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FINAL SCIENTIFIC REPORT

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PHOSPHORUS-NITROGEN COMPOUNDS

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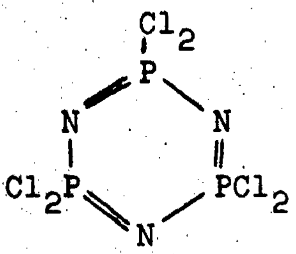
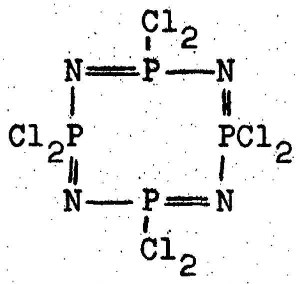
A. DERIVATIVES OF SIX MEMBERED AND EIGHT MEMBERED P-N RING COMPOUNDS:

The chemistry of P-N compounds is characterized by the existence of polymeric compounds. There are many ring compounds with relatively low molecular weight and there are also chain-molecules.

It is well known that there are P-N ring systems with six or eight members in the ring, e.g. I and II:



I

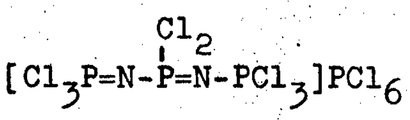


II

Both substances are formed by the reaction of PCl_5 with NH_4Cl[1]. Intermediates of this reaction are III and IV:

$[Cl_3P{=}N{-}PCl_3]PCl_6$

III



$[Cl_3P{=}N{-}\overset{Cl_2}{P}{=}N{-}PCl_3]PCl_6$

IV

Many useful products were prepared when starting with I or II. For instance insectizides[2].

P-N-chain V, which was also derived from PCl_5 and NH_4Cl, was used very often in research and industry as starting material for other useful products.

$$Cl_3P{=}N\{PCl_2{=}N\}_nPCl_2{=}NH$$

V

Thermally stable products were obtained by the reaction of polymeric $NPCl_2$ with metal oxydes, e.g. Na_2O, CaO, PbO, Bi_2O_3, Cu_2O, CuO or ZnO:

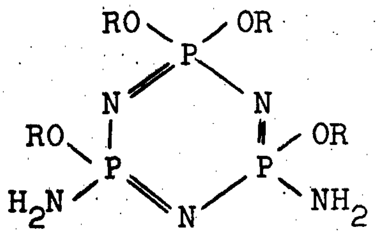
$$(NPCl_2)_n + n\ MO \xrightarrow[78\ at]{150-400^\circ} n\ MCl_2 + PON$$ 3)

VI

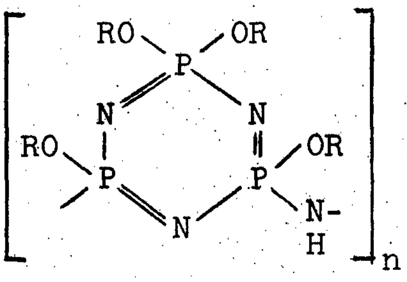
Even glass fibres may be protected when coated with $(PON)_x$.

If the Cl-atoms of I, II or V are replaced by OR groups, compounds are obtained which may be used for protection of fibres against ignition6).

Derivatives of I and II which are thermally stable are for instance VII and the compound which is formed when VII is heated, e.g. VIII4).



VII



VIII

$R = -CH_2-(CF_2)_2-CF_3$

$R = -CH_2-(CF_2)_3-CHF_2$

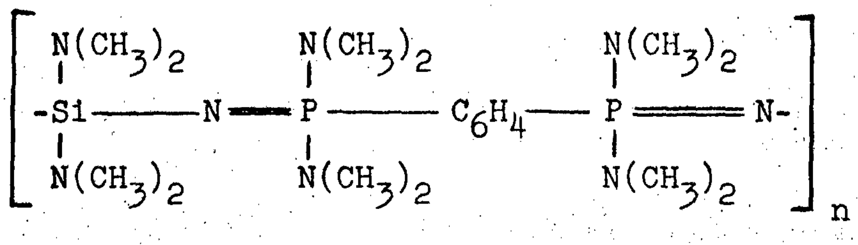
$R = -CH_2-CF_3$

$R = -CH_2-CF_2-CHF_2$

$R = -CH_2-CF_2-CF_3$

Many other derivatives of I and II with desired properties are known. A survey was given by G. Horn5). Here, this survey of recent literature may be mentioned without comments.

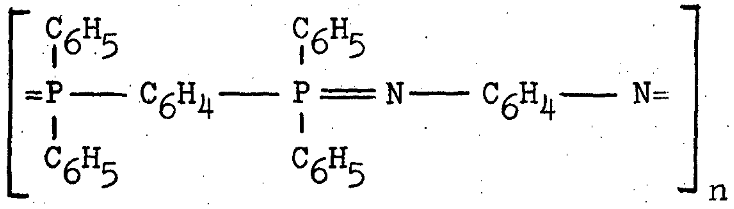
Another type of polymeric substances is IX7).



$$\left[\begin{array}{c}\overset{N(CH_3)_2}{\underset{N(CH_3)_2}{-Si}}\end{array}-N=\overset{N(CH_3)_2}{\underset{N(CH_3)_2}{P}}-C_6H_4-\overset{N(CH_3)_2}{\underset{N(CH_3)_2}{P}}=N-\right]_n$$

IX

Here, the benzene ring system is stabilizing the P, N and Si or Ge or Sn containing chain. Without the elements Si, Ge or Sn X was recommended8).



$$\left[=\overset{C_6H_5}{\underset{C_6H_5}{P}}-C_6H_4-\overset{C_6H_5}{\underset{C_6H_5}{P}}=N-C_6H_4-N=\right]_n$$

X

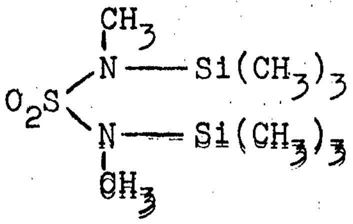
The ring systems of I or II may be polymerized to a phosphonitrilic caoutchouc. This may be obtained at 250-350°C without solvents. If no O_2 was present these polymerisation products have a molecular weight of 10^6. With O_2 further linkage occurs. Many catalytic effects were observed, which have influence in this reaction. A survey of such reactions will be given by M. Becke-Goehring and S. Pantel in a book which will be published by Springer-Verlag 1969.

The P-N polymers may be split off by hydrolysis. Therefore, one tried to substitute the Cl-atoms in this polymers by OR groups. Indeed, the esters are very useful30-43) for flame proofing or as coats which are not flammable44-69).

Glasses were also obtained with the formula $[NPF_2]_n$ or $[NPCl_2]_n$70).

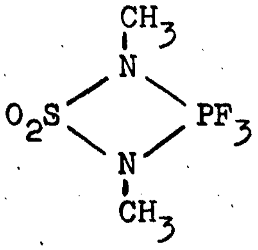
B. DERIVATIVES OF FOUR MEMBERED P-N RING COMPOUNDS:

PF_3Cl_2 reacts with N,N'-dimethylsulfamide, which was used as its bis trimethylsilyl derivative (XI),

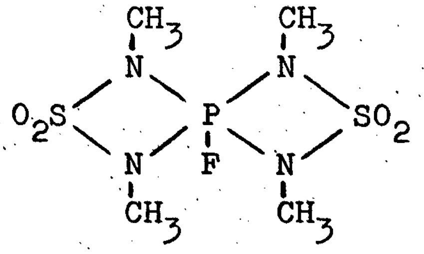


XI

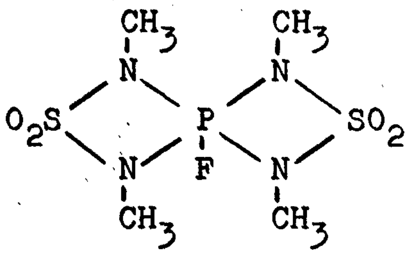
in the molecular ratio 1:1 to give the new four membered ring system XII. Further reaction of XII with XI and N,N'-bis(trimethylsilyl)-N,N'-dimethyurea yields XIII and XIV⁽⁹⁾. Compound XV is known since 1965⁽¹⁰⁾.



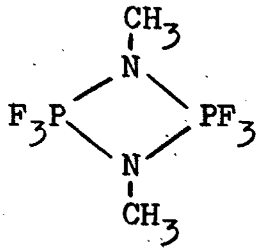
XII m.p. 54°C



XIII m.p. 182°C



XIV m.p. 118°C



XV m.p. -10.3°C

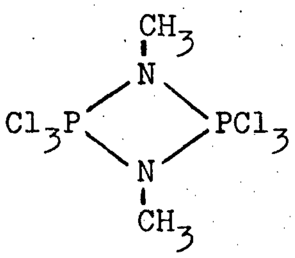
The nmr spectra are given in table 1.

Table 1

	^1H		^{19}F		^{31}P	
	δ_H	J_{HP}	δ_F	J_{PF}	δ_P	J_{PF}
XII	2.28 ppm	15.0 Hz D	77.8 ppm	968 Hz D	76.8 ppm D	968 Hz Q
XIII	2.44 ppm	16.0 Hz D	88.5 ppm	1035 Hz D	85.0 ppm	1030 Hz D
XIV	2.38 ppm D 2.44 ppm D	15.5 Hz 14.8 Hz	102.8 ppm	1038 Hz D	67.0 ppm	1035 Hz D
XV	2.48 ppm	14.5 Hz T	78.8 ppm	894 Hz D	71.6 ppm	

D = dublett, T = triplett, Q = quadruplett

An other substance was easier obtainable, substance XVI$^{11)}$.



XVI m.p. 178°C

XVI was obtained in very good yield by the reaction of PCl_5 with $[H_3NCH_3]Cl$. We prepared XVI also from N,N'-dimethylsulfamide, $CH_3\overset{H}{N}-SO_2-\overset{H}{N}CH_3$ and PCl_5. The phosphorus atoms are all chemically equivalent in this compound, since the ^{31}P-nuclear magnetic resonance spectrum of the material in bromoform solution has a single peak with a chemical shift of $+78.2 \cdot 10^{-6}$ (relative to a standard of 85 % phosphoric acid).

This markedly positive chemical shift indicates that the phosphorus is pentavalent, the comparable chemical shift of PCl_5 being $+80\cdot10^{-6}$.

