

mercury and also for a small deviation of the local g value (979.60 *vs.* the standard 980.665). The equation gives the normal boiling point as 71.1° and the Trouton constant as 21.05 e.u. The consistency of the results indicates good purity, and the value at 0° can be used as a test of purity.

The chlorophosphines (CF₃)₂PCl and CF₃PCl₂ were made from the highly purified iodophosphines by reaction with well-dried HgCl₂, present in excess. Both were purified by high-vacuum distillation methods, until each showed a uniform volatility for a series of fractions. The vapor tension data for middle fractions are shown with equations in Tables V and VI. For (CF₃)₂PCl the normal boiling point is calculated as 23.2° and the Trouton constant as 22.05 e.u. For CF₃PCl₂, the boiling point is 39.4° and the Trouton

TABLE V
VAPOR TENSIONS OF (CF₃)₂PCl

$$\log P = 4.1432 + 1.75 \log T - 0.002582T - 1429/T$$

Temp., °C.	-80.8	-64.8	-46.0	-31.4	-22.7	0.00
$P_{\text{obsd.}}$, mm.	1.64	6.34	24.8	59.8	97.5	295.3
$P_{\text{calcd.}}$, mm.	1.64	6.38	24.5	60.1	97.5	295.3

TABLE VI
VAPOR TENSIONS OF CF₃PCl₂

$$\log P = 4.2229 + 1.75 \log T - 0.002743T - 1516/T$$

Temp., °C.	-64.8	-46.0	-19.5	0.00	10.15	17.3
$P_{\text{obsd.}}$, mm.	2.72	11.3	57.2	154.0	243.4	329.1
$P_{\text{calcd.}}$, mm.	2.72	11.2	57.3	154.0	243.4	329.1

constant is 21.75 e.u.; also, its melting point was observed as $-129.6 \pm 0.1^\circ$ (ethylene vapor tension thermometer).

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID COMPANY, STAMFORD, CONNECTICUT]

Phosphonitrilic Compounds. II.¹ Reactions of Phosphonitrilic Chlorides with Catechol and Triethylamine

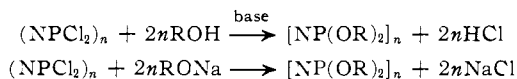
By H. R. ALLCOCK

RECEIVED JANUARY 23, 1964

Phosphonitrilic chloride trimer undergoes dehydrochlorination reactions with catechol and triethylamine to form tris(*o*-phenylenedioxy)phosphonitrile trimer and polymers. An unusual side reaction, involving phosphorus-nitrogen ring cleavage, yields the triethylamine salt of 2-(*o*-hydroxyphenoxy)-2,2'-spirobi[1,3,2-benzodioxaphosphole], which appears to exist as the hexavalent phosphorus anion tautomer in the crystalline state. This product was also formed when phosphonitrilic chloride tetramer or polymer was treated with catechol and triethylamine. The results are interpreted in terms of possible reaction mechanisms.

Introduction

Several authors have reported the reactions of phosphonitrilic chlorides with alcohols or phenols, or with their alkali metal salts, to give alkyl or aryl phosphonitrilates according to the equations²



Such reactions have been investigated principally for the cyclic trimeric and tetrameric phosphonitrilic chlorides (where n is 3 or 4) under conditions which led to complete substitution of chlorine atoms by alkoxy or aryloxy groups.³⁻⁹

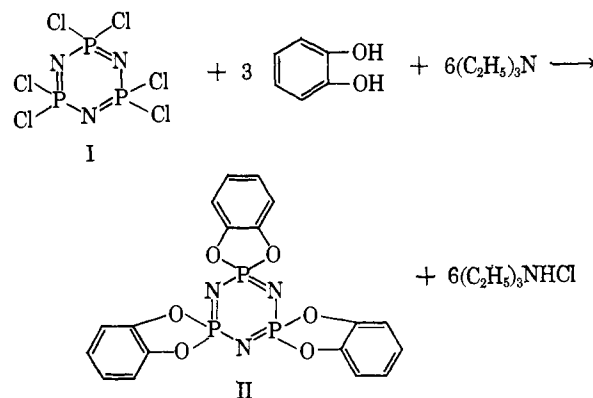
It was of interest, therefore, to ascertain if similar reactions could be employed to effect ring closure at each phosphorus atom using an aromatic *ortho* diol such as catechol,¹⁰ and to establish if a cyclization reaction of this type could be used to prepare partially substituted phosphonitrilic chlorides in which the exact location of the unreacted chlorine atoms would be known. Although no partially substituted products

were isolated, the results suggested the mechanism of chlorine replacement in these reactions.

