POLYMERS CONTAINING PHOSPHORUS—I. SYNTHESIS AND POLYMERIZATION OF ETHYLENEALKYLPHOSPHATES*

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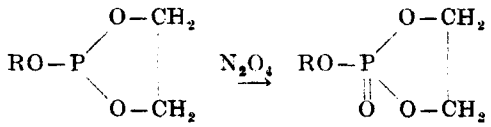
THE ordinary phosphates are well studied compounds, used in industry and in agriculture. However phosphates have not yet been synthesized having a five-membered, cyclic, ether grouping in their composition, nor high-molecular phosphates condensed other than through vinyl ester groups. A simple method is put forward in this paper for the preparation of ethylenealkylphosphates and for their conversion to polymers.

The synthesis of ethylenealkylphosphates was achieved by oxidation of ethylenealkylphosphites, which are available compounds [1]†, with nitrogen dioxide:



$R = C_3H_7$; C_4H_5; *iso*-C_4H_9; C_5H_{11}; C_6H_{13}; C_6H_5

Experiment showed that the best yield of the phosphates was obtained when oxidation was carried out without solvent at -5 to $+5°$, with subsequent displacement of the oxides of nitrogen by dry nitrogen, and distillation of the product immediately after oxidation. When the material was allowed to stand for a long time at room temperature and then distilled, considerable resinification occurred. Evidence on the structure of these compounds was obtained from the infrared spectrum of ethylenepropylphosphate. The spectrum has an intense absorption band at a frequency of 1286 cm^{-1} which corresponds to the vibration of the P=O bond and appears in phosphates in the 1300—1275 cm^{-1} region [2]. The compound in question cannot be the isomeric propylvinylphosphoric acid, the formation of which on distillation might be suggested, because there is no band in the spectrum in the 1850 and 1650 cm^{-1} regions, characteristic of the double bond, or a band at 2700 cm^{-1} corresponding to the P—OH group [2].

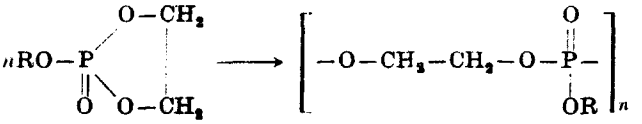
We used these cyclic phosphates for the preparation of phosphorus-containing polymers. It has been shown previously that ethylenephosphonates form poly-

* Vysokomol. soedin. **2**: No. 3, 417–420, 1960.

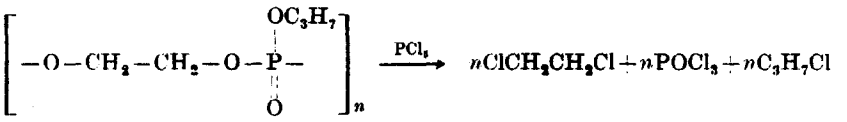
† Two of the phosphates ($R = C_6H_{13}$ and C_6H_5) were prepared for the first time by us, by the interaction of ethylenechlorophosphite with hexanol and phenol.

meric products with a degree of polymerization of 3–4 on heating in sealed tubes [3]. We found that the cyclic phosphates (in contrast to phosphonates) form products of higher molecular weight (degree of polymerization, 10–14) on polymerizing under the same conditions. The polymers obtained were of approximately the same molecular weight, and had the same properties, in experiments with and without a catalyst (sodium).

The macromolecular phosphates are neutral substances. In structure they belong to the class of polyesters, formed as a result of the opening of the cyclic phosphates:



When the polymers are treated with phosphorus pentachloride, phosphorus oxychloride, dichloroethane and the corresponding alkyl chloride are formed, for example:



The macromolecular phosphates described in this communication can be used as plasticizers.

EXPERIMENTAL

Ethylenehexylphosphite. 300 ml of absolute ether, 126·5 g (1 mole) of ethylenechlorophosphite and 152 g (1·5 moles) of triethylamine were placed in a three-necked flask fitted with a reflux condenser, stirrer and dropping funnel. 102 g (1 mole) of hexyl alcohol was then added dropwise, with stirring, to the flask cooled in ice-water. The reaction mixture was allowed to stand for 10–15 hours, filtered and again allowed to stand for the same period. After a second filtration the ether was distilled from the mother liquor and the residual oil distilled *in vacuo*. After a second distillation 143 g (72% of theory) of ethylenehexylphosphite was obtained; b.p. 115–118°/13 mm; n_D^{20} 1·4480; d_4^{20} 1·1090; $MR_{D\,found}$ 46·70; $MR_{D\,calc.}$ 46·72.

