

1,3-Addition-Type Ring-Opening Polymerization of Cyclic Phosphonites

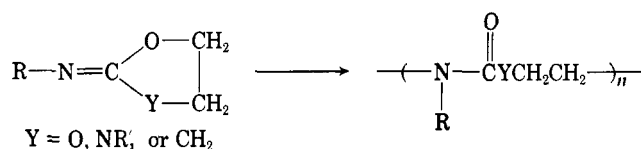
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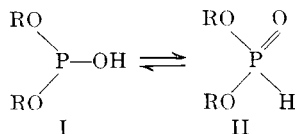
Ethylene and trimethylene phenylphosphonites were prepared from phenylphosphonous dichloride and corresponding glycols. Ethylene *n*-propylphosphonite was obtained by reacting ethylene phosphorochloridite with *n*-propylmagnesium bromide. The phosphonites, being reacted with such acids as hydrogen chloride and carboxylic acids, have given ring-opening addition compounds, which suggests the possibility that these phosphonites may be polymerized. Various polyphosphinates were produced by the ring-opening polymerization of the cyclic phosphonites in the presence of cationic catalysts or Arbusov reaction-type reagents at elevated temperatures. This type of polymerization can be termed as "1,3-addition-type ring-opening polymerization" because it consists of the repetition of ring-opening 1,3-additions of the cyclic monomers, cyclic phosphonites.

Preceding papers¹⁻⁴ on 1,4-addition-type ring-opening polymerization have shown that *exo*-imino cyclic compounds, such as ethylene iminocarbonates, 2-imino-1,3-oxazolidines, and 2-iminotetrahydrofurans, polymerize in the presence of cationic catalysts to give polyurethanes, polyureas, and polyamides, respectively, as shown in the following equation.



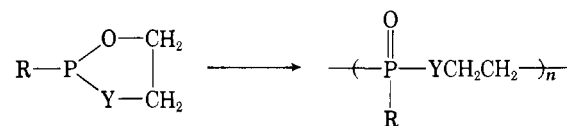
As shown in the preceding papers, the following two factors play important roles in the ring-opening polymerization of these *exo*-imino compounds. Since the *exo*-imino cyclic compounds are enol isomers of cyclic urethane, cyclic urea, or lactam, which seem to be more unstable than the corresponding keto-form structures, it is reasonable to consider that these compounds are readily converted into the polymers having keto-form structures. Furthermore, the imino groups of the cyclic compounds have a strongly basic character due to alkoxy group, by which the compounds react easily with cationic catalysts to form reactive intermediate salts for the ring-opening polymerization.

With a view to extending the scope of this type of ring-opening polymerization, the ring-opening polymerization of cyclic phosphonites has been tried under the assumption that they would, when polymerized, yield polymers containing pentavalent phosphorus atoms. What has prompted the assumption expounded here are the following facts about trivalent phosphorus compounds. It is known that a tautomeric pair of trivalent and pentavalent structures exists in the phosphorus compound as in enol- and keto-form structures of urethane, urea, or amide. The phosphorus com-



pound of the pentavalent structure (II) corresponding to the keto form seems to be more stable than that of the trivalent structure (I) corresponding to the enol form. Secondly, a trivalent phosphorus compound possesses

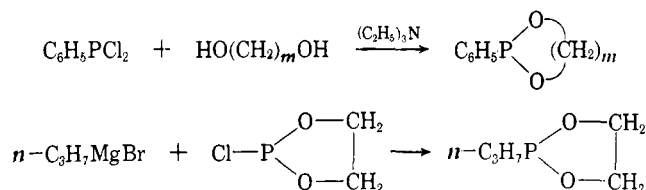
a lone electron pair, by which it may form a reactive salt with electrophiles. Under this assumption, it can be expected that cyclic trivalent phosphorus compounds such as cyclic phosphite, phosphonite, or phosphinite, afford polymers containing pentavalent phosphorus atoms—polyphosphonate, polyphosphinate, or polyphosphine oxide—by ring-opening polymerization.