Results and Discussion

Treatment of phosphonitrilic chloride trimer (I) with catechol, in tetrahydrofuran or benzene, using triethylamine as a hydrogen chloride acceptor, resulted in three distinguishable reactions. These were: (a) cyclization reactions at the three phosphorus atoms, (b) polymer formation by cross-linking reactions between different phosphonitrilic chloride molecules, and (c) reaction of the cyclized phosphonitrilic ester formed in (a) with excess catechol and base to cleave the phosphorus-nitrogen ring system. These three processes are considered separately.

Cyclization Reactions at Phosphorus.—Ring closure at the three phosphorus atoms of I yielded tris(*o*-phenylenedioxy)phosphonitrile trimer (II) according to the reaction



- (1) Part I: H. R. Allcock and R. J. Best, *Can. J. Chem.*, **42**, 447 (1964).
- (2) For reviews of this topic, see (a) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962); (b) C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 275 (1962).
- (3) B. R. Dishon, *J. Am. Chem. Soc.*, **71**, 2251 (1949).
- (4) C. Hamalainen and J. D. Guthrie, *Textile Res. J.*, **26**, 141 (1956);
- (5) R. Rätz and M. Hess, *Ber.*, **84**, 889 (1951).
- (6) B. W. Fitzsimmons and R. A. Shaw, *Chem. Ind.* (London), 109 (1961).
- (7) M. Yokoyama, *J. Chem. Soc. Japan*, **80**, 1192 (1959).
- (8) R. Rätz, H. Schroeder, H. Ulrich, E. Kober, and C. Grundmann, *J. Am. Chem. Soc.*, **84**, 551 (1962).
- (9) M. S. Chang and A. J. Matuszko, *Chem. Ind.* (London), 410 (1962).
- (10) For a preliminary account of parts of this work, see H. R. Allcock, *J. Am. Chem. Soc.*, **85**, 4050 (1963).

The structure of II was confirmed by both analytical and physical data. Both infrared and ultraviolet spectra (Tables I and II) are consistent with structure II. The fact that the ultraviolet spectrum of II was very similar to that of *o*-dimethoxybenzene indicates that there is negligible interaction between the phenyl and phosphonitrilic rings in II.

TABLE I
PRINCIPAL INFRARED BANDS^a

	[NP- (O ₂ C ₆ H ₄) ₂] (II)	[NP(OC ₆ H ₅) ₂] ₃	[P(O ₂ C ₆ H ₄) ₂] ⁻ [(C ₆ H ₅) ₂ NH] ⁺ (VIIb)	(<i>o</i> -HOC ₆ - H ₄ O) ₂ - P=O (IX)
OH				3300
NH			3200 sharp	
O-phenyl	1270	1265	1250	1190
P=O				1260
P=N	1220	1160-1200 ^b		
P-O-phenyl	835	950	825	970
Phenyl	745	770, 730, 690	750, 730	750

^a Values quoted are in wave numbers (cm.⁻¹). The smaller characteristic phenyl bands are not listed. ^b Three closely spaced peaks are evident in this region. The general shape of this band resembles the P=N stretching peaks in other trimeric phosphonitrilic compounds and this assignment now appears preferable to the one made previously¹ in which the 1265-cm.⁻¹ peak was attributed to this mode.

TABLE II
ULTRAVIOLET SPECTRA^a

[NP(O ₂ C ₆ H ₄) ₂] (II)	[NP(OC ₆ H ₅) ₂] ₃	1,2-(CH ₃ O) ₂ C ₆ H ₄	[P(O ₂ C ₆ H ₄) ₂ (<i>o</i> - OC ₆ H ₄ O)] ⁻ [(C ₆ H ₅) ₂ NH] ⁺ (VII)
276 (3.72)	272 (3.18)	282 sh (3.33)	290 sh (4.07)
271 (3.79)	266 (3.31)	276 (3.40)	284 (4.17)
266 sh (3.68)	259 (3.23)	^b	280 sh (4.14)
209 (4.38)	206 sh (4.70)	227 (3.89)	227 sh (4.17)

^a The spectra are for acetonitrile solutions: λ_{max}, mμ (log ε).
^b This peak at 273 mμ is present in cyclohexane solution but absent in acetonitrile.

