Decomposition of Diphosphine.—If $P_2H_3{}^+$ is not formed by the process given in eq. 2, then it is formed by simple ionization of the P_2H_3 radical (eq. 3). Therefore this radical could well be an intermediate in the thermal decomposition of diphosphine. Such a conclusion is not unreasonable, for the N_2H_3 radical has been postulated in mechanisms for the decomposition of hydra-zine.[18,19] If P_2H_3 is an intermediate, as suggested by our study, the convinctions of Evers and Street[2] concerning the active species in the room temperature decomposition of diphosphine may have to be revised.

(18) J. C. Elgin and H. S. Taylor, *J. Am. Chem. Soc.*, **51**, 2059 (1929).

(19) C. H. Bamford, *Trans. Faraday Soc.*, **35**, 1239 (1939).

Positional and *cis-trans* Isomeric Dimethylaminotriphosphonitriles. The Use of H¹ Nuclear Magnetic Resonance in Configurational Analysis

BY C. T. FORD, F. E. DICKSON, AND I. I. BEZMAN

Through aminolysis with dimethylamine, arylation with benzene or xylene in the presence of aluminum chloride, and a combination of both, a series of derivatives of trimeric phosphonitrilic chloride has been made. H¹ nuclear magnetic resonance spectra were obtained for these compounds and used to determine both their positional and *cis-trans* configurations. The structural analysis is based on consideration of the number of chemical shifts and the values of the coupling constants.

Introduction

Although complete substitution of the halogen atoms on the lower cyclic phosphonitrilic chlorides, $(NPCl_2)_{3,4}$, has received considerable study in the past several years,[1-3] it is only quite recently that attention has been focused on progressive replacement of halogens with elucidation of the positions at which such replacement occurs.[4-9] Trimeric phosphonitrilic chloride is an essentially planar ring,[10,11] with the chlorine atoms lying above and below the plane of the ring. Compounds such as $P_3N_3A_2B_4$, $P_3N_3A_3B_3$, and $P_3N_3A_2B_2C_2$ can, therefore, be formed as positional and *cis-trans* isomers.

Becke-Goehring and co-workers[4,5] found that treatment of $(NPCl_2)_3$ with strong nucleophiles such as methyl- and dimethylamine in amounts less than required for full replacement of chlorine gave di- and trisubstituted products in which each amino group was attached to a separate phosphorus atom. This was an important and somewhat surprising finding because it had been generally assumed that replacement reactions to give $P_3N_3A_4B_2$ compounds resulted in geminal substitution of B for A. This assumption was based almost entirely on the fact that treatment of

$(NPCl_2)_3$ with C_6H_6 in the presence of $AlCl_3$ gave $P_3N_3Cl_4(C_6H_5)_2$ with the phenyls both attached to the same phosphorus.[12] Recently we have shown that even Friedel–Crafts phenylation can give nongeminal substitution.[13]

Subsequent to Becke-Goehring's report there have been several publications on the reactions of $(NPCl_2)_3$ with restricted amounts of amines to give $P_3N_3Cl_4A_2$, $P_3N_3Cl_3A_3$, and $P_3N_3Cl_2A_4$ derivatives (A representing an amino group). In several cases two compounds of the same composition but differing melting point were obtained. Disregarding the possibility of boat and chair configurations, these represent positional and/or *cis-trans* isomers. A compilation of such compounds is given in a recent review.[3]

Even more clear-cut evidence for *cis-trans* isomers was found for the lower cyclic phenylchlorophosphonitriles, $[(C_6H_5)(Cl)PN]_{3,4}$, obtained by the action of NH_4Cl on $(C_6H_5)PCl_4$. Two trimeric[14,15] species and three tetrameric[15] species have been reported. However, despite the isolation of a fair number of isomers of aminochloro- and phenylchlorophosphonitriles, there are only two reports in which *cis-trans* configuration has been indicated. Our own report[13] is one; the other is by Moeller and Nannelli[16] and reports identification of the *cis* and *trans* forms for each of two isomers of $P_3N_3(C_6H_5)_3(n\text{-}C_3H_7NH)_3$ and $P_3N_3(C_6H_5)_3$-$(n\text{-}C_4H_9NH)_3$. In both cases assignment was based on proton magnetic resonance data. Recently,[17] Moeller

(1) N. L. Paddock and H. T. Searle, *Advan. Inorg. Chem. Radiochem.*, **1**, 348 (1959).

(2) C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 275 (1962).

(3) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).

(4) M. Becke-Goehring and K. John, *Angew. Chem.*, **70**, 657 (1958).

(5) M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. allgem. Chem.*, **302**, 103 (1959).

(6) L. F. Audrieth, *Record Chem. Progr.*, **20**, 57 (1959).

(7) W. E. Bull, Ph.D. Thesis, University of Illinois, 1957.

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(9) Y. Kobayashi, L. A. Chasin, and L. B. Clapp, *Inorg. Chem.*, **2**, 212 (1963).

