63-3-2

UNITED STATES RUBBER COMPANY
Research Center
Wayne, New Jersey

April 8, 1963

PHOSPHONITRILIC POLYMERS STABLE AT HIGH TEMPERATURES

CONTRACT NO. NObs 88232
PROJECT SERIAL NO. SR007-03-03 TASK 1000
SUBPROJECT 113-1000-3

TECHNICAL REPORT NO. 1
COVERING THE PERIOD
NOVEMBER 19, 1962 - FEBRUARY 28, 1963

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ABSTRACT

The object of this investigation is the development of thermoplastic and thermosetting high-temperature-stable resins for electrical applications from phosphonitrilic chloride trimer is reported.

This report covers the synthesis of monomeric phosphonitrilic derivatives in which the functionality of the phosphonitrilic ring has been reduced to ~~two~~ 2, ~~three~~ 3, or ~~four~~ 4 are covered. This ~~has been~~ was done by replacing some of the chlorines with stable phenyl or phenoxy groups. ~~In addition~~, in some derivatives, chlorines ~~have also been~~ were replaced with reactive ethoxy or dimethylamino groups.

SUMMARY

The Problem. To reduce the functionality of phosphonitrilic chloride trimer to two, and to prepare from the monomer thus obtained, linear, thermoplastic polymers, stable at high temperatures, for electrical applications. An additional phase of the problem is to crosslink the polymers obtained in a controlled manner, by use of trifunctional monomer prepared from phosphonitrilic chloride. In each case, polymers are to be formed by joining the phosphonitrilic rings through suitable heat-stable bridging groups.

Findings.. It has been possible to reduce the functionality of the phosphonitrilic ring from six to the desired level by several synthetic routes. The following monomers have been prepared:

A. $P_3N_3(OC_6H_5)_4(OC_2H_5)_2$
B. $P_3N_3(OC_6H_5)_3(OC_2H_5)_3$
C. $P_3N_3(OC_6H_5)_4[N(CH_3)_2]_2$
D. $P_3N_3(C_6H_5)_2(OC_6H_5)_2Cl_2$
E. $P_3N_3(C_6H_5)_4[N(CH_3)_2]_2$

In these, C_6H_5 and OC_6H_5 are thermally and hydrolytically stable blocking groups which reduce the functionality. The groups Cl, OC_2H_5, and $N(CH_3)_2$ are reactive, and it is through replacement of these with difunctional bridging groups that polymerization will be attempted.

Compounds A and B have been prepared in sufficient amount to begin polymerization studies.

Compounds C, D, and E have been prepared only on a small scale. Additional characterization of these is underway.

ADMINISTRATIVE INFORMATION

Phosphonitrilic Polymers Stable
at High Temperatures

April 8, 1963

Prepared under Navy, Bureau of Ships
Contract No. NObs 88232
Project Serial No. SR007-03-03 Task 1000
Subproject 113-1000-3

Technical Report No. 1
Covering the Period
November 19, 1963 - February 28, 1963

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INTRODUCTION

The objective of this project is the development of better polymers for electrical applications in a high temperature environment. The ordinary organic polymers in general are lacking in thermal stability and in flame resistance. Silicones are widely used, but are unsatisfactory in electric motors which operate at high temperatures. Excessive wear of the brushes is observed, apparently caused by abrasive decomposition products of silicones.

Polymers derived from phosphonitrilic chloride trimer appeared promising for these applications. A search of the literature and some preliminary experimental work showed that the thermal stability was adequate, the electrical properties were good, and the polymers possessed a high degree of flame resistance. However, due to the high chemical functionality (six) of the phosphonitrilic trimer ring, polymers reported in the literature became crosslinked and intractable at low degrees of polymerization. The approach to the problem under this Contract, NObs 88232, involves reduction of the functionality of the phosphonitrilic ring to two in order to obtain linear polymers. Controlled crosslinking is to be obtained through the use of trifunctional phosphonitrilic compounds in the proper ratio.

This report covers the initial synthetic work leading to monomers of reduced functionality. Four difunctional, two trifunctional, and four tetrafunctional phosphonitrilic compounds are described. One difunctional monomer has been prepared on a half-pound scale, and is ready for the start of polymerization studies.

RESULTS

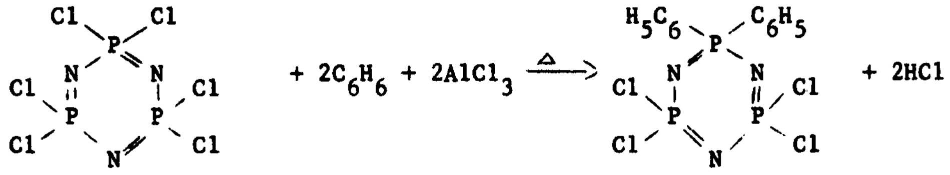
The synthetic routes to phosphonitrilic trimers of lowered functionality are here classified into four groups depending upon the nature of the initial replacement reaction. These are as follows:

1. Substitution by phenyl groups.
2. Substitution by dimethylamino groups.
3. Substitution by phenoxy groups.
4. Substitution by alkoxy groups.

Substitution by Phenyl Groups

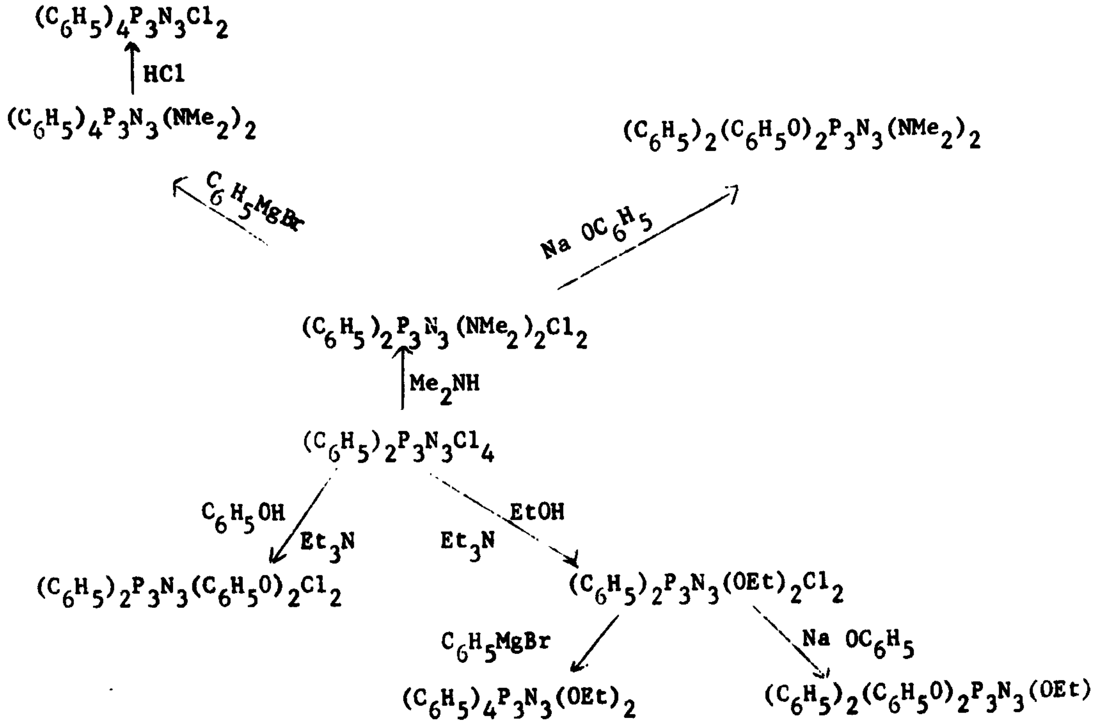
Initial replacement of part of the chlorine on phosphonitrilic chloride trimer by phenyl groups through the Friedel-Craft reaction is a convenient starting point for the synthesis of a series of monomers of reduced functionality. Two difunctional monomers have so far been synthesized by this route.

