REACTION OF ELEMENTAL PHOSPHORUS WITH EPOXIDES

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The synthesis of phosphorus-containing polyols from elemental phosphorus and epoxides, which have been proposed as flame retardants for textile materials and urethane foams, has been described in the patent literature [1-3]. In the present work, we studied the mechanism and other features of the reactions of elemental phosphorus P_4 with epoxides in order to synthesize phosphorus-containing oligomers with a given structure and properties. A series of organic bases was selected as the nucleophiles inducing the reaction of P_4 with epoxides since, in the presence of alkalis and alcoholates, the reactions are complicated by the formation of phosphines, hypophosphites, phosphites and H_2 [4, 5]. This reaction does not proceed in the absence of a proton donor (HX). In the presence of HX, the reaction begins several minutes after mixing of the components. In this regard, we studied the reaction of P_4 with epoxides in the presence of various bases and proton donors.

The data in Tables 1-3 indicate that the reaction rate depends on the pK_a value of the base, epoxide structure and nature of the proton donor. The greatest reactivity is found for ethylene oxide and propylene oxide (PO) and Me₃N. Strong acids such as HCl, HBr, and HI do not enter the reaction. The conversion of P_4 in the presence of acetic acid is 4%. This finding is apparently related to deactivation of the amine. The greatest conversion occurs for phenols. The conversion drops with increasing pK_a of the proton donor. In the reaction of P_4 and PO in the presence of Me_3N and PhOH, we studied the effect of the reagent concentration on the conversion rate and the composition of theoligomer formed under identical experimental conditions. The greatest conversion is achieved using 0.5-1 mole phenol and 0.8-1 mole Me₂N per mole phosphorus. A further increase in the reagent concentration does not lead to an increased conversion of P_4 (Fig. 1). The optimal amount of PO is 4-5 moles. A lesser amount of PO leads to the formation of insoluble products. With increasing PO concentration, the composition of the oligomer is not altered substantially. The hydroxyl group content in the oligomer found by the acylation method [6] does not change within experimental error and is 8.5% for $P_4/Me_3N/PhOH/PO = 1:0.8:1:5$, 9.4% for $P_4/Me_3N/PhOH/PO =$ 1:0.8:1:8, and 8.9% for $P_4/Me_3N/PhOH/PO = 1:0.8:1:12$. We expected an increase in the polyglycol chain of the oligomer and increase in the content of hydroxyl groups due to reaction of the excess oxide with the PH fragments of the oligomer. The possibility of incorporating polyoxide chains into the chain was determined by treatment of the sample with 45% HBr/CH₃CO₂H with subsequent analysis of the product formed by gas-liquid chromatography [7] using polypropyleneglycol-250 as the standard. The formation of 1,2-dibromopropane was not detected in any experiment. This failure indicates the absence of an oxypropyl chain in the oligomer. The composition of the oligomers formed was determined by chemical decomposition through chlorination with PCl₅ or SOCl₂ with subsequent treatment with EtONa and hydrolysis with 18% hydrochloric acid. The products were identified by ³¹P NMR spectroscopy, Fourier IR spectroscopy, mass spectrometry and gas-liquid chromatography. The mass spectra of the reaction mixtures showed four molecular ion peaks with m/z 170, 178, 182 and 194. The ³¹P NMR spectra show signals at 19.5, 86.9 and -0.4 ppm. Preparative chromatography on a column packed with 15% FS-16 on Chromosorb gave a product with δP 19.5 ppm and M⁺ m/z 178. The precise mass of the molecular ion indicated the chemical formula $C_7H_{15}PO_3$. IR spectrum: $v_{P=O}$ 1200, $v_{C=C}$ 1650 cm⁻¹, n_D^{20} 1.4360, d_4^{20} 1.052, MR_{exp} 44.24, MR_{calc} 44.82. This product was identified as the diethyl ester of 2-methylvinylphosphonic acid [8]. We also identified 1-phenoxy-2-chloropropane, M⁺ m/z 170, IR spectrum: 3047, 3078, 1601, 1041, 1242, 694 cm⁻¹, C₉H₁₁ClO [9], triethyl phosphate, M⁺ m/z 182, $\delta P = -0.4$ ppm, $v_{P=0}$ 1200 cm⁻¹, $C_6H_{15}O_4P$ [10], and the diethyl ester of 2-methylvinylthiophosphonic acid, M⁺ m/z 194, δP 86.9 ppm, IR spectrum: vp-OC 953, 1038, vp=S 779, vC=C 1643 cm⁻¹, C₇H₁₅PO₂S, which is formed

