

atoms in the F-C-S-O-C-F bond and space system. The decomposition of the peroxide,  $(CF_3SO_3)_2$ , was followed by n.m.r. spectrometry. When an impure sample of the peroxide which had been kept cold was scanned at low temperature in the C-F region, two large peaks were observed. The larger one at +77.19 p.p.m. could be ascribed to  $CF_3SO_3H$  while the smaller one at +72.36 p.p.m. could be ascribed to  $(CF_3SO_3)_2$ . Two small peaks were also observed for  $(CF_3)_2SO_3$  at +54.66 and +75.30 p.p.m. as well as a trace peak for the anhydride of trifluoromethanesulfonic acid at +74.05 p.p.m. When the sample was taken out of the spectrometer and allowed to warm to room temperature, a reaction occurred in the tube with the evolution of heat. When the sample was again scanned in the C-F region, the spectrogram revealed that the peroxide peak had disappeared, the ester peaks had grown, and a new peak at +89.06 p.p.m. (attributable to perfluoroethane) had appeared. A rerun of the same sample when cold did not produce the original spectrum, but the ester and perfluoroethane peaks were enlarged still further due to the gas phase being more highly dissolved in the liquid phase at lower temperatures.

**Mass Spectrum.**—A Consolidated Engineering Corp. Type 21-103 mass spectrometer was used to record the mass spectrogram for  $(CF_3)_2SO_3$ , which showed peaks corresponding to the following ions in order of decreasing intensity:  $CF_3^+$ ,  $SO^+$ ,  $SO_2^+$ ,  $CF^+$ ,  $CF_2^+$ ,  $COF^+$ ,  $S^+$ ,  $CF_3SO^+$ ,  $COF_2^+$ , and  $CF_3SO_2^+$ . In addition, small peaks which could have been due to  $CF_3O^+$ ,  $SO_3^+$ , and  $CF_3SO_3^+$  were observed at about the same low intensity level as some impurity peaks in the mass spectrometer background. No peak corresponding to the molecule ion was noted.

**Infrared Spectrum.**—A Perkin-Elmer Model 21 infrared spectrometer with a sodium chloride prism was used to obtain the spectrum of  $(CF_3)_2SO_3$  in the gas phase at 5 mm. pressure in a

10-cm. cell. Strong absorptions were found at 1461, 1258, 1230, 1134, and 954  $cm^{-1}$ . Two medium absorptions were noted at 786 and 766  $cm^{-1}$ . At 10 mm. pressure a weak band appeared at 888  $cm^{-1}$ . Some of these bands are close to those reported by Gramstad and Haszeldine for the S=O asymmetric vibration (1435  $cm^{-1}$ ) and the S=O symmetric vibration (either 1227 or 1156  $cm^{-1}$ ) in  $CF_3SO_3CH_3$ .<sup>4</sup>

**Chemical Reactions.**—An impure sample of  $(CF_3SO_3)_2$  immediately liberated iodine from cold KI solution.

A sample of  $(CF_3)_2SO_3$  was allowed to remain in contact with water at room temperature for 16 hr. The compound was immiscible and did not appear to react; sample wt. 0.7496 g., recovered 0.7291 g. Infrared analysis showed the recovered material to be the unchanged ester.

A sample of  $(CF_2)_2SO_3$  was held in contact with 0.1 *N* sodium hydroxide at 100° for about 12 hr. (with occasional shaking). Then 5 ml. of a 5%  $BaCl_2$  solution was added to precipitate barium carbonate. The excess base was titrated to the phenolphthalein end point and the milliequivalents of base used per milliequivalent of  $(CF_3)_2SO_3$  calculated; calcd. mequiv. of base used per mmole of  $(CF_3)_2SO_3$ , 6.0; found, 5.7. Apparently the basic hydrolysis proceeded:  $6OH^- + (CF_3)_2SO_3 = CF_3SO_3^- + 3F^- + CO_3^{2-} + 3H_2O$ , but did not go to completion under these conditions.

**Acknowledgment.**—This work was performed in part with the support of a fellowship from the Allied Chemical Co. The authors thank the Minnesota Mining and Manufacturing Co. for furnishing the barium salt of trifluoromethanesulfonic acid. They also thank Mr. B. J. Nist for the n.m.r. spectra.