The Friedel-Craft Phenylation of Phosphonitrilic Trimer



The Friedel-Craft phenylation of the phosphonitrilic chloride trimer was studied by Bode(1) who observed that the reaction required at least 2 moles of aluminum chloride per mole of trimer and that the product with two phenyls on the same phosphorus atom was obtained exclusively. These results were later confirmed by Shaw(2) who studied the reaction conditions extensively and could not obtain the 40% yield reported by Bode.

The preparation of this compound was undertaken to provide a source of tetrafunctional phosphonitrilic trimer as a starting material for further reduction of functionality as illustrated below.



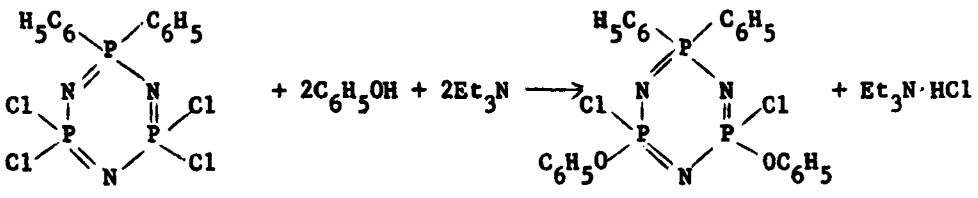
Both phenyl and phenoxy groups when attached to the phosphorous atom of the phosphonitrilic ring have been observed to possess high thermal and hydrolytic stability and have been found to be resistant to many chemical reagents.(3)

Four runs were made of this reaction. It had been previously observed that the use of high purity benzene resulted in a higher yield and a much more easily purified product. The reaction yield was consistently 68-69% upon separation of the unreacted trimer from the reaction mixture and 81%-84% conversion when the recovery of the trimer was considered. The unreacted trimer was always present in the crude product. The amount of unreacted trimer could be reduced by using a higher ratio of $AlCl_3$ to $P_3N_3Cl_6$; however, the product became more difficult to purify at the higher ratio of $AlCl_3$.

The unreacted trimer could not be separated by recrystallization from petroleum ether, heptane or acetone but could be sublimed out of the reaction mixture at 80-95°C (1-3 mm. pressure). The residue from the sublimation melted from 70-85°C and contained some oily material. The presence of unreacted $P_3N_3Cl_6$ would raise this range up to 111°C. Recrystallization of the diphenyl derivative from petroleum ether (81% yield) improved the melting point. High purity material could be obtained which melted between 93.8°C-94.8°C. (Bode et al(1) give 92.5°C). There were no difficulties or changes in yield or purity when reaction was scaled up to a one pound batch.

The oily impurity in the product is believed to be some linear $(PNCl_2)_n$ polymer which can be obtained with Lewis acid catalysts such as $AlCl_3$.(3)

The Reaction of $P_3N_3(C_6H_5)_2Cl_4$ with Phenol and Triethylamine



I

II

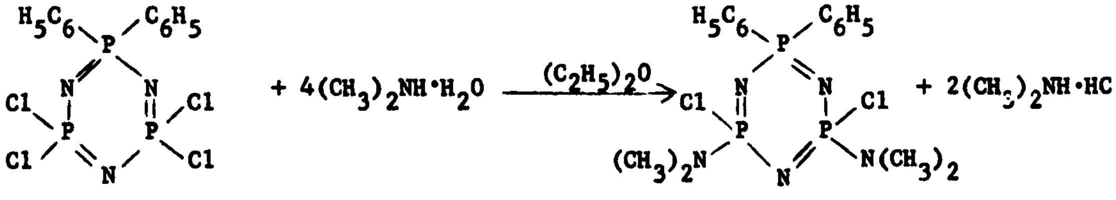
The reaction of $P_3N_3Cl_6$ in acetone with phenol and triethylamine yields $P_3N_3Cl_3(OC_6H_5)_3$ and indicates that the non-geminal mode of substitution occurs in this reaction. The reaction of phenol with the diphenyl derivative $(C_6H_5)_2P_3N_3Cl_4$ should be a convenient method of obtaining the difunctional, dichloro derivative $(C_6H_5)_2P_3N_3(OC_6H_5)_2Cl_2$ (II) which could then be reacted with difunctional bases to form linear polymers or with monofunctional groups which can be easily polymerized, i.e.

$$(C_6H_5)_2(C_6H_5O)_2P_3N_3Cl_2 + Na^+OC_2H_5 \longrightarrow (C_6H_5)_2(C_6H_5O)_2P_3N_3(OC_2H_5)_2$$

$$(C_6H_5)_2(C_6H_5O)_2P_3N_3(OC_2H_5)_2 \longrightarrow \{(C_6H_5)_2(C_6H_5O)_2P_3N_3\text{-}O\}_n$$

The reaction of $(C_6H_5)_2P_3N_3Cl_4$ (I) with phenol in the presence of triethylamine in acetone goes to the replacement of two chlorines after seven days at reflux. Further replacement is indicated but at a much slower rate. The reaction is much slower in ethers and alcohols. Diglyme and dimethyl formamide are exceptions and more than two chlorines are replaced in these solvents. The reaction product can be separated from unreacted $(C_6H_5)_2P_3N_3Cl_4$ and phenol by column chromatography on silica gel. The presence of a monosubstituted phenoxy derivative $(C_6H_5)_2P_3N_3(OC_6H_5)Cl_3$ (III) in the reaction product has not been established. Fractions eluted from the silica gel did not show any clear differences in their infrared spectra when the reaction products at 25% conversion are compared to the 98% conversion product except that the unreacted starting material (I) in the former has a weak absorption at 1600 cm^{-1} while the phenoxy containing derivative shows a strong band in this region. Preliminary analysis for phosphorus on the opaque, semi-solid oil from the latter product is consistent with the formulation $(C_6H_5)_6P_3N_3(OC_6H_5)_2Cl_2$ (II). Purification and complete analyses are in progress.

The Reaction of $P_3N_3(C_6H_5)_2Cl_4$ with Dimethylamine



I

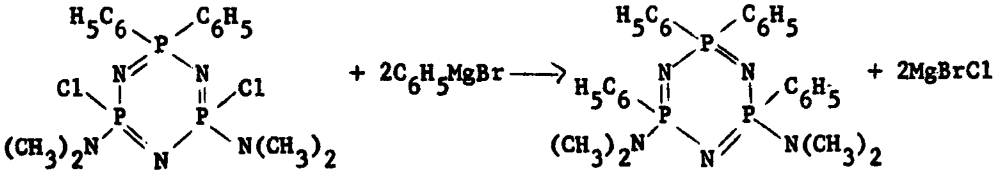
IV

By analogy to the reaction of $P_3N_3Cl_6$ with dimethylamine, compound IV is the expected product of this reaction. The compound $(C_6H_5)_2P_3N_3(NH_2)_2Cl_2$ (V) has been prepared by a similar method.(4) The compound (IV) represents another intermediate to a difunction derivative. Replacement of the remaining chlorines on IV by phenyl or phenoxy groups will give the desired difunctional derivatives; $(C_6H_5)_4P_3N_3[N(CH_3)_2]_2$ or $(C_6H_5)_2(C_6H_5O)_2P_3N_3[N(CH_3)_2]_2$.

The non-geminal formulation of compound IV is based on the evidence provided by nuclear magnetic resonance studies and substitution reactions of $P_3N_3Cl_3[N(CH_3)_2]_3$ and compound V.(4)

The isolation of the reaction product yielded 95% of the theoretical yield of compound IV. Recrystallization from heptane yielded 27% of the theoretical yield as a white, sharp melting solid. Recrystallization from acetone improved the melting point to 142.0-142.5°C. The rest of the product is an oil and is probably a liquid isomer of the solid compound. Analytical data and infrared spectra on the solid confirm the composition represented for compound IV. Carbon and hydrogen analyses do not agree but these difficulties were traced to the instrument. Other analyses were in excellent agreement with the expected value based on formula IV. The infrared spectrum of the liquid isomer was similar to that of the solid. A larger scale reaction has been run and the product is being purified.