R = alkoxy, aryloxy, alkyl, or aryl group
Y = O or CH₂

In the present experiment, the preparation and ring-opening polymerization of cyclic phosphonites were studied.

Ethylene and trimethylene phenylphosphonites were prepared as cyclic aromatic phosphonites by reacting phenylphosphonous dichloride with corresponding glycols in the presence of triethylamine. An aliphatic derivative, ethylene *n*-propylphosphonite, was obtained by the reaction of ethylene phosphorochloridite with *n*-propylmagnesium bromide. The yields, physical properties, and analysis of these cyclic phosphonites are listed in Table I.



Next, in order to confirm the possibility of the ring-opening polymerization, the reaction of the cyclic phosphonites with acids, such as hydrogen chloride and carboxylic acids, was carried out as established in the case of *exo*-imino cyclic compounds.^{5,6}

When hydrogen chloride was passed into a solution of ethylene phenylphosphonite in dry benzene at room temperature, a violent reaction took place and β -chloroethyl phenylphosphinate was obtained as expected. The reaction of trimethylene phenylphosphonite with hydrogen chloride in a benzene solution at room temperature gave only an undistillable oily substance, al-

(1) T. Mukaiyama, T. Fujisawa, H. Nohira, and T. Hyugaji, *J. Org. Chem.*, **27**, 3337 (1962).

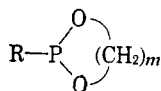
(2) T. Mukaiyama and K. Sato, *Bull. Chem. Soc. Japan*, **36**, 99 (1963).

(3) T. Fujisawa, Y. Tamura, and T. Mukaiyama, *ibid.*, **37**, 793 (1964).

(4) H. Nohira, Y. Nishikawa, and T. Mukaiyama, *ibid.*, **37**, 797 (1964).

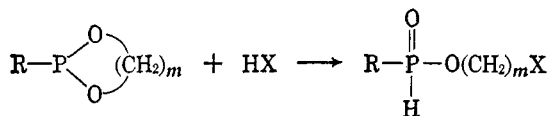
(5) T. Mukaiyama, T. Fujisawa, and T. Hyugaji, *ibid.*, **35**, 687 (1962).

(6) T. Mukaiyama, Y. Tamura, and T. Fujisawa, *ibid.*, **37**, 628 (1964).

TABLE I
 PREPARATION OF CYCLIC PHOSPHONITE


Phosphonite	R	m	Yield, %	B.p., °C. (mm.)	Formula	Carbon, %		Hydrogen, %		Phosphorus, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
Ethylene phenylphosphonite	C ₆ H ₅	2	62	79–80 (0.8)	C ₈ H ₉ O ₂ P	57.14	56.78	5.36	5.19	18.5	18.1
Trimethylene phenylphosphonite	C ₆ H ₅	3	66	72–74 (0.15) ^a	C ₉ H ₁₁ O ₂ P	59.37	59.06	6.09	6.84	17.0	17.1
Ethylene <i>n</i> -propylphosphonite	<i>n</i> -C ₃ H ₇	2	15	68–69 (20)	C ₅ H ₁₁ O ₂ P	44.77	44.49	8.20	8.28	23.1	22.7

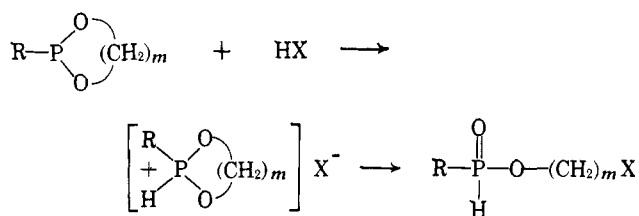
^a Lit.⁹ b.p. 86–89° (2 mm.).