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CORONA, CALIFORNIA

## Synthesis of a Cyclic Hexaphenyldichlorophosphonitrile Tetramer and Its Reactions with Diols

By D. L. HERRING AND C. M. DOUGLAS

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The reaction of sodium azide with a mixture of diphenylchlorophosphine and phenyldichlorophosphine yields hexaphenyldichlorophosphonitrile tetramer. This tetramer undergoes condensation with diols to form ring-linked polymeric products. The corresponding cyclic diphenoxy-, diethoxy-, and dihydroxyhexaphenylphosphonitrile tetramers are reported.

### Introduction

The reaction of sodium azide with trivalent phosphorus halides has previously been employed in the synthesis of cyclic phosphonitriles. Diphenylphosphonitrile tetramer,  $[(C_6H_5)_2PN]_4$ , can be prepared by treatment of diphenylchlorophosphine with sodium azide at 220° followed by pyrolysis of the reaction products at 270°.<sup>1</sup> Phenyl chlorophosphonitrile tetramers,  $[C_6H_5(Cl)PN]_4$ , are formed from phenyldichlorophosphine and sodium azide at 165–170°.<sup>2</sup> While the bulk of the reaction mixture is composed of higher molecular weight species, two tetrameric compounds can be isolated. These isomers, m.p. 202 and 248°,

have also been prepared by Shaw and Stratton *via* the reaction of phenyltetrachlorophosphorane and ammonium chloride.<sup>3</sup>

During our previous investigation of the reaction of iminobis(aminodiphenylphosphorane) chloride,  $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$  (I), with phenyltetrachlorophosphorane, two hexaphenyldichlorophosphonitrile tetramers were prepared (m.p. 154–155 and 192–193°).<sup>4</sup> Based on the composition and most probable structure of I,<sup>5</sup> these compounds were believed to be *cis-trans* isomers of the following structure.

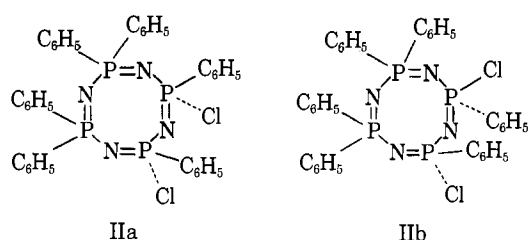
(1) D. L. Herring, *Chem. Ind.* (London), 717 (1960).

(2) D. L. Herring, unpublished results.

(3) R. A. Shaw and C. Stratton, *J. Chem. Soc.*, 5004 (1962).

(4) D. L. Herring and C. M. Douglas, *Inorg. Chem.*, **3**, 428 (1964).

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In the present work, the azide method has been extended to the synthesis of difunctional phosphonitriles by employing a mixture of halophosphines, and a third nongeminal hexaphenyldichlorophosphonitrile tetramer (III), m.p. 294°, has been prepared.

The reaction of cyclic phosphonitriles with dihydroxy aromatic compounds has been reported by several investigators. The *o*-phenylenedioxyphosphonitrile trimer and tetramer have been prepared by the interaction of the cyclic chlorides with catechol. Cross-linked polymers containing readily hydrolyzable chlorine are also formed during this synthesis.<sup>6</sup> Pyrolysis of the cyclic products yielded insoluble polymers.<sup>7</sup> Other aromatic diols, e.g., resorcinol, hydroquinone, and 4,4'-isopropylidenediphenol, have also been employed as coupling agents.<sup>8-10</sup> The preparation of polymers by the condensation of the cyclic trimer and tetramer with polyhydroxy compounds has been described in the patent literature.<sup>11-13</sup>

In this paper the coupling of III with mono- and difunctional alcohols is described. Polymers have been prepared from the reaction of III with aromatic diols and by the condensation of III with the corresponding diethoxy- and dihydroxyhexaphenylphosphonitrile tetramers.