The Reaction of $P_3N_3(C_6H_5)_2[N(CH_3)_2]_2Cl_2$ with Phenyl Magnesium Bromide



IV

VI

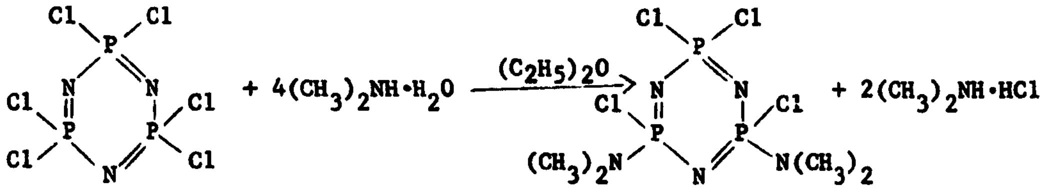
The reaction between $P_3N_3Cl_6$ and Grignard reagents does not yield products with definite compositions; however, Tesi(5) has observed that smooth reactions can be carried out between $P_3N_3Cl_3[N(CH_3)_6]_3$ and Grignard reagents at low temperatures to yield $P_3N_3R_3[N(CH_3)_2]_3$ where R = methyl or phenyl. Compounds of the type $P_3N_3R_3[N(CH_3)_2]_3$ were then converted with HCl to $P_3N_3R_3Cl_3$. The experimental details provided by Tesi were very sketchy. The formation of the difunctional monomers $P_3N_3(C_6H_5)_4[N(CH_3)_2]_2$ and $P_3N_3(C_6H_5)_4Cl_2$ (VII) are the goal of this study.

The reaction between C_6H_5MgBr and $(C_6H_5)_2P_3N_3[N(CH_3)_2]_2Cl_2$ (IV) did not appear to go in diethyl ether even at reflux. No solid was formed which would indicate reaction. Since there was no more of solid compound IV available, monoglyme was added and the ether was partially removed. A solid was formed on the addition of monoglyme but this also occurred when monoglyme and C_6H_5MgBr in ether were mixed in the absence of compound IV. A gummy solid was isolated after reaction and removal of solvent which could not be extracted with petroleum ether. The solid was hydrolyzed and extracted with ether. An oil resulted which had an infrared spectrum consistent with the structure of compound IV after removal of phenol in the oil. The spectrum showed that the PN ring was intact and that phenyl and dimethylamino groups were present. There was less than 1/2% chlorine in the crude oil. A larger scale reaction will be run in order to obtain enough product for complete identification.

Substitution by Dimethylamino Groups

Since the reaction of $P_3N_3Cl_6$ with dimethylamine to give the bis-dimethylamino derivative has already been described, this seemed to be a convenient starting point for the preparation of difunctional derivatives. Subsequent blocking of the remaining four positions would give a difunctional monomer directly, since the amino groups undergo such reactions as transamination. Replacement of the amino groups by chlorine is also possible.

The Reaction of $P_3N_3Cl_6$ with Dimethylamine



VIII

The preparation of the bis-dimethylamino derivative of $P_3N_3Cl_6$ has been previously described and the non-geminal replacement of chlorines has been established.(6) This compound was prepared as an intermediate in the preparation of a difunctional phosphonitrilic trimer. Replacement of the remaining chlorines by stable phenoxy ligands(3) should result in a difunctional monomer in a short, convenient route as illustrated by the equation:

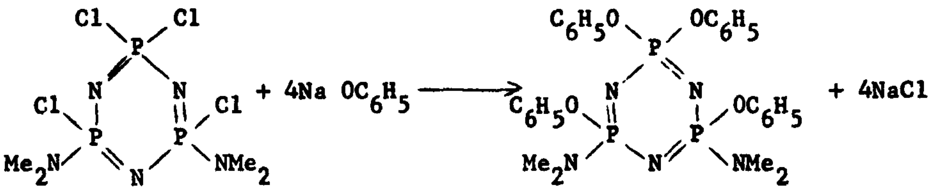
$$P_3N_3[(CH_3)_2N]_2Cl_4 + 4Na\ OC_6H_5 \longrightarrow P_3N_3(OC_6H_5)_4[N(CH_3)_2]_2 + 4NaCl.$$

This intermediate (VIII) was isolated in order to obtain a standard to verify analytical procedures.

The reaction was made on a mole scale. The initial yield of crude residue (91%) was apparently not completely free of volatile material. Only 191 g. of product (52%) were obtained as the solid material which corresponds to the compound described in the literature.(6) Another 100 g. of liquid (28%) was obtained which had a similar spectrum and is believed to be another isomer of the compound. This brings the total yield of both isomers to 80%.

Heptane was found to be a good solvent for recrystallization of the solid (VIII). The best melting point obtained was 104.2-104.5°C on a sample recrystallized several times from this solvent. Analytical results were excellent except for nitrogen which was, however, acceptable. This indicates that normal methods of microanalysis are satisfactory for this type of compound.

The Reaction of $P_3N_3[N(CH_3)_2]_2Cl_4$ with Sodium Phenoxide



VIII IX

The preparation of the hexaphenoxide of phosphonitrilic trimer, $P_3N_3(OC_6H_5)_6$ has been described and its thermal stability measured; both here and by other workers.(3) We have found the reaction between sodium phenoxide and $P_3N_3Cl_6$ to be complete in acetone or THF to give a high yield of this compound. The extension of this reaction to $P_3N_3Cl_4(NMe_2)_2$ should provide us with a monomer which could be polymerized to a linear polymer by transamination reactions, i.e.:

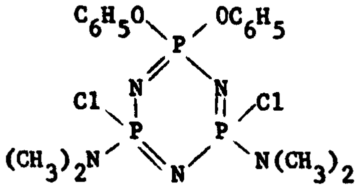
$$P_3N_3(OC_6H_5)_4(NMe_2)_2 + C_6H_5NH_2 \longrightarrow [P_3N_3(OC_6H_5)_4NC_6H_5]_n$$

or lead to other reactive monomers, i.e.:

$$P_3N_3(OC_6H_5)_4(NMe_2)_2 + HCl \longrightarrow P_3N_3(OC_6H_5)_4Cl_2$$

$P_3N_3(OC_6H_5)_4[N(CH_3)_2]_2$ (IX) appears to be the major product when sodium phenoxide and $P_3N_3Cl_4[N(CH_3)_2]_2$ are refluxed for 8 days in monoglyme. Isolation and identification of the compound has not been completed but chlorine analysis and the infrared spectrum are consistent with this conclusion. The reaction in acetone is incomplete in five days. Acetone is not as convenient a reaction medium, since a condensation product of the solvent is formed, apparently when sodium is reacted with phenol to form sodium phenoxide "in situ". The condensation product is difficult to separate from IX especially after long reaction times.

The condensation product of acetone was not observed in the reaction of potassium phenoxide with VIII in acetone when the potassium phenoxide was isolated and recrystallized before use. The reaction product in this case was isolated when the amount of KCl produced indicated that the reaction was about one-half complete. The product of this reaction was isolated by molecular distillation. This product was not, however, the single compound (X) as expected.



X

The analysis was low in chlorine and indicated a mixture; hence there was less selectivity for phenoxide ion than expected on the basis of the vast differences in rate of removal of Cl's. The reaction after 12 hours in refluxing acetone is almost 65% complete and only 85% after 5 days. The formation of the hexaphenoxide $[P_3N_3(OC_6H_5)_6]$ from $P_3N_3Cl_6$ and sodium phenoxide is much more rapid and is complete in 48 hours in refluxing acetone.

A qualitative study of solvents for the reaction showed that higher boiling solvents, therefore higher reflux temperatures, resulted in a more rapid reaction. Complete displacement of the chlorines occurred in dimethylformamide after 20 hours at reflux but this treatment apparently decomposed the trimer.

The reaction products were all viscous oils which could be distilled in a molecular still at high vacuum (10^{-5} to 10^{-6}) but decomposed at 1 to 2 mm. before distillation.