 TABLE II
 REACTION OF CYCLIC PHOSPHONITES WITH ACIDS


R	m	X	Solvent	Temp.	Time, hr.	Yield, %	B.p., °C. (mm.)	Formula	Carbon, %		Hydrogen, %	
									Calcd.	Found	Calcd.	Found
C ₆ H ₅	2	Cl	Benzene	Room	2	49	132–136 (0.2)	C ₈ H ₁₀ ClO ₂ P	46.94	47.03	4.90	5.09
C ₆ H ₅	3	Cl	Benzene	Reflux	2	60	117–120 (0.015)	C ₉ H ₁₂ ClO ₂ P	49.44	49.68	5.53	5.41
C ₆ H ₅	2	CH ₃ COO	Benzene	Reflux	5	37	139–141 (0.04)	C ₁₀ H ₁₃ O ₄ P	52.63	52.20	5.70	5.67
C ₆ H ₅	2	C ₂ H ₅ COO	Benzene	Reflux	8	56	125–126 (0.18)	C ₁₁ H ₁₅ O ₄ P	54.54	53.90	6.24	6.32
C ₆ H ₅	3	CH ₃ COO	Acetic acid	Reflux	11	28	160–162 (0.01)	C ₁₁ H ₁₅ O ₄ P	54.54	53.33	6.24	6.36
<i>n</i> -C ₃ H ₇	2	CH ₃ COO	Benzene	Reflux	6	21	72–74 (0.15)	C ₇ H ₁₃ O ₄ P	42.27	40.76	7.73	7.63

though heat liberation was observed, but γ -chloropropyl phenylphosphinate was obtained in a 60% yield when the solution was refluxed under passing hydrogen chloride.

No noticeable reaction occurred at room temperature when ethylene phenylphosphonite was treated with carboxylic acids such as acetic and propionic acids; however, β -acyloxyethyl phenylphosphinates were obtained when the same reagents were refluxed in dry benzene. On the other hand, there appeared to be no reaction when equimolar amounts of trimethylene phenylphosphonite and acetic acid were refluxed in dry benzene for 13 hr. and the starting materials were recovered, but, when acetic acid was used in large excess, γ -acetoxypropyl phenylphosphinate was produced in a yield of 28% along with trimethylene diacetate (51% yield). The formation of the acetate may be attributed to transesterification between acetic acid and the phosphinate initially formed. Similarly, ethylene *n*-propylphosphonite reacted with acetic acid giving β -acetoxyethyl *n*-propylphosphinate, when they were refluxed in dry benzene for 6 hr.



HX = HCl or R' COOH

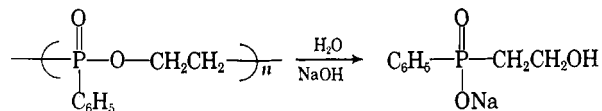
These products were confirmed to be the corresponding phosphinates by means of infrared absorption spectra which have characteristic bands attributable to the P–H linkage (2350 cm.⁻¹) and to the phosphoryl group (1280–1260 cm.⁻¹). The reaction conditions, yields, physical properties, and analysis of the products are shown in Table II.

As shown above, it is reasonable to assume that the cyclic phosphorus compounds react with acids to give intermediate salts, which in turn decompose to give the corresponding addition compounds by ring opening.

Further, bulk polymerization of the cyclic phosphonites was tried. When a catalytic amount of sulfuric acid was added to ethylene phenylphosphonite, heat liberation was observed and the viscosity of the mixture increased. However, the infrared absorption spectrum of the mixture was found to be identical with that of ethylene phenylphosphonite, and the mixture failed to show any characteristic band attributable to the phosphoryl group which was assumed to have been formed by ring opening. Furthermore, when a catalytic amount of Lewis acids, such as boron trifluoride etherate, titanium tetrachloride, or aluminum chloride, was added to ethylene phenylphosphonite, the mixture became gruelly with heat liberation, but they also failed to show any infrared absorption attributable to the phosphoryl group. On the other hand, it was found that a solid polymer was obtained when the phosphonite was heated at temperatures above 150° in the presence of cationic catalysts, such as boron trifluoride etherate or sulfuric acid. The polymerization was also successfully carried out in the absence of catalyst, when it was

heated at 200° for 9 hr. The infrared spectrum of the polymer showed a new absorption peak in the region of 1265 cm.⁻¹. According to Bellamy,⁷ the spectrum in this region originates in the phosphoryl stretching vibration.