The dipole moment of II was found to be 1.9 ± 0.2 D. at 70°. Under the same conditions, the values for (NPCL₂)₃ (I) and [NP(OC₆H₅)₂]₃ were 0.92 ± 0.1 and 3.0 ± 0.2 D., respectively. The high dipole moment of [NP(OC₆H₅)₂]₃ was attributed previously to nonplanarity of the phosphonitrilic ring¹ and the lower value of II is consistent with a greater planarity of the phosphorus-nitrogen ring in this compound although the symmetry is clearly less than for (NPCL₂)₃ (I). Preliminary X-ray diffraction results suggest that if the phosphorus-nitrogen ring of II is not planar, it is slightly puckered in a chair conformation.¹² Nuclear magnetic resonance proton spectra of II in cyclohexane at 95° showed one sharp peak at τ 2.83, which was displaced to τ 2.68 at 25°. This is consistent with the proposed structure of this compound, since 1,2-dioxymethylenebenzene and *o*-dimethoxybenzene also show only a single peak at τ 3.25 and 3.24, respectively.

When heated above the melting point (244-245°), II rearranged to a vitreous, low molecular weight polymeric material.¹³ Infrared spectra of this product suggested a retention of the cyclic phosphorus ester

(11) The dipole moment in benzene was determined by Dr. R. J. Best using the Guggenheim method and employing the equipment described in ref. 1.

(12) H. R. Allcock and L. A. Siegel, unpublished results.

(13) The polymer melted over the range 80-125°. In dimethylformamide the reduced specified viscosity was 0.05 (1% concentration at 30°). Elemental analysis indicated that the polymer had the same composition as II.

grouping. This thermal behavior contrasts markedly with that of the hexaphenoxy analog, [NP(OC₆H₅)₂]₃, which is unchanged by prolonged heating at 300°. These two compounds also differed in their reactivity toward primary amines. Treatment of II with *n*-propylamine at room temperature resulted in a rapid, exothermic reaction. Infrared spectra of the reaction products suggested that although the phosphonitrilic ring was still present, phenoxy groups had been displaced from phosphorus by alkylamino units. The hexaphenoxy compound was recovered unchanged from solution in propylamine. The greater reactivity of II reflects a release of steric strain at the phosphorus atoms in this compound, in a manner which is comparable to the accelerated hydrolysis of cyclic phosphorus esters.¹⁴

Attempts were made to prepare 1,1,3,3-tetrachloro-5-(*o*-phenylenedioxy)phosphonitrile trimer (III), 1,1-dichloro-3,5-di-(*o*-phenylenedioxy)phosphonitrile trimer (IV), and 1,3,5-trichloro-1,3,5-tri-(*o*-hydroxyphenoxy)-phosphonitrile trimer (V) by variations in the stoichiometry of I, catechol, and triethylamine. A near theoretical amount of triethylamine hydrochloride was obtained from each of these reactions, but no partially substituted trimeric derivatives were isolated. In each case the reaction products were II, unreacted I, phenoxychlorophosphonitrilic polymers, and phosphorus-nitrogen ring degradation products.

These results are of interest in establishing the mechanism and sequence of chlorine replacement in phosphonitrilic chloride trimer. Following replacement of one chlorine atom by *o*-hydroxyphenoxy, further substitution could proceed by a geminal (1,1-cyclization) or a nongeminal (1,3-di-*o*-hydroxyphenoxy substitution) mechanism.¹⁵ The isolation of the fully substituted phosphonitrilic ester (II) and unreacted phosphonitrilic chloride trimer from these reactions indicates that a geminal-type substitution is preferred, and that replacement of the chlorine atoms on one phosphorus atom by aryloxy activates the remaining chlorine atoms to substitution. The ease of ring closure in these compounds is understandable in view of the favored steric arrangement of the reacting groups. Electron withdrawal from phosphorus by the phenoxy group also facilitates cyclization. Similarly, the enhanced reactivity at the *meta* positions to the benzodioxaphosphole group is consistent with the greater electropositivity of the phosphorus atoms at those positions.

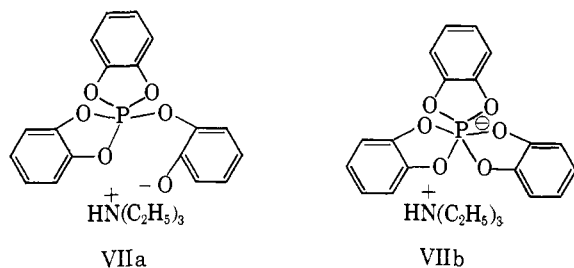
Polymer Formation.—Ring closure at each phosphorus atom is accompanied by an alternative reaction in which dehydrochlorination takes place between 1 molecule of catechol and 2 molecules of phosphonitrilic chloride. (Cyclization involving *m*-phosphorus atoms is also possible but no evidence was obtained for such a step). The ultimate extension of the polymer-forming substitution reaction would be the production of a cross-linked polymeric network. Such products (VI) were isolated from nearly all the reactions studied and were found to contain aryloxy groups and readily hydrolyzable chlorine. Although polymer formation is clearly competitive to ring closure in this reaction, it is significant that the yields of II were invariably

(14) P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961).