$C_{18}H_{17}PO_3$	Found %:	*P* 16·07
	Calculated %:	*P* 16·14

Ethylenephenylphosphite. As described above, 148 g (85 per cent of theory) of ethylenephenylphosphite was obtained from 126·5 g of ethylenechlorophosphite, 152 g of triethylamine and 96 g of phenol; b.p. 133–135°/13 mm; n_D^{20} 1·5350; d_4^{20} 1·2225; $MR_{D\,found}$ 49·22; $MR_{D\,calc.}$ 49·19.

$C_8H_9PO_3$	Found %:	*P* 16·20
	Calculated %:	*P* 16·84

According to the literature [4], b.p. 73°/0·3 mm, n_D^{20} 1·5342.

Ethylenealkylphosphates. The phosphite was placed in a four-necked flask, protected from moisture and fitted with a stirrer, thermometer and capillary gas inlet, and nitrogen peroxide in a current of dry nitrogen was passed through. The rate at which the gases were passed was such that the temperature of the reaction mixture did not exceed 0°. At the end of the reaction (appearance of a green colour) the excess of oxide of nitrogen was swept out by a current of dry nitrogen and the product was twice distilled *in vacuo* at 0·4 mm. The experimental results are shown in Table 1, where R is the radical in the formula

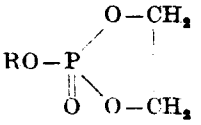


TABLE 1. SYNTHESIS OF ETHYLENEALKYLPHOSPHATES

R	Yield (%)	Boiling point (°C) at 0·4 mm Hg	n_D^{20}	d_4^{20}	MR_D		Phosphorus content %	
					Found	Calculated	Found	Calculated
C_3H_7	62·7	103–104	1·4297	1·2020	36·65	35·65	18·58	18·67
C_4H_9	70·0	115–116	1·4330	1·1850	39·48	39·70	16·84	17·22
iso-C_4H_9	76·6	110–111	1·4310	1·1740	39·48	39·70	16·96	17·22
C_5H_{11}	55·0	123·5–124	1·4345	1·1410	44·34	44·32	16·61	15·98
C_6H_{13}	83·0	137–138·5	1·4361	1·1160	49·20	48·94	14·78	14·90
C_6H_5	53·0	149–150·5 (melting point 29°)	—	—	—	—	15·15	15·50

Polymerization of ethylenealkylphosphates. Polymerization was carried out by heating in sealed tubes in an atmosphere of nitrogen. In some experiments a catalyst (sodium) to the extent of 1% by weight of the phosphate, was used. The polymer from ethylenepropylphosphate was obtained after standing for three months in an atmosphere of nitrogen. The polymers were soluble in benzene, chloroform and carbon tetrachloride, and insoluble in water, alcohol and ether. The viscosity of 1·5 per cent solutions of the polymers in benzene at 20° was measured. Data on the polymers are shown in Table 2.

Reaction of polyethylenepropylphosphate with phosphorus pentachloride. 3·2 g of phosphorus pentachloride was added in portions to 0·84 g of the polymer in 3 ml of dry carbon tetrachloride, with stirring and cooling in ice-water. The mixture was then stirred for a further two hours at 35°. Unreacted phosphorus pentachloride was removed by passing sulphur dioxide through the mixture which was then distilled. The following fractions were obtained: I b.p. 44–46°; II b.p. 69–78°; III b.p. 82–84°; IV b.p. 100–107°.

TABLE 2. CONDITIONS OF POLYMERIZATION OF ETHYLENEALKYLPHOSPHATES AND PROPERTIES OF THE POLYMERS

Basic unit	Reaction time (hr)	Temperature (°C)	Catalyst	η_{sp}^{20}	Molecular weight
$C_3H_7OP(O)O-CH_2-CH_2-O-$	10	140	Na	0·186	2320
	4 months	20	—	0·14	2090
	10	140	—	0·15	2280
$C_4H_9-OP(O)OCH_2CH_2-O-$	10	140	—	0·192	2320
$C_5H_{11}OP(O)OCH_2CH-O-$	10	140	—	0·23	2420
	10	140	Na	0·31	2950

Fraction I after redistillation had b.p. 45–46°, n_D^{20} 1·3869 and consisted of propyl chloride. According to the literature [5], b.p. 46·4°; n_D^{20} 1·3873.

Fraction III after redistillation had b.p. 83–84°, n_D^{20} 1·4426 and consisted of 1,2-dichloroethane. According to the literature [5], b.p. 83·7°, n_D^{20} 1·4431.

Fraction IV after redistillation had b.p. 103–106° and was phosphorus oxychloride. According to the literature [5], b.p. 105·7°.

CONCLUSIONS

(1) A synthesis of ethylenealkylphosphates by oxidation of ethylenealkylphosphites with nitrogen peroxide has been developed.

(2) It is shown that the ethylenealkylphosphates polymerize on prolonged standing or on heating. The structure of the products is discussed.

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