(10) A. Wilson and D. F. Carroll, *Chem. Ind.* (London), 1558 (1958).

(11) F. Pompa and A. Ripamonti, *Ricerca Sci.*, **29**, 1516 (1959).

(12) H. Bode and H. Bach, *Ber.*, **75B**, 215 (1942).

(13) I. I. Bezman and C. T. Ford, *Chem. Ind.* (London), 163 (1963).

(14) F. S. Humiec and I. I. Bezman, *J. Am. Chem. Soc.*, **83**, 2210 (1961).

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

(16) T. Moeller and P. Nannelli, *Inorg. Chem.*, **1**, 721 (1962).

(17) P. Nannelli and T. Moeller, *ibid.*, **2**, 896 (1963).

has reported similar findings for [(C₆H₅)(Br)PN]₃ based on P³¹ resonance measurements.

This paper is a continuation of our previous report and involves the synthesis of certain aminochloro- and arylaminochlorotriphosphonitriles. It will be demonstrated that proton magnetic resonance measurements are particularly useful in assignment of both positional and *cis–trans* configurations to cyclic trimeric phosphonitriles of the type $P_3N_3A_x[N(CH_3)_2]_{6-x}$, where A represents chlorine and/or aryl groups. The specific structures are shown to be related both to the magnitude of the coupling constants and the number of chemical shifts observed in the p.m.r. spectra.

Experimental

Using (NPCl₂)₃ as a starting material and carrying out aminolyses with dimethylamine, arylation with benzene or xylene in the presence of AlCl₃, and a combination of both, various derivatives were made as shown in Charts I–III. The specific configurations as shown for the compounds capable of existing in isomeric forms are based on proton magnetic resonance spectra and these will be discussed separately.

Aminolyses were carried out by two procedures. Method A involved treatment of an ether solution of the phosphonitrile with an aqueous amine solution in a pressure flask. In method B, the anhydrous gaseous amine was passed into a chilled ether solution of the phosphonitrile. The procedures are described below; variations are noted in the discussions of specific syntheses.

Method A.—A solution of 0.04 mole of the phosphonitrile in 80 ml. of (C₂H₅)₂O was placed in a pressure flask. To this was added a 25% aqueous solution of (CH₃)₂NH. The flask was stoppered and shaken for 5 min. The reactions were generally rapid and exothermic. After phase separation, the organic phase was dried over calcium sulfate, filtered, and evaporated to dryness. In all cases, the products obtained were purified by repeated recrystallizations from petroleum ether.

Method B.—A solution of 0.03 mole of the phosphonitrile in 200 ml. of (C₂H₅)₂O was cooled in an ice bath and saturated with (CH₃)₂NH while being stirred constantly. This mixture was brought slowly to reflux and held there for 4 hr. Amine addition was continued during the entire operation, which lasted about 8 hr. At the end of the reaction, excess amine was removed by purging with N₂. By-product (CH₃)₂NH·HCl was removed by filtering the warm solution. The filtrate was evaporated to dryness and the final products purified by repeated recrystallizations from petroleum ether.

Method C. Friedel–Crafts Arylation.—A solution of 0.03 mole of the phosphonitrile in 120 ml. of C₆H₆ was added to anhydrous AlCl₃ in 80 ml. of C₆H₆. The mixture was refluxed for 3 days, cooled, and treated slowly with H₂O until HCl evolution ceased. The C₆H₆ layer was washed twice with H₂O, dried over calcium sulfate, and filtered, and the filtrate was evaporated to dryness leaving an oily material. The products were obtained by chilling a petroleum ether solution of the oil for a few days and purified by repeated recrystallizations from petroleum ether.

Benzene, diethyl ether, and petroleum ether (b.p. 30–60°) were dried over freshly extruded sodium wire. Trimeric phosphonitrilic chloride, (NPCl₂)₃, purchased commercially, was recrystallized to constant melting point from petroleum ether before use.

Aminochlorotriphosphonitriles. $P_3N_3Cl_4[N(CH_3)_2]_2$ (II).—Using method A and a 1:4.3 (NPCl₂)₃:(CH₃)₂NH mole ratio, II was made repeatedly in approximately 60% yield and melting at 106° (lit.⁴ m.p. 103°). Becke-Goehring⁵ and Ray and Shaw⁸ have indicated that in II the –N(CH₃)₂ groups are on separate phosphorus atoms. We not only confirm this, but offer evidence that II exists in a *cis* configuration. *Anal.* Calcd. for C₄H₁₂Cl₄N₅P₃: C, 13.16; H, 3.31; Cl, 38.86; N, 19.19; P, 25.47. Found: C, 13.60; H, 3.47; Cl, 38.67; N, 19.51; P, 25.64.