### Experimental

The phenyldichlorophosphine and diphenylchlorophosphine used in these experiments were obtained from Victor Chemical Works. Sodium azide (Fisher Purified grade) was dried *in vacuo* at 110–120° for 24 hr. Dichlorobenzene, chlorobenzene, and heptane were dried by distillation from lithium aluminum hydride.

Resorcinol, hydroquinone, *p,p'*-biphenol, and phloroglucinol were purified by vacuum sublimation. 2,2,3,3-Tetrafluorobutanediol, supplied by Peninsular ChemResearch, was recrystallized from benzene. Except where noted, all molecular weight measurements were determined osmotically in benzene using a Mechrolab Model 301A osmometer.

**Preparation of Hexaphenyldichlorophosphonitrile Tetramer (III).**—A mixture of phenyldichlorophosphine (179 g., 1.0 mole) and diphenylchlorophosphine (220 g., 1.0 mole) was heated to 200° in an inert atmosphere chamber. Anhydrous sodium azide (65 g., 1.0 mole) was added while the mixture was stirred vigorously with a mechanical stirrer. By adding 4-g. portions every

15 min., the addition of sodium azide required 4 hr. The nitrogen evolution and refluxing of the chlorophosphines occurred in an easily-controllable manner. The temperature of the reaction mixture was then raised to 300° and maintained at this temperature for 16 hr. An efficient air condenser of the glass coil type was employed during this phase of the reaction to prevent the loss of phosphines by evaporation.

The reaction product was filtered at 300° to remove sodium chloride and unreacted sodium azide and the filtrate was vacuum distilled at 275° to remove chlorophosphines. The residue was washed with boiling heptane and then dried to yield a brown glassy material. Elemental analysis indicated that the crude product had the composition  $(C_6H_5)_2PN \cdot C_6H_5Cl)PN$ .

*Anal.* Calcd. for  $C_{18}H_{16}P_2N_2Cl$ : C, 60.7; H, 4.2; P, 17.4; N, 7.8; Cl, 9.9. Found: C, 60.5; H, 4.5; P, 17.6; N, 8.0; Cl, 9.8.

By treating this material with refluxing chlorobenzene, a tan crystalline product was isolated (28.2 g., 15% yield based on total sodium azide). Recrystallization from toluene yielded a white crystalline compound (III), m.p. 294°.

*Anal.* Calcd. for  $C_{36}H_{30}P_4N_4Cl_2$ : C, 60.7; H, 4.2; P, 17.4; N, 7.8; Cl, 9.9; mol. wt., 713. Found: C, 60.8; H, 4.3; P, 17.4; N, 7.8; Cl, 10.1; mol. wt., 690 (ebullioscopically in benzene).

The infrared spectrum of III exhibited strong peaks attributable to phosphorus-phenyl at 1420  $cm^{-1}$  and to the P—N=P linkage associated with the tetrameric phosphonitriles at 1280  $cm^{-1}$ .

When the reaction was carried out at temperatures of from 165 to 200°, only trace amounts of III were isolated along with diphenylphosphonitrile tetramer. The main product (8–10%) was a compound (IV) which when recrystallized from pyridine gave diphenylphosphonitrile trimer. Heating IV above 50° *in vacuo* resulted in the same conversion with the liberation of hydrogen chloride.

The infrared spectrum of IV exhibits very strong bands at 1235 and 930  $cm^{-1}$  and a medium band at 600  $cm^{-1}$ , none of which is present in the spectra of the diphenylphosphonitrile trimer.

*Anal.* Calcd. for  $C_{36}H_{31}P_3N_3Cl$ : P, 14.7; N, 6.6. Found: P, 15.2; N, 6.6.

**Hydrolysis of Hexaphenyldichlorophosphonitrile Tetramer.**—A suspension of 20 ml. of aqueous pyridine (1% water) and 2.0 g. of III was refluxed for 30 min. The crystalline product was removed by filtration, washed with four 50-ml. portions of ether, and then dried *in vacuo* at 80°. This material, dihydroxyhexaphenylphosphonitrile tetramer (V), melted sharply at 272°. It was very slightly soluble in ethanol and insoluble in other organic solvents and water.

