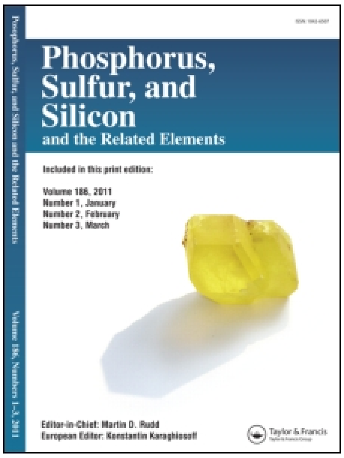

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THE INTERACTION BETWEEN TRIS(CHLOROMETHYL)- AND BIS(CHLOROMETHYL)METHYLPHOSPHINE OXIDE WITH VICINAL DIOLS

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THE INTERACTION BETWEEN TRIS(CHLOROMETHYL)- AND BIS(CHLOROMETHYL)METHYLPHOSPHINE OXIDE WITH VICINAL DIOLS

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It is shown that the interaction between phosphine oxides containing at least two chloromethyl groups (bis(chloromethyl)methylphosphine oxide and tris(chloromethyl)phosphine oxide) with vicinal diols (ethyleneglycol, 1,2-propanediol and pyrocatechol) proceeds simultaneously affording cyclic and acyclic compounds. The seven-membered ring compounds 6-oxo-1,4,6-dioxaphosphepane and 6-oxo-2,3-benzo-tetrahydro-1,4,6-dioxaphosphepin were isolated. In some of the syntheses the acyclic compounds were isolated also. The structure of the products were elucidated with analytical methods, infrared, ^{1}H and ^{31}P-NMR spectroscopy.

INTRODUCTION

It has been reported earlier that the interaction between tris(chloromethyl)phosphine oxide (TCPO) and monosodium diol derivatives leads to the formation of oligoethers.[7] It was found that the interaction between TCPO and vicinal diols (ethyleneglycol and 1,2-propanediol) affords products of lower molecular mass and lower functionality in comparison with the other α,ω-diols. These results were explained with the assumed presence of seven-membered cyclic compounds, which however were not isolated.

Seven-membered cyclic compounds containing P–CH$_2$–O– bonds have not been described hitherto in the literature. Structurally nearest to them are the six-membered cyclic 1,3,5-dioxaphosphorinanes generally prepared by condensing aldehydes with phosphine oxides containing at least two hydroxy alkyl groups. Valetdinov and coworkers have prepared in the ring unsubstituted phosphorinanes.[2,3] Phosphorinanes are also known which contain aliphatic and aromatic substituents attached to a ring carbon.[4,5]

Data in the literature describing an oligoether from bis(chloromethyl)methyl phosphine oxide (BMPO) and ethyleneglycol[6] and a chloro-containing polyether from TCPO and ethyleneglycol[7] do not mention molecular mass and functionality anomalies in the products.

The aim of the present work is to elucidate the causes of the by us observed decreased molecular mass and functionality of the products arising from the interaction between TCPO and vicinal diols.

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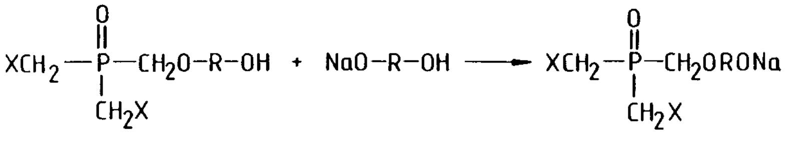
RESULTS AND DISCUSSION

The following equation can be used to describe the interaction between TCPO and monosodium diol derivatives:

$$O{=}P(CH_2Cl)_3 + 3\ NaO{-}R{-}OH \longrightarrow O{=}P(CH_2OROH)_3 + 3\ NaCl \qquad (1)$$

Phosphorus-containing alkoxides are, however, formed through exchange reactions taking place between partially or completely substituted products which arise from the reaction of TCPO with diols and their monosodium derivatives:

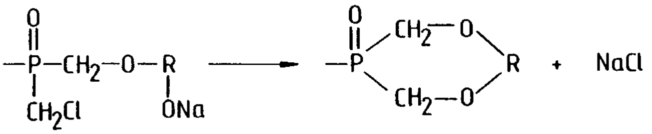


$$XCH_2-\overset{\overset{O}{\|}}{\underset{\underset{CH_2X}{|}}{P}}-CH_2O-R-OH + NaO-R-OH \longrightarrow XCH_2-\overset{\overset{O}{\|}}{\underset{\underset{CH_2X}{|}}{P}}-CH_2ORONa$$

(2)

where X = Cl, —OROH

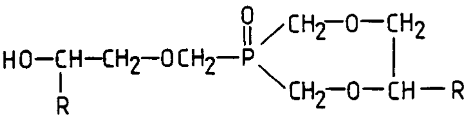
The intermolecular interaction between the alkoxide and the chloromethyl groups leads to the formation of oligomeric products. However, cyclic products can also arise as a result of the flexibility of the moiety attached to the phosphorus atom:



(3)

The number of the atoms in the cycle varies depending on the diol used. With vicinal diols such as ethyleneglycol and 1,2-propanediol the ring is seven-membered and its formation was shown by models to be quite feasible.

