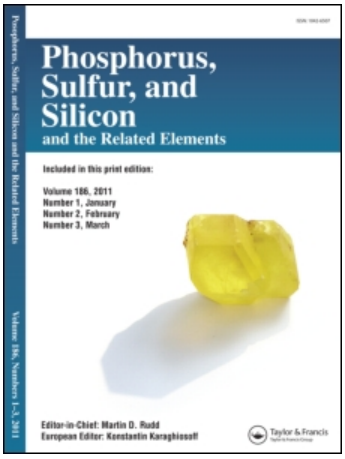

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SYNTHESIS OF α-(DIMETHYLPHOSPHINYL-METHYLENOXY)-ALKAN-ω-OLS AND α, ω-BIS(DIMETHYLPHOSPHINYL-METHYLENOXY) ALKANES

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SYNTHESIS OF α-(DIMETHYLPHOSPHINYL-METHYLENOXY)-ALKAN-ω-OLS AND α, ω-BIS(DIMETHYLPHOSPHINYL-METHYLENOXY) ALKANES

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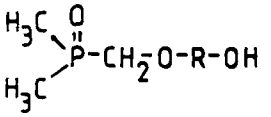
The Williamson reaction is applied in the preparation of new tertiary phosphine oxides i.e. α-(dimethylphosphinylmethylenoxy) alkan-ω-ols (**I**) and α,ω-bis(dimethylphosphinylmethylenoxy)alkanes (**II**) from dimethyl-chloromethyl-phosphine oxide (DMPO) and aliphatic sodium glycolates. It is established that the two types of products are simultaneously formed. Their ratio depends on the DMPO: glycol: sodium ratio. Thus, the excess of DMPO and sodium affords mainly α,ω-bis(dimethylphosphinylmethylenoxy)-alkanes, while their use in 1.1 : 1 : 1.1 ratio affords **I** and **II** in comparative yields.

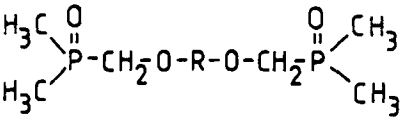
INTRODUCTION

The interaction between methyl-bis(chloromethyl)phosphine oxide or tris(chloromethyl)phosphine oxide and the sodium glycolates of α, ω-glycols affords, depending on the ratio of the reactants, low-molecular weight or oligomeric products.[1,2] Some of them have been examined as starting materials in the synthesis of phosphorus-containing polyurethanes. It has also been found that the employment of vicinal sodium glycolates leads to cyclic products.[2]

We presently wish to report the results from the investigation of the interaction between dimethyl-chloromethyl-phosphine oxide (DMPO) and aliphatic sodium glycolates affording α-(dimethylphosphinylmethylenoxy)alkan-ω-ols (**I**) and α, ω-bis(dimethylphosphinylmethylenoxy)alkanes (**II**), respectively:



I



II

where R = CH_2CH_2—O—CH_2CH_2 or $(CH_2)_n$ n = 2 to 6.

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RESULTS AND DISCUSSION

It is well known that the substitution of the chlorine atoms in tertiary phosphine oxides containing chloromethyl groups proceeds smoothly in aromatic hydrocarbons.[1,3,4,5] We, therefore, carried out the interaction of DMPO with the sodium glycolates of the aliphatic glycols by reflux in xylene.[6] It was found that under these conditions using as the starting compounds DMPO, glycol and sodium in ratio 1.1 : 1 : 1.1 the reaction afforded in comparative yields (with respect to DMPO) α-(dimethylphosphinylmethylenoxy)alkan-ω-ols (**I**) and α,ω-bis(dimethylphosphinylmethylenoxy)alkanes (**II**). The simultaneous formation of the two kinds of products can be explained with the presence of exchange reactions proceeding via monosubstituted reaction products on the one hand, and by the formation of disodium glycolates on the other:

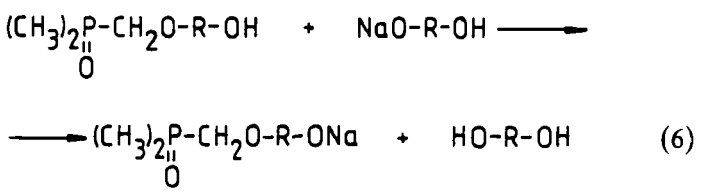
$$HO\text{-}R\text{-}OH + CH_3ONa \longrightarrow HO\text{-}R\text{-}ONa + CH_3OH \quad (1)$$

$$HO\text{-}R\text{-}ONa + CH_3ONa \longrightarrow NaO\text{-}R\text{-}ONa + CH_3OH \quad (2)$$