Substitution by Phenoxy Groups

Since direct replacement of four chlorines in $P_3N_3Cl_6$ by phenoxy groups would give a difunctional monomer in a single step, it was deemed desirable to study this reaction. Difunctional monomers have not been obtained in this way as yet, but it has been possible to prepare tri- and tetrafunctional compounds which will be useful both as intermediates and as crosslinking monomers.

The Reaction of $P_3N_3Cl_6$ with Phenol in the Presence of Triethylamine

In the phase of the research program prior to the contract period, thermal stability studies were conducted on a number of phosphonitrilic polymer prototypes. It was found that the aryl esters were thermally stable to 375°C and in addition were extremely stable in acidic, basic and aqueous media. Further, these derivatives could be made in high yields by a simple method. Based on this data, it was concluded that the aryloxy groups could be used effectively to synthesize phosphonitrilic monomers of reduced functionality.

The method of synthesizing aryloxy derivatives consisted in treating trimeric phosphonitrilic chloride with an alkali metal salt of the phenol in an appropriate solvent, usually acetone or xylene. At that time, however, it appeared that it would be extremely difficult to control this substitution reaction to give a single partially substituted product. It was thought that mixtures of several products of the type, $P_3N_3(OC_6H_5)_xCl_{6-x}$ would result from this approach. Therefore, it seemed a logical course to develop other methods of synthesis. It was found that the degree of substitution could be controlled by treating trimeric phosphonitrilic chloride with phenol and triethylamine in a particular solvent. Experiments showed that the degree of substitution was controlled by the nature of the solvent. In non-polar solvents such as xylene a disubstituted product, $P_3N_3(OC_6H_5)_2Cl_4$ resulted. However, in polar solvents, such as acetone, a trisubstituted product was obtained.

Efforts to prepare the tetrasubstituted $P_3N_3(OC_6H_5)_4Cl_2$ by this synthetic method have been unsuccessful.

Substitution by Alkoxy Groups

Since it was found possible to cleanly restrict the degree of substitution by phenoxy groups to two or three, it was decided to investigate substitution by alkoxy groups under similar conditions. It was indeed found possible to similarly restrict the degree of substitution by alkoxy to two in the presence of triethylamine in xylene. In acetone, however, the degree of substitution was also two, not three as in the case of phenoxy substitution. Subsequent blocking of the remaining positions by phenoxide in the usual manner then yielded a difunctional monomer in a straightforward manner.

Mixed Alkyl-Aryl Esters of Phosphonitrilic Trimer

In our previous studies, it was found that the alkyl esters were thermally unstable. These studies showed that $(C_6H_5)_2P_3N_3(OC_2H_5)_4$ decomposed on heating into a film. The infrared studies showed a P-O-P bond in addition to the characteristic cyclic PN, $P(C_6H_5)$ and $-C_6H_5$ absorptions. It was proposed at this time that the alkyl ester thermal instability could be used to synthesize polymeric materials from monomers of the type $P_3N_3(OC_6H_5)_x(OC_2H_5)_{6-x}$.

Therefore, a series of the alkyl-aryl derivatives were synthesized. These materials are, however, difficult to purify by techniques such as recrystallization or distillation. Therefore, chromatographic techniques had to be used.

One of the alkyl-aryl esters, $P_3N_3(OC_6H_5)_4(OC_2H_5)_2$, has been prepared in sufficient amount so that about one-half pound is now available for polymerization studies.

EXPERIMENTAL

The Preparation of $P_3N_3(C_6H_5)_2Cl_4$

Materials: $P_3N_3Cl_6$ was obtained in high purity from Millmaster Chemical Corporation and anhydrous aluminum chloride (99.1%, Baker Analyzed Reagent) was used without further purification. Benzene (Baker Analyzed Reagent) was passed through a column of activated charcoal and silica gel and stored over sodium-lead amalgam under argon.

Procedure: A typical experiment is described as follows:

$P_3N_3Cl_6$ (140 g., 0.4 mole) and $AlCl_3$ (113.4 g., 0.85 mole) are charged into a one liter, one necked flask containing 550 ml. of purified benzene. The reaction mixture is stirred by a magnetic stirrer and the flask is equipped with a reflux condenser and nitrogen atmosphere. The mixture is refluxed for 72 hours with a heating mantle and cooled. It is then poured onto 400 g. of crushed ice in 200 ml. of HCl solution (6N) with stirring. The complex breaks down slowly and 100-200 g. more of crushed ice are added if necessary. The benzene and water layers are separated. The benzene layer is washed twice with 50 ml. portions of distilled water; twice with 100 ml. portions of 10% $NaHCO_3$ and then again twice with 50 ml. distilled water portions. The benzene layer is then dried over molecular sieve 4A; treated with decolorizing charcoal; filtered and the benzene is then stripped from the solution leaving a waxy residue (141 grams). $P_3N_3Cl_6$ (46 g.) was sublimed from the residue at 90°C (1-3 mm presure) leaving 94 grams (67.5% yield, 83% conversion, 0.27 mole) of crude $(C_6H_5)_2P_3N_3Cl_4$. An 89 g. portion of the crude product was dissolved in about 350 ml. of petroleum ether (30°C-60°C) and cooled to -20°C. The $(C_6H_5)_2P_3N_3Cl_4$ obtained weighed 58 g. (64% yield), and melted at 89-92°C (Fisher-Johns Block). The volume of the mother liquor was reduced to about one-half and 14 more grams of $(C_6H_5)_2P_3N_3Cl_4$ separated out on cooling.

Summary of Data on Various Preparations of $(C_6H_5)_2P_3N_3Cl_4$

Exp. No.	Moles $AlCl_3$	Moles $P_3N_3Cl_6$	Ratio $AlCl_3/P_3N_3Cl_6$	ml. Benzene	Time (hrs.)	Total Product (grams)	Crude Yield $\phi_2P_3N_3Cl_4$ (grams)	Recovered $P_3N_3Cl_6$ (grams)
2-96	0.9	0.4	2.3/1.0	600 (6.8 mole)	48	141	78	25
2-106	0.85	0.4	2.1/1.0	550	72	141	94	46
2-122-II	0.85	0.27	3.1/1.0	550	72	106	82	20
2-136	3.40	1.6	2.1/1.0	2000	72	571	478	89

The Preparation of $P_3N_3(C_6H_5)_2(OC_6H_5)_2Cl_2$

Materials: All reactants were common laboratory chemicals or their preparation has been previously described. Acetone was purified by distillation from molecular sieve 4A at atmospheric pressure.

A. Procedure: Three reactions were run under similar reaction conditions with changes in solvent, reactant ratios and time. A typical experiment is described as follows:

$P_3N_3(C_6H_5)_2Cl_4$ (21.6 g., 0.05 mole) was added to 300 ml. of dry acetone in a 500 ml., three-necked flask equipped with a reflux condenser closed with a drying tube containing Drierite. Then, 10.4 g. (0.11 mole) of phenol was added as a solid to the reaction mixture and dissolved by stirring with a magnetic stirrer. Triethylamine (75 ml., 0.5 mole) was added to the reaction mixture and it was heated to reflux with a heating mantle with continued stirring. After 15 hours at reflux, the solution was cooled to -78°C and the triethylamine hydrochloride was filtered from the reaction mixture and the residue washed with some cold acetone. The filtrate and washings were evaporated on a Rinco evaporator, taken up in 200 ml. benzene, washed twice with 100 ml. portions of distilled water, twice with 100 ml. portions of 10% $NaHCO_3$ solution and then twice more with 100 ml. portions of distilled water. The benzene solution was then dried over 4A Molecular Sieve passed through an aluminum column to remove excess phenol and then stripped of benzene on the Rinco evaporator. A yellow oil remained (22.0 g.).