The hydrolytic degradation of the polymer, which was carried out by refluxing it in an aqueous 0.1 *N* sodium hydroxide solution, gave a sodium salt of β -hydroxyethylphenylphosphinic acid in a 55% yield.



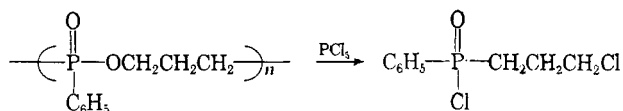
This polymer was confirmed to be poly(ethylene phenylphosphinate) by the above-mentioned experiments.

In addition, the polymerization initiated by alkyl halide was studied by the use of the concept of the Arbusov reaction. When ethylene phenylphosphonite was heated in the presence of methyl iodide at 120° for 4 hr., poly(ethylene phenylphosphinate) was also obtained in the solid state. It was noted that the polymerization took place vigorously at 170° and the internal temperature rose to more than 250° with decomposition. In a similar fashion, the polymerization was successfully carried out in the presence of dimethyl sulfate or bromocycanoacetamide⁸ in place of an alkyl halide.

The inherent viscosities of the polyphosphinate measured in chloroform are relatively low and the polymer was a flame-proof, glass-like substance which softened at a temperature of about 80°. It changed to a tacky material when left exposed to air. It is soluble in chloroform and dimethylformamide, but is insoluble in any other organic solvent and water.

It was also established that the ring-opening polymerization of trimethylene phenylphosphonite and ethylene *n*-propylphosphonite was successfully carried out in the presence of cationic catalysts or Arbusov reaction-type reagents at elevated temperatures.

After a volatile material was removed from the oily product obtained by the polymerization of trimethylene phenylphosphonite, a brittle glass-like polymer was obtained, whose property resembles that of the polymer of ethylene phenylphosphonite. The structure of the polymer was confirmed to be poly(trimethylene phenylphosphinate) by decomposition with phosphorus pentachloride, which yielded γ -chloropropylphenylphosphinyl chloride.



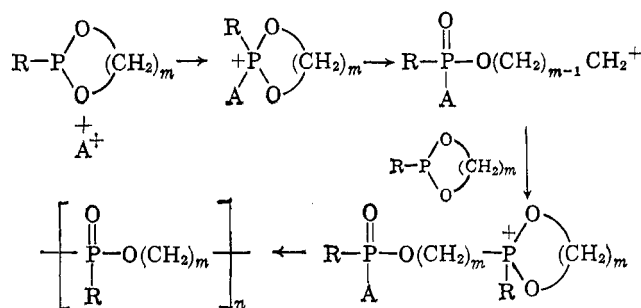
Concerning this type of polymerization, Petrov, *et al.*,⁹ have already published that the compounds prepared from phenylphosphonous dichloride and 1,3-butandiol or trimethylene glycol were polymerized in the presence of methyl iodide.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 312.

(8) This compound is effective for the Perkov reaction; T. Hata and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **35**, 1106 (1962).

(9) K. A. Petrov, E. E. Nifant'ev, and I. I. Sopikova, *Vysokomolekul. Soedin.*, **2**, 685 (1960); *Chem. Abstr.*, **55**, 9935 (1961).

On the other hand, a viscous jelly-like polymer was obtained from the polymerization of ethylene *n*-propylphosphonite by a similar treatment and its structure was established to be poly(ethylene *n*-propylphosphinate) by means of its infrared spectrum.



This polymerization can be represented by the above equation, which involves the initial formation of the intermediate salt of the phosphonites with catalysts, analogous to the explanation proposed for the reaction with acids. On heating, the salt subsequently decomposes to give an open-chained carbonium cation having a phosphoryl group by bond fission of oxygen-carbon linkage, and the step is repeated giving the polyphosphinates.