*Anal.* Calcd. for  $C_{36}H_{32}P_4N_4O_2$ : C, 63.7; H, 5.0; P, 18.3; N, 8.3; O, 4.7. Found: C, 63.6; H, 4.6; P, 18.2; N, 8.5; O, 5.1.

Treatment of III with aqueous dimethylformamide also gave V. Compound V was resistant to hydrolysis by hydrochloric acid in refluxing ethanol.

The infrared spectrum of V exhibited a band of medium intensity at 2620  $cm^{-1}$  which has been reported as characteristic of P—OH stretching.<sup>14</sup>

**Preparation of Hexaphenyldiphenoxyphosphonitrile Tetramer (VI).**—Sodium (3.0 g., 0.13 g.-atom) was added to a solution containing 100 ml. of ethanol and 12.2 g. of phenol (0.13 mole). This reaction was carried out in an inert atmosphere chamber. After the solution was boiled for 10 min., the ethanol was distilled *in vacuo*, and the resultant sodium phenoxide was allowed to react with 25.0 g. of III (0.035 mole) in dichlorobenzene (1200 ml.) for 25 hr. at 170–174°. The reaction mixture was filtered to remove sodium chloride and unreacted sodium phenoxide. Evaporation of the solvent yielded a brown solid which was recrystallized from acetonitrile to give 18.9 g. (65%) of hexaphenyl-

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(13) R. G. Rice, B. H. Geib, and L. A. Kaplan, U. S. Patent 3,121,704 (1964).

(14) D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, 4555 (1954).

diphenoxyphosphonitrile tetramer (VI) as white needles, m.p. 129–130°.

*Anal.* Calcd. for  $C_{48}H_{40}P_4N_4O_2$ : C, 69.6; H, 4.8; P, 15.0; N, 6.8; O, 3.9; mol. wt., 828. Found: C, 69.2; H, 4.9; P, 14.8; N, 7.0; O, 3.7; mol. wt., 808.

**Preparation of Hexaphenyldiethoxyphosphonitrile Tetramer (VII).**—Sodium (3.0 g., 0.13 g.-atom) was added to 100 ml. of ethanol. The solution was boiled for 10 min. and the excess ethanol was distilled *in vacuo*. The solid sodium ethoxide was allowed to react with III (25.0 g., 0.035 mole) in dichlorobenzene (500 ml.) at 170–175° for 24 hr. in an inert atmosphere chamber. Sodium chloride and unreacted sodium ethoxide were then removed by filtration. Evaporation of the solvent yielded a brown product which was dissolved in acetonitrile and treated with decolorizing charcoal to give 18.0 g. (70%) of white crystalline VII; m.p. 183–185°.

*Anal.* Calcd. for  $C_{40}H_{40}P_4N_4O_2$ : C, 65.6; H, 5.5; P, 16.9; N, 7.6; O, 4.4; mol. wt., 732. Found: C, 65.9; H, 5.6; P, 16.9; N, 7.9; O, 4.5; mol. wt., 721.

**Hydrolysis of VII.**—An aqueous ethanol solution of VII (0.47 g.) was acidified with concentrated hydrochloric acid. Both diphenylphosphinic acid (m.p. 194–195°) and phenylphosphonic acid (m.p. 158–159°) were recovered and their identities confirmed by infrared spectra. The residue from the hydrolysis was ammonium chloride (0.115 g., 85%).

**Condensation of III with Diols.** (1) **Resorcinol.**—A mixture of 12.5 g. (0.017 mole) of III and 2.0 g. (0.017 mole) of resorcinol was heated under vacuum. At 220° the reactants melted and gas evolution began. The reaction was continued at 310° for 12 hr. During the heating cycle, 91% of the calculated amount of hydrogen chloride (identified by infrared spectrum) was collected. The product was a light tan resin (m.p. 110–130°) and was soluble in common organic solvents.

*Anal.* Calcd. for  $C_{42}H_{34}P_4N_4O_2$ : C, 67.2; H, 4.5; P, 16.5; N, 7.5; O, 4.3; mol. wt. per unit, 747. Found: C, 67.3; H, 4.5; P, 16.3; N, 7.4; O, 4.3; Cl, 0; mol. wt., 12,400, determined at concentrations of 72.1, 55.9, and 30.1 g./l.