$P_3N_3Cl_3[N(CH_3)_2]_3$ (III).—The use of method A with a 1:6.3 (NPCl₂)₃:(CH₃)₂NH mole ratio gave the trisubstituted product (III) in 27% yield melting at 107°, in agreement with literature values of 107°⁴ and 104.5–105.5°.⁸ A second species of P₃N₃Cl₃-[N(CH₃)₂]₃ (IV), melting at 149°, was obtained in 9% yield by method B and a large excess of (CH₃)₂NH. Both III and IV have each amino group attached to a separate phosphorus atom. Compound III has a *trans* configuration and IV has a *cis* configuration. *Anal.* Calcd. for C₆H₁₈Cl₃N₆P₃: C, 19.29; H, 4.86; Cl, 28.48; N, 22.50; P, 24.88. Found (compound III, m.p. 107°): C, 19.18; H, 4.61; Cl, 28.56; N, 22.85; P, 24.86; (compound IV, m.p. 149°): C, 19.26; H, 5.02; Cl, 28.32; N, 22.60; P, 25.38.

$P_3N_3Cl_2[N(CH_3)_2]_4$ (V).—From the same reaction which gave IV, compound V was obtained in 70% yield, melting at 100°. By repeated recrystallization from petroleum ether, as many as 10–12 times, compounds IV and V were separated cleanly, with IV being obtained first. Ray and Shaw⁸ report two species of V melting at 103.5–104 and 101–101.5° and a mixture melting point of 71–87°. Our data show that in V two amino groups are attached to a single phosphorus and the other two are attached to separate phosphorus atoms and are *cis* to each other. It is interesting to note that no trace of P₃N₃[N(CH₃)₂]₆ was found even though a large excess of amine was used. *Anal.* Calcd. for C₈H₂₄Cl₂N₇P₃: C, 25.14; H, 6.33; Cl, 18.56; N, 25.61; P, 24.32. Found: C, 25.43; H, 6.66; Cl, 18.24; N, 25.80; P, 24.41.

$P_3N_3(NH_2)_2[N(CH_3)_2]_4$ (VII).—P₃N₃Cl₄(NH₂)₂ (VI), prepared by treating (NPCl₂)₃ with NH₃(g) according to de Fiquelmont,¹⁸ was treated as in method B with a large excess of (CH₃)₂-NH. Repeated recrystallization from (C₂H₅)₂O gave VII in 75% yield, melting at 157° (lit.⁴ m.p. 144°). [Although some samples of VII were found to melt sharply at 145°, a few more recrystallizations gave material which melted at 157°, with some sign of change at 145°. A mixture melting point of the two samples always was sharp at 145°.] Two –N(CH₃)₂ groups are attached to a single phosphorus and the other two are attached to separate phosphorus atoms and are *trans* to each other. This, then, implies that in VI, the –NH₂ groups are on separate phosphorus atoms and are *trans* to each other. *Anal.* Calcd. for C₈H₂₈N₉P₃: C, 27.98; H, 8.22; N, 36.72; P, 27.07. Found: C, 27.82; H, 8.30; Cl, 0; N, 36.56; P, 26.78.

Arylaminotriphosphonitriles.—Phenylation of (NPCl₂)₃ followed by aminolysis and the same reactions carried out in reverse order have given isomeric species indicating that the course of phenylation is influenced by the specific ring substituents.

$P_3N_3Cl_4(C_6H_5)_2$ (VIII).—This was made by method C with a 1:4 mole ratio of (NPCl₂)₃:AlCl₃. Compound VIII was obtained in 45% yield, melting at 97° (lit.¹²,¹⁹ m.p. 95°). Degradative hydrolysis gave diphenylphosphinic acid, proving the geminal configuration of the phenyl groups.

$P_3N_3Cl_2(C_6H_5)_2[N(CH_3)_2]_2$ (IX and IXa).—Using method A with a 1:4.3 mole ratio of VIII:(CH₃)₂NH, the diamino derivatives, IX and IXa, were prepared in 27% yield, melting at 146° (lit.²⁰ m.p. 143–144°). This proved to be a mixture of *cis* and *trans* isomers with the –N(CH₃)₂ groups on separate phosphorus atoms. These compounds could not be separated even after intensive purification. *Anal.* Calcd. for C₁₆H₂₂Cl₂N₅P₃: C, 42.87; H, 4.95; Cl, 15.82; N, 15.63; P, 20.73. Found: C, 43.42; H, 4.93; Cl, 15.33; N, 16.74; P, 19.37.

$P_3N_3(C_6H_5)_2[N(CH_3)_2]_4$ (X).—Substituting C₆H₆ with its higher reflux temperature for (C₂H₅)₂O in method B and treating VIII with an excess of (CH₃)₂NH gave X in 99% yield, melting at 121° (lit.³,¹⁹,²⁰ m.p. 120°). Hydrolysis again gave diphenylphosphinic acid, showing the retention of the geminal configuration of the phenyl groups. *Anal.* Calcd. for C₂₀H₃₄N₇P₃: C, 51.60; H, 7.37; N, 21.07; P, 19.96. Found: C, 51.44; H, 7.42; N, 21.31; P, 20.38.

(18) A. M. de Fiquelmont, *Ann. Chim.*, **12**, 169 (1939).