Since this type of ring-opening polymerization[†] proceeds by the repetition of ring-opening 1,3-additions of the cyclic monomers, *i.e.*, cyclic phosphonites, it may better be termed as "1,3-addition-type ring-opening polymerization."

Experimental

Phenylphosphonous Dichloride.—This compound was prepared from benzene, phosphorus trichloride, and aluminum chloride according to the method of Buchner and Lockhart.¹⁰

Ethylene Phenylphosphonite.—Into a mixture of 3.1 g. (0.05 mole) of ethylene glycol and 10.1 g. (0.10 mole) of triethylamine in 50 ml. of dry benzene was added dropwise a solution of 9.0 g. (0.05 mole) of phenylphosphonous dichloride in 50 ml. of dry benzene with stirring under cooling in an ice-water bath. Then the reaction mixture was refluxed on a water bath for 1 hr. and triethylamine hydrochloride was filtered off. After the benzene was removed from the filtrate, ethylene phenylphosphonite was distilled; yield 5.3 g. (62%), b.p. 79–80° (0.8 mm.). The infrared absorption bands are at 2950 (ms), 1443 (ms), 1215 (s), 1129 (s), 1040 (ms), 960 (s), and 750 (s) cm.⁻¹.

Trimethylene phenylphosphonite was prepared from trimethylene glycol and phenylphosphonous dichloride in the same way as ethylene phenylphosphonite. The infrared absorption bands are at 2950 (ms), 1440 (ms), 1240 (ms), 1135 (ms), 1050 (s), 940 (s), and 750 (s) cm.⁻¹.

These phosphonites gradually changed to viscous materials even when they were stored in a sealed tube at room temperature.

Ethylene Phosphorochloridite.—This compound was prepared from ethylene glycol and phosphorus trichloride according to the method of Lucas, *et al.*¹¹

Ethylene *n*-Propylphosphonite.—Into a solution of *n*-propylmagnesium bromide, which was prepared from 12.0 g. (0.5 mole) of magnesium and 61.5 g. (0.5 mole) of *n*-propyl bromide in 200 ml. of dry ether, was added very slowly a solution of 63.3 g. (0.5 mole) of ethylene phosphorochloridite in 100 ml. of dry ether with vigorous stirring. During the addition, the temperature was maintained below 10° and then the reaction mixture was refluxed on a water bath for 2 hr. The precipitate was filtered off and extracted repeatedly with dry ether. The combined ethereal solution was concentrated and the distillation of the

(10) B. Buchner and L. B. Lockhart, Jr., *Org. Syn.*, **31**, 88 (1951).

(11) H. J. Lucas, F. W. Mitchell, Jr., and C. N. Scully, *J. Am. Chem. Soc.*, **72**, 5494 (1950).

residue at 68–69° (20 mm.) gave 10.0 g. (15%) of ethylene *n*-propylphosphonite. Its infrared absorption bands are at 2950 (s), 2924 (s), 1460 (s), 1211 (m), 1065 (ms), 980 (s), 924 (s), 795 (s), and 730 (s) cm^{-1} .

Reaction of Ethylene Phenylphosphonite with Hydrogen Chloride.—Dry hydrogen chloride was saturated into a solution of 5.0 g. (0.03 mole) of ethylene phenylphosphonite in 10 ml. of dry benzene for 2 hr. On evaporation of the benzene, β -chloroethyl phenylphosphinate was obtained by distillation; yield 3.0 g. (49%), b.p. 132–136° (0.2 mm.). The infrared absorption bands showed at the peaks of 2950 (m), 2350 (m), 1495 (m), 1442 (ms), 1265 (s), 1225 (s), 1130 (s), 1030 (s), 925 (s), and 750 (s) cm^{-1} .

Reaction of Trimethylene Phenylphosphonite with Hydrogen Chloride.—Into a solution of 7.0 g. (0.04 mole) of trimethylene phenylphosphonite in 15 ml. of dry benzene was passed dry hydrogen chloride for 2 hr. under refluxing. After removal of the benzene, γ -chloropropyl phenylphosphinate was distilled; yield 5.1 g. (60%), b.p. 117–120° (0.015 mm.). The infrared spectrum resembled that of β -chloroethyl phenylphosphinate.