Similar reaction conditions were used in the coupling of III with other diols.

(2) **Hydroquinone.**—III (12.5 g., 0.017 mole) and hydroquinone (2.0 g., 0.017 mole) were allowed to react to give a tan glass (m.p. 120–130°).

*Anal.* Calcd. for  $C_{42}H_{34}P_4N_4O_2$ : C, 67.2; H, 4.5; P, 16.5; N, 7.5; O, 4.3; mol. wt. per unit, 747. Found: C, 65.2; H, 4.4; P, 14.4; N, 7.3; O, 4.9; Cl, 1.7; mol. wt., 5500, determined at a concentration of 34.7 g./l.

(3) **4,4'-Oxydiphenol.**—The reaction of equimolar quantities of III and 4,4'-oxydiphenol resulted in the evolution of 92% of the calculated hydrogen chloride. The product melted at ~120°.

*Anal.* Calcd. for  $C_{48}H_{38}P_4N_4O_3$ : C, 68.5; H, 4.5; P, 14.7; N, 6.7; O, 5.7; mol. wt. per unit, 839. Found: C, 68.5; H, 4.7; P, 14.5; N, 6.7; O, 5.6; Cl, 0; mol. wt., 8250, determined at a concentration of 41.2 g./l.

(4) **2,2,3,3-Tetrafluorobutanediol.**—The product of the condensation of III and 2,2,3,3-tetrafluorobutanediol was a brown glass which melted at 70–80°.

*Anal.* Calcd. for  $C_{40}H_{34}P_4N_4O_2F_4$ : C, 59.8; H, 4.2; P, 15.5; N, 7.0; O, 4.0; F, 9.5; mol. wt. per unit, 802. Found: C, 60.2; H, 4.2; P, 16.2; N, 7.2; F, 8.5; Cl, 1.5; mol. wt., 4450, determined at a concentration of 33.4 g./l.

(5) ***p,p'*-Biphenol.**—A mixture of III (6.25 g., 0.008 mole), *p,p'*-biphenol (1.58 g., 0.008 mole), and phloroglucinol (0.052 g., 0.0004 mole) was heated to 285° for 14 hr. Hydrogen chloride (93% of the calculated amount) was liberated. The product was a light brown resin which softened slightly at 320° but did not melt. The polymer could be molded into transparent disks at 200° under 30,000 p.s.i.-pressure for 30 min. Extensive swelling of the material occurred in benzene.

*Anal.* Calcd. for  $C_{48}H_{38}P_4N_4O_2$ : C, 69.7; H, 4.6; P, 15.0; N, 6.8; O, 3.9. Found: C, 69.5; H, 4.7; P, 15.0; N, 7.0; O, 3.5; Cl, 0.3.

**Reaction of Hexaphenyldichlorophosphonitrile Tetramer (III) with Hexaphenyldiethoxyphosphonitrile Tetramer (VII).**—A mixture of III (1.9 g., 0.0028 mole) and VII (2.0 g., 0.0028 mole) was gradually heated *in vacuo* to 280–290° for 10 hr. Initially the mixture melted into a clear liquid at 130–135°, then on further heating resolidified into an opaque white glass. A volatile product was collected and identified as ethyl chloride by infrared and mass spectral analyses; yield 98%. The product softened over the range 220–300°.

*Anal.* Calcd. for  $C_{36}H_{30}P_4N_4O$ : C, 65.6; H, 4.6; P, 18.8; N, 8.5; O, 2.4; mol. wt. per unit, 658. Found: C, 65.7; H, 4.9; P, 18.9; N, 8.4; O, 2.1; Cl, 0. This material was too insoluble in organic solvents to permit the determination of the molecular weight.

**Reaction of Hexaphenyldichlorophosphonitrile Tetramer (III) with Hexaphenyldihydroxyphosphonitrile Tetramer (V).**—Compound III (2.47 g., 0.00345 mole) and compound V (2.33 g., 0.00345 mole) were heated for 16 hr. at 310–320°. Only 65% of the calculated amount of hydrogen chloride was generated. The polymer was a brown resin (m.p. 100–120°).