(19) M. Becke-Goehring and K. John, *Z. anorg. allgem. Chem.*, **304**, 126 (1960).

(20) K. Hills and R. A. Shaw, unpublished results, quoted in ref. 4.

CHART I

AMINOCHLOROTRIPHOSPHONITRILES
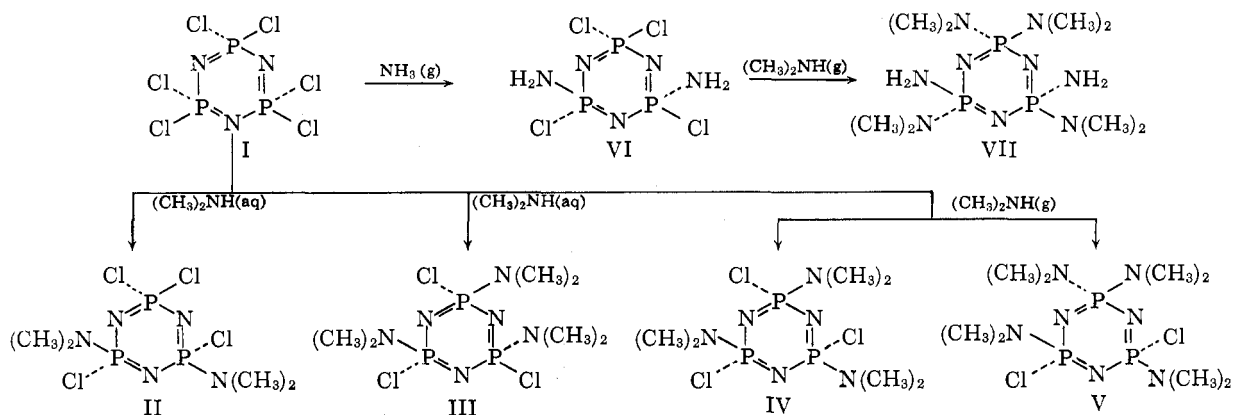
CHART II

DERIVATIVES OBTAINED BY AMINOLYSIS OF DIPHENYLTETRACHLOROTRIPHOSPHONITRILE

obtained as mixture
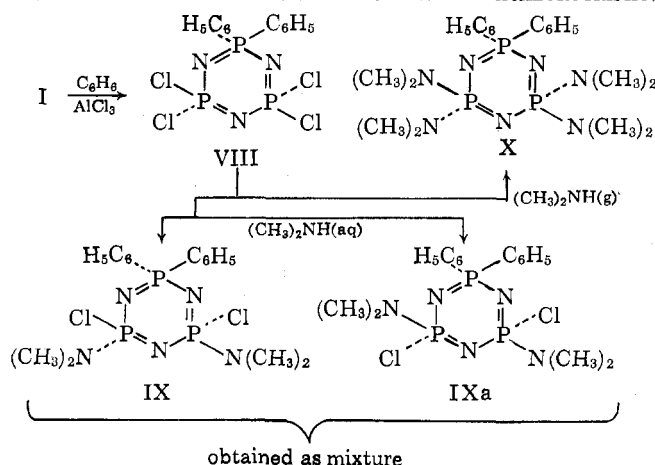
CHART III

ARYLATION AND AMINOLYSIS DERIVATIVES OF BIS-N-DIMETHYLAMINOTETRACHLOROTRIPHOSPHONITRILE
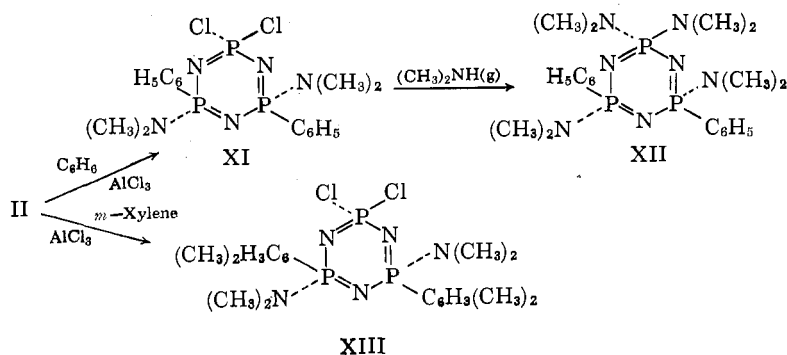
$P_3N_3Cl_2(C_6H_5)_2[N(CH_3)_2]_2$ (**XI**).—Treatment of II by method C with a 1:4 mole ratio of II:AlCl₃ gave XI in 37% yield, melting at 99°. The nongeminal position of the phenyl groups was established by hydrolytic degradation to phenylphosphonic acid. The –N(CH₃)₂ groups are each on a phosphorus atom which carries a phenyl group. Further, the –N(CH₃)₂ groups are *cis* to each other. *Anal.* Calcd. for C₁₆H₂₂Cl₂N₅P₃: C, 42.87; H, 4.95; Cl, 15.82; N, 15.63; P, 20.73. Found: C, 42.87; H, 5.09; Cl, 15.82; N, 15.75; P, 20.98.