Reaction of Ethylene Phenylphosphonite with Acetic Acid.—A mixture of 5.0 g. (0.03 mole) of ethylene phenylphosphonite and 2.0 g. (0.03 mole) of acetic acid in 10 ml. of dry benzene was refluxed on a water bath for 5 hr. and then the benzene was removed. β -Acetoxyethyl phenylphosphinate was obtained by distillation; yield 2.0 g. (37%), b.p. 139–141° (0.04 mm.). Its infrared absorption bands are at 2950 (w), 2350 (w), 1735 (s), 1443 (ms), 1260 (s), 1230 (s), 1133 (ms), 1040 (ms), 925 (ms), and 750 (m) cm^{-1} .

Anal. Calcd. for $\text{C}_{10}\text{H}_{13}\text{O}_4\text{P}$: C, 52.63; H, 5.70; P, 13.6. Found: C, 52.20; H, 5.67; P, 14.1.

In a similar fashion, β -propionyloxyethyl phenylphosphinate and β -acetoxyethyl *n*-propylphosphinate were prepared by the equimolar reactions of the corresponding cyclic phosphonites with acids under the conditions as indicated in Table II.

Reaction of Trimethylene Phenylphosphonite with Acetic Acid.—A mixture of 5.4 g. (0.03 mole) of trimethylene phenylphosphonite and 30.0 g. (0.5 mole) of acetic acid was refluxed on an oil bath for 11 hr. After removal of the acetic acid, the fractionation of the residue gave 2.3 g. (51%) of trimethylene diacetate, b.p. 36–38° at 0.07 mm. (*Anal.* Calcd. for $\text{C}_7\text{H}_{12}\text{O}_4$: C, 52.50; H, 7.50. Found: C, 52.39; H, 7.63, lit.¹² b.p. 209–210°, and 2.0 g. (28%) of γ -acetoxypropyl phenylphosphinate, b.p. 160–162° at 0.01 mm. This infrared spectrum closely resembled that of β -acetoxyethyl phenylphosphinate.

Polymerization of Ethylene Phenylphosphonite.—One gram of ethylene phenylphosphonite was polymerized by heating with a catalytic amount of boron trifluoride etherate in a sealed glass tube under nitrogen for 5 hr. at 150°. The resultant poly(ethylene phenylphosphinate) had an inherent viscosity in chloroform of 0.13, which was measured after it was kept standing *in vacuo* for 30 min.

Anal. Calcd. for $(\text{C}_8\text{H}_9\text{O}_2\text{P})_n$: C, 57.14; H, 5.36; P, 18.5. Found: C, 54.47; H, 5.74; P, 18.9.

Similarly, the phosphonite was polymerized by heating at 120–200° in the presence of the following catalysts or in the absence of catalyst until its fluidity was hardly observed ($\eta_{\text{inh}}^{30^\circ}$ CHCl_3): aluminum chloride (0.04), sulfuric acid, 96% (0.03), phosphoric acid (0.07), hydrochloric acid, 37% (0.05), acetic acid (0.05), methyl iodide (0.06), dimethyl sulfate (0.04), bromocycanoacet-

amide (0.06), no catalyst (0.09). The polyphosphinate polymerized in the presence of phosphoric acid or in the absence of catalyst softened, respectively, at 83 or 70°, bubbling occurred at 142 or 135°, and it finally colored to dark brown at 258 or 264° with decomposition. The infrared absorption bands are at 2950 (m), 1495 (ms), 1440 (ms), 1270 (s), 1215 (ms), 1125 (ms), 1030 (ms), and 750 (ms) cm^{-1} .