The interaction between TCPO and ethyleneglycol or 1,2-propanediol was conducted at 100–110°C for the duration of 10 hrs employing the corresponding diol as a solvent system and using a 10% excess of its monosodium derivative. Distillation under reduced pressure of the products afforded a fraction which was found to be a 1,4,6-dioxaphosphepane derivative:



(4)

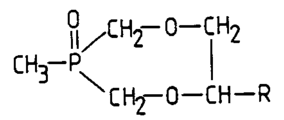
I (R = H); II (R = CH_3)

The reaction between TCPO and 1,2-propanediol affords a mixture of two isomers i.e., 2-methyl-6(3-methyl-2-oxa-4-hydroxybutyl)-6-oxo-1,4,6-dioxaphosphepane and

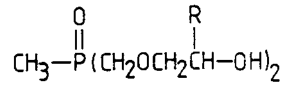
2-methyl-6(2-oxa-4-hydroxypentyl)-6-oxo-1,4,6-dioxaphosphepane. This is the result of the close acidities of the primary and secondary hydroxyl groups.

The acyclic compounds were not isolated.

It was to be expected that the interaction between BMPO and vicinal diols or *o*-diphenols will also lead to the formation of seven-membered ring systems. For this reason BMPO was reacted with ethyleneglycol or 1,2-propanediol under conditions similar to the ones employed with TCPO. Distillation under vacuum of the products afforded two fractions, the first being a phosphepane and the second a phosphorus-containing diol:



(5)



$$CH_3-\overset{\overset{O}{\|}}{P}(CH_2OCH_2\overset{\overset{R}{|}}{C}H-OH)_2$$

(6)

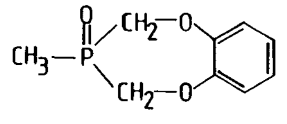
III (R = H)
IV (R = CH_3)

V (R = H)
VI (R = CH_3)

Compound III was also prepared in toluene solution.

The acyclic product VI contains the isomeric radicals 3-methyl-2-oxa-4-hydroxybutyl and 2-oxa-4-hydroxypentyl. The phosphepanes II and IV are a mixture of cis and trans isomers (with respect to the plane of the ring). The isolation of the individual isomers was not envisaged in the present investigation.

6-Methyl-6-oxo-2,3-benzo-tetrahydro-1,4,6-dioxaphosphepin was prepared from BMPO and the disodium salt of pyrocatechol:



(7)

(VII)

The isolated compounds are colourless, viscous liquids or solid (III and VII) products. The products I–VI are soluble in water, alcohol and chloroform, III and IV are soluble in benzene, I and II are poorly soluble while the remaining ones are insoluble. The product VII is soluble in chloroform and ethylmethyl ketone.

The products are characterized by elemental and functional analysis, molecular mass (as determined by the vapour pressure method) and refractive index and melting point. The results are listed in Table I. It can be seen that the elemental data as well as the experimentally determined molecular mass and hydroxyl group content are close to the calculated values. A good confirmation of the suggested structure is the molecular mass of product VII determined by mass spectrometry.

The infrared and PMR data also corroborate the structure of the products. The infrared spectra of products I–VI exhibit the following absorption bands: at 1105–1140 cm^{-1} due to ether linkage; at 1160–1180 cm^{-1} due to phosphoryl groups; and at 2850–2950 cm^{-1} due to methylene groups. The phosphepanes obtained from

TABLE I

Properties of the synthesized cyclic and acyclic compounds

Product	Yield	B.p., °C/ mm Hg	n_D^{20}	M.p., °C	Content of C, %		Content of H, %		Content of P, %		Content of OH groups, %		Molecular mass	
					calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
I	50	200/0.2	1.5045	—	40.00	40.45	7.14	7.27	14.76	14.52	8.10	8.63	210	197
II	34	190/0.3	1.4952	—	45.38	45.28	7.98	8.53	13.02	13.12	7.14	7.12	238	221
III	35	108/0.2	—	46.5–47	40.00	39.84	7.33	7.87	20.67	20.31	—	—	150	148
IV	28	120/0.3	1.4930	—	43.90	43.50	7.93	8.29	18.90	18.44	—	—	164	156
V	27	194/0.2	1.4958	—	39.62	39.62	8.02	8.35	14.62	14.32	16.04	16.00	212	200
VI	23	195/0.3	1.4815	—	45.00	45.05	8.75	8.87	12.92	12.98	14.17	13.92	240	238
VII	36	—	—	170–171	54.50	54.60	5.60	5.70	15.60	15.60	—	—	198	198[a]

[a] Determined by mass-spectrometry.

