound is at 1.20 (s).

observation indicated that the used phenolate agents were comparatively highly nucleophilic under the reaction conditions. All TPO were easily isolated and purified by recrystallization from the solvents indicated in Table I. The products are crystalline: compounds **2**, **5** and **6** are hygroscopic. They, also **3** and **4** are water soluble. The remaining **1**, **7**, **8** and **9** are insoluble in water, but dissolve in aliphatic solvents. This can be explained by the long hydrocarbon chains present in their molecules. All compounds are soluble in methylene chloride, chloroform and ethanol. The supposed structures of the newly prepared TPO were supported by elemental analysis for phosphorus, IR, ^{1}H NMR and ^{31}P NMR spectra.

The infrared spectra revealed the presence of bands due to phosphoryl groups (P=O) at 1170–1190 cm^{-1}, methyl groups bonded to a phosphorus atom at 1280–1300 cm^{-1}, aromatic ethers at 1040–1050 cm^{-1} and aromatic rings at 1610 cm^{-1}.

The ^{1}H NMR spectra (Table II) showed doublets for the methyl and methylene group protons attached to a phosphorus atom at δ = 1.5–1.7 ppm and δ = 4.0–4.4 ppm, respectively, and aromatic proton resonances at 6.5–7.3 ppm. In all cases the integral intensities of the signals corresponded to the expected number of protons.

The ^{31}P NMR spectra of all TPO compounds possessed a one multiplet signal, which was in agreement with the assumed structures of compounds **1–9** (see Table II).

EXPERIMENTAL

All phenols and the dimethyl-chloromethyl-phosphine oxide were commercial products. The melting points were determined on a Kofler instrument. The IR spectra were recorded in KBr tablets using a UR-20 spectrometer. The ^{1}H-NMR spectra were taken at room temperature in $CDCl_3$ against tetramethylsilane as internal standard on a Tesla B487C/80 MHz apparatus. The ^{31}P NMR spectra were obtained without decoupling with a Bruker 250 spectrometer in $CHCl_3$.

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

Procedure A: 2,6-di-tert-butyl-1-dimethylphosphinylmethyleneoxy-4-methyl-benzene (**1**). A solution of dimethyl-chloromethyl-phosphine oxides (2.53 g, 0.02 mol) in xylene (30 ml) was added portionwise to the refluxing suspension of sodium phenoxide in xylene, prepared by subsequent addition of 2,6-di-*tert*-butyl-4-methylphenol (4.9 g, 0.022 mol) and sodium (0.5 g, 0.022 g.at.), to a mixture of xylene (30 ml) and methanol (20 ml) followed by the latter's distillation. The reaction mixture was refluxed under argon with stirring for 8 hrs, then cooled to room temperature and the sodium chloride filtered off. The distillate was evaporated to dryness to give 5.0 g of product which was recrystallized from *n*-heptane.

Procedure B: 1,2,3-tris(dimethylphosphinylmethyleneoxy)benzene (**6**). Sodium (1.4 g, 0.06 g.at.) was added portionwise under argon to the stirred mixture of pyrogallol (2.5 g, 0.02 mol), methanol (30 ml) and xylene (35 ml). The methanol is distilled off after the end of the reaction of the sodium. A solution of dimethyl-chloromethyl-phosphine oxide (7.6 g, 0.06 mol) in xylene (25 ml) was added to the boiling suspension of the trisodium salt of pyrogallol. The reaction mixture was refluxed for 20 hrs under argon, the solvent removed by distillation and the residue treated with chloroform for removing the sodium chloride. Distilling off the chloroform gave 7.3 g of the crude product, which was recrystallized from methylene chloride-diethyl ether.

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