Consequently, the assignment of this compound of structural formula XVI was reasonable. Also the proton magnetic resonance spectrum, investigated by Tripett[16], was in a agreement with this structure. The crystallography of XVI was examined by Hess and Forst[11]; the data of these authors are presented in Figures 1 and 2:

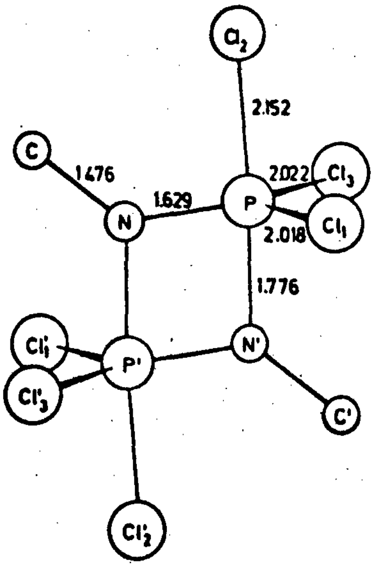


Fig. 1
Bond lengths of XVI

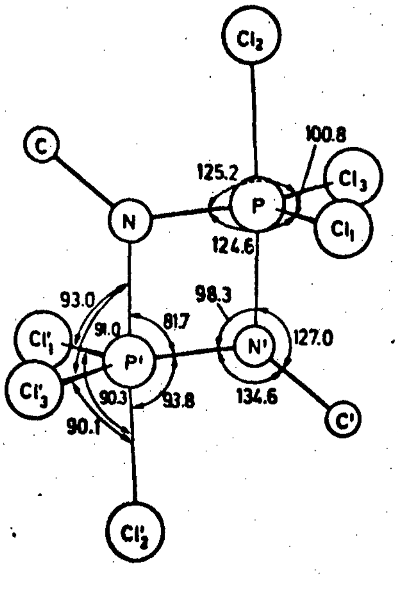
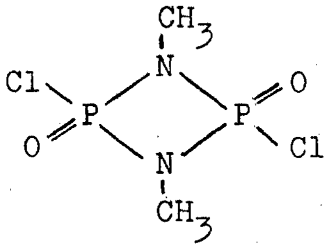


Fig. 2
Bond angles of XVI

Thus it was found that substitution reactions could be performed on phosphorus pentachloride, which yielded not only tetra-coordinated products but also penta-coordinated substances. Compound XVI melts at 178°C, showing that penta-coordinated phosphorus and this four membered ring possess a great deal of thermal stability. Nevertheless this material can readily undergo chemical reaction to form different compounds in which the phosphorus is tetra-coordinated. Compound XVI shows many reactions.

1. Compound XVI was reacted with sulphur dioxide[15)]. Substance XVIIIa could be isolated with an excellent yield. XVIIIa is a crystalline colorless material which is sensitive to moisture. In benzene solution only one ^{31}P-nuclear magnetic resonance signal is detected, having a chemical shift of $+5.3 \cdot 10^{-6}$. This indicates that compound XVIIIa has its phosphorus in a tetra-coordinated state, as shown below[17)]:



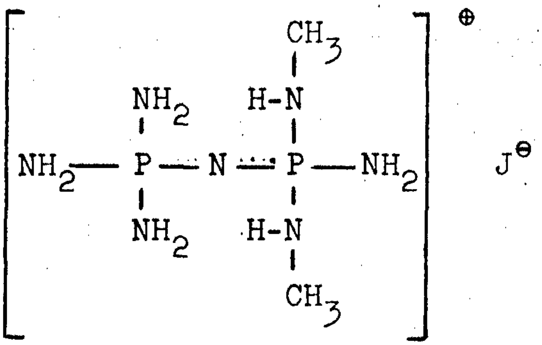
XVIIIa

2. Refluxing of a solution of chromiumhexacarbonyl and 2.2.2.4.4.4-hexachloro-N,N'-dimethyl-cyclo-diphosphazene (XVI) in benzene yields a light red compound of the empirical formula $[(OC)_4Cr(CH_3NPCl_3)_2]$. The substance is stable at room temperature. Thermal degradation at 350-450°C of this substance yields a polymer, whose structure seems to be similar to $(P_3N_5)_x$ because of its infrared spectrum. The polymer has the formula $(Cr_7P_5N_2)_x$[12)]. This polymer is not destroyed when heated up to 790°C.

Infrared spectrum:

$(P_3N_5)_x$:	1250	950	500	-	cm^{-1}
$(Cr_7P_5N_2)_x$:	1242	1073	485	400	cm^{-1}

3. Ammonolysis of XVI leads$^{13)}$ to $P_2N_7C_2H_{16}Cl$. This compound was converted into the iodide $P_2N_7C_2H_{16}J$. The structure of this compound could be elucidated by X-ray structure analysis. Formula XVII is the right one for this compound$^{14)}$:



XVII

4. XVI could easily be transformed to XVIII$^{15)}$. Crystallographic examination of this substance revealed a planar four membered ring system. The bond lengths of this ring are remarkably uniform in contrast to compound XVI. The phosphorus is sp^3 hybridized, while the nitrogen is sp^2.

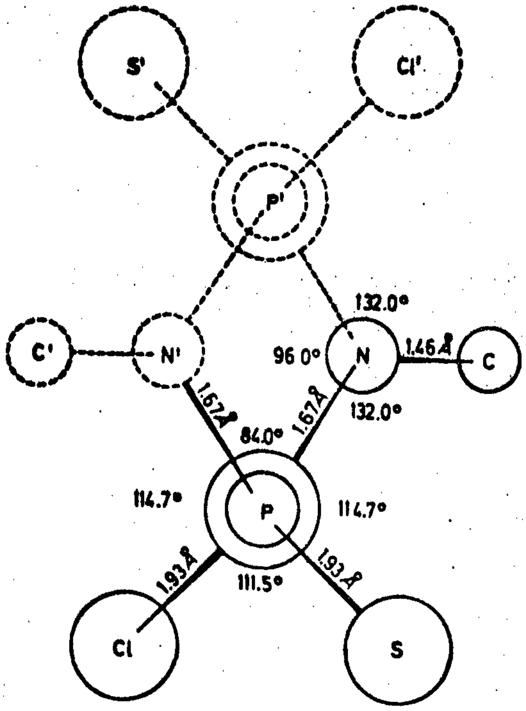
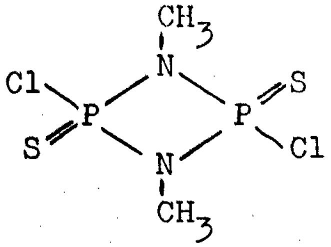


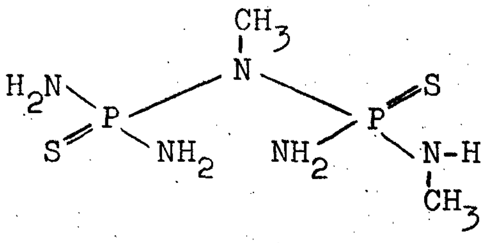
Fig. 3

Bond lengths and bond angles of compound XVIII

4.1. This substance, however, was very useful for further reactions. With ammonia XIX was obtained, and this substance may be thermally condensated.



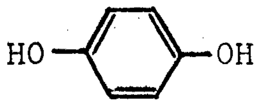
XVIII



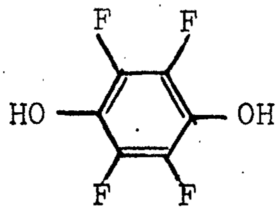
XIX

4.2. Especially interesting, however, were the reactions of XVIII with aromatic dihydroxy compounds. The thermal stability of the condensation polymers thus yielded should depend on the following points:

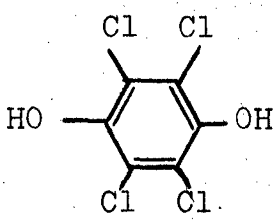
(1) the electro negativity and the bond dissociation energy of the substituents bonded to the aromatic dihydroxy compounds (XXII, XXIII, XXIV):



XXII

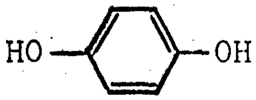


XXIII

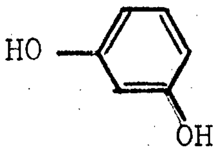


XXIV

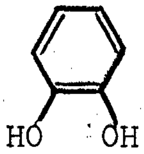
(2) the relative position (o-, m-, p-) of the dihydroxy groups to each other in the benzene ring (XXII, XXV, XXVI):



XXII

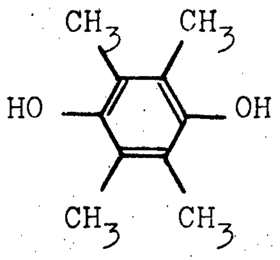


XXV

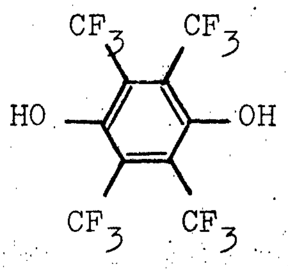


XXVI

(3) the possible sterical influence of four methyl and trifluoromethyl groups which may be substituted for the four hydrogen atoms on the benzene ring of hydroquinone.

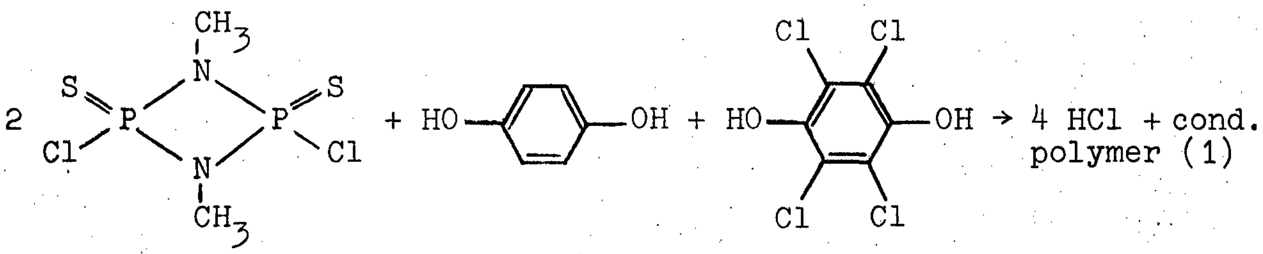


XVII



XVIII

On the other hand, one can try to change the mechanical and in some way the thermal properties of the condensation polymers yielded by mixing two different dihydroxy benzenes (molecular ratio, e.g. of XVIII, XXII, XXIV-2:1:1) by following the scheme of eq. (1):



(1)

Thus we can expect that the polymers obtained by the condensation reaction of XVIII and XXIII or XVIII should be the most thermally stable polymers, while the condensation products of XVIII and XXVII or XXVI should be less stable. Perfluorinated polymers (e.g., Teflon) have very good thermal qualities. (Estimation of the bond dissociation energy of the C-F bond in CF_4 gives 124 kcal/mole; the same energy for the C-H bond in CH_4 is 101 kcal/mole.) Therefore a condensation polymer yielded by condensation of a perfluorinated organic monomer and a diazadiphosphetidine should be thermally more stable than the unfluorinated counterpart.

5. Experimental

2.2.2.4.4.4-hexachloro-1.3-dimethylcyclodiphosphazane (XVI):

74.3 g of methylammonium chloride (1.1 mole) and 208.5 g of PCl_5 (1 mole) were placed in 750 ml of dry tetrachloroethane and heated to boiling. Evolution of HCl set in at 60° and continued for about 6 hours. After this time the solution was allowed to cool to about 40°C and then concentrated in a thin-layer evaporator under partial pressure (20 mm Hg) until crystals appeared. The mixture was then cooled to 0° and the crystals filtered off. The yield of XVI is about 150 g, corresponding to 90 % of theory. The product can be recrystallised from benzene, CCl_4, di- and tetrachloroethane, and acetonitrile. With the latter solvent and repeated recrystallization, it is possible to obtain a sample which melts at 178° (uncorr.) as opposed to the melting point of 160°C reported by Chapman et al.$^{23)}$. It is essential that the melting point determination be carried out in a sealed tube. In all other aspects, this substance is identical with that obtained by the authors mentioned above$^{23)}$.

2.4-dioxo-2.4-dichloro-1.3-dimethylcyclodiphosphazane (XVIIIa):

100 g of $P_2(NCH_3)_2Cl_6$ (XV) were dissolved in 500 ml of dry methylene chloride; dry SC_2 was then passed into the cooled solution (ice bath) with stirring. At first, a portion of the starting material remained undissolved, but this was consumed in the course of the reaction. SO_2 is sparged into the clear, colourless solution until approximately twice the theoretical amount has been absorbed. The reaction mixture is then allowed to stand at 0°C over night, after which the

solvent is removed in a thin-layer evaporator under aspirator vacuum. The residue consists of a pale yellow oil which soon crystallises; this product can be recrystallised from cyclohexane or, preferably, sublimed at 60°C/0.01 mm Hg. The melting point is unsharp (101-103°C). Yield: 92.5 %, based on $P_2(NCH_3)_2Cl_6$.