TABLE II

Chemical shifts δ (ppm) and coupling constants J (Hz) of the synthesized cyclic and acyclic compounds

Product	$O\text{-}CH_2\text{-}CH_2\text{-}O$ δ	$O\text{—}\underline{CH}_2\text{-}CH$ δ	$CH_3\text{-}\underline{CH}\text{-}CH_2$ δ	$OCH_2\text{-}P$ δ	$OCH_2\text{-}P$ $^2J_{H-P}$	$CH_3\text{-}P$ δ	$CH_3\text{-}P$ $^2J_{H-P}$	$\underline{CH}_3\text{-}CH$ δ	$\underline{CH}_3\text{-}CH$ $^3J_{H-H}$	C_6H_4 δ	OH δ	^{31}P δ
I	3.73 (s)[a]			3.87 (d)	2.8						4.30 (s)	+54.1
	4.18 (q)[b]											CH_3OH
		3.55 (d)[a]	3.40 (m)[a]	4.00 (d)[a]	6.0			1.16 (d)[a]	6.2			
II		4.40 (m)[b]	4.40 (m)[b]	4.11 (d)[b]	4.0			1.13 (d)[b]	6.2		4.30 (s)	
				4.08 (d)[b]	4.0							
III	3.86 (s)			4.16 (d)	4.4	1.65 (d)	12.8					+50.9
												$CHCl_3$
IV		3.91 (d)	3.87 (m)	4.11 (d)	4.4	1.63 (d)	12.8	1.13 (d)	6.2			
				4.06 (d)	4.4	1.65 (d)	12.8					
V	3.71 (s)			3.97 (d)	5.0	1.57 (d)	12.4				4.20 (s)	
VI		3.55 (d)	3.47 (sex)	3.98 (d)	5.0	1.58 (d)	13.2	1.14 (d)	6.2		4.20 (s)	
VII				4.70 (s)		1.70 (d)	13.0			7.2		+41.8
				4.50 (d)	3.0							$CHCl_3$

[a] Refers to the cyclic fragment.
[b] Refers to the acyclic fragment.
s—singlet; d—doublet; q—quartet; sex—sextet; m—multiplet.

TCPO and the phosphorus-containing diols show an intensive absorption band at about 3400 cm^{-1} characteristic of hydroxyl groups, while the products prepared from BMPO possess a band at 1300 cm^{-1} ascribed to the $P-CH_3$ moiety.

The PMR spectral data are listed in Table II. The doubling of the signals for the methyl and methylene protons of the $P-CH_3$ and $P-CH_2O$ moieties in the spectrum of compound IV is due to the presence of two isomers i.e. cis- and trans-2,6-dimethyl-6-oxo-1,4,6-dioxaphosphepane. For the same reason the signals for the methylene protons of the $P-CH_2O$ moiety of the compound II in the ring are also doubled. The complex spin system due to the signals of the methylene and methine protons of the $O-CH_2-CH(CH_3)O$ group in the spectrum of compound II is not resolved. A multiplet is observed at about 4.4 ppm.

The hydroxyl group proton signals in the spectra of compounds I, II, V and VI disappear on addition of D_2O. A signal due to DHO appears at about 4.8 ppm. The integral intensities correspond to the number of the protons in the studied cyclic and acyclic compounds which is a reliable indication for the correctness of the suggested structures.

The ^{31}P-NMR spectra were recorded for compounds I, III and VII. The results are listed in Table II.

The data obtained in the present work indicate that the interaction between phosphine oxides with at least two chloromethyl groups and vicinal diols affords concurrently acyclic and cyclic compounds.

EXPERIMENTAL

Reagents: tris(chloromethyl)phosphine oxide (TCPO) was obtained via oxidation of tris(chloromethyl) phosphine with bromine according to ref. 8 followed by recrystallization from water, m.p. 100–100, 5°C (lit.[9] 100–101, 5°C; bis(chloromethyl)methyl phosphine oxide (BMPO) was prepared according to refs. 10 and 11, m.p. 49–50°C.[10] The diols were commercial products. They were purified by dissolving 2–3 g of sodium in 100 ml of the corresponding diol and distilling under reduced pressure 1,6-hexanediol was purified by vacuum distillation. Dowex 50 and Dowex 21X were the ion-exchange resins employed.