The following table describes the variations tried:

Exp. No.	Amount of $(C_6H_5)_2P_3N_3Cl_4$	Amount of C_6H_5OH	Ratio C_6H_5OH/ $(C_6H_5)_6P_3N_3Cl_4$	Solvent	Ratio Et_3N/ $(C_6H_5)_2P_3N_3Cl_4$
2-111	21.6 g. (0.05 mole)	10.4 g. (0.11 mole)	2.02/1.00	300 ml. Acetone	10/1
2-122	21.6 g. (0.05 mole)	27.7 g. (0.22 mole)	4.04/1.00	300 ml. diethyl ether	10/1
2-152	21.6 g. (0.05 mole)	27.7 g. (0.22 mole)	4.04/100	300 ml. Acetone	10/1

Exp. No.	Reaction Time	Grams $Et_3N\cdot HCl$ obtained	% Completion to $(C_6H_5)_2(C_6H_5O)_2P_3N_3Cl_2$	Yield (Grams of Crude Oil)
2-111	15 hrs.	3.5	25%	22
2-122	2 wks.	6.6	49%	-
2-152	7 days	13.5	98%	27.2

B. Comparison of Reaction Rates: A rough qualitative comparison of the reaction rates were made in acetone and in diethyl ether by cooling the refluxed solutions at intervals, filtering and collecting the solid as described in section A.

Acetone			Diethyl Ether		
Time	Gms. $Et_3N\cdot HCl$	No. of Cl's Removed	Time	Gms. $Et_3N\cdot HCl$	No. of Cl's Removed
24 hrs. (1 day)	8.61	1.25	24 hrs. (1 day)	4.2	0.61
48 hrs. (2 days)	10.2	1.46	72 hrs. (3 days)	4.9	0.71
120 hrs. (5 days)	12.6	1.84	7 days	5.4	0.78
7 days	13.5	1.96	2 weeks	6.6	0.96
			3 weeks	7.4	1.07
			4 weeks	8.0	1.16

C. Separation of Products: Unreacted $(C_6H_5)_2P_3N_3Cl_4$ could not be separated by crystallization either from a solvent or the oil but was preferentially eluted from a silica gel column by a 20% benzene-80% petroleum ether mixture. Benzene eluted the phenoxy substituted product. About 8 grams were collected from a middle benzene fraction in Exp. 2-152. Phosphorus analysis indicated that the product was the expected compound. Complete separation and identification of the product is still in progress.

For $P_3N_3(OC_6H_5)_2(C_6H_5)_2Cl_2$	P = 17.01%
Observed value	P = 16.98%

D. Effect of Solvent on the Reaction: $P_3N_3(C_6H_5)_2Cl_4$ (2.15 g., 0.005 mole) was put into each of seven 125 ml. erlenmeyer flasks with 1.88 g. (0.02 moles) of phenol. Solvent (50 ml.) and 10 ml. of triethylamine were added to each flask and shaken periodically. The solutions began to turn yellow and triethylamine hydrochloride began precipitating from the reaction mixture. After one week, the solutions were cooled in a -78°C bath, and filtered. The amount of $(C_2H_5)_3N\cdot HCl$ formed was determined from the weight of the solid removed after washing with cold acetone. The filtrates were returned to the flasks and kept another week. A few more were then filtered again.

No.	Solvent	Sol'n. Color	Grams $(C_2H_5)_3N\cdot HCl$ (1 week)	No. of Cl's Removed	Grams $(C_2H_5)_3N\cdot HCl$ (2 weeks)	No. of Cl's Removed
1	Tetrahydrofuran	light yellow	1.09	1.62	-	-
2	Acetone	yellow-orange	1.39	2.01	1.45	2.10
3	Dimethylformamide	amber	2.45	3.57	-	-
4	Ethanol	light yellow	0.45	0.66	-	-
5	1-Butanol	light yellow	0.60	0.88	-	-
6	Monoglyme	yellow-orange	1.16	1.69	1.21	1.75
7	Diglyme	amber	1.48	2.16	1.87	2.71

The Preparation of $P_3N_3(C_6H_5)_2[N(CH_3)_2]_2Cl_2$

Run #1: $P_3N_3(C_6H_5)_2Cl_4$ (21.5 g., 0.05 mole) was dissolved in 300 ml. of anhydrous ether (Mallenckrodt, A.R.) in a 1000 ml. round bottom, 3-necked flask equipped with a reflux condenser, thermometer and pressure equalized dropping funnel. Then 42 grams (0.2 mole) of a 25% solution of dimethylamine in water was added dropwise to the solution with stirring by a magnetic stirrer. The solution was kept at 0°C during the addition with an ice bath and the amine was added in a period of one hour. Distilled water (150 ml.) was added and the solution was left overnight to warm to room temperature. After 12 hours, the ether and water layers were separated. The ether layer was washed three times with 50 ml. portions of distilled water, then dried over moleuclar sieve 4A. The ether was evaporated and 20.4 g. (95% of theoretical yield) of semi-solid residue was left. Recrystallization from heptane yielded 6.1 g. (27% of theoretical yield) of a white solid (m.p. 136.5-138.0°C). Recrystallization from acetone yielded 3.0 g. of white solid (m.p. 142-142.2°C).

Analysis for $(C_6H_5)_2P_3N_3[N(CH_3)_2]_2Cl_2$:

Calculated C = 42.87%, H = 4.95%, N = 15.63%, P = 20.73%, Cl = 15.82%

Observed (average) C = 35.53%, H = 4.77%, N = 15.33%, P = 20.49%, Cl = 15.97%

Molecular Weight: Calculated, 448.2; found (osmometer, benzene), 444. The low observed carbon value was traced to an instrument error.

Run #2: The reaction was repeated on a larger scale using 86.2 g. (0.20 mole) of $(C_6H_5)_2P_3N_3Cl_4$ with 150 g. (0.8 mole) of $(CH_3)_2NH \cdot H_2O$ solution in 500 ml. of diethyl ether at -5°C. Workup yielded 81.2 g. (91% of theoretical) of product. The crude material is being recrystallized from acetone.

The Preparation of $P_3N_3(C_6H_5)_4[N(CH_3)_2]_2$

Materials: Phenyl magnesium bromide was obtained as a 3M solution in diethyl ether from Arapahoe Chemicals, Inc.

Procedure: $P_3N_3(C_6H_5)_2[N(CH_3)_2]_2Cl_2$ (2.4 g., 0.005 mole) was dissolved in 100 ml. of diethyl ether in a 3-necked, 200 ml. flask equipped with a reflux condenser, magnetic stirrer and a rubber septum. The solution was put under a nitrogen atmosphere and 50 ml. (0.12 mole) of 3 molar C_6H_5MgBr solution were added by a hypodermic syringe to the solution through the rubber septum. The solution was cooled to -78°C with a dry ice-trichloroethylene bath before and during the addition of C_6H_5MgBr. No reaction was observed so the solution was heated to room temperature and finally left overnight at reflux. No reaction was observed under these conditions. The solution was cooled to room temperature and a distilling head was put in between the reflux condenser and the flask. Monoglyme (50 ml.) was added to the solution and then the solution was heated to reflux. Ether was removed from the reaction until the reflux temperature was raised to 50°C. About 25 ml. more of monoglyme was added and the solution was refluxed for two hours. About 25 ml. of triethylamine were added after cooling to complex any unreacted C_6H_5MgBr. The solution was stripped. A gummy solid was found which was extracted in a soxhlet extractor overnight with petroleum ether. The solid was insoluble and only traces of a yellow oil could be removed by this treatment. The solid was dissolved in a mixture of 100 ml. of diethyl ether and 100 ml. of water. The yellow ether layer was separated, washed 3 times with 50 ml. portions of distilled water and dried over 4A molecular sieve. The ether was evaporated and the oil dissolved in benzene and passed through alumina to remove phenol which was observed in the infrared spectrum. The oil that was obtained on evaporation of the benzene was light yellow in color. The infrared spectrum showed bands for aliphatic and aromatic C-H in the 3000 cm^{-1} region, P_3N_3 ring absorptions at 1200 cm^{-1}, and C_6H_5 ring absorptions at 695 cm^{-1}. The analyses showed less than 0.5% residual chlorine in the oil.

The Preparation of $P_3N_3[N(CH_3)_2]_2Cl_4$

Materials: Dimethylamine hydrate, 25% solution in water (Matheson, Coleman & Bell), anhydrous ether (Mallenckrodt A.R.) and the phosphonitrilic chloride trimer were used without further purification.