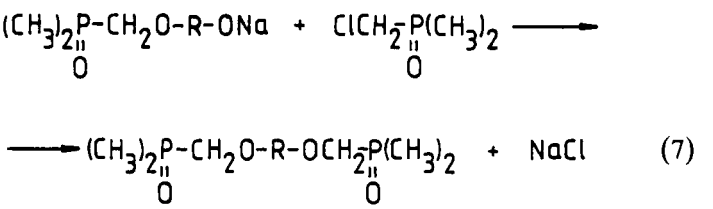
$$(CH_3)_2\overset{\overset{O}{\|}}{P}\text{-}CH_2Cl + NaO\text{-}R\text{-}OH \longrightarrow (CH_3)_2\overset{\overset{O}{\|}}{P}\text{-}CH_2O\text{-}R\text{-}OH + NaCl \quad (3)$$

$$(CH_3)_2\overset{\overset{O}{\|}}{P}\text{-}CH_2Cl + NaO\text{-}R\text{-}ONa \longrightarrow (CH_3)_2\overset{\overset{O}{\|}}{P}\text{-}CH_2O\text{-}R\text{-}ONa + NaCl \quad (4)$$

$$(CH_3)_2\overset{\overset{O}{\|}}{P}\text{-}CH_2O\text{-}R\text{-}OH + CH_3ONa \longrightarrow (CH_3)_2\overset{\overset{O}{\|}}{P}\text{-}CH_2O\text{-}R\text{-}ONa + CH_3OH \quad (5)$$

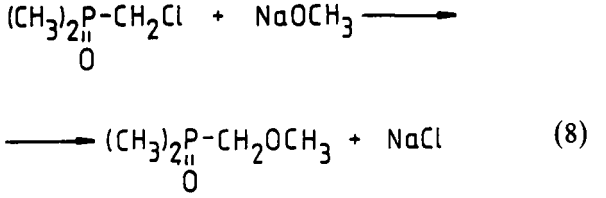


(6)



(7)

In the first-fractions obtained during the isolation of products **1**, **2**, **5** and **6** there was also detected (by thin-layer chromatography) the presence of dimethyl-methoxymethyl-phosphine oxide (Kieselgel 60 F_{254}, DC Alufolien, Merck, R_f = 0.61). This observation can be explained by the reversible character of reactions **1**, **2**, **5** and **6**. Because of that, in spite of increasing the reaction temperature to about 140°C i.e. the temperature of xylene at reflux, in the preparation of the glycolates, a part of sodium methoxide remains in the reaction mixture. The latter reacts in the next stage along reaction **5** on addition of DMPO or via formation of dimethyl-methoxymethyl-phosphine oxide according to the reaction:



(8)

Changing the reactants ratio in favour of DMPO and sodium with respect to the amount of glycol introduced leads to an increase in the yields of α,ω-bis(dimethyl-phosphinylmethylenoxy)alkanes at the expense of those of the α-(dimethylphos-phinylmethylenoxy)alkan-ω-ols. Thus, from ethylene glycol (EG) at a ratio of DMPO : EG : Na of 1.1 : 1 : 1.1 are obtained the two products, 1-(dimethylphos-phinylmethylenoxy)ethan-2-ol and 1,2-bis(dimethylphosphinylmethylenoxy)ethane in 35% and 47% yield, respectively (see Table I). At the DMPO : EG : Na ratio of 1.6 : 1 : 1.6 the corresponding yields are 10% and 83%, respectively. With 1,4-butanediol (BD) and a reactants ratio of DMPO : BD : Na = 1.1 : 1 : 1.1 the yields of 1-(dimethylphosphinylmethylenoxy)butan-4-ol and of 1,4-bis(dimethylphosphinyl-

TABLE I

α-(dimethylphosphinylmethylenoxy)alkan-ω-ols and α,ω-bis(dimethylphosphinylmethylenoxy)alkans

