STRUCTURE OF THE PRODUCT OF THE REACTION OF ELEMENTAL PHOSPHORUS, PROPYLENE OXIDE, PHENOL, AND TRIETHYLAMINE

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The composition and structure of an oligomer has been studied, formed in the reaction of elemental phosphorus (P_4) with propylene oxide, phenol, and triethylamine in the ratio 1:5:0.8:1. It has been found by using mass spectrometry, IR and ³¹P NMR spectrometry, chromatography and ebulliometry that the oligomer represents a chain consisting of fragments of isopropylphosphonous acid. Products of side reactions have been identified.

It has been shown earlier that the interaction in the system P_4 -propylene oxide (PO)-NMe-PhOH in the ratio 1:5:0.8:1 leads to the formation of an oligomer in which -C-P(O)-Ofragments alternate in sequence. The composition of the fragments in the oligomer has been established by chemical destruction (chlorination, hydrolysis) and ³¹P NMR [1]. In order to determine the composition of the oligomer and to obtain additional information on the structure of products formed, we have investigated the oligomer by mass spectrometry, liquid chromatography, preparative fractionation on a column packed with an inert support, and ebulliometry.

Chromatography of the products on a liquid chromatograph showed that they contained three groups of substances (Fig. 1). Separation of the products on a column, filled with an inert support (glass) in the system methanol (solvent):ether (precipitant) gave three fractions. Ebulliometry was used to determine the number average molecular mass of the fractions (Mn) in methanol and isopropanol (Table 1). The composition and structure of the products were investigated by chemical ionization mass spectrometry and electron impact mass spectrometry and by measuring the exact masses of the ions. The electron impact mass spectrometric data for fraction I and measurement of the exact mass of the ions (Table 2) identified the main component of this fraction as 2-hydroxypropylphenyl ether.

According to the chemical ionization mass spectra fraction II contains, besides a small amount of fraction I, a product which corresponds to the intensive MH⁺ ion peak with m/z 169, having the composition $C_5H_{14}O_4P$. The ³¹P NMR spectrum of fraction II contains a signal at 28.6 ppm, indicating a phosphonate structure of the product. The electron impact spectrum of II is presented in Table 3, obtained by subtracting the mass spectrum of product I. Based on all the data obtained the product can be identified as the methyl-2-hydroxypropyl ester of methylphosphonic acid. The absence of the molecular ion with m/z 168 in the electron impact



Fig. 1. Chromatogram of the product of the reaction of P_4 -PO-Me₃N-PhOH in the ratio 1:5:0.8:1 (5 h at 55-65°C in benzene).

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TABLE 1. Composition of the Products of the Reaction of P_4 -PO-Me₃N-PhOH = 1:5:0.8:1

Frac- tion	Weight frac- tion of the group of substances, g	n_D^{20}	$in {\overline{M}n \atop MeOH}$	іп ^{Mn} in i-PrOH	Found, %			
					С	н	N	Р
(I) (II) (III)	0,0937 2,475 6,545	1,5197 1,4865 1,4887	150 170 200	. 150 170 240	57 32,19 32,5	6,56 6,73 7,16	1.29 1.35 3,41	6,91 19,0 18,37

TABLE 2. Electron Impact Mass Spectrum of 2-Hydroxypropylphenyl Ether

m/z	Found, %	Calculated, %	Formula	I, %
74 76 77 99 93 107 108 119 127 152	$\begin{array}{c} 74,0148\\ 76,0310\\ 77,0382\\ 78,0456\\ 79,0538\\ 93,0347\\ 107,0500\\ 108,0577\\ 119,0503\\ 127,0159\\ 152,0841 \end{array}$	$\begin{array}{c} 74.0156\\ 76.0313\\ 77.0391\\ 78.0469\\ 79.0548\\ 93.0340\\ 107.0497\\ 108.0575\\ 119.0497\\ 127.0184\\ 152.0837 \end{array}$	$\begin{array}{c} C_{6}H_{2} \\ C_{6}H_{4} \\ C_{6}H_{5} \\ C_{6}H_{6} \\ C_{6}H_{7} \\ C_{6}H_{5}O \\ C_{7}H_{7}O \\ C_{7}H_{8}O \\ C_{7}H_{8}O \\ C_{8}H_{7}O \\ C_{8}H_{3}O \\ C_{9}H_{12}O_{2} \end{array}$	$\begin{array}{c} 3.4\\ 3.9\\ 60.6\\ 43.4\\ 19.3\\ 6.5\\ 14.3\\ 48.7\\ 6.0\\ 2.7\\ 100\\ \end{array}$