Procedure: $P_3N_3Cl_6$ (348 g., 1 mole) was added to 1.2 liters of diethyl ether in a 3 liter, 3-necked flask equipped with a reflux condenser, magnetic stirrer and pressure equalized dropping funnel. A nitrogen atmosphere was kept over the reaction mixture and it was cooled to 0°C by an ice bath. Dimethylamine hydrate (721 g., 4 moles, 850 ml.) was added dropwise to the stirred solution in about two hours. The two layer solution was left to warm to room temperature overnight. The layers were separated. The water layer was evaporated and yielded 169 g. of $Me_2NH{\cdot}HCl$ (theoretical 163 g.). The ether layer was washed twice with water, dried with 4A molecular sieve and evaporated. 332 Grams (91% yield) of a semi-solid material was obtained as the residue. The residue was dissolved in petroleum ether and solid was crystallized from the solution. The petroleum ether was evaporated and more solid was separated until only a clear liquid was left. The solid material, $P_3N_3Cl_4(NMe_3)_2$, 191 g. (52%) melted at 101°C-102°C. The liquid weighed 100 g. and is possibly a liquid isomer of the solid. 135 Grams of the solid (VIII) were dissolved in 270 ml. of heptane and yielded 118 g. (87%) of recrystallized material which melted at 103.5-104.5°C (literature(6) 103°C). A sample was analyzed and the results are listed below with a comparison with literature values.(6)

$P_3N_3(Me_2N)_2Cl_4$

Theoretical	C = 13.17	H = 3.31	Cl = 38.86	N = 19.20	P = 25.47
Found	C = 13.12	H = 3.32	Cl = 38.99	N = 18.81	P = 25.37
Literature(4)	C = 13.3	H = 3.1	Cl = 38.8	N = 19.4	P = 25.6

The Preparation of $P_3N_3(OC_6H_5)_4[N(CH_3)_2]_2$

Materials: Sodium phenoxide was prepared "in situ" by the reaction of sodium metal with a slight excess of phenol in the solvent of choice. Potassium phenoxide was prepared by the reaction of phenol with KOH in xylene. The solvents were dried by treatment with molecular sieve. Acetone was distilled from molecular sieve 4A at atmospheric pressure.

Variation I: Sodium phenoxide (0.7 mole) was prepared "in situ" from 16.1 g. of sodium metal and 65.8 g. of phenol in 400 ml. of acetone under nitrogen in a one liter three-necked flask equipped with a reflux condenser. The flask was cooled with a dry ice-trichloroethylene bath to around 0°C and the solution was stirred with a magnetic stirrer. $P_3N_3Cl_4[N(CH_3)_2]_2$ (61 g., 0.167 mole) in 300 ml. of acetone was added to the solution at 0°C through a pressure equalized dropping funnel in a period of about one hour. The mixture was then heated to reflux and left at reflux for 12 hours. It was then stripped of acetone and treated with 700 ml. of anhydrous diethyl ether and 700 ml. of distilled water. The ether layer was separated, washed four times with 150 ml. portions of distilled water and dried over molecular sieve 4A. It was treated with 2 grams of decolorizing charcoal, filtered and stripped of solvent ether.

Vacuum distillation at 38 mm. pressure and up to 55°C removed an acetone condensation product from the reaction mixture. The residue, 83 g. (crude yield 83%) was passed into an alumina column and eluted with benzene and diethyl ether. The benzene fraction, 56.4 g. was light yellow in color; a lighter color than the crude product. The ether layer, 18.0 g. was yellow-orange in color; a deeper color than the crude. Both samples showed a similar infrared spectrum.

An attempt to distill the fraction eluted with benzene at 1 mm. pressure on a micro distillation apparatus was unsuccessful. Decomposition became evident at a pot temperature of 220°C (darkening of solution). The decomposition products were removed by passing the contents of the distillation pot through an alumina column in benzene. The benzene was stripped and the light yellow oil was distilled under high vacuum (10^{-5} to 10^{-6} mm.) in a molecular still at a heating mantle temperature of about 185°C. The product was redistilled at 10^{-6}. A thermocouple in the molecular still read 120°C. About 20 grams from the middle fraction were collected as a pale yellow oil; $n_D^{20} = 1.5675$.

Analytical data on the oil indicated that this was a mixture of compounds with an average chlorine content of 1.5 per P_3N_3 ring compound.

		% C	% H	% N	% P	% Cl	Mol. Wt.
A.	$(C_6H_5O)_4P_3N_3[N(CH_3)_2]_2$	56.47	5.42	11.76	15.60	0	595
B.	$(C_6H_5O)_3P_3N_3[N(CH_3)_2]_2Cl$	49.13	5.06	13.02	17.27	6	538
C.	$(C_6H_5O)_2P_3N_3[N(CH_3)_2]_2Cl_2$	40.02	4.62	14.59	19.35	14.76	480
D.	60% B + 40% C	45.53	4.91	13.64	18.24	9.88	515
E.	Observed Results	44.45	4.51	13.34	18.11	9.80	504

<u>Variation II</u>: Phenol, 47.1 g. (0.5 mole); sodium, 11.5 g. (0.5 mole) and 36.4 g (0.1 mole) of $P_3N_3Cl_4[N(CH_3)_2]_2$ were reacted in 700 ml. of acetone under conditions similar to those described in Variation I. The reaction time was extended to five days at reflux. Workup was the same as in Variation I. The crude oil, isolated from ether, weighed 99 g., 39 g. more than theoretical for complete reaction. Rough distillation and passage through alumina separated most of this large amount of acetone condensation product, leaving 48 g. (80% of theoretical) of yellow oil. 27 Grams of light yellow oil (darker than in Variation I); $n_D^{70} = 1.5716$ were collected after two molecular distillations at 10^{-5} to 10^{-6} mm. (thermocouple temperature 145-160°C).

Analysis showed that complete replacement of chlorines on the ring was not achieved:

found: C = 51.47% H = 5.5% P = 16.91% N = 12.38% Cl = 4.70%
Mol. wt. (osmometer) = 548.

<u>Variation III</u>: The effect of solvent on the reaction was determined by reacting 1.15 g. (0.05 mole) of sodium and 5.2 g. (0.055 mole) of phenol in 50 ml. of solvent. In all but one solvent (Ansul Ether 121, monoglyme) completed solubility of $NaOC_6H_5$ was obtained. More solvent was added to the monoglyme to complete solution. Addition of 3.65 g. (0.01 mole) of $P_3N_3Cl_4[N(CH_3)_2]_2$ was followed by 20 hours of refluxing of the mixture in each of the solvents. The solid, presumably NaCl, was separated by filtration, washed with ether and weighed.

Solvent	B.P. of Solvent	NaCl Obtained (gms.)	No. of Cl's/ P_3N_3 Ring
Tetrahydrofuran	66°C	0.7	0.8
Dimethylformamide (reflux)	153	3.5	4.0
Dimethylformamide (R.T.)	-	1.1	1.2
Monoglyme (Ansul Ether 121)	85	2.5	2.7
Diglyme (Ansul Ether 141)	162	3.0	3.3
Ethanol	78	2.0	2.2
1-Butanol	117	2.2	2.4
1-Hexanol	157	2.3	2.5

Variation IV: Sodium, 2.9 g. (0.125 mole); phenol, 12.7 g. (0.135 mole) and $P_3N_3[N(CH_3)_2]_2Cl_4$, 9.1 g. (0.025 mole) were reacted in a total of 160 ml. of dimethylformamide in a 250 ml, 3-necked round bottom flask as in the procedure described in Variation I. The reaction mixture was refluxed for three days. The workup was similar to Variation I. The DMF was removed at 1-2 mm pressure up to about the last 10-20 ml. which was washed out during the washing of the ether layer with water. The residue at this point was tarry. Evaporation of the ether was followed by passage through an alumina column in benzene. The oil that was collected after this treatment was light yellow but did not show the characteristic PN trimeric ring absorption in its infrared spectrum.