(15) This subject is discussed in some detail in the reviews mentioned in ref. 2.

much higher than the yields of polymer and this, presumably, is also due to steric and electronic assistance in the ring-closure step.

Phosphorus-Nitrogen Ring Cleavage Reactions.—The reactions described above, between phosphonitrilic chloride trimer and catechol in the presence of triethylamine, also yielded varying quantities of a white, insoluble, sublimable powder. This product was formed in greater quantities when catechol and triethylamine were in excess. It could also be prepared quantitatively by treatment of the phosphonitrilic ester (II) in tetrahydrofuran or toluene with 6 equiv. of catechol and 3 equiv. of triethylamine. Ammonia was evolved during the reaction. This product is believed to be 2-(*o*-hydroxyphenoxy)-2,2'-spirobi[1,3,2-benzodioxaphosphole] triethylamine salt (VIIa), or its hexavalent phosphorus anion tautomer (VIIb).



The evidence on which the structure of this compound is based is as follows. Carbon, hydrogen, nitrogen, and phosphorus analyses corresponded closely to this structure. The infrared spectrum of the solid (Table I) showed no phosphorus-nitrogen absorption in the 1200-cm.⁻¹ region and was consistent with structure VIIb. The ultraviolet spectrum (Table II) was very similar to that of II but was displaced 15 mμ toward the visible. Nuclear magnetic resonance proton spectra in warm dimethyl sulfoxide or dimethylformamide indicated the presence of phenyl groups, and ethyl groups attached to nitrogen. The methyl to phenyl proton ratio in dimethylformamide at 130° was 2.9 to 4.0, and in deuteriodimethylformamide, 3.0 to 4.0. In the latter solvent the phenyl proton spectrum was an A₂B₂ pattern, centered at τ 3.0. Clearly, the presence of the negative charge in VII is sufficient to split the single peak observed for II. Attempts to obtain P³¹ n.m.r. spectra of VII were unsuccessful due to the low solubility of the compound in dimethylformamide. A mass spectroscopic examination of the compound gave a spectrum which was consistent with the products formed by the vapor state dissociation of VIIa into triethylamine and VIII, followed by fragmentation and hydrolysis of VIII.¹⁶ An X-ray powder diffraction study of VII was also made.¹⁷ The rela-

(16) Mass spectrometric analyses were performed in a Consolidated Electrodynamics Model 21-103 spectrometer. When samples of VII were introduced through a heated glass inlet at 250–300° a complex mixture of products was formed due presumably to reaction of VII with the walls of the hot inlet. In one particular case (when VIII was detected) a sample was introduced directly into the ion beam at a temperature of 80–100°, and peaks were detected at the following mass numbers: 418 (vw), unknown; 356 (vw), VIII; 264 (w), (*o*-C₆H₄O₂)₂POH; 247 (s), (*o*-C₆H₄O₂)₂P; 172, (*o*-C₆H₄O₂)P(O)OH; 156, (*o*-C₆H₄O₂)POH; 139 (s), (*o*-C₆H₄O₂)P; 110, *o*-C₆H₄(OH)₂; 101, N(C₂H₅)₃; 92, C₂H₅O. This latter experiment was performed by Dr. K. Biemann at Massachusetts Institute of Technology.

(17) The X-ray diffraction data were obtained using a Debye-Scherrer camera with 114.6-nm. nickel-filtered copper radiation. The hexagonal cell constants found were *c* = 8.75 and *a* = 12.10 Å., and the density of the solid was found to be 1.36 by a flotation method in chloroform-methylene chloride.

tively simple pattern was explained in terms of a hexagonal, two molecule unit cell in which the molecular weight of VII was 457 ± 1%.

A number of degradation reactions also served to confirm the structure of this product. When VII was treated with pyridine or ethanolic sodium hydroxide, triethylamine was evolved. Triethylamine was also liberated when VII was heated for long periods of time at 100–130° in dry dimethylformamide. The soluble product (VIII), when prepared under anhydrous conditions, appeared to be the compound (C₆H₄O₂)₂P-(*o*-C₆H₄OH), derived by detriethylamination of VIIa, since treatment of VIII with triethylamine yielded VII. However, when VII was heated with aqueous dimethylformamide, detriethylamination occurred as before, but the product was shown by phosphorus nuclear magnetic resonance and infrared spectra to be a hydroxyphenyl phosphate, (*o*-HOC₆H₄O)₂P=O (IX). This product presumably was formed by direct hydrolysis of VIII. The same hydroxyphenyl phosphate was formed when VII in tetrahydrofuran was treated with mineral acid.