Analysis of $P_2(NCH_3)_2C_2Cl_2$ (222.9):

calc.:	12.57 N	27.79 P	31.81 Cl	10.77 C	2.71 H %
found:	12.49 N	27.40 P	31.83 Cl	10.72 C	2.70 H %

Molecular weight (ebullioscopically in benzene and dichloroethane): 222±1.5 (mean from 6 determinations).

2.4-dithio-2.4-dichloro-1.3-dimethylcyclodiphosphazane (XVIII):

103 g of dry pyridine were added to a solution of 100 g of V (0.3 mole) in 1 l of dry benzene. Dry H_2S was passed into the stirred solution at room temperature. After a short time, a precipitate of pyridinium chloride appeared, which was formed in approximately theoretical amount in the course of 15 hours. The precipitate was then filtered off and washed repeatedly with benzene. The filtrate was subsequently evaporated in aspirator vacuum, care being taken to exclude moisture throughout each phase of the operations. A yellowish crystalline residue is obtained following removal of the solvent; this product can be recrystallised from cyclohexane or (preferably) from petroleum ether. Purification can also be achieved by sublimation at 70°C/0.1 mm Hg. Melting point: 120-122°C (unsharp). Yield: 60 g (78.3 % of theory).

Analysis of $P_2S_2(NCH_3)_2Cl_2$ (255.1):

calc.: 24.29 P 10.98 N 25.14 S 27.80 Cl
found: 24.14 P 10.77 N 24.75 S 27.50 Cl

Molecular weight (ebullioscopically in benzene and dichloroethane): 256 ± 0.5 (mean for 7 determinations).

2.4-dithio-2.4-dianilino-1.3-dimethylcyclodiphosphazane:

37 g of aniline were added dropwise with stirring in the course of 20 min. to a solution of 25.5 g $P_2(NCH_3)_2S_2Cl_2$ (XVIII) in 800 ml of dry benzene. The reaction mixture was allowed to stand under continuous stirring for 24 hours, after which it was heated to boiling for a short time and filtered while still hot through a frit to separate the anilinium chloride formed in the reaction. The solvent was removed in aspirator vacuum, leaving a colourless crystalline residue. When this was dissolved in 600 ml of hot carbon tetrachloride and the solution allowed to cool, star-shaped crystals separated. These were recrystallised in the same way. Yield: 8 g (25 % of theory). The substance melted at 146°C and was readily soluble in dichloroethane, benzene, and CCl_4. It is not hygroscopic, although it is slowly darkened by the action of light.

Analysis of $P_2(NCH_3)_2S_2(NCH_6H_5)_2$ (368.4):

calc.: 15.21 N 16.81 P 17.40 S 45.64 C 4.92 H
found: 14.96 N 17.00 P 17.37 S 45.66 C 4.88 H

Molecular weight (ebullioscopically in benzene): 368 (mean from 3 determinations).

2.4-dithio-2.4-bis-diethylamino-1.3-dimethylcyclophosphazane:

A solution of 6 g of diethylamine in 100 ml of benzene was dropped in the course of 20 min. with stirring into a solution of 13 g of $P_2(NCH_3)_2S_2Cl_2$ in 350 ml of dry benzene at room temperature. The reaction was mildly exothermic and a white precipitate was formed, which was filtered off on a frit after two hours. The filtrate was concentrated to 50 ml in aspirator vacuum and allowed to cool, whereupon crystals separated. These were recrystallised from 700 ml of cyclohexane. The substance melts at 169°C and is not hygroscopic. Yield: 12 g (75 % of theory).

Analysis of $P_2(NCH_3)_2S_2[N(C_2H_5)_2]_2$ (328.4):

calc.: 17.06 N 18.86 P 19.53 S 36.57 C 7.98 H %
found: 16.77 N 19.20 P 19.78 S 37.01 C 8.04 H %

Molecular weight (ebullioscopically in benzene): 328 (graphic mean from 3 determinations).

N-methylimidodithiophosphoric tetra-N-methylamide:

13.4 g of XVIII were added in one portion to 100 ml of methylamine which had been condensed at -50°C under exclusion of moisture. The clear solution which resulted was allowed to stand at room temperature until most of the excess methylamine had evaporated and then residual amine was pumped off in vacuum. The white solid which remained was boiled with several separate portions of benzene, care being taken to apply heat for only a short time in order to avoid loss of amine by chemical fission. The benzene solutions were subsequently concentrated in vacuum, whereupon the product crystallised out on cooling. Purification was accomplished by recrystallization from carbon tetrachloride or methylene chloride. Yield: 12.5 g (86.4 % of theory). Melting point: 92°C.

Analysis of $P_2S_2(NCH_3)(NHCH_3)_4$ (275.3):

calc.: 22.50 P 25.44 N 23.29 S %
found: 22.70 P 25.22 N 23.64 S %

Molecular weight (ebullioscopically in benzene): 278±6 (mean from 4 determinations).

2.4-dithio-2.4-bis-N-methylamino-1.3-dimethylcyclodiphosphazane:

Sublimation of the substance which is described above at 180-200°C/15 mm Hg led to the desired compound in ca. 80 % yield. The product was recrystallised from dichloroethane or acetonitrile. Melting point: 224°C.

Analysis of $P_2S_2(NCH_3)_2(NHCH_3)_2$ (244.3):

calc.: 25.37 P 22.94 N 26.25 S %
found: 25.36 P 23.04 N 26.50 S %

Molecular weight (ebullioscopically in acetone): 243±2 (mean from 4 determinations).

Preparation of $[(OC)_4Cr(CH_3NPCl_3)_2]$ (Ia):

5.3 g $(CH_3NPCl_3)_2$ (0.016 mole) and 3.3 g $Cr(CO)_6$ (0.015 mole) were refluxed in dry benzene under dry nitrogen for 20 hours. Then the reaction mixture was cooled and the deep blue precipitate was collected by filtering the whole through a frit.

The product came into a round-bottomed sublimation flask and was heated for 4 hours to 50-60°C in an oil bath. So benzene and unreacted $Cr(CO)_6$ was separated. The remaining light red product was analysed:

calc.:	10.48 Cr	42.90 Cl	5.63 N	12.49 P %
found:	10.06 Cr 11.91	43.42 Cl 41.52	6.10 N	13.88 P % 13.96

Preparation of $(Cr_7P_5N_2)_x$:

After carefully heating 4.0 g of (Ia) in a trap under dry nitrogen with an open flame the remaining product which had the same qualities (IR, solubility, X-ray diffraction pattern) as a substance yielded on an thermal balance, was analysed: $(Cr_7P_5N_2)_x$.

calc.: 66.41 Cr 28.22 P 5.11 N %
found: 64.29 Cr 28.07 P 5.10 N % (C: 1.21 H: 0.23 %)

The evolved gas during the thermal degradation was collected in a trap cooled with liquid nitrogen. Its identification followed from IR-measurements.

Experimental concerning the reaction of XVIII with aromatic dihydroxy compounds:

The diazadiphosphetidine (XVIII) was prepared by the method of Becke-Goehring et al.$^{15)}$ and has been further purified by sublimation. Its purity was shown by analysis.

Analysis:

calc.: 27.79 Cl 24.24 P 25.18 S %
found: 27.45 Cl 24.67 P 24.39 S %

(The S analysis may be low because of some hydrolysis while weighing the sample.)
Its ^{31}P-NMR-spectrum and its infrared spectrum agreed very well with the literature$^{15)}$.

The hydroquinone was obtained from commercial sources (reinst, E. Merck AG., Darmstadt).

Tetrafluorohydroquinone (XXIII) was obtained from Imperial Smelting Corp. Several recrystallizations from petrol ether (100-140°C) yielded a product of m.p. 159-162°C. Its composition is confirmed by its infrared spectrum. The ^{19}F NMR spectrum of XXIII consists only of a single peak with a chemical shift of 164.4 ppm towards an internal standard of $CFCl_3$.

Tetrachlorohydroquinone (XXIV) was obtained from Farbenfabriken Bayer; it was used without further purification.

Tetramethylhydroquinone (XXVIII) was prepared after the procedure of Rügheimer and Hankel[19]. It has been found that it is necessary to purify the tetramethylquinone by sublimation. Reduction of this quinone takes place most readily with $SnCl_2$ and hydrochloric acid in a water-alcohol mixture. The melting point after drying was 230-231°C.

Analysis

calc.: 72.30 C 8.48 H %
found: 72.08 C 8.12 H %

The m- and o-dihydroxybenzenes (XXV and XXVI, respectively) were commercial products (reinst, E. Merck AG., Darmstadt).

Tetrakis(trifluoromethyl)hydroquinone (XXVIII) was not prepared (see results and discussion).

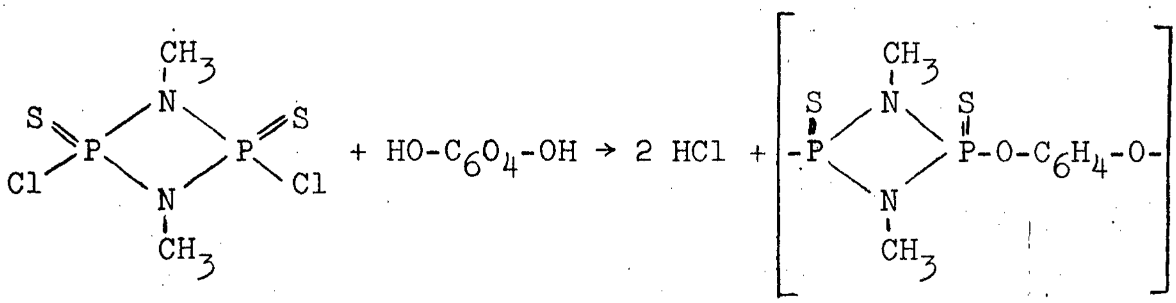
Procedures:

Condensation reactions were carried out in an oil bath at 200, 180, and in one case at 100°C. The oil was stirred and temperature controlled automatically. The reaction vessel was a round-bottomed flask fitted with two necks. One of these necks was used for a stirrer, while the other was used as exit for a gas inlet tube (two coaxial glass tubes).

Throughout the reaction dry nitrogen, containing less than 15 ppm O_2, passed through the apparatus. The reaction vessel was put into the oil bath at reaction temperature. Some time later reaction started, as could be seen by hydrogen chloride evolved. HCl evolved throughout the reaction passed the reaction flask through a glass tube into a cooling trap cooled with liquid nitrogen. Weighing of the condensed HCl followed after removal of N_2 from the cooling trap.

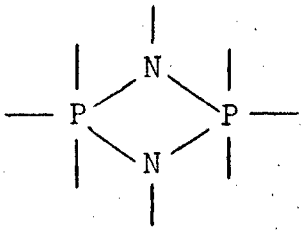
Infrared spectra were recorded with a Perkin-Elmer Model 221 and a Perkin-Elmer Model 457 spectrophotometer. It was very difficult to powder the polymers for preparation of the KBr disks, especially those obtained by the reaction of hydroquinone and resorcinol. The substances were powdered under dry nitrogen.