Variation V: Sodium, 9.2 g. (0.4 mole); phenol, 37.6 g. (0.4 mole) and $P_3N_3Cl_4[N(CH_3)_2]_2$, 32.8 g. (0.09 mole) were reacted in 400 ml. of monoglyme at reflux for 5 days according to the procedure described in Variation I. After 5 days, 18.7 g. of solid was filtered from the mixture, washed with ether and titrated for sodium phenoxide. Only 0.4 g. of $NaOC_6H_5$ was found; therefore, 3.5 chlorines per P_3N_3 ring were replaced. 0.1 Mole of sodium phenoxide was added to the reaction mixture and the mixture was refluxed for 3 days more. It was then worked up in the manner specified under Variation I. A colorless, slightly opaque oil was isolated after chromatography on alumina which weighed 47 g. (88% of theoretical). Chlorine analysis on this crude material showed less than 1.5% Cl which indicates the formation of the desired compound.

Attempted Preparation of $P_3N_3(OC_6H_5)_2[N(CH_3)_2]_2Cl_2$: The reaction between 29.10 g. (0.08 mole) of $P_3N_3Cl_4[N(CH_3)_2]_2$ and 51.5 g. (0.40 ml.) of potassium phenoxide in 600 ml. of acetone was carried out in the manner described in the preparation of $P_3N_3(OC_6H_5)_4[N(CH_3)_2]_2$. After 24 hours at reflux a solid was separated which weighed 15.4 g. and indicated that about one-half of the total chlorine was replaced. The oil, which was isolated from ether as described previously, weighed 35.7 g. Chromatography through alumina yielded 34.7 g. of very pale yellow oil. The first molecular distillation yielded 25.6 g, $n_D^{70} = 1.5668$, of a center fraction of almost colorless oil. Redistillation of this fraction yielded a center fraction, 13.5 g, $n_D^{20} = 1.5642$. The analysis of the product, however, did not agree with the expected product, $P_3N_3(OC_6H_5)_2[N(CH_3)_2]_2Cl_2$ but indicated a mixture.

Calculated for:

$P_3N_3(OC_6H_5)_2[N(CH_3)_2]_2Cl_2$ C = 40.02% H = 4.62% N = 14.59%
P = 19.35% Cl = 14.76% Mol. Wt. = 480.2

Observed (average) C = 41.99% H = 4.68% N = 14.00%
P = 19.00% Cl = 12.63%
Mol. Wt. (osmometer) = 491.

The Preparation of $P_3N_3(OC_6H_5)_3Cl_3$

$P_3N_3Cl_6$, technical grade (34.7 g, 0.1 mole) was placed in a 3-necked, 500 ml. flask fitted with a dropping funnel, reflux condenser and a magnetic stirrer. Acetone (200 ml., distilled over $CaSO_4$) was added and the mixture was stirred until all of the $(PNCl_2)_3$ dissolved. Phenol, technical grade (30.3 g., 0.37 moles) was then added to the solution. No evolution of heat or discoloration of the solution occurred. Triethylamine (84 ml.) was placed in the dropping funnel and added dropwise to the solution. Heat was evolved during this process. The temperature of the reaction vessel rose to 42°C. A white precipitate of $(C_2H_5)_3NHCl$ started to form. When the base was added, the reaction mixture was heated to reflux and maintained at reflux for 3 hours.

The reaction mixture was then cooled to 0°C and filtered. The solid, $(C_2H_5)_3N \cdot HCl$, was then washed with cold acetone and dried in a vacuum oven for 2 1/2 hours at 80°C.

$$\text{weight } (C_2H_5)_3N \cdot HCl = 41.3 \text{ g.}$$
$$\text{calc. for } \frac{3(C_2H_5)_3NHCl}{(PNCl_2)_3} = 41.1 \text{ g.}$$

The filtrate was distilled under vacuum thus removing the excess acetone, $(C_2H_5)_3N$ and phenol. A brownish oil remained (52.0 g.).

A 10.0 g. portion of the oil was dissolved in 90 ml. of benzene and passed through an alumina column (6" x 3/4"). The column was washed with benzene. The effluent was colorless. The benzene was removed under vacuum and a clear colorless oil remained.

The infrared spectrum of the oil indicated the presence of the cyclic PN structure and in addition $P\text{-}OC_6H_5$ bonds and characteristic $-C_6H_5$ absorptions.

The chromatographed oil was further purified by distillation under high vacuum. A 5 gram sample of the oil was placed in a molecular still and evacuated to $\sim 10^{-6}$ mm. The pot was heated to $\sim$165°C at which temperature distillation occurred. Nearly all of the oil distilled.

The infrared spectrum of the distillate was identical to that of the undistilled product.

Analytical Data:

Found: P, 17.85, 17.80; N, 8.16, 8.16; Cl, 21.60, 21.44; C, 40.22, 40.18, H, 2.88, 3.07.

Calc.: P, 17.85; N, 8.09; Cl, 20.40; C, 41.60; H, 2.91.

The Preparation of $P_3N_3(OC_6H_5)_2Cl_4$

$P_3N_3Cl_6$ (34.7 g., 0.1 mole) was placed in a 3-necked, 500 ml. flask fitted with stirrer, reflux condenser, dropping funnel and thermometer. Xylene (200 ml.) was added and the mixture was stirred until all of the $(PNCl_2)_3$ dissolved. Phenol (20.0 g.) was then added to the solution. Triethylamine (84 ml.) was added dropwise to the solution. The mixture became turbid and a voluminous white precipitate, $(C_2H_5)_3NHCl$, formed. The reaction mixture was kept at room temperature for a period of 18 hours. At that time, the reaction mixture was cooled to 0°C and filtered. The solid $(C_2H_5)_3N \cdot HCl$ was washed with cold xylene and dried in a vacuum oven at 80°C for a 2 hour period (weight 27.3 g.).

The filtrate was distilled under reduced pressure to remove any excess base and xylene. A viscous brown oil remained. The oil was dissolved in 300 ml. of benzene and passed through an alumina column (6" x 3/4"). The effluent was clear and colorless. The benzene was evaporated under vacuum and an oily product which was somewhat brownish in color remained.

A 10.0 g. sample of the oil was placed in a molecular still and evacuated to $\sim 10^{-6}$ mm Hg. The still was heated to 110°C at which temperature distillation occurred. The distillate was collected.

The infrared spectrum of the distillate was nearly identical to that of $P_3N_3(OC_6H_5)_3Cl_3$; however, the relative intensities of some of the bands were different.

Analytical Data:

Found: P, 19.79, 19.82; N, 9.32, 9.24; Cl, 33.52, 33.99; C, 28.69, 28.44; H, 2.54, 2.50.

Calc.: P, 20.08; N, 9.15, Cl, 30.40; C, 31.20; H, 2.34.

The Preparation of $P_3N_3(OC_6H_5)_3(OC_2H_5)_3$

Absolute ethanol (100 ml.) was placed in a 250 ml. flask which was fitted with a reflux condenser, stirrer and nitrogen inlet. Then 3.5 grams of sodium were cut into thin slices and added to the ethanol. Evolution of a gas (hydrogen) was noted. When the sodium had completely dissolved, 15.6 g. of $P_3N_3(OC_6H_5)_3Cl_3$ were dissolved in 50 ml. of ethanol and added dropwise to the $NaOC_2H_5$ solution. A white precipitate formed. The mixture was refluxed for a period of 18 hours. At this time the solution was cooled to 0°C and filtered. Celite was used as a filter aid. The filtrate was neutralized with gaseous HCl. The NaCl which resulted was filtered. The filtrate was then evaporated under vacuum, leaving a clear viscous oil.

The infrared spectrum of the oil confirmed the presence of the PN ring, POC_6H_5 bonds and POC_2H_5 bonds.

The product will be chromatographed and then an attempt will be made to purify the material by molecular distillation.