The stoichiometry of the reaction between II, catechol, and triethylamine to form VII also supports the proposed composition of the product. When II was treated with either catechol or triethylamine, in the absence of the other reagent, in tetrahydrofuran at 25°, VII was not formed. When the molar ratio of II to catechol to triethylamine was varied according to the following proportions the moles of VII (relative to II) changed as shown in parentheses: 1:3:0.36 (0.75), 1:3:6 (1.55), 1:3:1.5 (1.39), 1:3:3 (1.52), 1:6:3 (2.7). These results suggest that formation of VII from II requires the presence of both catechol and triethylamine in the ratio of 1:6:3, respectively.

The exact mechanism of this process has not been elucidated, but the initial reaction may involve a base-catalyzed addition of catechol molecules to the phosphonitrilic ring, followed by phosphorus-nitrogen ring cleavage and elimination of ammonia. It is significant that the final reaction product (VII) was also isolated when phosphonitrilic chloride tetramer, (NPCl₂)₄, or polymer, (NPCl₂)_{~1500}, was treated with catechol and triethylamine. No tetrameric or polymeric products analogous to II, [NP(O₂C₆H₄)₂]_{4 or n}, were isolated from these reactions. Apparently, these species are formed initially but are rapidly degraded to VII in the reaction mixtures, presumably because the phosphorus-nitrogen bonds are less protected against degradative attack than in the case of the trimeric compound.

In solution or in the vapor state, VII probably exists as the pentavalent phosphorus form (VIIa), as indicated by the mass spectrometric data and by the ultraviolet spectrum (Table II). The bathochromic ultraviolet shift of VII compared to II is consistent with an increase in phenoxidic character as might be expected for the triethylamine salt of a phenol. The fact that one chromophore rather than two is observed indicates, however, that VIIa exists as a resonance hybrid in which all the carbon-oxygen bonds are equivalent but in which the negative charge is localized at the oxygen atoms. The existence of a symmetrical A₂B₂ phenyl proton n.m.r. spectrum affirms this interpretation.

In the solid state however, the structure of VII can be more accurately represented by the hexavalent

phosphorus anion form (VIIb).^{17a} The high symmetry of the molecule in the solid state, as demonstrated by the infrared spectrum and the X-ray diffraction data, does not, of course, distinguish between a resonance hybrid of VIIa and structure VIIb. However, the stability of the solid material to loss of triethylamine during thermal or hydrolytic degradation precludes a significant contribution from the phenolic structure (VIIa). The infrared spectrum of the solid shows a sharp N-H peak at 3200 cm^{-1} , which is strong evidence that a significant charge separation exists in this compound and that the negatively charged site is sterically shielded from the triethylammonium ion.¹⁸ The proposed structure of the anion (VIIb) in the solid state is similar to that of the hexachlorophosphorus anion, $(\text{PCl}_6)^-$ and the hexafluorophosphorus anion $(\text{PF}_6)^-$.¹⁹ In the latter structure, the high electronegativity of the fluorine atoms is frequently cited as a reason for the stability of this unit. For structure VIIb, however, the formation of the hexavalent phosphorus anion can be attributed to resonance and to the steric effects which result from a separation of the sterically hindered counterions within the crystal lattice. Presumably the triethylammonium ion occupies a fixed, symmetrical position relative to each phosphorus atom, in which case the negative charge would be stabilized more readily on phosphorus than on the oxygen atoms.

Experimental²⁰

Phosphonitrilic chloride trimer and tetramer (Hooker Chemical Corp.) were recrystallized from *n*-heptane before use. Triethylamine and catechol (Eastman Organic Chemicals), tetrahydrofuran (Fisher Certified Reagent), and benzene (Baker and Adamson Reagent) were used as received. Pyridine (Baker and Adamson Reagent) was refluxed for 2 hr. over potassium hydroxide pellets and was distilled into a flask which contained barium oxide before storage at reduced pressure on a vacuum system.