No	Compound	Yield[a] %( )[b]	M.P. °C	B.P. °C/Terr	d_4^{20}	n_D^{20}	Molecular refraction		Phosphorus content, %		Hydroxyl group content, %	
							Theoretical	Found	Calcd.	Found	Calcd.	Found
1	2	3	4	5	6	7	8	9	10	11	12	13
1	1-(dimethylphosphinyl-methylenoxy)ethan-2-ol	35 (82)	—	160–162/0.2	1.1521	1.4758	37.15	37.19	20.4	20.4	11.2	11.3
2	1,2-bis(dimethylphos-phinylmethylenoxy)ethan	47	83–85	212–214/0.1	—	—	—	—	25.6	26.1	—	—
3	1-(dimethylphosphinyl-methylenoxy)propan-3-ol	30 (67)	—	173–175/0.5	1.1190	1.4735	41.79	41.65	18.7	17.4	10.2	10.3
4	1,3-bis(dimethylphos-phinylmethylenoxy)propan	37	72–74	210/0.1	—	—	—	—	24.2	24.5	—	—
5	1-(dimethylphosphinyl-methylenoxy)butan-4-ol	42 (78)	—	177/0.5	1.0899	1.4729	46.45	46.32	17.2	17.3	9.4	9.5
6	1,4-bis(dimethylphos-phinylmethylenoxy)butan	36	95–97	220–221/0.1	—	—	—	—	22.9	22.3	—	—

7	1-(dimethylphosphinyl-methylenoxy)pentan-5-ol	36 (67)	—	177–178/0.1	1.0674	1.4735	51.09	51.04	16.0	16.0	8.7	8.1
8	1,5-bis(dimethylphosphinylmethylenoxy)pentane	31	74–76	235/0.1	—	—	—	—	21.8	21.5	—	—
9	1-(dimethylphosphinyl-methylenoxy)hexan-6-ol	39 (69)	—	171–174/0.1	1.0635	1.4722	55.74	54.70	14.9	15.0	8.2	8.4
10	1,6-bis(dimethylphosphinylmetylenoxy)hexane	30	89–93	229–233/0.1	—	—	—	—	21.6	20.6	—	—
11	1-(dimethylphosphinyl-methylenoxy)-3-oxa-pentan-5-ol	42 (93)	—	185–190/0.1	1.1517	1.4759	48.09	47.97	15.8	15.2	8.6	8.7
12	1,5-bis(dimethylphosphinylmethylenoxy)-3-oxa-pentan	51	—	252–255/0.1	1.1640	1.4844	70.81	70.41	21.7	21.1	—	—

[a] The yields are calculated on the base of DMPO.
[b] Total yield.

methylenoxy)butane are 42% and 36%, respectively (see Table I), while at a DMPO : BD : Na ratio of 1.6 : 1 : 1.6 these yields are 23% and 73%, respectively.

The hydroxyl group-containing tertiary phosphine oxides (see Table I, Nos **1**, **3**, **5**, **7**, **9** and **11**) and 1,5-bis(dimethylphosphinyl-methylenoxy)-3-oxa-pentane (Table I, No **12**) are colourless and odourless oils.† The diphosphine dioxides, with the exception of the mentioned one above (see Table I, compounds **2**, **4**, **6**, **8** and **10**) are colourless, crystalline, highly hygroscopic compounds. Those among them with an even number of methylene units in the glycol moiety melt higher than their immediate neighbours with an odd number of methylene units. All products are well soluble in water, chloroform, alcohols, acetone and sparingly soluble in benzene and toluene at elevated temperatures. The compounds are insoluble in diethyl ether and carbon tetrachloride. Their structures were determined by elemental analysis for phosphorus, determining the number of hydroxyl groups present, molecular refraction and infrared and ^{1}H NMR spectra.

The infrared spectra exhibit absorption bands characteristic for a phosphoryl group (P=0) at 1160–1185 cm^{-1}, for an aliphatic ester at 1100–1150 cm^{-1} and for methylenes at 2800–3000 cm^{-1}. The hydroxyl group containing compounds reveal intensive broad bands in the 3100–3600 cm^{-1} region (compounds **1**, **3**, **5**, **7**, **9** and **11**).