$P_3N_3(C_6H_5)_2[N(CH_3)_2]_4$ (**XII**).—Again substituting C₆H₆ for (C₂H₅)₂O in method B and treating XI with an excess of (CH₃)₂NH gave XII in 38% yield, melting at 83–86°. Two –N(CH₃)₂ groups are attached to the same phosphorus and the other two to separate phosphorus atoms and are *cis* to each other. *Anal.*

Calcd. for C₂₀H₃₄N₇P₃: C, 51.60; H, 7.37; N, 21.07; P, 19.96. Found: C, 51.29; H, 7.15; Cl, 0; N, 21.58; P, 20.21.

Compounds XII and XI are isomers of X and IX, respectively. Configurations as shown were reported previously.[13]

$P_3N_3Cl_2[C_6H_3(CH_3)_2]_2[N(CH_3)_2]_2$ (**XIII**).—This compound was prepared by merely stirring a 1:4 mole ratio of II:AlCl₃ in *m*-xylene for a few hours without heating and processing as in method C. Crystallization took place only after chilling a solution of the oily product in petroleum ether for 6 months. Compound XIII was obtained in 13% yield, melting at 122°. Its structure is similar to XI, each –N(CH₃)₂ group being on a phosphorus carrying a xylyl group and *cis* to each other. *Anal.* Calcd. for C₂₀H₃₀Cl₂N₅P₃: C, 47.64; H, 6.00; Cl, 14.05; N

13.88.; P, 18.42. Found: C, 48.66; H, 6.29; Cl, 13.95; N, 14.00; P, 18.09.

The synthesis of compound XIII indicates that the directing influence of the ring substituents is general for Friedel–Crafts arylation.

Table I gives the principal characterizing infrared absorption peaks for the various compounds.

TABLE I
Principal Characteristic Infrared Absorption Peaks

Compound	Formula	$P{=}N$ stretch[a]	$P{-}C_6H_5$[b]
II	$P_3N_3Cl_4[N(CH_3)_2]_2$	1215 (s), 1180 (m)	
III	$P_3N_3Cl_3[N(CH_3)_2]_3$	1210 (s), 1180 (m)	
IV	$P_3N_3Cl_3[N(CH_3)_2]_3$	1210 (s), 1180 (m)	
V	$P_3N_3Cl_2[N(CH_3)_2]_4$	1225 (s), 1200 (s)	
VII	$P_3N_3(NH_2)_2[N(CH_3)_2]_4$	1185 (s)	
VIII	$P_3N_3Cl_4(C_6H_5)_2$	1220 (s), 1190 (s)	1440
IX, IXa	$P_3N_3Cl_2(C_6H_5)_2[N(CH_3)_2]_2$	1210 (s), 1180 (s)	1440
X	$P_3N_3(C_6H_5)_2[N(CH_3)_2]_4$	1190 (s), 1170 (s)	1440
XI	$P_3N_3Cl_2(C_6H_5)_2[N(CH_3)_2]_2$	1230 (s), 1180 (s)	1440
XII	$P_3N_3(C_6H_5)_2[N(CH_3)_2]_4$	1200 (s), 1170 (s)	1440
XIII	$P_3N_3Cl_2[C_6H_5(CH_3)_2]_2[N(CH_3)_2]_2$	1210 (s), 1170 (s)	

[a] L. W. Daasch, *J. Am. Chem. Soc.*, **76**, 3403 (1954). [b] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

observed chemical shift, 2.60 p.p.m., is consistent with previously published values for protons of this type.[8,23]

The observed number of doublets, values for the apparent coupling constants, J'_{PH}, and for the average shifts (δ) for each compound studied are given in Table II. Each doublet is taken to represent a specific $-N(CH_3)_2$ group or pair of $-N(CH_3)_2$ groups in a particular chemical environment in the molecule. By environment is meant the nuclei in close proximity to the $-N(CH_3)_2$ group, specifically the groups attached to the other phosphorus atoms in the ring. The J'_{PH} values are significant in that they are dependent on the nature of the second substituent bonded directly to the phosphorus carrying the $-N(CH_3)_2$. In Table II it can be seen that a $\equiv P(Cl)[N(CH_3)_2]$ grouping gives J'_{PH} of about 17.5, a $\equiv P(aryl)[N(CH_3)_2]$ gives about 12.8, and $\equiv P[N(CH_3)_2]_2$ gives about 11.8 c.p.s. Thus the coupling constants indicate the groups attached to the phosphorus atoms and