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TABLE 1. Dependence of the Conversion of P_4 on the Base pK_a Value ($P_4/PO/HX/base$ mole ratio = 1:5:1:0.8)

Base	рК _а	нх	Reaction	D convon-	
			Time, h	т., °С	sion, %
$\begin{array}{c} Me_{3}N\\ Et_{3}N\\ (EtO)_{2}PNEt_{2}\\ (Et_{2}N)_{2}POEt\\ C_{5}H_{5}N\end{array}$	9,8 10,87 5,25	$\begin{array}{c} PhOH\\ H_2O\\ PhOH\\ PhOH\\ H_2O\end{array}$	5 7 8 8 96	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	91 70 60 56 0

TABLE 2. Dependence of the P_4 Conversion on the Epoxide Structure ($P_4/Me_3N/PhOH/oxide$ mole ratio = 1:0.8:1:5)

Owido	Reaction	P_{μ} conversion,		
	Time, h	т., °С	%	
Ethylene oxide Propylene oxide Epichlorohydrin THF	7,8 5 30,5 96	30-55 50-75 60-80 50-60	96 91 38 0	

TABLE 3. Dependence of the P_4 Conversion on the Nature of the Proton Donor ($P_4/OP/Me_3N/HX$ mole ratio = 1:5:0.8:1)

HX	рК _а	P ₄ Conver- sion, %	Reaction conditions
MeCO ₂ H	4,75	4	Time 5 h at 55-65°C
PhOH	9,98	91	
MeC ₆ H ₄ OH	10,4	98	
H ₂ O	15,7	18	
<i>t</i> -BuOH	19	9	



Fig. 1. The dependence of the conversion of P_4 on the concentration of Me_3N (1) and PhOH (2) in the system with P_4/PO = 1:5.

upon treatment of the oligomer with SOCl₂. Thus, the chlorination of the sample leads to the identification of three major products. Hydrolysis of the oligomer gives a viscous, colorless liquid which gradually crystallizes. The hydrolysis products were identified by ³¹P NMR spectroscopy and compared with the unhydrolyzed oligomer (Table 4). The compositions of both reaction mixtures are in rather good accord.

It has been reported that 1:1:1 mixtures of tertiary amines, epoxides and water (or alcohol or phenol) are catalysts for many chemical reactions [11]. Quaternary ammonium bases or zwitterions or, depending on the acidity of the proton donor, $R_3N...PO...HX$ trimolecular complexes may be responsible for initiation of the reactions of P_4 with epoxides

$$R_3N + H_2C \xrightarrow{HX} CHR \xrightarrow{+HX} [R_3NCH_2CHROH]^+X^- \rightleftharpoons R_3NCH_2CHRO^- + HX$$

Literature data and the present results indicate that the action of $Me_3NCH_2CH(CH_3)O^$ or PhO⁻ anions in the reaction medium leads to cleavage of the P-P bond in the P₄ molecule and formation of a phosphide anion (I) (a strong base) which is protonated by phenol to form phosphine (II) and the PhO⁻ anion which reacts with one of the unsubstituted phosphorus atoms of the P₄ molecule or with PO to form a new alkoxy anion, PhOCH₂CHMeO⁻ capable of attacking one of the phosphorus atoms with the formation of new phosphide anions. The reaction of phosphide anions with PO is also possible. This reaction would lead to the

formation of alkoxy anions PCH_2CHMeO^- . Apparently, successive transformations of the

anions formed with P_4 lead to the formation of an oligomer with the -C-P(0)-O- sequence shown in Table 4. The probability of such transformations is indicated by the finding that in the absence of a proton donor, the reaction does not proceed and 1-phenoxy-2-chloropropane



is found in the products of chemical decomposition. The mechanism for the formation of the oligomer is presently under study.