In the ^{1}H NMR spectra (Table II) are present in all cases doublets for the vicinal to the phosphorus methylene protons at 1.5–1.7 ppm with a $^2J_{H,P}$ of 13–14 Hz. This signal overlaps or is close to the signals due to the protons of the methylene groups directly bonded to carbon, with the exception of compounds **1**, **2**, **11** and **12** which are devoid of such protons and compounds **3** and **4** in which the signals for the C—CH_2—C protons appear at 1.8–1.9 ppm with a $^2J_{H,H}$ of 6 Hz. There is a doublet ascribed to the methylene group protons bonded to phosphorus at 3.7–3.9 ppm with $^2J_{H,H}$ = 5–7 Hz. The hydroxyl group protons were identified by deuterium exchange. In all case the integral intensities corresponded to the number of protons expected according to the molecular formula.

EXPERIMENTAL

The starting glycols and DMPO were commercial products. The glycols were dried over a molecular sieve (4A) and distilled before use. The melting points were determined on a Kofler apparatus. The infrared spectra were determined using a neat sample or KBr pellets on a UR-20 instrument. The proton NMR spectra were recorded on a Tesla B487/80 MHz apparatus against TMS as internal standard using deuterochloroform as solvent. The hydroxyl group content was determined by acetylation.[8] The refractive indexes were recorded with the aid of an Abbe refractometer. The relative densities were obtained via pycnometry. The theoretical molecular refractions were obtained by summation of the refractions of the individual atoms and groups, while the experimental ones were calculated from the corresponding equation.[9]

Synthesis of 1-(dimethylphosphinylmethylenoxy)-ethane-2-ol and 1,2-bis(dimethylphosphinyl-methylenoxy)ethane. To the stirred under argon mixture of ethylene glycol (15.4 g, 0.25 mole), dry methanol (40 ml) and xylene (100 ml) is added sodium (5.7 g, 0.25 g.at.). A solution of DMPO (28.5 g,

†After completion of our work, ref. 7, appeared in print in which the synthesis of compounds **1**, **2** and **12** (see Table I) was described.

TABLE II

^{1}H NMR data of α-(dimethylphosphinylmethylenoxy)alkan-ω-ols and α,ω-bis-(dimethylphosphinylmethylenoxy)alkanes (δ in ppm; $^2J_{H-H}$ and $^2J_{H-P}$ in Hz)

	Protons							
	$(CH_3)_2P{=}O$		$C{-}(CH_2)_n{-}C$		$O{-}CH_2{-}C$	$O{=}P{-}CH_2O$		$C{-}OH$
Compound number	δ	$^2J_{P-H}$	δ	$^2J_{H-H}$	δ	δ	$^2J_{P-H}$	δ
1	2	3	4	5	6	7	8	9
1	1.65 (*d*)	13	—	—	3.69	3.81 (*d*)	7	4.22 (*s*)
2	1.50 (*d*)	13	—	—	3.70	3.80 (*d*)	7	—
3	1.50 (*d*)	13	1.79 (*m*)	6	3.68	3.70 (*d*)	6	3.60
4	1.52 (*d*)	13	1.88 (*m*)	6	3.62	3.72 (*d*)	7	—
5	1.52 (*d*)	13	1.5	—	3.60	3.72 (*d*)	7	3.40
6	1.52 (*d*)	13	1.5	—	3.58	3.72 (*d*)	7	—
7	1.50 (*d*)	13	1.5	—	3.58	3.71 (*d*)	7	3.50
8	1.50 (*d*)	13	1.5	—	3.55	3.71 (*d*)	7	—
9	1.5 (*d*)	14	1.5	—	3.55	3.70 (*d*)	7	3.40
10	1.50 (*d*)	13	1.5	—	3.50	3.70 (*d*)	7	—
11	1.50 (*d*)	14	—	—	3.70	3.90 (*d*)	5	3.40
12	1.50 (*d*)	14	—	—	3.70	3.80 (*d*)	7	—

0.22 mole) in xylene (50 ml) is added portionwise to the refluxing mixture after the end of the reaction and distillation of methanol. Refluxing is maintained for 8 hrs more, the mixture is cooled to room temperature and the solvent decanted. The residue is dissolved in chloroform and filtered. After evaporation of the solvent the residue is subjected to distillation under reduced pressure to afford two fractions i.e. one with b.p. 152–174°C/0.1 torr (12.1 g) and a second with b.p. 195–213°C/0.1 Torr (12.7 g). The two fractions were subjected to additional distillation to give, the first a product with b.p. 160–162°C/0.2 Torr and the second a product with b.p. 212–214°C/0.1 Torr.

All remaining products, listed in Table I, were prepared analogously.

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