Phosphonitrilic Diphenoxide Trimer, $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$.—This compound was prepared and purified as described previously.¹

Tris(*o*-phenylenedioxy)phosphonitrile Trimer (II). A. Using Triethylamine in Tetrahydrofuran.—A solution of catechol (95 g., 0.864 mole) and triethylamine (175 g., 1.728 moles) in tetrahydrofuran (500 ml.) was added dropwise to a stirred solution of phosphonitrilic chloride trimer (100 g., 0.288 mole) in tetrahydrofuran (1000 ml.) at 30°. After completion of addition, the mixture was refluxed for 2 hr. and was stirred at 30° for a further 48 hr. The white precipitate was filtered off, dried (350 g.), and was then washed thoroughly with water to remove triethylamine hydrochloride. The powdery residue (136 g.) was then subjected to a prolonged extraction with benzene in a Soxhlet apparatus. The extracts, when cooled, yielded tris(*o*-phenylenedioxy)phosphonitrile trimer (II, 74 g., 50% yield). Recrystallization from benzene followed by sublimation at 230° (0.05 mm.) gave material with m.p. 244–245°. *Anal.* Calcd. for $\text{C}_{18}\text{H}_{12}\text{O}_6\text{N}_3\text{P}_3$: C, 47.0; H, 2.61; N, 9.15; P, 20.3; mol. wt., 459. Found: C, 46.85; H, 2.85; N, 9.16; P, 20.3; mol. wt., 459 (mass spectrometry). The original tetrahydrofuran filtrate was evaporated under reduced pressure at 30–40° to leave an oily resin (16 g.), which solidified, evolved hydrogen chloride, and became insoluble when exposed to the atmosphere.

(17a) NOTE ADDED IN PROOF.—Evidence in favor of a hexavalent silicon dianion analog of similar structure, $[(\text{C}_6\text{H}_5\text{O})_2\text{Si}]^{2-}$, has recently been described by H. Bartels and H. Erlenmeyer. *Helv. Chim. Acta*, **47**, 7 (1964).

(18) P. Chevalier and C. Sandorfy. *Can. J. Chem.*, **38**, 2524 (1960).

(19) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 238, 805.

(20) Ultraviolet spectra were recorded using a Cary Model 14 automatic recording spectrometer. Infrared spectra were measured as Nujol or halocarbon mulls on a Perkin-Elmer Model 21 spectrometer. Nuclear magnetic resonance measurements were performed using a Varian DP 60 apparatus with proton spectra measured at 56.4 Mc. and P^{31} spectra at 16.2 Mc. Melting points are corrected.

This material appeared to be a polymer derived from species such as VI. The white residue from the Soxhlet extraction (27 g.) was purified by sublimation at 280° (0.05 mm.), and was shown to be 2-(*o*-hydroxyphenoxy)-2,2'-spiropi[1,3,2-benzodioxaphosphole] triethylamine salt (VII). The examination and identification of this material is described below.

B. Vacuum Line Reaction in Pyridine.—Phosphonitrilic chloride trimer (6.96 g., 0.02 mole) and catechol (6.6 g., 0.06 mole) were placed in a 250-ml. flask attached to a vacuum system, and the system was evacuated. Dry pyridine (100 ml.) was then condensed into the flask. The mixture was melted and stirred at 0° at which temperature no reaction appeared to take place in the yellow solution. The solution temperature was then raised slowly to 20° and precipitation of a white solid took place. The reaction mixture was stirred at 70° for 8 hr., and at 30° for a further 18 hr. The precipitate was filtered off, washed with pyridine, and dried under vacuum. This material was recrystallized from benzene and sublimed to give II (2 g.), m.p. 245°. The identity of this product was confirmed by its infrared spectrum.