The Preparation of $P_3N_3(OC_6H_5)_2(OC_2H_5)_4$

Ethanol (100 ml.) was placed in a 250 ml. flask which was fitted with a reflux condenser, stirrer and nitrogen inlet. Sodium (5.0 g.) was cut into thin slices and added to the ethanol. Hydrogen was evolved. When the sodium had completely dissolved, 13.8 g. of $P_3N_3(OC_6H_5)_2Cl_4$ were dissolved in ethanol and added dropwise to the $NaOC_2H_5$ solution. A white precipitate formed. The mixture was refluxed for a period of 18 hours. The mixture was then cooled to 0°C and filtered. Celite was used as a filter aid. The filtrate was neutralized with gaseous HCl and the resulting NaCl was filtered. The ethanol was then evaporated off under vacuum leaving a viscous oil.

The infrared spectrum of the oil was very similar to that of $P_3N_3(OC_6H_5)_3(OC_2H_5)_3$. It showed the presence of the cyclic PN structure, POC_6H_5 bonds and POC_2H_5 bonds.

The sample will be chromatographed in the near future.

The Preparation of $P_3N_3(OC_2H_5)_6$

Absolute ethanol (100 ml.) was placed in a 250 ml. flask which was fitted with a condenser and magnetic stirrer. Sodium (4.2 g.) was cut into thin slices and added to the ethanol. Hydrogen was evolved. Then 10.4 g. of $(PNCl_2)_3$ were dissolved in 50 ml. of ethanol and added dropwise to the ethanol solution. A white precipitate (NaCl) formed. The mixture was then refluxed for a period of 4 hours. At that time the mixture was cooled to 0°C and filtered. The fine particles of NaCl went through the filter paper, thus, celite had to be used for efficient filtration.

The filtrate which was basic due to the excess $NaOC_2H_5$ was neutralized with HCl gas to a phenolphthalein end point. The NaCl formed was removed by filtration (celite added). The filtrate was decolorized with 1/2 gram of activated charcoal for a period of 3 hours. It was then filtered. The ethanol was removed and a clear viscous oil remained.

The infrared spectrum of the oil was obtained. It showed the presence of the PN ring, POC_2H_5 and characteristic alkyl absorptions.

The Preparation of $P_3N_3(OC_2H_5)_2Cl_4$ in Xylene

$P_3N_3Cl_6$ (34.7 g.) was placed in a 3-necked, 500 ml. flask fitted with a dropping funnel, stirrer and reflux condenser. Xylene (200 ml.) was added and the mixture stirred until all of the $P_3N_3Cl_6$ dissolved. Ethanol (35 ml.) was then added to the xylene solution and 60 ml. of triethylamine were added dropwise to the solution. A white precipitate started to form. The reaction mixture was then maintained at room temperature for 48 hours. At that time the reaction mixture was cooled to 0°C and filtered. The solid $(C_2H_5)_3NHCl$ was washed with cold xylene. It was then dried in a vacuum oven at 80°C for 2 hours (weight = 27.1 g; theory for 2 chlorines replaced = 27.4 g.).

The filtrate was neutralized with gaseous HCl and the $(C_2H_5)_3NHCl$ which formed in this process was filtered.

A 25 ml. portion of the filtrate was evaporated under vacuum. A brownish oil remained. Attempts to distill this product under high vacuum led only to a decomposition of the material.

The infrared spectra of the oil indicated the presence of the PN ring and the POC_2H_5 structure.

The Preparation of $P_3N_3(OC_2H_5)_2Cl_4$ in Acetone

$P_3N_3Cl_6$ (34.7 g.) was placed in a 500 ml. 3-necked flask which was fitted with a stirrer, thermometer and reflux condenser. Then 200 ml. of acetone were added and the mixture stirred until all of the $(PNCl_2)_3$ dissolved. Ethanol (30 ml.) was added to the reaction mixture and triethylamine (60 ml.) was then added dropwise. A white precipitate formed. The reaction mixture was kept at room temperature and stirred for 24 hours. It was then cooled to -78°C and filtered. The solid was washed with cold acetone and dried (weight = 27.1 g; theory for 2 chlorines replaced = 27.4 g.).

The filtrate was neutralized with gaseous HCl. The amine hydrochloride that formed during this process was filtered. The filtrate was then decolorized with charcoal and dried over molecular sieve.

A portion of the filtrate was distilled leaving a non-volatile oil. The infrared spectrum of the oil was identical to the compound prepared in xylene solvent.

The Preparation of $P_3N_3(OC_2H_5)_2(OC_6H_5)_4$ in Acetone

An acetone solution containing $P_3N_3(OC_2H_5)_2Cl_4$ (0.1 mole) was placed in a 3N 500 ml. flask which was fitted with a reflux condenser and stirrer. Potassium phenoxide (60 g.) was added to the acetone solution. Heat was evolved during the addition of the KOC_6H_5. The solution was then refluxed for 24 hours. A white precipitate formed. The solution was cooled to 0°C and filtered. Celite was used as a filter aid.

The filtrate was neutralized with HCl gas and the KCl which formed was removed by filtration. The filtrate was brownish in color and was treated with charcoal but this apparently had little effect on the color. The acetone was removed and a highly viscous brown oil remained.

The infrared spectrum of the oil indicated the presence of PN cyclic structure, POC_6H_5 and POC_2H_5 bonds.

Three runs on the above scale have been combined to give approximately one-half pound of the ester. This will be used for polymerization studies.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are based on the experimental work completed:

1. The functionality of the phosphonitrilic trimer ring can be successfully reduced to four, three, or two in several ways.

2. Either phenyl or phenoxy groups can be used to reduce the functionality of the ring. When chlorine is replaced by either of these, the resulting bonds are thermally and hydrolytically stable.

3. The positions on the phosphonitrilic ring at which it is desired to retain reactivity may be left with chlorine as the substituent, or the chlorine may be replaced with ethoxy or dimethylamino groups.

4. Preliminary experiments have shown that the monomers with reduced functionality are polymerizable. If the reactive positions contain chlorine, the materials react with hydroquinone to give polymers. If ethoxy groups are present, heating eliminates diethyl ether to produce P-O-P bridges, or reaction with hydroquinone liberates ethyl alcohol with polymer formation. If dimethylamino groups are present, they can be made to undergo transamination reactions with, for example, aniline or phenylenediamine to give P-N-P bridges or P-N--N-P bridges.

Future work is to be concentrated in several areas. To date, the following new phosphonitrilic derivatives have been synthesized as monomers:

A. $P_3N_3(OC_6H_5)_4(OC_2H_5)_2$

B. $P_3N_3(OC_6H_5)_3(OC_2H_5)_3$

C. $P_3N_3(OC_6H_5)_4[N(CH_3)_2]_2$

D. $P_3N_3(C_6H_5)_2(OC_6H_5)_2Cl_2$

E. $P_3N_3(C_6H_5)_4[N(CH_3)_2]_2$

Investigations during the next quarter will include:

1. A study of the polymerization of A and B and combinations of the two. Both compounds are on hand in sufficient quantity to begin this investigation.

2. Complete the characterization of C, D, and E, and select the best synthetic conditions for their preparation.

3. Scale up the preparation of monomers C, D and E.

4. Begin the study of the polymerization of monomers C, D, and E. Transamination of C and E with difunctional amines, and reaction of D with difunctional amines, alcohols, or phenols are the most obvious approaches.

5. Continue the study of the reactions of the numerous intermediates that are described in this report, in order to develop additional synthetic routes to compounds of the proper functionality for polymerization studies.

/lml

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Contract NObs 88232, Project Ser. No. SR007-03-03 Task 1000
Phosphonitrilic Polymers Stable at High Temperatures
TR 1 by H. K. Garner, G. J. Klender, J. E. Owen

The object is the development of thermoplastic and thermosetting high temperature stable resins for electrical applications from phosphonitrilic chloride trimer.

This report covers the synthesis of monomeric phosphonitrilic derivatives in which the functionality of the phosphonitrilic ring has been reduced to two, three, or four. This has been done by replacing some of the chlorines with stable phenyl or phenoxy groups. In addition, in some derivatives chlorines have also been replaced with reactive ethoxy or dimethylamino groups.

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