TABLE 3. Electron Impact Mass Spectrum of the Methyl-2-hydroxypropyl Ester of Methylphosphonic Acid

m/z	Found, %	Calculated, %	Formula	I, %
31 32 57 58 93 94 95 109 110 121 124 137 153	$\begin{array}{c} 31.0244\\ 32.0245\\ 57.0464\\ 58.0524\\ 78.9945\\ 93.0109\\ 94.0181\\ 94.9894\\ 109.0059\\ 110.0137\\ 121.0054\\ 124.0285\\ 137.0365\\ 153.0317 \end{array}$	$\begin{array}{c} 31.0184\\ 32.0262\\ 57.0340\\ 58.04187\\ 78.9949\\ 93.0105\\ 94.0184\\ 94.9898\\ 109.0055\\ 110.0133\\ 121.0055\\ 124.0289\\ 137.0367\\ 153.0318 \end{array}$	$\begin{array}{c} CH_{3}O\\ CH_{4}O\\ C_{3}H_{5}O\\ C_{3}H_{6}O\\ CH_{4}O_{2}P\\ C_{2}H_{6}O_{2}P\\ C_{2}H_{7}O_{2}P\\ CH_{4}O_{3}P\\ C_{2}H_{7}O_{3}P\\ C_{2}H_{7}O_{3}P\\ C_{3}H_{6}O_{3}P\\ C_{3}H_{6}O_{3}P\\ C_{4}H_{10}O_{3}P\\ C_{4}H_{10}O_{4}P\end{array}$	100 14.7 7.4 26.1 99.8 9.7 73.8 20.0 27.2 18.2 11.0 84.9 10.7 89.1

spectrum of the methyl-2-hydroxypropyl ester of methylphosphonic acid is due to the radical -OCH₂CH(Me)OH, since methylphosphonates, containing simple radicals such as OMe, OEt, or OPr, form stable (10%) molecular ions [2]. The formation of P-OMe and P-Me bonds in the identified compounds can be attributed to the alkylating power of the quaternary ammonium

salts in the reaction with the anions P^- or by the thermal decomposition of

the reaction products in the chamber of mass spectrometer.

The chemical ionization mass spectra of fraction III are complicated (Table 4). Heating of the sample leads to an increase of the peaks in the region of high mass numbers. The ion peak with m/z 351 and the composition $C_{10}H_{25}O_7P_3$ is the most pronounced peak. The molec-

TABLE 4. Chemical Ionization Mass Spectrum of Fraction III

MH+	Found,	Calcu- lated, %	Formula	MH+	Found, %	Calcu- lated, %	Formula
351 277 263	351,0821 277,0184 263,0331	351,0892 277,0016 263,0368	$\begin{array}{c} C_{10}H_{26}O_7P_3\\ C_6H_{16}O_6P_3\\ C_6H_{15}O_4P_2\end{array}$	255 243 213	255,0908 243,0552 213,0445	255,0916 243.0552 213,0446	$\begin{array}{c} C_9H_{21}O_4P_2\\ C_7H_{17}O_5P_2\\ C_6H_{15}O_4P_2 \end{array}$