TABLE II
Proton Magnetic Resonance Data

			J'_{PH} for $\equiv P(X)[N(CH_3)_2]$, c.p.s.			Chemical
No.	Formula	No. of doublets	X = Cl	X = N(CH₃)₂	X = aryl	shift (av.) δ, p.p.m.
II	$P_3N_3Cl_4[N(CH_3)_2]_2$	1	17.8			2.72
III	$P_3N_3Cl_3[N(CH_3)_2]_3$	2	17.6 (2)			2.70
IV	$P_3N_3Cl_3[N(CH_3)_2]_3$	1	17.7			2.67
V	$P_3N_3Cl_2[N(CH_3)_2]_4$	3	16.9	11.7 (2)		2.65
VII	$P_3N_3(NH_2)_2[N(CH_3)_2]_4$	2		11.7; 11.1[a]		2.59
IX, IXa	$P_3N_3Cl_2(C_6H_5)_2[N(CH_3)_2]_2$	2	17.1 (2)			2.69
X	$P_3N_3(C_6H_5)_2[N(CH_3)_2]_4$	1		11.6		2.48
XI	$P_3N_3Cl_2(C_6H_5)_2[N(CH_3)_2]_2$	1			13.4	2.63
XII	$P_3N_3(C_6H_5)_2[N(CH_3)_2]_4$	3		11.9 (2)	12.3	2.46
XIII	$P_3N_3Cl_2[C_6H_5(CH_3)_2]_2[N(CH_3)_2]_2$	1			13.5	2.52

[a] These J'_{PH} values are so close that it is not possible to state which is for $\equiv P(NH_2)[N(CH_3)_2]$ and which is for $\equiv P[N(CH_3)_2]_2$.

Proton Magnetic Resonance

Proton magnetic resonance spectra were obtained for 20% solutions in $CHCl_3$ at a 50 c.p.s. sweep width on a Varian Model A-60 spectrometer. Chemical shift measurements were made from tetramethylsilane as an internal reference. Figure 1 is the spectrum for compound II and is typical of the entire group. The N-methyl proton resonance gives a doublet with additional broadened structure between the major peaks. This spectrum is consistent with one proton environment coupled to the nearest phosphorus atom by an apparent coupling constant, J'_{PH}, ranging from 10 to 17 c.p.s.[21] (Table II). Because these absorptions result from a multiplicity of lines in the spectrum, deriving primarily from neighboring and long-range phosphorus coupling, the J'_{PH} value is related to but not the same as the actual P–H coupling constant. The additional splitting and broadening are attributed to longer range coupling to the phosphorus atoms further removed and to quadrupole broadening by the adjacent nitrogen atom.[22] The average value of the

the number of doublets indicate different sets of environments. These data have clearly and consistently delineated both positional and *cis–trans* isomerism.

To illustrate the derivation of structure from the resonance spectra, reference is made to Table II. For compound IV, $P_3N_3Cl_3[N(CH_3)_2]_3$, the spectrum shows only one doublet, indicating a single environment for the protons. This immediately indicates that each $-N(CH_3)_2$ group is located on a separate phosphorus atom, that each phosphorus atom has the structure $\equiv P(Cl)[N(CH_3)_2]$, and that the observed coupling constant, $J'_{PH} = 17.7$ c.p.s., is characteristic of this grouping. Further, the single proton environment also indicates that IV has a *cis* configuration. The *trans* form would have given two proton environments, *i.e.*, two doublets.

Compound III is an isomer of IV. For III, however, two doublets are observed, each with $J'_{PH} = 17.6$ c.p.s. The J' value is in accord with that found for IV and indicates that in III, the $-N(CH_3)_2$ groups are each located on a separate phosphorus atom. The presence of two doublets confirms that III is the *trans* isomer.

(21) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p. 351.

(22) R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, **2**, 377 (1963).

(23) Varian Spectra Catalog, Varian Associates, Palo Alto, Calif., Spectrum Number 145, hexamethylphosphoramide, $P[N(CH_3)_2]_3$.
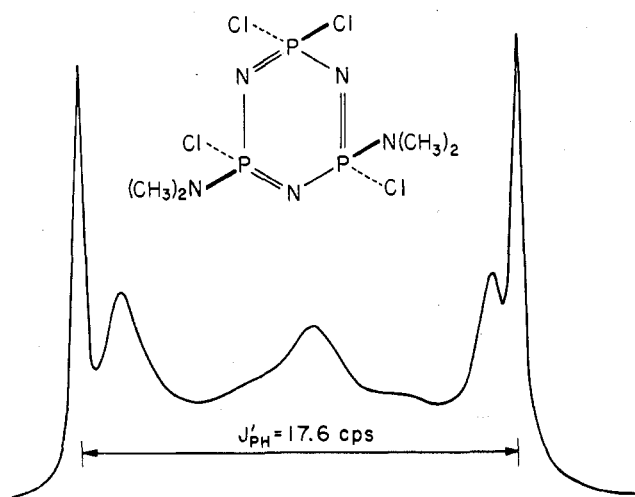
Fig. 1.—H^1 n.m.r. spectrum of compound II.