Hydrolysis of Poly(ethylene phenylphosphinate).—A mixture of 5.0 g. of poly(ethylene phenylphosphinate), 10 ml. of 0.1 *N* aqueous solution of sodium hydroxide and 60 ml. of dioxane was refluxed on an oil bath for 4 hr. and kept standing overnight at room temperature. During this period, the sodium salt of β -hydroxyethylphenylphosphinic acid was precipitated, and was recrystallized from ethanol; yield 3.1 g. (55%), m.p. above 360°. Its infrared absorption bands are at 3330 (s), 1440 (ms), 1275 (m), 1255 (m), 1170 (s), 1130 (s), 1060 (s), 1030 (ms), and 730 (s) cm^{-1} .

Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{NaO}_3\text{P}$: C, 46.16; H, 4.84; P, 14.9. Found: C, 46.09; H, 4.53; P, 14.6.

Polymerization of Trimethylene Phenylphosphonite.—By a similar method to that of ethylene phenylphosphonite, 1.0 g. of trimethylene phenylphosphonite was polymerized in the presence of the following catalysts by heating at 160–200° for 10–12 hr. and then a volatile material was removed from the resulting polymer at 150° at 0.1 mm. (% yield and $\eta_{\text{inh}}^{30^\circ}$ CHCl_3): boron trifluoride etherate (45, 0.06), aluminum chloride (60, 0.07), sulfuric acid (45, 0.06), methyl iodide (80, 0.11), dimethyl sulfate (40, 0.06), no catalyst (95, 0.14). Poly(trimethylene phenylphosphinate) polymerized in the absence of catalyst, softened at 60°, and decomposed at 280°. Its infrared absorption bands closely resembled that of poly(ethylene phenylphosphinate).

Anal. of the polymer obtained in the presence of methyl iodide. Calcd. for $(\text{C}_8\text{H}_{11}\text{O}_2\text{P})_n$: C, 59.37; H, 6.09; P, 17.0. Found: C, 57.79; H, 6.24; P, 16.3.

Decomposition of Poly(trimethylene phenylphosphinate) with Phosphorus Pentachloride.—A mixture of 3.0 g. of poly(trimethylene phenylphosphinate) and 3.5 g. of phosphorus pentachloride in a sealed tube was heated on an oil bath at 100° for 3 hr. The mixture was fractionated giving γ -chloropropylphenylphosphinyl chloride, which was redistilled; yield 1.0 g. (39%), b.p. 125–127° (0.05 mm.). Its infrared absorption bands are at 2950 (m), 1595 (m), 1442 (s), 1270 (ms), 1255 (ms), 1230 (s), 1115 (s), 940 (ms), 750 (s), and 695 (s) cm^{-1} .

Anal. Calcd. for $\text{C}_8\text{H}_{11}\text{Cl}_2\text{OP}$: C, 45.59; H, 4.68; P, 13.1. Found: C, 45.60; H, 4.65; P, 13.3.

Polymerization of Ethylene *n*-Propylphosphonite.—The polymerization of ethylene *n*-propylphosphonite was carried out by heating at 140–180° for several hours by means of an analogous procedure to that of ethylene phenylphosphonite mentioned above. Poly(ethylene *n*-propylphosphinate) initiated by the following catalysts was obtained in the viscous jelly state after removal of a volatile material from the resulting polymer at 150° at 0.05 mm. (% yield and $\eta_{\text{inh}}^{30^\circ}$ DMF): boron trifluoride etherate (95, 0.05), aluminum chloride (100, 0.03), titanium tetrachloride (100, 0.04), ferric chloride (100, 0.07), phosphoric acid (90, 0.06), methyl iodide (85, 0.05), methyl iodide–magnesium metal (88, 0.04), no catalyst (90, 0.06). Its infrared absorption bands are at 2950 (s), 1465 (m), 1260 (s), 1210 (m), 1120 (m), 1050–960 broad (s), and 750 (s) cm^{-1} .

Anal. of the polymer obtained in the presence of boron trifluoride etherate. Calcd. for $(\text{C}_8\text{H}_{11}\text{O}_2\text{P})_n$: C, 44.77; H, 8.20; P, 23.1. Found: C, 42.88; H, 7.86; P, 22.5.

(12) N. A. Lange, "Handbook of Chemistry" McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 711.