EXPERIMENTAL

All the reactions were carried out in a glass reactor equipped with a stirrer, dropping funnel, bubbler, thermometer and condenser cooled with liquid nitrogen/acetone in a dry argon atmosphere. The IR spectra were taken on a Specord spectrometer. The ³¹P NMR spectra were taken on a Bruker CXP-100 spectrometer. The mass spectra were taken on a Varian MAT-212 spectrometer. The reaction products were studied by gas-liquid chromatography on a Tsvet-6 chromatograph.

Reaction of P_4 and Propylene Oxide in the Presence of Me₃N and PhOH. A sample of 23.g (0.4 mole) PO and 3.8 g (0.06 mole) Me₃N was added dropwise with stirring to a mixture of 10 g (0.08 mole) P₄ in 80 ml benzene and 7.6 g (0.08 mole) PhOH heated until the phosphorus melted. The reaction was carried out for 5 h at 55-65°C. Then, the mixture was dissolved in 250 ml methanol and 0.9 g unreacted P₄ was filtered off. The filtrate was evaporated and the residue was reprecipitated three times from methanol by the addition of ether and dried in vacuum to give 11.3 g oligomer as a thick viscous liquid. Found: C 40.83; H 8.03; N 3.80; P 22.7%.

<u>Hydrolysis of the Oligomer</u>. A sample of 5 g oligomer was heated with 40 ml 18% hydrochloric acid for 14 h at 120-140°C. The solution was evaporated. The residue was washed until there were no traces of HCl and dried in vacuum. The products were identified by ³¹P NMR spectroscopy (see Table 4).

<u>Chlorination of the Oligomer</u>. A sample of 11 g oligomer was triturated in a dry argon stream with PCl_5 until a mobile liquid was formed or heated at reflux for 10 h in the presence of 70 ml SOCl₂. The chlorination products were extracted by three 30-ml portions of dry ether. The extracts were combined and treated with EtONa. The products were identified by gas-liquid chromatography, IR and ³¹P NMR spectroscopy and mass spectrometer.

CONCLUSIONS

The reactions of P_4 /propylene oxide/Me₃N/HX (mole ratio = 1:5:0.8:1) leads to the formation of an oligomer. The chain of this oligomer features the sequence of -C-P(0)-O- fragments. Features were determined which control the rate of P_4 conversion depending on the composition of the reaction mixture. The oligomer composition was determined.

Oligomer fragment prior to hydroly- sis*	ôªP, ppm	J _{PH} , Hz	Fragment content,%	Product of oligomer hydrolysis	widd ' dreg	J _{PH} , Hz	Fragment content, %
R P(0)CH2CH(Me)OY H	$43,9\\42,9\\39,2$	$555 \\ 566,5 \\ 549,3$	25,5	OH P(O)CH ₂ CH(Me)OH H	34,0	549,3	26,9
R₂P(O)CH₂CH(Me)OY	33,2 28,9 27,0 25,3 22,7		24,5	R₂P(O)CH2CH(Me)OH	40,4 35,0 28,4 23,0 17,2		18,5
R₂P(O)H	14,1 11,2 8,4 5,8	708 720 610 634,8	36,2	H₃₽O₃	5,67	653	41,4
R₅P==O	$^{0,8}_{0,4}$		14,0	P ₃ P=O	$1,6 \\ 6,1 \\ 0,5$		13,2

TABLE 4. Distribution of the Fragments in the Oligomer Before and After Hydrolysis $(P_4/PO/PhOH/Me_3N \text{ mole ratio} = 1:5:1:0.8)$

 \dot{R} is the residue of the proton donor, Me₃ $\dot{N}CH_2CH(Me)O^-$ and RCH₂CH(Me)O⁻, and Y is hydrogen or one of the fragments indicated in the table.

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