*Anal.* Calcd. for  $C_{36}H_{30}P_4N_4O$ : C, 65.6; H, 4.6; P, 18.8; N, 8.5; O, 2.4; mol. wt. per unit, 658. Found: C, 64.1; H, 4.8; P, 18.2; N, 8.5; Cl, 1.3.

The products from the III–VII and the III–V condensations gave infrared spectra which were identical. Both contained a strong band at 935  $cm^{-1}$  which has been assigned to P–O–P.<sup>15</sup>

**Reaction of VII with Resorcinol.**—Compound VII (5.0 g., 0.0068 mole) and resorcinol (0.75 g., 0.0068 mole) were heated for 16 hr. at 280–290°. The volatile product of the reaction was identified by infrared and mass spectral analysis as a mixture of ammonia, ethylene, and ethylamine. The residue was a yellow glass which melted over the range 75–85°.

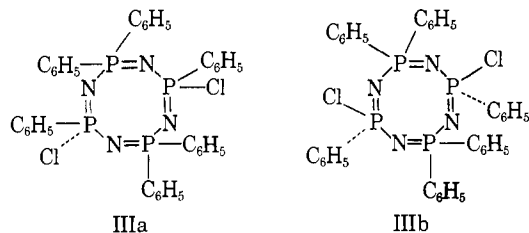
## Discussion

The data presented above describe a new one-step method for the preparation of hexaphenyldichlorophosphonitrile tetramer (III) in yields which are relatively large considering all the possible mixed and unmixed cyclic and linear configurations. From the experimental evidence, the prolonged heating at 300° is necessary for the formation of any appreciable quantity of the desired compound; however, no effort was made to characterize the complex mixture of products to be found in the residue after the isolation of III. It may be noted that at lower temperatures (165–200°) the cyclic diphenylphosphonitriles or their precursors are the major (10%) identified products and little or no III was obtained, a result which suggests further rearrangement at 300°.

The data which bear on the structure of compound III are: the elemental analysis and molecular weight measurements which are in excellent agreement with the formula  $(C_6H_5)_6Cl_2P_4N_4$ ; the infrared absorption at 1280  $cm^{-1}$  which has been assigned to eight-membered phosphonitrilic ring systems; the hydrolysis of the diethoxy derivative of III which gave equal quantities of  $(C_6H_5)_2POOH$  and  $C_6H_5P(O)(OH)_2$ , indicating that the chlorine substitution of III is nongeminal; and the melting point of 294° which distinguishes III from the two previously reported hexaphenyldichlorophosphonitrile tetramers. Although no absolute configuration was determined for these two isomers, their method of preparation leads to the assumption that the phosphorus atoms bearing the chlorine ligand are adjacent.

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 318.

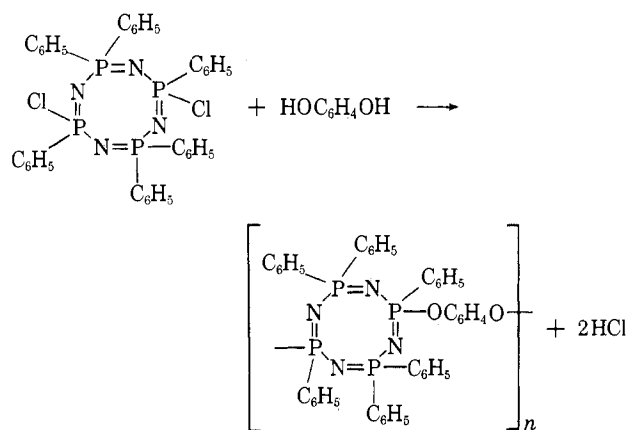
Since neither the well-characterized octaphenyl- nor octachlorophosphonitrile tetramers have been shown to exist in more than one stable ring configuration (boat or chair), the most logical assignment of configuration for compound III is one in which the phosphorus atoms bearing the chlorine ligands are not adjacent



More concrete evidence concerning the configuration of all three hexaphenyldichlorophosphonitrile tetramers will be provided by crystallographic studies which have recently been initiated.