The condensation reactions yield polymers that are hard, brittle (with exception of the condensation product of XVIII with pyrocatechol, which is waxy or a viscous liquid) and to a certain extent flame-resistant. The polymer containing perchloro-hydroquinone begins to swell on heating with an open flame, and gas is evolved. Equation (2) describes the condensation reactions carried out (molecular ratio 1:1):



(2)

Properties of the condensation polymers obtained are listed in Table 2. Thermal degradation curves (of some of the polymers) are shown in Figure 4. From Table 2 and Fig. 4 we see that the thermally most stable polymers are obtained if the hydrogen atoms are not substituted by halogen atoms and the OH groups are not too close to each other (o-dihydroxybenzenes). The unexpected thermal instability of the polymers containing halogen atoms on the benzene ring may be explained by the fact that the monomeric halogen substituted hydroquinones (especially the quinones) have halogenating qualities. On the other hand, Kozlov and Drach[20] found on chlorinating $(CH_3NPCl_3)_2$ that splitting



of the N-P-N-P ring occurred. The main product was $CCl_3N{=}PCl_3$. A similar reaction may take place on thermal degradation of the above polymers containing halogenated benzene rings. From the data obtained one can get the following series of thermal stability for polymers of the composition mentioned above:

hydroquinone ≈ resorcinol > tetramethylhydroquinone ≫ tetrachlorohydroquinone ≈ tetrafluorohydroquinone ≫ pyrocatechol.

Table 2

Reaction Conditions and Properties of the Synthesized Condensation Polymers

Polymer	Reaction Conditions Time min	Temp. °C	HCl, g Calcd	Found	Polymer Properties	Decomp. Temp. °C
XVIII + hydroquinone	60	180	1.1	1.2	Not soluble	540
	45	200	0.8	0.7	Very hard, tenacious, pale yellow	590
XVIII + tetrafluorohydroquinone	60	162	0.8	1.0	Dark brown	
	60	160	0.4	0.4	Hard, brittle	
	130	133)	Not determined		Not soluble	180
	150	133)			Dark brown brittle	190
	50	162)				
XVIII + tetrachlorohydroquinone	120	180	0.7	1.0	Dark brown	
	35	180	0.6	0.6	Hard, brittle	180
	45	180	0.8	0.6	Not soluble	160
	150	160	0.4	0.5		160
XVIII + tetramethylhydroquinone	20	210)	0.5	0.5	Brown, hard brittle, not soluble	510
	60	160)				
XVIII + resorcinol	150	180	0.5	0.3	Hard tenacious	570
	105	165	0.6	0.6	Pale yellow, not soluble	560
	120	180				
XVIII + Pyrocatechol	240	160	0.4	0.4	Waxy, pale yellow	170
	60	100	0.5	0.7	Mixture of pale yellow viscous liquid and white solid	
XVIII + hydroquinone + tetrachlorohydroquinone (2:1:1)	120	180	0.7	0.3	Very hard brown	165 550
	20	180)	0.7	1.0	brittle, not soluble	
	90	180)				180

The degradation curves of the thermally more stable polymers first show a slight decrease, which may be caused by some unreacted material. A strong decrease indicates decomposition. As can be seen from the degradation curve, the same polymer (XVIII + XXII) shows a somewhat higher decomposition point (50°C) after being extracted with ether for several hours. In contrast to the above polymers, the condensation products of XVIII and XXIII or XIV decompose continuously. The mixed condensation polymer (XVIII + XXII + XXIV) shows similar behavior on heating.

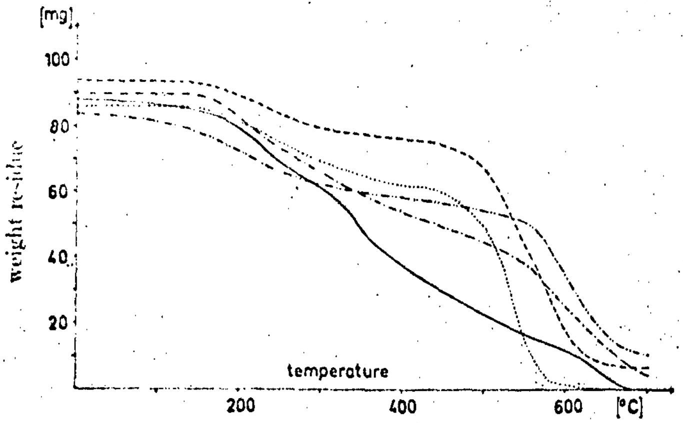
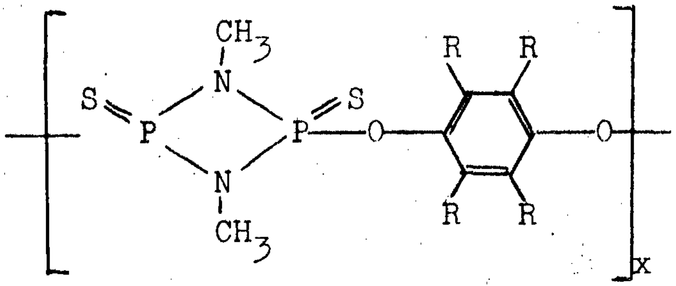


Fig. 4. Thermal degradation curves: (--) polymer of XVIII and XXII; (-..-) XVIII and XXII (after extraction with ether); (——) polymer of XVIII and XVIII and XXIII; (-.-) polymer of XVIII and XXIV); (---) polymer of XVIII and XXVII).

The formulae of the polymers (with exception of products obtained from condensation of XVIII and XXV or XXVI) are given by XXIX, where R may be H or F, Cl, $CH_3(CF_3)$.



XXIX

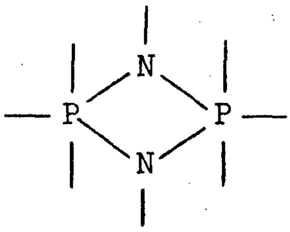
In all cases the same diazadiphosphetidine (XVIII) was used for the condensation reaction. Only the substituents R and the relative position of the hydroxy groups to each other were changed.

In case of the polymer prepared from XVIII and XXV compared with the corresponding product obtained from XVIII and XXII, no steric hindrance is found for two diazadiphosphetidine rings connected with the aromatic dihydroxy compound. The decomposition point of these polymers is nearly the same. In contrast to these polymers, the polymer prepared from XVIII and XXVI is a waxy solid or a viscous liquid. Strong mutual hindrance of the diazadiphosphetidine rings bonded to the pyrocatechol leads to low molecular weight products. Therefore volatilization of the low molecular weight fractions overlaps thermal degradation. A weight loss is recorded at a much lower temperature than in the case of the polymers from XVIII + XXII and XVIII + XXV. The possible influence of the substituents, e.g. F and H, could not be determined by thermal degradation studies, because the polymers obtained by condensation of XVIII and tetrafluoro- (XXIII) or tetrachlorohydroquinone (XXIV) show halogenating qualities, which cause decomposition of the P-N heterocycle- This is the reason for not preparing a condensation polymer of XVIII and XXVIII.

Infrared Spectra:

The increasing reaction between XVIII and the aromatic dihydroxy benzenes was followed by infrared spectroscopy. The infrared spectra from the polymers are very complex. Therefore it is difficult, if not impossible, to assign all bands to characteristic group frequencies. In Table 3 infrared data of the condensation polymers are listed. The assignments naturally depend on assigned spectra of the diazadiphosphetidine and the dihydroxy-benzenes. Unfortunately we have found little material about the infrared spectra of four-membered P-N heterocycles. Downs[21)] has published a complete assignment of $(CH_3NPF_3)_2$. But this is of limited value for our investigations, because his assignment depends on a vapor-phase infrared spectrum. Yagupsky[22)] has published a complete assignment of the bands found in the infrared spectra of $(CH_3NPF_3)_2$ and $(CH_3NPCl_3)_2$. He compares calculated and measured spectra. Chapman et al.[23)] assign only a strong band in the 847 cm^{-1} region to the P-N stretching vibration. This is confirmed by Haszeldine[17)], who investigated several four-membered P-N heterocycles with various substituents and found a band of strong to very strong intensity in the range of 845-910 cm^{-1}.

According to the above assignments, we assign a strong band at 861 cm^{-1} found in the solid state of $[CH_3NP(S)Cl]_2$ (XVIII) not only to the P-N stretching frequency but as characteristic for four-membered rings,



as proposed by Yagupsky[22)] for $(CH_3NPCl_3)_2$ and $(CH_3NPF_3)_2$. In all spectra of the polymers this band could be found (see Table 3). Fortunately the dihydroxy-benzenes do not in general give rise to bands in this region; those bands which do occur can easily be separated from the P-N band. Thus we can conclude, that the four-membered P-N heterocycle is not decomposed during the time of condensation.

Two bands[24)] for the P=S stretching vibration should be found in the range 550-872 cm^{-1}, but only one band in the region of 668 cm^{-1} of medium intensity found for both the polymers and XVIII should be assigned tentatively to this vibration.

A band of strong to very strong intensity in the range of 905-996 cm^{-1} is correlated with the P-O-C vibration[25)], while a weak band[26)] is found in the 1030 cm^{-1} region. Such absorption bands are found (Table 3) indicating reaction between XVIII and XXII-XXVII. In the case of the condensation polymer XVIII + XXIII, this assignment is of tentative character because of the appearance of a "triplet" of bands near 1000 cm^{-1} which may be due to aromatic C-F stretching frequencies[27)28)]. On the other hand[29)], strong bands in the range 420-587 cm^{-1} due to P-Cl-bonds $[CH_3NP(S)Cl]_2$: 500 cm^{-1} and a very strong and often broad band[+)] indicating OH groups disappear during the reaction.

A weak band in the range of 2940-2948 cm^{-1} was found to be the C-H stretching frequency of the CH_3 group bonded to nitrogen. XVIII absorbs in this case 2944-2946 cm^{-1}. Aromatic C-H stretching vibration[23)] occurs in the 3030 cm^{-1} region.

[+)] p-HO-C_6H_4-OH, 3250; m-HO-C_6H_4-OH, 3240; o-HO-C_6H_4-OH, 3360, 3490; p-HO-C_6F_4-OH, 3335; p-HO-C_6Cl_4-OH, 3390; p-HO-$C_6(CH_3)_4$-OH, 3395 cm^{-1}.

very few infrared data have been reported for organic compounds containing C-Cl bonds. Therefore was assign tentatively a medium to strong band at 718 cm^{-1} of the polymers to the C-Cl stretching vibration. We are confirmed in this way, for some substances+) contain bands in this region which can be correlated to C-Cl bonds. No attempts have been made to assign observed bands between 1650 and 1450 cm^{-1} to C-C stretching vibrations.

Therefore the infrared measurements confirm our assumption that the polymers are linear and agree very well with the formulae given.

+) p-H_2N-C_6Cl_4-NH_2, 677 (s); p-H_2N-CH_2-C_6Cl_4-CH_2-NH_2, 657 (s); p-HO-C_6Cl_4-OH, 715 (vs) cm^{-1}.