The acetylation procedure was employed in the evaluation of the hydroxyl group content. The molecular mass was determined by the Knauer method using an osometer to evaluate the vapour pressure. The melting interval of the cyclic products was determined in mass. The infrared spectra were recorded neat on a UR-10 apparatus. The proton NMR spectra were recorded on a TESLA BS 487C (80 MHz) instrument with TMS as internal standard and on a Perkin-Elmer R-20 (60 MHz) ref. HMDS in $CDCl_3$. The ^{31}P-NMR spectra were taken on a Bruker HX-90 (36, 43 MHz) with Fourier technique using $CHCl_3$ and CH_3OH as a solvent reference 85% phosphoric acid.

Interaction between TCPO and ethyleneglycol. Ethylene glycol (0.165 mole and 50 ml as solvent) and sodium (3.77 g, 0.165 g-atom) added slowly in small portions under nitrogen are placed in a flask provided with a stirrer, thermometer, a reflux condensor and an in- and outlet for the inert gas. After the final amounts of sodium have dissolved (the final portions require some heating) the reaction mixture is brought to room temperature and TCPO (9.61 g, 0.05 mole) is added. The reaction is conducted for 10 hrs at 100–110°C under a flow of nitrogen and under stirring. The precipitate of sodium chloride is filtered off after cooling, the residue dissolved in water and the resultant solution passed through ion-exchangers (an anion and cation exchanger). The water is distilled off and the product dried via azeotropic distillation with benzene. The excess diol is removed by distillation under reduced pressure. The vacuum distillation of the product afforded a fraction, b.p. 200°C/0.2 mm Hg, which was 6 (2-oxa-4-hydroxybutyl)-6-oxo-1,4,6-dioxaphosphepane(I), yield 5.1 g (50%).

The reaction with 1,2-propanediol was conducted analogously.

Interaction between BMPO and ethyleneglycol in ethyleneglycol solution. The reaction is carried out similarly to that with TCPO and ethyleneglycol. Ethyleneglycol (46 ml, 0.088 mole and 40 ml as solvent), sodium (2.0 g, 0.088 g-atom) and BMPO (6.5 g, 0.04 mole). Distillation of the product under reduced pressure afforded two fractions: (a) 6-methyl-6-oxo-1,4,6-dioxaphosphepane(III), b.p. 108°C/0.2 mm Hg; and (b) bis(2-oxa-4-hydroxybutyl)methyl phosphine oxide(V), b.p. 194°C/0.2 mm Hg in yields of 2.1 g (35%) and 2.35 g (27%), respectively.

The reaction between BMPO and 1,2-propanediol was conducted analogously.

Interaction between BMPO and ethyleneglycol in toluene solution. Sodium (6.3 g, 0.27 g-atom) is dissolved in ethyleneglycol (50 ml) under nitrogen at 70–120°C. The glycol is removed by vacuum distillation. To the solid residue are added 30 ml of dry toluene and the mixture is brought to 90–100°C at which temperature is added the solution of BMPO (20 g, 0.12 mole) in dry toluene (40 ml). The reaction mixture is heated at reflux for 8.5 hrs after which are added acetic anhydride (10 ml) and acetyl chloride (10 ml). The addition is exothermic and the temperature reaches 90°C. Acetic anhydride (50 ml) is added dropwise and the reaction mixture is heated for 2 hrs at 100°C. The precipitate is filtered off, the filtrate taken to dryness under vacuum and the residue distilled under reduced pressure to give two fractions: (a) b.p. 130–185°C/3 mm Hg; (b) b.p. 185°C/3 mm Hg. A second distillation of the first fraction afforded 6-methyl-6-oxa-1,4,6-dioxaphosphepane(III), b.p. 142–143°C/3 mm Hg, 6.2 g (35%).

Interaction between BMPO and pyrocatechol. Pyrocatechol (3.4 g, 0.031 mole) is added to the solution of sodium (1.6 g, 0.068 g-atom) in dry methanol (30 ml) under an atmosphere of dry nitrogen. The solvent is removed and the residue distilled under vacuum during 2 hrs at 90–100°C (bath) 10 mm Hg. The finely ground pyrocatechol disodium salt is added to dry *o*-xylene (40 ml), the mixture heated at 100°C and BMPO (5.0 g, 0.031 mole) added. The reaction mixture is heated under reflux for 8 hrs and the solvent removed under vacuum. The residue is treated with 10% aqueous sodium hydroxide (2 × 20 ml) and extracted with chloroform. The combined extracts are dried over Na_2SO_4 and the solvent distilled off under reduced pressure. Yield 3.1 g (50.5%), m.p. 168.5–170°C, after recrystallization from ethyl methyl ketone 2.2 g (36%) of 6-methyl-6-oxa-2,3-benzotetrahydro-1,4,6-dioxaphosphepin(VII).

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