Although III reacted readily with sodium phenylate and sodium ethylate to form VI and VII, respectively, the preparation of V occurred unexpectedly when pyridine and dimethylformamide were being tried as recrystallizing agents for III. Compound III, although resistant to hydrolysis in boiling water, was hydrolyzed readily in these solvents which had not been dried. Subsequently, it was observed that III was not affected by anhydrous pyridine in dichlorobenzene solution.

The preparation of compound III yielded a material which could be linked in a systematic linear manner with diols without cross linking to produce a polymer free of unreacted chlorine atoms on phosphorus which are potential sites of hydrolytic degradation. In an attempt to prepare thermally and chemically stable polymers, III was allowed to react with the several diols described in the experiments above. Initially the reaction was run in solvent with a hydrogen halide acceptor at temperatures up to 180° for 60 hr. As much as 50% unreacted starting materials was recovered. Use of the sodium salts of the diols did not

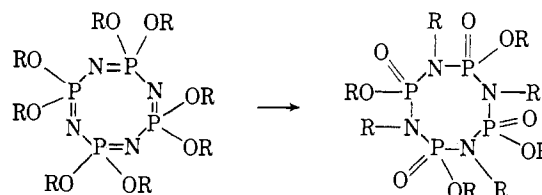


improve the results. The more successful melt reactions yielded polymers of similar characteristics. These materials melted between 100 and 140°; they were hard glassy amber solids at 25°; the molecular

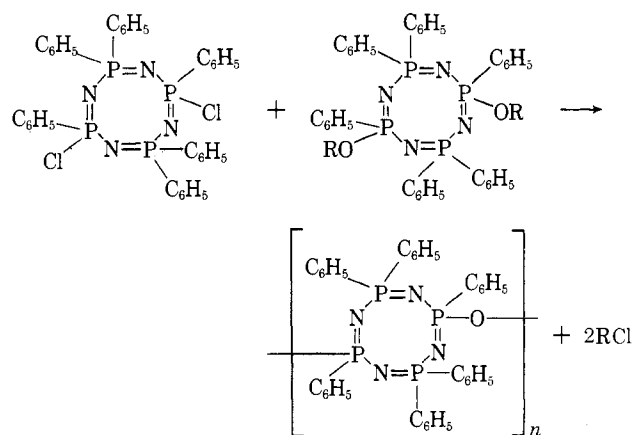
weights showed the number of monomer units to be 5–15; and their differential thermograms in nitrogen showed no events up to 500°, except for softening points. The reactions between III and the diols may be illustrated by the preceding equation.

The addition of 5% phloroglucinol to the reaction of III with *p,p'*-biphenol resulted in a polymer whose softening point was increased from 120 to 320° as a result of cross linking of the polymer chains by the trihydroxy aromatic compound. No molecular weight measurements could be made because the resulting polymers were insoluble in all the solvents used in osmometric determinations.

In an attempted polymerization by transesterification between hexaphenyldiethoxyphosphonitrile tetramer (VII) and resorcinol, ethylene, ethylamine, and ammonia were recovered, but no ethanol was formed. Shaw<sup>16</sup> has reported that the cyclic phosphonitrile alkoxides can undergo a thermal disproportionation to the corresponding cyclic phosphonamides



Although the infrared spectrum of VII showed no unusual features and the analytical data would not differentiate between the expected diethoxide and the rearranged product, a complete acid hydrolysis of VII was carried out to establish the identity unambiguously. Only ammonium chloride was found and no ethylamine hydrochloride was present. Presumably, under the vigorous conditions of the attempted polymerization, a disproportionation similar to that described above occurred; however, the preparation of polymers by transesterification of hexabutoxyphosphonitrile trimer with resorcinol and hydroquinone has been reported.<sup>17</sup>



The condensation of V and VII with the dichloro tetramer III liberates ethyl chloride and hydrogen

(16) B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.*, 1735 (1964).