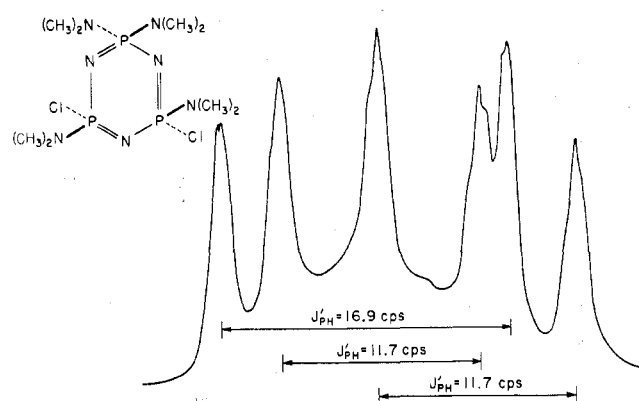Fig. 2.—H^1 n.m.r. spectrum of compound V.

The spectrum of compound V, shown as Fig. 2 and included as an example of the most complex type of spectrum, consists of three doublets; for one J'_{PH} = 16.9 and for the others J'_{PH} = 11.7 c.p.s. The 16.9 value is in line with that for ≡P(Cl)[N(CH$_3$)$_2$] based on the data for compounds III and IV and indicates the presence of at least one such grouping. Because V contains four –N(CH$_3$)$_2$ groups, there must be two ≡P(Cl)[N(CH$_3$)$_2$] structures, with the other two –N(CH$_3$)$_2$ groups attached to the third phosphorus. The 11.7 value is indicative of the ≡P[N(CH$_3$)$_2$]$_2$ grouping and the fact that two doublets are found with this value shows that the ≡P(Cl)[N(CH$_3$)$_2$] groups are in a *cis* configuration; the *trans* configuration would give only one doublet with J'_{PH} = 11.7 c.p.s.

For compound II, the spectrum, per se, is not sufficient to give the complete configuration. The presence of only one doublet (the only possibility) with J'_{PH} = 17.8 c.p.s. shows that both –N(CH$_3$)$_2$ groups are on separate phosphorus atoms. Differentiation between *cis* and *trans* forms is not possible.

Compound VII gives two doublets indicating the presence of ≡P[N(CH$_3$)$_2$]$_2$ and ≡P(NH$_2$)[N(CH$_3$)$_2$], with two of the latter in a *trans* arrangement. The J'_{PH} values are 11.7 and 11.1 c.p.s. That the J'_{PH} values for ≡P(NH$_2$)[N(CH$_3$)$_2$] and ≡P[N(CH$_3$)$_2$]$_2$ are similar is related to the similarity of electronegativity of the –NH$_2$ and –N(CH$_3$)$_2$ groups. The *trans* configuration of VII indicates that compound VI, P$_3$N$_3$Cl$_4$(NH$_2$)$_2$, from which VII was made has two ≡P(Cl)NH$_2$ groups in a *trans* configuration.

Turning to the aryl derivatives, compound X, with one doublet, shows all protons are equivalent and are arranged in ≡P[N(CH$_3$)$_2$]$_2$ groups. The J'_{PH} value of 11.6 c.p.s. is in accord with that found for the same grouping in compounds V and VII.

The isomer of X, compound XII, has a distinctly different spectrum showing three doublets, one with J'_{PH} = 12.3 and two with J'_{PH} = 11.9 c.p.s. The situation is similar to that found for V and the only structure which can give this spectrum is one in which there is

one ≡P[N(CH$_3$)$_2$]$_2$ group and two ≡P(C$_6$H$_5$)[N(CH$_3$)$_2$] groups, the latter being in a *cis* configuration.

Compound XI, from which XII was made as shown in Chart III, should also have ≡P(C$_6$H$_5$)[N(CH$_3$)$_2$] groups in a *cis* configuration. For it, the spectrum should contain only one doublet with a J'_{PH} value typical of ≡P(C$_6$H$_5$)[N(CH$_3$)$_2$]. The observed spectrum does, indeed, show only one doublet with J'_{PH} = 13.4 c.p.s., substantially different from the J'_{PH} values for ≡P(Cl)[N(CH$_3$)$_2$] and ≡P[N(CH$_3$)$_2$]$_2$, and taken as characteristic of the ≡P(C$_6$H$_5$)[N(CH$_3$)$_2$] grouping. Having established that the –N(CH$_3$)$_2$ groups in XII and, de facto, in XI are in a *cis* configuration, it is now possible to state that in II, the starting compound for XI, the –N(CH$_3$)$_2$ groups are also in a *cis* configuration.

Compounds IX and IXa, P$_3$N$_3$Cl$_2$(C$_6$H$_5$)$_2$[N(CH$_3$)$_2$]$_2$, represent an isomeric mixture which could not be separated despite intensive efforts and in which each species is different from compound XI. The spectrum clearly indicates that a mixture exists. Two doublets are present, each with J'_{PH} = 17.1 c.p.s., showing that the ≡P(Cl)[N(CH$_3$)$_2$] grouping is the only one present, but must exist in two configurations, and further indicating that these are *cis* and *trans* isomers.

Compound XIII is similar to XI as indicated by the spectrum which shows only one doublet, J'_{PH} = 13.5 c.p.s. Here the ≡P[C$_6$H$_3$(CH$_3$)$_2$][N(CH$_3$)$_2$] group is present and the –N(CH$_3$)$_2$ groups are *cis* to each other.