Attempted Preparation of $\text{N}_3\text{P}_3\text{Cl}_4(\text{O}_2\text{C}_6\text{H}_4)$ (III), $\text{N}_3\text{P}_3\text{Cl}_2(\text{O}_2\text{C}_6\text{H}_4)_2$ (IV), and $\text{N}_3\text{P}_3\text{Cl}_3(o\text{-OC}_6\text{H}_4\text{OH})_3$ (V).—These reactions were carried out using a similar technique to that described for the synthesis of II (method A). Solutions of catechol and triethylamine in tetrahydrofuran were added dropwise over 3 hr. to stirred solutions of I in tetrahydrofuran at 25°. After completion of the reaction the white precipitate was filtered off and dried. The filtrate was evaporated at 25–30° (~10 mm.), and the semisolid residue was extracted with boiling benzene to remove unchanged I. The residue was insoluble phenoxychlorophosphonitrilic polymer. Extraction of the original white precipitate with boiling benzene removed II, and the residue was washed with water to remove triethylamine hydrochloride and leave VII. The various products were identified by their infrared spectra and, where possible, by melting points. None of the expected products (III, IV, and V) was isolated. The following reactions were performed. (a) The reaction of catechol (6.6 g., 0.06 mole) and triethylamine (12.12 g., 0.12 mole) in tetrahydrofuran (100 ml.) with I (20.8 g., 0.06 mole) in tetrahydrofuran (400 ml.) after 18 hr. at 25° yielded I (~15 g., 0.04 mole), II (3.0 g., 6.5×10^{-3} mole), VII (0.3 g., 6.5×10^{-4} mole), $(\text{C}_2\text{H}_5)_3\text{NHCl}$ (14.6 g., 0.11 mole), and polymer (1.3 g.). (b) Reaction of catechol (13.2 g., 0.12 mole) and triethylamine (24.24 g., 0.24 mole) with I (20.8 g., 0.06 mole) under identical conditions yielded I (7.5 g., 0.022 mole), II (9.6 g., 0.021 mole), VII (1.5 g., 3.3×10^{-3} mole), $(\text{C}_2\text{H}_5)_3\text{NHCl}$ (28.5 g., 0.021 mole), and polymer (4.5 g.). (c) Addition of catechol (19.8 g., 0.18 mole) and triethylamine (18.8 g., 0.18 mole) in tetrahydrofuran (100 ml.) to I (20.8 g., 0.06 mole) in tetrahydrofuran (400 ml.) over 3 hr. at 25° followed by 1-hr. reaction at the same temperature yielded I (8.3 g., 0.024 mole), catechol (5 g., 0.046 mole), II (6.9 g., 0.015 mole), $(\text{C}_2\text{H}_5)_3\text{NHCl}$ (22.7 g., 0.17 mole), and polymer (5 g.). During the extraction steps the temperature was not allowed to exceed 30° in order to minimize the possibility of polymerization. (d) The procedure resembled that of reaction c except that triethylamine in tetrahydrofuran (50 ml.) was added over 4 hr. to a solution of catechol and I in tetrahydrofuran (450 ml.). After 36-hr. reaction at 25°, the products were I (11 g., 0.032 mole), catechol (8.1 g., 0.074 mole), II (8.0 g., 0.017 mole), $(\text{C}_2\text{H}_5)_3\text{NHCl}$ (24.9 g., 0.175 mole), and polymer (4.2 g.).

Preparation of VII from II.—A 250-ml. flask was fitted with a glass-covered magnetic stirrer bar and was charged with II (2 g., 0.0044 mole), catechol (2.92 g., 0.0244 mole), and toluene (100 ml.). The flask was attached to a vacuum line and the contents were frozen as air was removed. The mixture was then allowed to reach 25°, and triethylamine (2 ml., 0.0132 mole) was added by syringe through a rubber serum-cap stopper. The reaction mixture was stirred at 25° for 50 hr. After this time, the more volatile components were distilled into a side arm. A mass spectroscopic examination of the distillate demonstrated the absence of triethylamine and the presence of ammonia. The reaction mixture was then filtered, and the precipitate was extracted with boiling toluene in a Soxhlet apparatus to remove unchanged starting materials. The dried residue was sublimed at 280° (0.05 mm.) to give VII (6.0 g.). *Anal.* Calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_6\text{PN}$: C, 63.0; H, 6.17; P, 6.79; N, 3.06. Found: C, 62.8; H, 6.32; P, 6.95; N, 3.16. The infrared spectrum of this material was identical with those of samples obtained during the preparation of II, as were the sublimation temperature and

decomposition reactions. Other reactions using different stoichiometric amounts of the reagents were carried out in the same way.

Reactions of VII.—In addition to the physical data described previously, further evidence in favor of the proposed structure for VII was obtained from solvolytic degradation experiments. Compound VII (1 g.) was stirred with sodium hydroxide (3 g.) in absolute ethanol (25 ml.) at 25° for 18 hr. in a flask attached to a vacuum system. The solid dissolved slowly, and the initial dark green color was slowly bleached during the reaction. A gas sample from above the reaction mixture was shown, by mass spectrometry, to contain triethylamine. Acidification of the reaction mixture, followed by evaporation, extraction with ethanol, and removal of the solvent, yielded an oil which showed an infrared spectrum consistent with that expected for (*o*-HOC₆H₄O)₃P=O (IX).

The same product (IX) was formed by treatment of VII (3.1 g.) in tetrahydrofuran (200 ml.) with concentrated hydrochloric acid (1 ml.) at 25° for 18 hr. Prolonged treatment of VII (10 g.) with methanolic 20% hydrochloric acid (300 ml.) yielded a mixture which contained triethylamine hydrochloride and catechol. The latter compound presumably was formed by hydrolysis of IX.

A mixture of VII (3.2 g.) and dry pyridine (50 ml.) was stirred at 25° for 16 hr. within a glass vacuum system. A gas sample from above the mixture was shown by mass spectrometry to contain triethylamine. When VII was dissolved in hot pyridine, exposed to the atmosphere, triethylamine evolution was accompanied by hydrolysis. Phosphorus nuclear magnetic resonance spectra showed peaks at -16 and -1 p.p.m. which were attributed to a covalent phosphate structure. Isolation of the product by removal of the pyridine yielded an oil, which showed an infrared spectrum identical with that of IX.