TABLE 5. Electron Impact Mass Spectrum of Fraction III

m/z	Found, %	Calculated, %	Formula	I, %
79 80 81 95 96 105 106 107 110 121 123 136 137 169 211	79,0073 80,0154 81,0136 94,9899 95,9974 105,0106 106,0178 107,0263 110,0132 121,0058 123,0207 136,0289 137,0368 168,9886 211,0274	79,0061 80,0139 81,0105 94,9898 95,9976 105,0105 106,0184 107,0262 110,0133 121,0055 123,0211 136,0289 137,0367 168,9819 211,0289	$\begin{array}{c} H_4 N_2 OP \\ H_5 N_2 OP \\ CH_6 O_2 P \\ CH_4 O_3 P \\ CH_5 O_3 P \\ C_3 H_6 O_2 P \\ C_3 H_7 O_2 P \\ C_3 H_8 O_2 P \\ C_2 H_7 O_3 P \\ C_3 H_6 O_3 P \\ C_4 H_6 O_3 P \\ C_4 H_6 O_3 P \\ C_4 H_0 O_3 P \\ C_4 H_1 O_3 P \\ C_4 H_1 O_4 P_2 \\ C_6 H_1 O_4 P_2 \end{array}$	9,3 22,3 5,2 7,7 9,4 3,6 11,4 11,5 8,5 3,3 8,5 3,3 8,3 4,2 6,5 9,4 5,5

ular fragments correspond to the composition of the ions identified from the electron impact mass spectrum (Table 5).

Based on the comparison of the electron impact and chemical ionization mass spectra (Tables 4 and 5) the following structure of the product has been proposed

 $\begin{array}{ccc} O & O \\ M_{e}O - P - CH_{2}CH(M_{e})OPCH_{2}CH(M_{e})OPCH_{2}CH(M_{e})OH \\ I \\ H & H \\ H \end{array}$

This structure is in agreement with the IR and ³¹P NMR spectroscopic data. IR spectrum $(\nu, \text{ cm}^{-1})$: 1220 (P=O), 1055 (P-OC), 2290 (PH): δ^{31} P 19.5 ppm, $J_{P-H} = 502$ Hz (1:1). Thus, the main product of the reaction of elemental phosphorus with PO, phenol, and Me₃N is a product with an oligomer structure, while the 2-hydroxypropylphenyl ether and the methyl-2-hydroxypropyl ester of methylphosphonic acid are side products. The formation of these products is in agreement with the scheme proposed in [1].

The action of the initially formed anion $Me_3NCH_2CH(Me)O^-$ on the phosphorus molecule leads to the formation of a phosphide anion which can protonate itself with the phenol or add a molecule of the oxide. Due to its low nucleophilicity the liberated PhO anion does not interact with the phosphorus but reacts with PO to form the alkoxide anion PhOCH,CH(Me)O⁻ which can convert to the alcohol or participate in the initiation reactions of the phosphorus. The formation of the alcohol can also be expected in the interaction of phenol with propylene oxide at the reaction conditions. However, the consumption of phenol for this reaction is improbable, since the reaction does not take place in the absence of phenol. The reactivity of the phosphide anion formed is so strong [3] that its protonation by phenol is strongly preferred to the interaction of phenol with the oxide [4]. The absence of PhO-P bonds in the oligomer is also confirmed by the absence of chlorobenzene and phenol in the chlorination products of the oligomer as has been shown in [1]. We have also studied the interaction of P₄ with propylene oxide, N(Me)₃, and thiophenol in the ratio 1:5:0.8:1. According to ³¹P NMR data the oligomer formed in this case does not contain the signal characteristic for P-S and P=S and has the same structure as in the investigated case. This also confirms the absence of an interaction of the PhO- and PhS-anions with P₄.

EXPERIMENTAL

The investigated oligomer was prepared by the method given in [1]. The IR spectra were recorded on a Specord UV-VIS spectrometer, the ³¹P NMR spectra on a Bruker CXP-100 spectrometer, and the mass spectra on a Finnigan MAT-212 spectrometer. The reaction products were investigated by liquid chromatography on a Gilson chromatograph. The ebulliometric measurements were carried out on an ebulliometer with a multijunction thermocouple. A column 1000 mm long, with a diameter of 40 mm was used for the fractionations, packed with glass particles with a diameter of 0.15 mm, to which the oligomer was applied from a methanol solution. The eluent was methanol (solvent):ether (precipitant).

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