Table 3

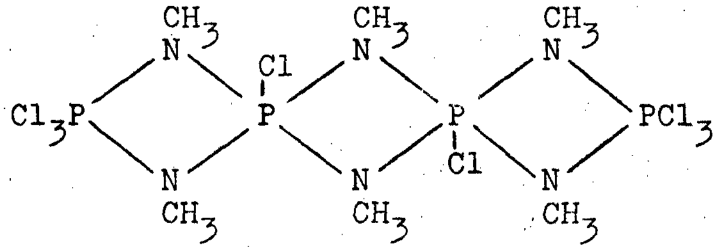
Infrared Data for Condensation Polymers

Polymer	Wavenumber cm^{-1} a						
	—C—H (aliphatic)	—C—H (aromatic)	—C—F (aromatic)	—C—Cl (aromatic)	P - O - (C) (aromatic)	P—N (ring)	P═S
XVIII + hydroquinone	2940 (vw)	3062 (m)	-	-	1018 (w) ? 922 (vs)?	860 (w) ?	-
XVIII + tetrafluoro-hydroquinone	2940 (vw)	-	1030 (vs)? 1015 (vs)?	-	-	870 (vs)	672 (m)
XVIII + tetrachloro-hydroquinone	2945 (w)	-	-	718 (s)	1030 (m) 950 (vs)	868 (vs)	668 (m)
XVIII + tetramethyl-hydroquinone	-	-	-	-	- 979 (vs)	860 (vs)	675 (m) 690 (m)?
XVIII + resorcinol	2940 (vw)	3060 (m)	-	-	1010 (vw)? 965 (vs)?	863 (vs)	671 (m)
XVIII + pyrocatechol	2938 (w)	3062 (w)	-	-	1030 (w)? 950 (vs)?	866 (vs)	680 (m)? 620 (m)?
XVIII + hydroquinone + tetrachloro-hydroquinone (2:1:1)	2938 (vw)	3060 (w)?	-	720 (w)?	1032 (w) 930 (vs)?	865 (vs)	-

a = Intensity: v = very; s = strong; w = weak; m = medium.

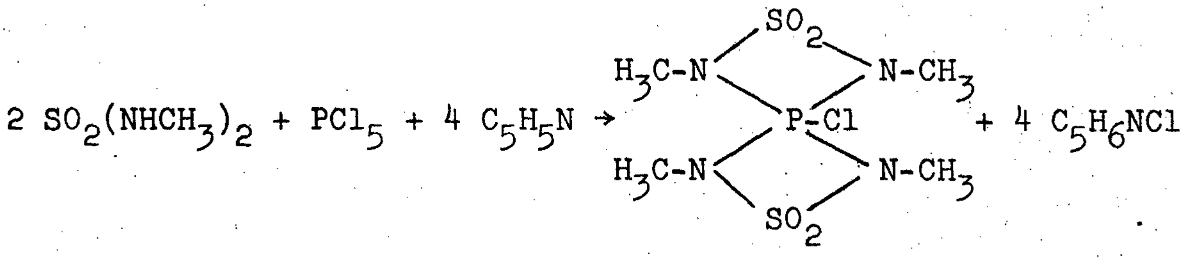
C. DERIVATIVES WITH MORE THAN ONE FOUR-MEMBERED PN OR PNS RING COMPOUNDS

The reaction product of PCl_5 and $[CH_3NH_3]Cl$ is not only compound XVI. There is also another reaction product of higher molecular weight. Compound XXX was synthezised in good yield$^{15)}$.



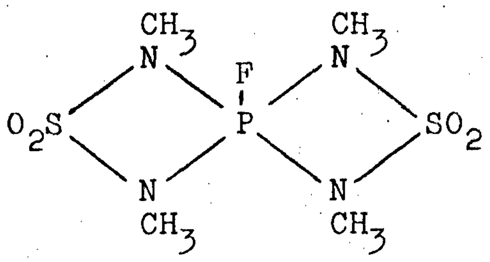
XXX

Later, we tried to prepare other ring systems with more than one four-membered PN ring. The reaction of PCl_5 and N,N'-dimethylsulfamide in the presence of pyridine yielded such a new ring system (XXXI):



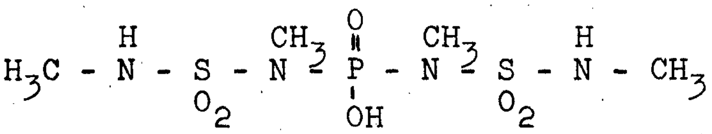
XXXI

XXXI is a colourless solid (m.p. 170-171.5°) which may be sublimed at 110-120° (0.6 torr). With AgF a fluorine compound (XXXII) is formed quantitatively.



XXXII (m.p. 184°)

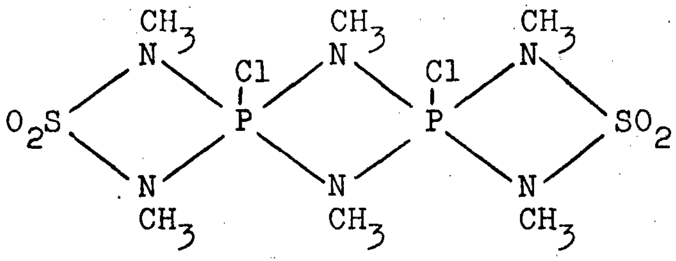
XXXI formes an adduct with $TiCl_4$ (1:1) and with $SbCl_5$ (1:2) and with BCl_3 (1:2). With formic acid and XXXI compound XXXIII is obtained. With ethanol, however, an ethyl ester of XXXIII is formed (m.p. 107-108°).



$$H_3C-\overset{H}{N}-\underset{O_2}{S}-\overset{CH_3}{N}-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-\overset{CH_3}{N}-\underset{O_2}{S}-\overset{H}{N}-CH_3$$

XXXIII (m.p. 135°C)

Reaction of XVI with N,N'-dimethylsulfamide led to compound XXXIV.



XXXIV (m.p. 221°C)

Especially XXXIV with the two chlorine atoms is suited for further reactions.

nmr spectra:

XXXI ^{31}P δ = +86.0 ppm (multiplett) $J_{^{31}P^{1}H}$ = 16.7 Hz

^{1}H δ = 1.395 ppm, -1.533 ppm with $(CH_3)_4Si$
as standard substance $J_{^{1}H^{31}P}$ = 17.0 Hz

XXXII ^{31}P δ = +63.5 ppm, +105.7 ppm $J_{^{31}P^{19}F}$ = 1025 Hz

^{19}F δ = +20.7 ppm, +2.3 ppm $J_{^{19}F^{31}P}$ = 1038 Hz

XXXIII ^{31}P δ = 3.7 ppm

XXXIV ^{31}P δ = 81.2 ppm

Infrared spectra

	XXXI	XXXII	XXXI·$TiCl_4$	XXXI·2 $SbCl_5$	XXXI·2 BCl_3	XXXIV
	4300 vw	4250 vw	4350 vw	4450 vw	4350 vw	
	3370 w	3280 w	3330 w	3380 s	3280 m	3180 w
$\nu_{sym.}$ CH(aliph.)	2945 m					2950 w
$\nu_{asym.}$ CH(aliph.)	2830 m					2830 w
	1670 vw			1625 w		
$\delta_{asym.}$ CH(aliph.)	1460 m					1466 w
$\delta_{sym.}$ CH(aliph.)	1408 w	1416 w	1428 w	1405 s	1420 s	1416 w
$\nu_{asym.}$ SO_2	1328 s	1328 s	1329 s	1342 vs	1370 s	1352 m
			1309 s			
	1265 m	1272 m	1250 w	1266 m	1270 m	1318 m
	1203 s	1195 s	1184 s			1270 m
	1168 vs					1196 vs
$\nu_{sym.}$ SO_2	1150 vs	1162 vs	1149 s	1173 vs	1190 s	1173 vs
$\nu_{asym.}$ N-S-N	1136 s	1130 s	1123 s	1141 s	1138 m	1130 m
$\nu_{sym.}$ N-S-N	1093 m	1083 w		1082 vs	1088 m	1086 m
	1003 m					
P-F		887 s				
$_1$ P-N	866 vs	866 vs	870 vs	853 vs	858 s	875 vs
$_2$ P-N	853 s	841 s				837 s
	808 m	817 s				788 m
	748 s	760 s				
$\nu_{sym.}$ P-N-C	722 m	712 m	708 m	738 w	719 s	720 m
	695 s	680 m	690 m	702 m	688 s	671 m
	645 m	643 w		653 m	664 s	631 w
	617 s	615 w	618 s		618 m	
	580 m	583 w	580 w	589 s		582 m
			562 w	573 s	567 m	
	553 s	547 s	543 m	548 s	553 s	551 s
	535 m			535 s	535 m	543 s
ν P-Cl	517 w		512 w	518 w	518 s	517 s
	502 w					
	480 m	492 s				452 m
	468 vs	477 vs	473 s	467 m	464 m	422 s
	420 vw	422 vw	403 s	420 w	418 w	

Experimental

$P_4(NCH_3)_6Cl_8$ (XXX):

208.5 g PCl_5 and 75 g methylammonium chloride (not previously dried) were placed in 750 ml tetrachloroethane and heated to boiling. The evolution of HCl ceased after about 6 hours. The reaction mixture was cooled to 0°C and the crystallised product (V) filtered. The filtrate was evaporated in aspirator vacuum in a thin-layer evaporator to about half the original amount and then cooled to 0°C. This procedure led to a further quantity of V. Next, tetrachloroethane was evaporated off in the same way and the residue warmed with 200 ml of carbon tetrachloride. In the absence of residual tetrachloroethane, this treatment permits removal of remaining traces of V and oily by-products from the finely crystalline crude product. The latter consists of a white material corresponding to XXX. The yield is variable, amounting to about 3 g (ca. 2 % of theory). XXX can be recrystallised from benzene. In a sealed tube, the substance melts with decomposition at 395°C.

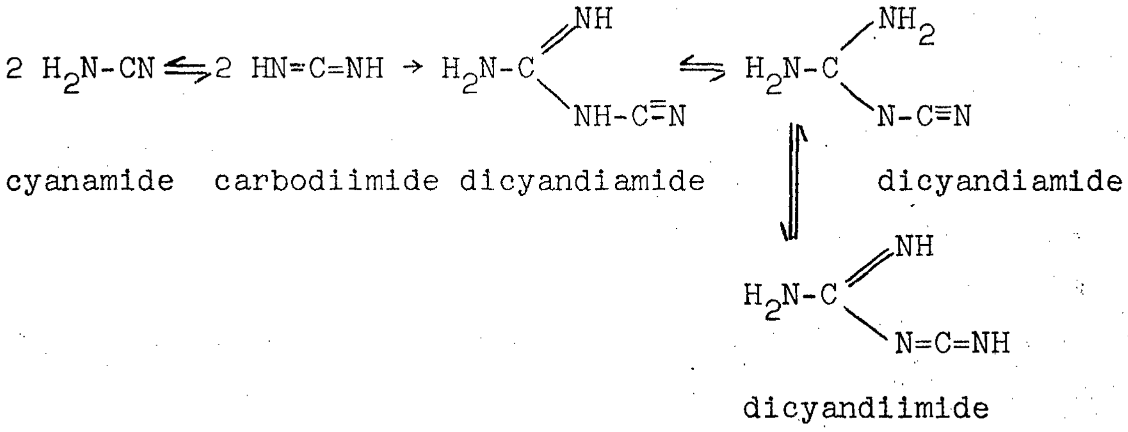
Analysis of $P_4(NCH_3)_6Cl_8$ (581.8):

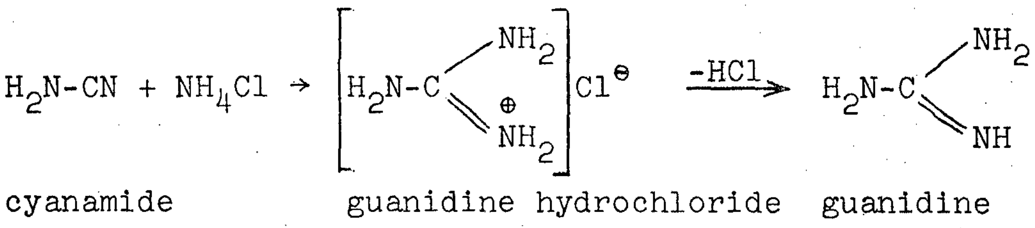
calc.:	21.30 P	14.45 N	48.75 Cl	12.38 C	3.12 H (%)
found:	21.24 P	14.36 N	47.63 Cl	12.9 C	3.29 H (%)

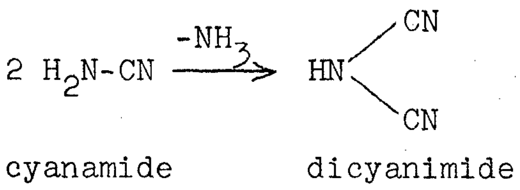
Molecular weight (ebullioscopically in benzene and in dichloroethane): 584±16 (mean from 6 determinations).