Compound VII (3 g.) was dissolved in hot dimethylformamide (50 ml., dried over MgSO₄), from which VII could be recovered when the solution was cooled rapidly. More prolonged heating under anhydrous conditions caused evolution of triethylamine. Removal of the solvent yielded an oil which showed an infrared spectrum consistent with that expected for VIII. Treatment of the dimethylformamide solution of VIII with triethylamine yielded VII. If the solution of VII or VIII in dimethylformamide was heated while exposed to the atmosphere or in the presence of water, VII could not be recovered by treatment with triethylamine. Phosphorus nuclear magnetic resonance measurements of this solution showed one strong peak at -16 p.p.m. and one weaker at -1 p.p.m., which was consistent with a covalent phosphate structure. Removal of the solvent yielded a glass which showed an infrared spectrum consistent with structure IX.

Reaction of Phosphonitrilic Chloride Tetramer with Catechol and Triethylamine.—A solution of catechol (26.4 g., 0.24 mole) and triethylamine (48.48 g., 0.48 mole) in tetrahydrofuran (200 ml.) was added dropwise to a stirred solution of phosphonitrilic chloride tetramer (27.84 g., 0.06 mole) in tetrahydrofuran (1000 ml.). A white mist of triethylamine hydrochloride formed immediately above the reaction mixture, which was stirred at 25° for 48 hr. The white precipitate was then filtered off, washed with tetrahydrofuran, and dried. Treatment with water removed triethylamine hydrochloride (66.3 g.) from the solid. The residue was subjected to a prolonged extraction with boiling toluene, but no soluble material was isolated. An infrared spectrum of the residue showed it to be VII (13.7 g.). The original tetrahydrofuran filtrate was evaporated to dryness, but subsequent extractions of the residue (28 g.) with boiling benzene and boiling toluene served only to render the material insoluble in all solvents. Infrared spectra of this material indicated that it was a partially substituted, cross-linked polymer. *Anal.* Found: C, 36.29; H, 6.10; N, 9.42; P, 13.57; Cl, 8.37.

Reaction of Phosphonitrilic Chloride Polymer with Catechol and Triethylamine. A. Preparation of (NPCl₂)_n Polymer.—Phosphonitrilic chloride trimer (I) was heated in an evacuated, thick-walled glass tube for 5 hr. at 300° in the absence of a catalyst, or for 30 hr. at 200° in the presence of 1% benzoic acid. The rubbery product was then extracted with toluene to remove unchanged starting material and was subdivided into small particles prior to reaction.

B. Reaction of Polymer.—A solution of triethylamine (175 g.) and catechol (95 g.) in tetrahydrofuran was added dropwise to a stirred suspension of phosphonitrilic chloride elastomer (100 g., swelled with 200 g. of toluene) in tetrahydrofuran (1 l.). The mixture was stirred at 25° for 7 days and the solid was filtered off, washed with toluene and tetrahydrofuran, and dried. The filtrate was evaporated to leave a brown oil (9 g.). The solid obtained by filtration (425 g.) was washed with a large excess of water and with methanol (2 l.) and was dried (132 g.). An infrared spectrum of this product was identical with that of VII.

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Electron Exchange Kinetics of the NO₃ Free Radical in Solution¹

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The NO₃ free radical can be generated photochemically in aqueous 6 *M* nitric acid by the primary electron-exchange reaction, Ce^{IV}NO₃⁻ + *hν* $\xrightarrow{I_a}$ Ce(III) + NO₃. Possible secondary reactions between NO₃ and added solutes are found to be in competition with the fast spontaneous bimolecular electron back-exchange process, NO₃ + Ce(III) $\xrightarrow{k_2}$ Ce^{IV}NO₃⁻. By means of an improved flash kinetic method which features a simplified photolysis lamp design and a new ignitron firing technique, we have measured *k*₂ = (1.70 ± 0.04) × 10⁶ M⁻¹ sec.⁻¹ at 23° with good precision. The back-exchange process is only slightly temperature dependent, with an apparent activation energy estimated to be approximately 1.0 ± 0.2 kcal./mole over the interval from 23 to 50°. An interpretation of these results and their role in explaining the slow decomposition of ceric nitrate salts in nitric acid solution is discussed.

Introduction

In an earlier note³ we have shown that the NO₃ free radical can be generated in aqueous media at room

temperature by the photolysis of ceric ammonium nitrate solutions. In contrast to the earlier methods of preparation, which are of value for studying the properties of NO₃ in either gas phase^{4,5} or frozen matrix,⁶ this photolysis technique represents not only

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