Discussion

Ray and Shaw[8] have shown that, for a series of aminochlorotriphosphonitriles, P$_3$N$_3$Cl$_x$[N(CH$_3$)$_2$]$_{6-x}$, where x is 0, 2, 3, 4, and 5, the value of the chemical shift obtained from p.m.r. measurements is indicative of the positions occupied by the –N(CH$_3$)$_2$ groups in the various compounds. However, they do not indicate, nor can chemical shift values, per se, indicate *cis* or *trans* configurations, although such isomers are possible in all compounds with the exception of P$_3$N$_3$[N(CH$_3$)$_2$]$_6$ and P$_3$N$_3$Cl$_5$[N(CH$_3$)$_2$]. Our procedure, based on high resolution measurements, gives information concerning both positional and *cis–trans* configurations.

With respect to the course of Friedel–Crafts aryla-

tion of aminochlorophosphonitriles such as compound II, it is evident that the basic $-N(CH_3)_2$ substituents are important in directing arylation. The free electron pair on the nitrogen atom probably is the position to which the Lewis acid, $AlCl_3$, is attracted most strongly. Although the PN ring nitrogens also have electron pairs, these are involved in the π-bonding system of the ring[24] and are less influential in attracting the $AlCl_3$.

The arylations require stoichiometric rather than catalytic amounts of $AlCl_3$. This is an indication that II has the properties of an acyl halide where the $AlCl_3$ is believed to complex first with the oxygen atom rather than the halogen with subsequent rearrangement to give the carbonium ion and $AlCl_4^-$.[25] Although we have made no study of mechanism, we believe that a comparable situation exists in the arylation of II using $AlCl_3$, *i.e.*, the $AlCl_3$ complex forms first with the nitrogen atom of the $-N(CH_3)_2$ group and rearrangement gives the phosphonium ion and $AlCl_4^-$ so that the chlorine replaced by the aryl group is that attached to the same phosphorus carrying the $-N(CH_3)_2$.

Although it would be interesting and important to find that nucleophilic substitution of chlorine in $(NPCl_2)_3$ follows specific paths, and the work of Becke-Goehring and of Shaw indicates some general pattern with respect to aminolysis reactions, it is necessary to employ caution in the interpretation of experimental findings.

The work described above does substantiate that of Becke-Goehring and Shaw in confirming that aminolysis of $(NPCl_2)_3$ with strong nucleophiles such as $(CH_3)_2NH$ or NH_3 does not occur geminally. However, we do not find a specific direction with respect to preferential formation of a *cis* or *trans* isomer. Indeed, our results indicate that $P_3N_3Cl_4[N(CH_3)_2]_2$ is formed in a *cis* configuration, while $P_3N_3Cl_4(NH_2)_2$ is *trans*. Further, $P_3N_3Cl_3[N(CH_3)_2]_3$ has been obtained both as *cis* and *trans* depending on experimental conditions, and compounds IX and IXa, $P_3N_3Cl_2(C_6H_5)_2[N(CH_3)_2]_2$, not only are *trans* and *cis*, respectively, but came from the same reaction.

Finally, it should be noted that in most syntheses, the yields were considerably below 100%. It may be that the compounds obtained were not necessarily the only ones formed. Rather they may be those most readily isolated and purified. For this reason generalizations concerning positions of attack on the phosphonitrile ring should be approached with prudence and caution.

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Rare Earth Compounds. I. Rare Earth Polysulfides[1a,1b]

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The polysulfides of Tb, Ho, and Er have been prepared for the first time. New information has been obtained for a number of rare earth polysulfides. A larger phase region with a more complex crystal structure has been shown to exist. Sulfur to metal atom ratios of 1.7 to 2.0 were found for the lightest rare earths and 1.7 to 1.8 for the heavier rare earths. As the atomic number of the metal component is increased, higher sulfur pressures at lower allowed temperatures are required to create the polysulfide phase.

Introduction

Flahaut, Picon, and co-workers have studied many of the rare earth polysulfides. They first prepared the sesquisulfides by reaction of the oxides with H_2S and then heated the sesquisulfides with excess sulfur to 600° to produce the polysulfides. In a summary article[2] the authors concluded that "polysulfides" are obtained, with the stoichiometry Ln_2S_4 and cubic crystal struc-

ture for the elements La through Nd and a stoichiometry close to $Ln_2S_{3.8}$, with a slight tetragonal distortion of the unit cell, for Eu, Gd, Dy, and Y. Sm exhibited both crystalline modifications. They could not prepare the polysulfide of Er (and do not report having worked on Ho or Tb). When syntheses of the polysulfides from the lighter rare earth sesquisulfides were performed employing insufficient sulfur, only starting product and cubic Ln_2S_4 forms were observed. These results led the investigators to conclude that the allowable range in sulfur content for the rare earth polysulfides must be very small.

In this work we continue to use the term "rare earth polysulfide" to describe this class of compounds