D. DERIVATIVES OF P-N-C RING COMPOUNDS:

Other attempts have been made to synthezise thermo-stable and flame resistant materials on the basis of P-N-C compounds. The new flame proof compounds described in the following chapter may be used for impregnation of e.g. fibres in order to get flame resistant materials. The way so synthezise such compounds was found by the reaction of phosphorus pentachloride and e.g. cyanamide, dicyanamide, guanidine and dicyanimide. The connection between cyanamide and the other compounds may be described in the following reaction schemes:

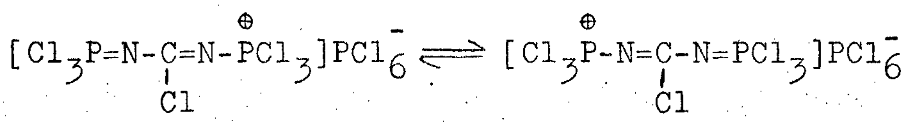






Results and Discussion:

Cyanamide yields on reaction with PCl_5 compound XL, which may be stabilized by mesomeric structures:

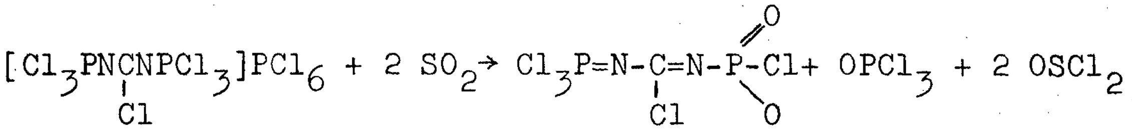


$$[Cl_3P{=}N{-}\underset{Cl}{C}{=}N{-}\overset{\oplus}{P}Cl_3]PCl_6^- \rightleftharpoons [Cl_3\overset{\oplus}{P}{-}N{=}\underset{Cl}{C}{-}N{=}PCl_3]PCl_6^-$$

XL

The ionogenic structure of XL was confirmed by its ^{31}P-NMR spectrum (standard 85 % H_3PO_4): One signal at +297.5 ppm is found for PCl_6^- and only one signal is found at -38.5 ppm, which is in agreement with the structure of the positive ion of XL with equivalent phosphorus atoms in the cation.

Molecular weight measurements of XL in 1.2-dichloroethane gave 350 to 365. This may be due to some dissociation and is consistent with our assumption of an ionogenetic structure of XL. On the other hand XL reacts with SO_2 to give an oxygenized product:

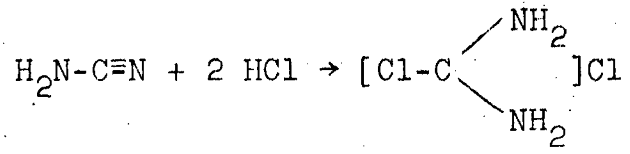


$$[Cl_3PN\underset{Cl}{C}NPCl_3]PCl_6 + 2\ SO_2 \rightarrow Cl_3P{=}N{-}\underset{Cl}{C}{=}N{-}\overset{O}{\underset{O}{P}}{-}Cl + OPCl_3 + 2\ OSCl_2$$

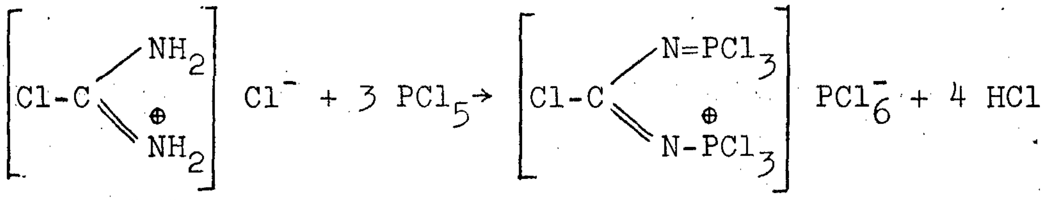
XL XLI

The ^{31}P-NMR spectrum consists of two signals at -23.8 and -0.1 ppm. The peak at -23.8 ppm belonge to the $Cl_3P=$ group and the -0.1 ppm value to the $-POCl_2$ group. From the positive ion XL we got the non-ionogenic XLI.

In reaction first hydrogen chloride is evolved by reaction of PCl_5 and the NH_2 group of the cyanamide, secondly we have formation of XLII, which reacts further with PCl_5 to give the ion XL:

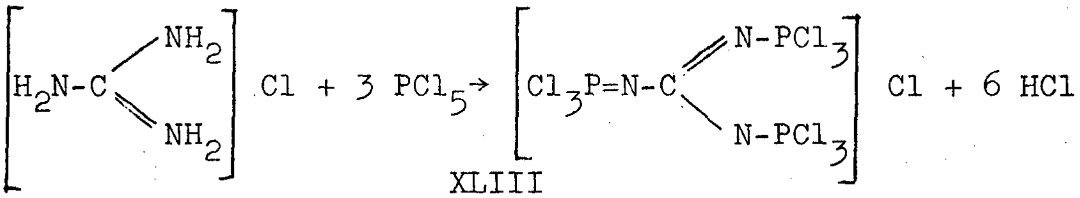


XLII



XLII XL

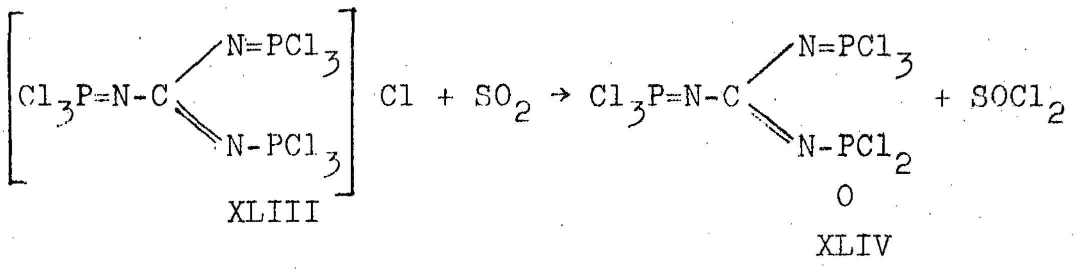
In a similar manner guanidine hydrochloride reacts with PCl_5 to give a similar resonance-stabilized salt XLIII:



XLIII

^{31}P-NMR measurements of XLIII show a peak at -33.5 ppm, which means that all three phosphorus nuclei have the same chemical surroundings. In the crude product a second signal at +295.0 ppm of low intensity is found, which vanishes after several recrystallizations of XLIII from 2:1 dichloroethane/trichloroethylene mixture. Therefore, one can say that a smaller part of the salt XLIII is first yielded as a PCl_6^- salt.

Molecular weight measurements of XLIII in 1.2-dichloroethane gave values between 360 and 373; dissociation of XLIII will be the reason for this behavior as it was for XL. After handling XLIII with SO_2 the ^{31}P-NMR spectrum shows two signals of the intensity 2:1 at -14.7 and -0.6 ppm; this leads to the reaction scheme (7) and compound XLIV:

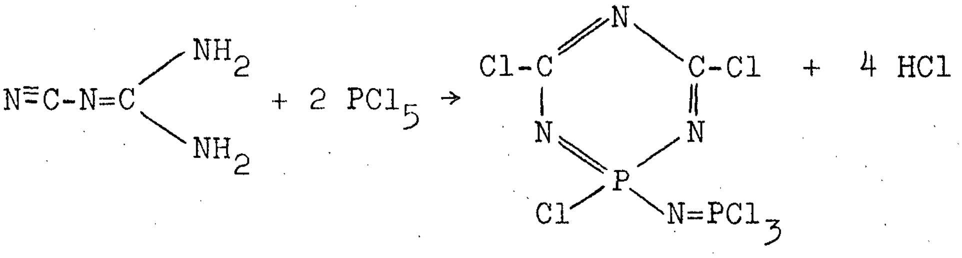


(7)

Thus we can say that the same conversion from a ionic to a non-ionic compound as in (4) took place.

On the reaction of PCl_5 and dicyandiamide in the molecular ratio 1:2 in dry 1.2-dichloroethane a product of the empirical formula $C_2N_4P_2Cl_6$ XLV, was found. Many possible linear and cyclic structures could be excluded for compound XLV by running ^{31}P-NMR spectra. These show two doublets centered at -57.0 ppm.

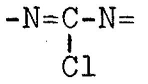
The reaction scheme therefore is given by (8)

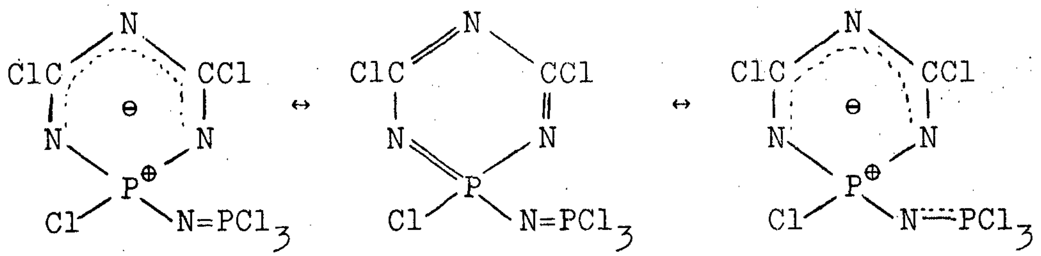


(8)

dicyandiamide phosphatriazine XLV

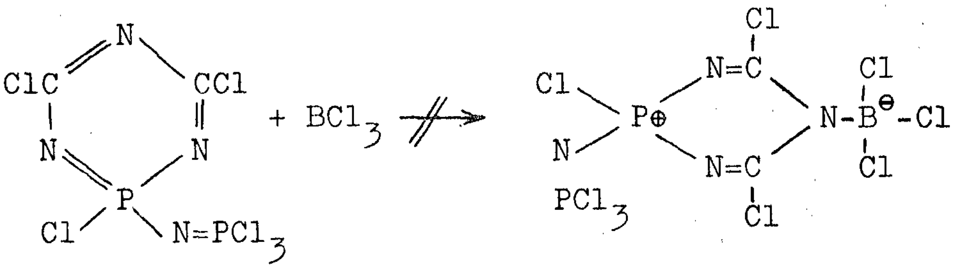
The correct name for this compound is: 1-chloro-1-trichlorophosphazo-3.5-dichloro-1-phospha-2.4.6-triazine. Molecular weight measurements gave the correct value of the P-N heterocycle XLV. No reaction took place with SO_2.