(17) S. M. Zhivukhin, V. B. Tolstoguzov, V. V. Kireev, N. V. Aulova, L. T. Gerasimenko, and F. I. Yakobson, *Plasticheskie Massy*, 19 (1964); *Chem. Abstr.*, 62, 659 (1965).

chloride, respectively, to yield polymers whose infrared spectra show a strong P—O—P absorption. The polymerization is described by the preceding equation where  $R = H$  or  $C_2H_5$ . Although the infrared spectra of the two polymers were very similar, the softening point of the III-VII polymer was 220–300°, while the softening point of the III-V polymer was only 100–120°. The polymer structures should be the same, but end-group analysis (terminal chloride) of the two materials indicates that the III-VII polymer has the higher molecular weight.

From this work, we have described a one-step synthesis of a difunctional phosphonitrilic tetramer which will react with several diols to form thermally stable low polymers. It has also been shown that small

amounts of phloroglucinol, acting as a cross-linking agent, will raise the softening point of the resulting polymer approximately 200°, and that the cross-linked material may be molded conveniently. Hexaphenyldichlorophosphonitrilic tetramer will also copolymerize with the dialkoxy and dihydroxy derivatives.

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CONTRIBUTION FROM SHIONOGI RESEARCH LABORATORY,  
SHIONOGI & Co., LTD., FUKUSHIMA-KU, OSAKA, JAPAN

## Reduction of B-Triethynylborazine Derivatives

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The catalytic hydrogenation of B-triethynylborazine derivatives was employed for the preparation of B-tris(*cis*-methyl vinyl)- and B-tris(*cis*-phenylvinyl)borazine derivatives which were not attainable by the usual Grignard reaction. The configurations and conformations at the vinyl groups were determined on the basis of the n.m.r., infrared, and ultraviolet spectra.

It was found<sup>1</sup> that a Grignard reagent prepared from *cis*- or *trans*- $\beta$ -bromostyrene gives a mixture of *cis*- and *trans*-styryl compound by an appropriate subsequent reaction. This fact suggests difficulties in the preparation of pure B-tris-*cis*- and B-tris-*trans*-styrylborazines by the usual Grignard reaction. Furthermore, in a preliminary experiment, B-tris(phenylethynyl)-N-triphenylborazine was the main product of the reaction between B-trichloro-N-triphenylborazine and the Grignard reagent prepared from *cis*- $\beta$ -bromostyrene in tetrahydrofuran. In a previous paper,<sup>2</sup> the preparation and properties of B-tris(phenylethynyl)borazine derivatives were described and a new route was suggested for the preparation of B-trivinylborazine derivatives by hydrogenating the B-triethynylborazines. The present work deals with the catalytic reduction of ethynyl groups on borazines and the conformation determination of B-trivinylborazines obtained therefrom.

An attempt to reduce B-tris(phenylethynyl)-N-triphenylborazine with sodium in liquid ammonia was unsuccessful due to the instability of the borazine ring. In contrast, B-tris(phenylethynyl)borazines and B-tris(alkylethynyl)borazines underwent the usual cata-

lytic hydrogenation in tetrahydrofuran to give the corresponding vinyl derivatives. The compounds listed in Table I were prepared by the catalytic reduction of ethynylborazines except B-tris(*trans*-phenylvinyl)-N-triphenylborazine, which was prepared for comparison by the Grignard reaction between B-trichloro-N-triphenylborazine and *trans*-styrylmagnesium bromide. Here, the procedure of Yoshino and Manabe<sup>1</sup> was followed to retain *trans* configuration at the double bond of the styryl group in good yield. The product was referred to and shown to be different from that obtained by the catalytic reduction. For these reduction products, four different structures are conceivable with respect to the configuration and the relative orientation of the three vinyl groups, as illustrated in Figure 1, when three vinyl groups in the molecule are solely of *cis* or *trans* configuration and the rotation around the B—C= bond is restricted.

Various chemical and physicochemical data showed that the hydrogenation products are the monomeric B-trivinylborazine derivatives and the three vinyl groups on boron atoms are of *cis* configuration and of symmetric conformation. In contrast, the Grignard reaction product was proved to be the *trans* isomer in which the rotation around the B—C= bond would be sterically allowed. Both of the *cis* and *trans*

(1) T. Yoshino and Y. Manabe, *J. Am. Chem. Soc.*, **85**, 2860 (1963).

(2) H. Watanabe, T. Totani, and T. Yoshikazi, *Inorg. Chem.*, **4**, 657 (1965).