The group  $-N{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}N{=}$ seems to be able to abstract electrons from phosphorus. This grouping we have twice in XLV, thus we can explain the strong chemical shift (-57.0 ppm) downfield for the phosphorus atom, which is a part of the heterocycle; while the doublet centered at -22.7 ppm is caused by the phosphorus atom of the side-chain. The coupling constant $P_{ring}-P_{chain}$ is found to be 40 cps. The best way to describe the structure of XLV is



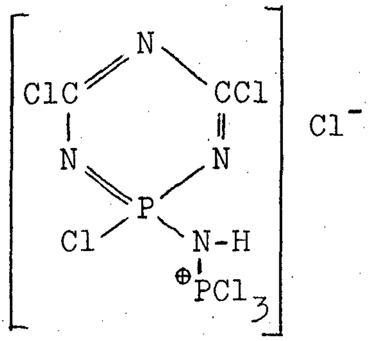
XLV

Some influence of the hetero-atoms (N) in the symmetrical 1.3.5-triazines on the aromatic character has been found. This influence seems to be much stronger in the phosphatriazine XLV: It was not possible to prepare an adduct of XLV and the Lewis-acid BCl_3:



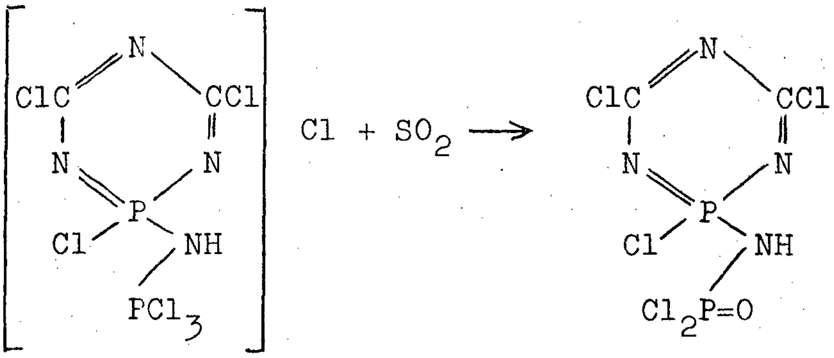
XLV

If the reaction (8) is carried out, however, at a temperature of 45-50°C with further heating to 65°C, one gets an other crystalline product. This product is unsoluble in common solvents. Only in 1.2-dichloroethane a ^{31}P-NMR spectrum, consisting of two peaks at -54.4 and -34.1 ppm, was obtained. The analytical formula of the product is: $C_2HN_4P_2Cl_7$. The conclusion of these data is a structure similar to XLV of $C_2HN_4P_2Cl_7$, XLVI:



XLVI

Compound XLVI is a salt; the peak at -54.4 ppm is caused by the phosphorus atom of the ring; the signal at -34.1 ppm belongs to the phosphorus of the side-chain. Due to the small solubility of XLVI no P-P coupling was observed. BCl_3 reacts with XLVI to give a tetrachloro-borate. In the above reactions of XL, and XLIII with SO_2 we got non-ionic molecules. The same reaction takes place with XLVI.

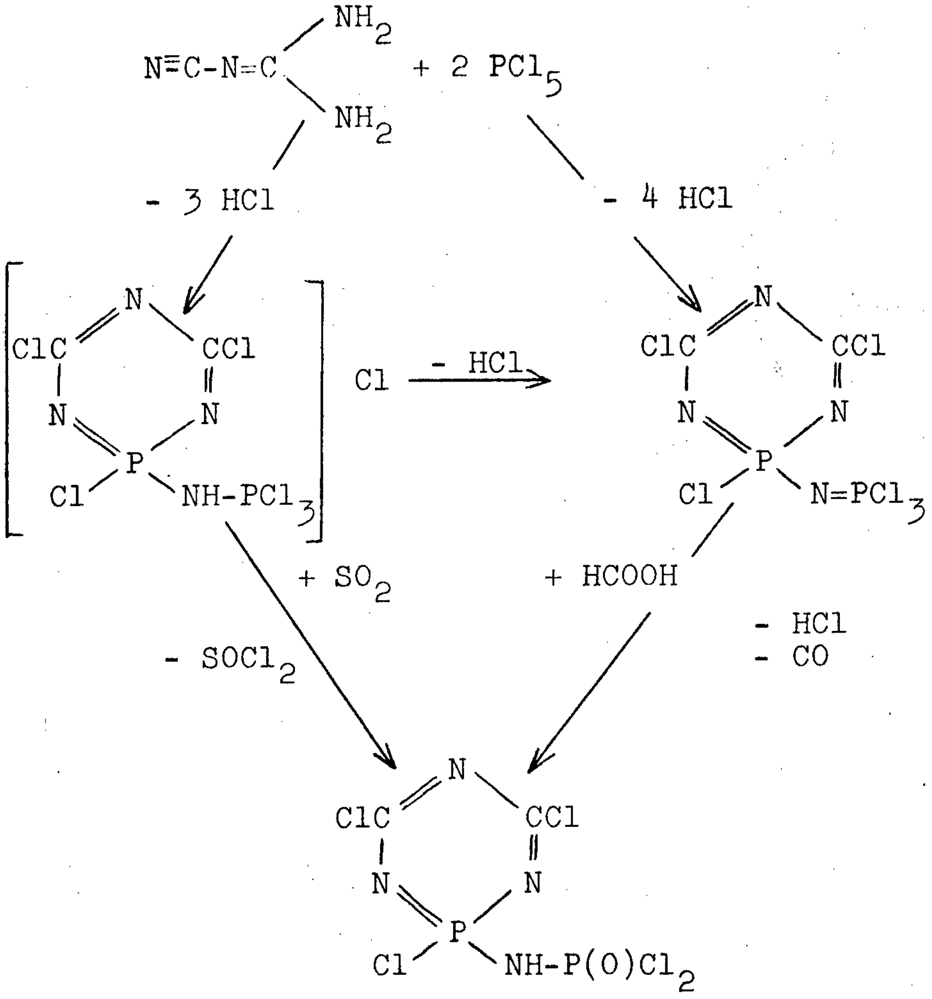


(9)

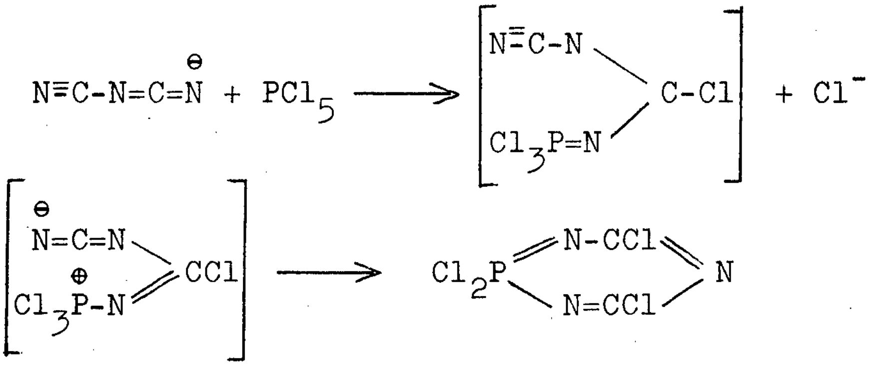
XLVI XLVII

^{31}P-NMR measurements showed two signals at -51.5 and -3.8 ppm. This can be explained in the same manner as it was for compound XLI and XLIV. The peak at -51.5 ppm belongs to the phosphorus atom of the ring, the other signal at -3.8 ppm is caused by the phosphorus atom of the $-P(O)Cl_2$ grouping.

It could be shown that one mole HCl per mole XLVI is evolved on heating of XLVI; thus compound XLV is obtained, and XLVI is shown to be an intermediate of the reaction (8). The following scheme gives a survey on the reactions of PCl_5 with dicyandiamide.



A similar 1-phospha-2.4.6-triazine as XLV could be obtained by the reaction of dicyandiimide and PCl_5.



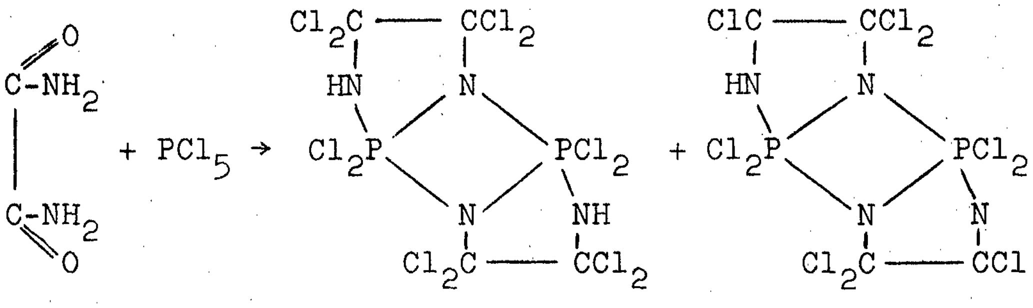
(10')

XLVIII

XLVIII does not react with SO_2; thus a ionic structure for this compound can be excluded. The ^{31}P-NMR spectrum shows only a single peak which is consistent with the structure given by XLVIII. The values is similar to that of XLV for the phosphorus atom of the ring.

Several other compounds containing phosphorus, nitrogen and carbon in heterocyclic ring systems have been synthetized by Russian investigators[82)].

It was possible to get some new heterocyclic four- and five-membered P-N ring systems by the reaction of oxamide and phosphorus pentachloride in an inert solvent (scheme):

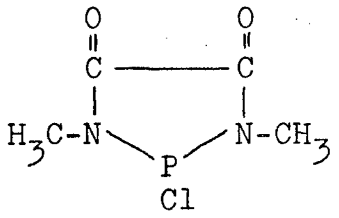


L LI

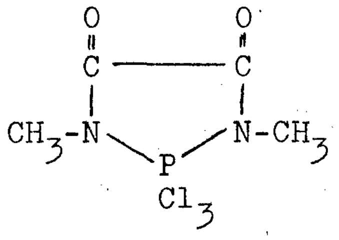
Only one signal is observed for both, (L) and (LI) in the ^{31}P-NMR spectrum. The chemical shifts, measured against an internal standard of 85 % H_3PO_4 are +55 ppm for (L) and +48 ppm for (L). These values indicate phosphorus nuclei of the coordination number 5, which is consistent with the structure given. The lower value than the normal (+80 ppm e.g. for PCl_5) may be explained by the electron attracting qualities of the CCl- and CCl_2-groups.

The new ring systems may be of interest for preparation of polymers and give resistant materials.

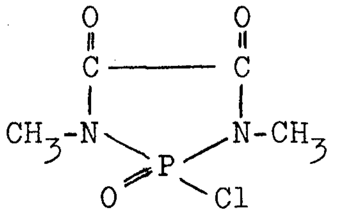
Reacting N,N'-dimethyloxamide with phosphorus trichloride produces another new heterocyclic ring system (LII) with coordination number 3 for phosphorus. This is supported by a chemical shift of -124 ppm of the ^{31}P-NMR-signal against an internal standard of 85 % H_3PO_4.


(LII)

Chlorination of (LII) yields an intermediate, whose ^{31}P-NMR-signal consists of one peak at +69 ppm, which means that the phosphorus atom has the coordination number 5 (LIII):

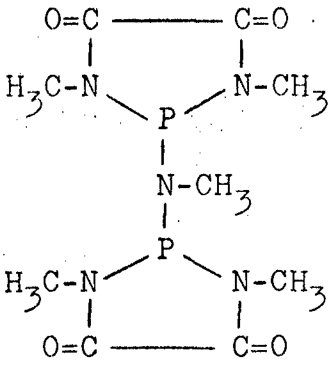

(LIII)

An intermolecular reaction of the PCl_3- with the CO-groups yields yields

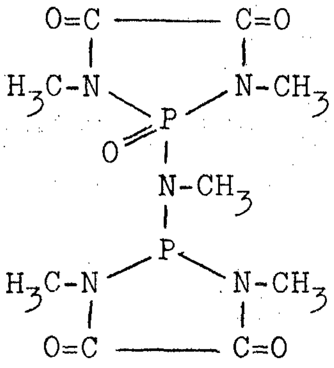

(LIV)

-8 ppm has been measured for a single peak in the ^{31}P-NMR-spectrum of (LIV).

Reaction of (LII) and (LIV) with heptamethyldisilazane yields compounds consisting of two five-membered heterocycles with an P-N-P bridge:



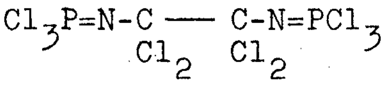
(LV)



(LVI)

The chemical shifts are -81 (LV) and -12.5 (LVI) ppm. It seems to be of interest that reaction of PCl_5 and $H_2N\text{-}C(S)\text{-}C(S)\text{-}NH_2$ doesn't produce the same compounds as PCl_5 does with oxamide.

Instead of this compound (LVII) is yielded:



$$Cl_3P{=}N{-}\underset{Cl_2}{C}{-}\underset{Cl_2}{C}{-}N{=}PCl_3$$

(LVII)

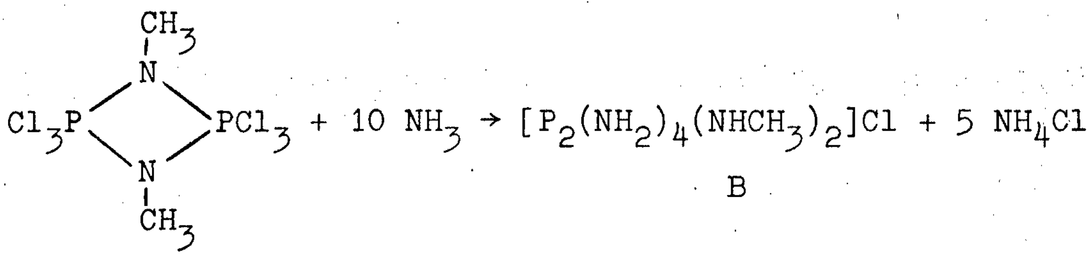
E. NITRIDO-DIPHOSPHORIC AND HEXA-AMIDO-CHLORIDE, A NEW PRODUCT OF THE REACTION BETWEEN PHOSPHORUS PENTACHLORIDE AND LIQUID AMMONIA:

The reaction between PCl_5 and liquid ammonia was first investigated by H. Moureau and P. Rocquet[71)]. They assumed that phosphorus pentaamide $P(NH_2)_5$ is first formed. However, they were able to isolate only polymeric products of the composition PN_3H_4, r.e., amides of the cyclic phosphornitrilic halides.

Later, M. Becke-Goehring and K. Niedenzu[72)] established that it is difficult to obtain completely oxygen-free substances out of the reaction between PCl_5 and liquid ammonia. The amide of imidophosphoric acid, $NH{=}P(NH_2)_3$, was postulated by them as the unstable and highly moisture-sensitive intermediate-product. Oxygen - containing products were obtained also by L.F. Audrieth and D.B. Sowerby[73)], who treated a solution of PCl_5 in chloroform at -50°C with liquid ammonia; they also got the amide of phosphonitrilic chloride $[NP(NH_2)_2]_3$ as a product.

In view of these observations, we considered it worthwhile to re-investigate the reaction of PCl_5 with liquid ammonia. On introducing PCl_5 to liquid ammonia under condition of careful exclusion of moisture, we found NH_4Cl and also a product, which could be freed from ammonium chloride by treating with diethylamine in chloroform. After recrystallisation from methanol, we got from it a substance (A) of the composition $P_2N_7H_{12}Cl$, which melts at 174-176°C. The ^{31}P-NMR-spectrum of this substance in methanol or liquid ammonia shows a signal at $-15.6\cdot 10^{-6}$.

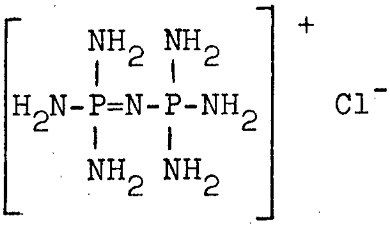
The chemical shift of A seems to us to indicate the formula LVIII. We had previously studied the reaction of compound XVI$^{76)}$ with NH_3. In agreement with Gutmann, Utvary and Bermann$^{75)}$, we had found the following reaction:



$$Cl_3P(NCH_3)_2PCl_3 + 10\ NH_3 \rightarrow [P_2(NH_2)_4(NHCH_3)_2]Cl + 5\ NH_4Cl$$

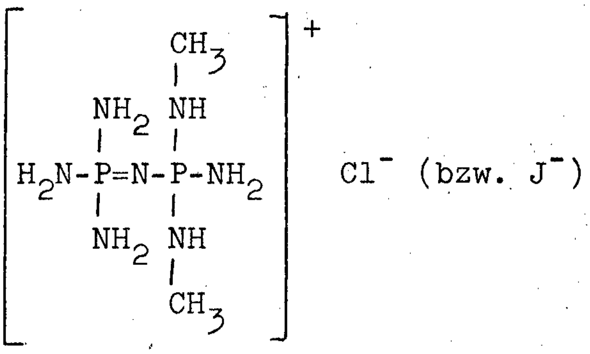
XVI

B



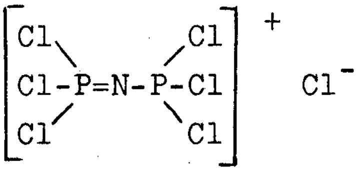
$$[H_2N-P(NH_2)_2=N-P(NH_2)_2-NH_2]^+\ Cl^-$$

LVIII



$$[H_2N-P(NH_2)_2=N-P(NHCH_3)_2-NH_2]^+\ Cl^-\ (bzw.\ J^-)$$

XVII



ILX

The structure of the reaction product B was established by X-ray analysis. It was shown that the structure is different from what Gutmann and co-workers$^{75)}$ had suggested. The structure of B is rather correctly represented by formula XVII. XVII shows a ^{31}P-NMR-signal at -16.5, i.e., a very similar signal as substance LVIII. A similar constitution for LVIII and XVII is therefore probable.

If our suggestion regarding structure is correct, one should be able to convert ILX smoothly into compound LVIII through the reaction with liquid ammonia. In this reaction, we isolated a substance, which is identical in composition, melting point, IR-spectrum, ^{31}P-NMR-spectrum and Debye-Scherrer diagram with the product A got from PCl_5 and liquid ammonia.

This result confirms formula LVIII.

Whereas in the reaction,

$$2\ PCl_5 + 16\ NH_3 \rightarrow [(NH_2)_3P{=}N{-}P(NH_2)_3]Cl + 9\ NH_4Cl$$

by-products are also formed, the reaction

$$[Cl_3P{=}N{-}PCl_3]Cl + 12\ NH_3 \rightarrow [(H_2N)_3P{=}N{-}P(NH_2)_3]Cl + 6\ NH_4Cl$$

runs almost quantitatively.

One may therefore make the following conclusions about the reaction of PCl_5 with liquid ammonia. At first, as we have earlier established$^{79)80)}$, PCl_5 reacts with ammonia to get the first isolable intermediate product, $[Cl_3P{=}N{-}PCl_3]^+$:

$$PCl_5 + NH_3 \xrightarrow{-2\ HCl} (Cl_3P{=}NH) \xrightarrow{+\ PCl_5} [Cl_3P{=}N{-}PCl_3]^+ + Cl^- + HCl$$

The cation reacts under condition of low ammonia concentration to give the linear and cyclic phosphonitrilic halides. However, when larger ammonia concentration are available, as they are in the case of the reaction of PCl_5 with liquid ammonia, then $[Cl_3P{=}N{-}PCl_3]^+$ is directly ammoniated to compound LVIII.

Experimental

Preparation of $P_2N_7H_{12}Cl$

a) From PCl_5 and NH_3

25 g PCl_5 were introduced in several lots into 200 ml of liquid ammonia, dried over sodium wire. A rigorous exothermic reaction took place on each addition. Under conditions of exclusion of moisture, the excess of ammonia was then distilled off, finally at reduced pressure (20 mm Hg). The white, moisture-sensitive residue was finely powdered, suspended in 600 ml absolute chloroform and boiled with 50 g diethylamine (previously dried over BaO) under reflux for 8 hours. The residue was then filtered hot and washed several times with chloroform. About 11.6 g of a white powdery substance were obtained. This was dissolved in 150 ml warm methanol and the solution was filtered off from undissolved residues and the bulk reduced to half and allowed to crystallise in a refrigerator. It was further recrystallised twice from methanol. It melts at 114-116^o; the yield amounts to 6 g, i.e., 48 % of theoretical yield.

b) From NP_2Cl_7 and NH_3

7.5 g of NP_2Cl_7, purified by sublimation, were introduced into 100 ml of liquid ammonia (dried over sodium wire) at -78^{o}C. When the ridorous reaction subsided, the excess ammonia was distilled off under conditions of careful exclusion of moisture. The white residue was finely powdered and suspended in 300 ml absolute chloroform, 13 g of BaO- dried diethylamine were added, boiled under reflux for 8 hours and filtered hot.

The residue was washed several times with chloroform. It was purified by recrystallisation from methanol. About 4.3 g, i.e., 84 % of theoretical yield, of the pure substance were obtained.

Analytical Data of $P_2N_7H_{12}Cl$

required:	P 29.85	N 47.24	H 5.83	Cl 17.08 %	
found:	P 30.09	N 47.47	H 6.12	Cl 17.07 %	(a)
found:	P 30.06	N 47.29	H 5.69	Cl 17.18 %	(b)

IR-spectrum of LVIII (in KBr)

3400 (ss), 3300 (ss), 1560 (ss), 1265 (ss), 1060 (schw), 1018 (m), 940 (s), 887 (m), 842 (m) cm^{-1}.

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13. ABSTRACT

The chemistry of P-N compounds is characterized by the existence of polymeric compounds. Many derivatives of the six membered ring system $(NPCl_2)_3$ and of the eight membered system $(NPCl_2)_4$ are known Therefore, the reaction of PCl_5 with NH_4Cl has been studied. The intermediates of this reaction could be isolated. In the report a short review of useful substances derived from the trimeric and the polymeric phosphonitrilic chlorides is given.

There are also four membered P-N ring compounds. These four membered ring systems their preparation and their properties, e.g. their structure, are described. Polymeric substances containing such a four membered ring system are formed with aromatic dihydroxy compounds and also with $Cr(CO)_6$. Some four membered ring systems may be condensated. .A compound with 3 four membered P-N ring systems was formed, in which the 3 ring systems are connected by a P-Cl bridge. There are also such ring systems in which 1 or more phosphorus atoms are substituted by SO_2-groups. Special attempts have been made to synthesize thermostable and flame resistant materials on the basis of P-N-C compounds. Therefore the reaction of guanidine and PCl_5 was studied Other compounds were prepared by the reaction of PCl_5 with cyanamide and with dicyandiamide, e.g. phosphatriazines could be prepared. New heterocycles with four and five membered P-N ring systems were obtained by the reaction of oxamide and PCl_5. Such ring systems can be connected with each other. Finally a very promissing product was obtained by the reaction of PCl_5 and liquid ammonia. The salt $[(NH_2)_3P{=}N{-}P(NH_2)_3]Cl$ was formed in very good yield. 5 This salt may be condensated by heating.

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