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Phenylphosphonitriles. I. *cis*- and *trans*-2,4,6-Trichloro-2,4,6-triphenyltriphosphonitriles

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Two isomers of $[NP(C_6H_5)Cl]_3$ have been prepared and identified by n.m.r. spectroscopy as the *cis* (m.p. 191–192°) and the *trans* (m.p. 158–159°) isomers. Both compounds were isolated from the reaction of phenyltetrachlorophosphorane, $C_6H_5PCl_4$, with ammonium chloride in an inert solvent such as chlorobenzene. Optimum conditions for making the cyclic trimers require the slow addition of a chlorobenzene solution of $C_6H_5PCl_4$ to a suspension of excess NH_4Cl in refluxing chlorobenzene. Chlorinated aliphatic solvents, such as *sym*-tetrachloroethane, which is the solvent most often used for the reaction, and pentachloroethane, were found to undergo dehydrohalogenation and render the reaction mixture more complex, with resultant poor yields of cyclic trimers.

Introduction

The reaction of $C_6H_5PCl_4$ with NH_4Cl

$$nC_6H_5PCl_4 + nNH_4Cl \longrightarrow \underset{\text{I}}{[NP(C_6H_5)Cl]_n} + 4nHCl \quad (1)$$

as reported by Humiec and Bezman[1] gave 26% of a cyclic trimer (I, $n = 3$; m.p. 161–163°) and a small amount of tetramer which was not isolated. Shaw and Stratton,[2] studying the same reaction under somewhat different conditions, obtained only trivial amounts of a different trimer (0.3% yield, m.p. 188°) and three different tetramers (I, $n = 4$) in a total yield of about 14%.

Moeller and Nannelli[3] recently have isolated and identified, by phosphorus nuclear magnetic resonance, two isomers of the closely related cyclic bromo trimer $[NP(C_6H_5)Br]_3$. The *trans* isomer exists in two crystalline forms (m.p. 152–153° and 162–163°), whereas the *cis* isomer exists as a higher melting (194–195°) species.

In this laboratory a careful study of conditions for reaction 1 has given significantly improved yields of cyclic products. In addition, *cis* and *trans* chloro isomers of the cyclic trimer have been identified by phosphorus n.m.r. spectroscopy, and synthetic conditions for obtaining either cyclic trimeric isomer have been defined.

Experimental

Materials.—Phenyldichlorophosphine, obtained from Victor Chemical Works, was distilled at 77° (1 mm.). All solvents were of reagent grade except for pentachloroethane. Pentachloroethane, obtained from Eastern Chemical Corp., was distilled at 161° prior to being used. All reaction solvents were dried over CaH_2. The NH_4Cl was of reagent grade quality. It was dried at 108° for at least 8 hr. before being used.

Analyses.—Microanalytical data were obtained from the Huffman Microanalytical Laboratory, Wheatridge, Colorado.

Instrumental Studies.—The crystal system of *trans*-trichlorotriphenyltriphosphonitrile was established from single crystal photographs taken with a precession camera. The phosphorus-31 nuclear magnetic resonance spectra of *cis*- and *trans*-$[NP(C_6H_5)Cl]_3$ were obtained on a Varian DP60 high resolution instrument. Spectra were obtained for chloroform solutions of the compounds at 15.1 Mc. and referred to 85% H_3PO_4 (external).

Synthesis of $[NP(C_6H_5)Cl]_3$. (A) Slow Addition of $C_6H_5PCl_4$ to NH_4Cl in Chlorobenzene (Experiment F of Table I).—A solution of 2.0 moles of $C_6H_5PCl_2$ in 2 l. of chlorobenzene was chlorinated until the solution turned bright yellow. Nitrogen was then bubbled through the solution until the yellow color disappeared. By using this procedure, one can quantitatively prepare $C_6H_5PCl_4$ in the solution to be used for the reaction without the necessity for isolating the extremely moisture-sensitive solid.

The chlorobenzene solution of $C_6H_5PCl_4$ was slowly added to a suspension of 4.0 moles of NH_4Cl in 8 l. of refluxing chlorobenzene. A nitrogen sweep through the reaction solution was maintained to facilitate removal of HCl. Evolved gas was passed into water and continuously titrated with standard base. The $C_6H_5PCl_4$ feed rate was regulated so that the total HCl evolved corresponded to within 5% of four times the total molar amount of $C_6H_5PCl_4$ already added.

In order to maintain this condition, the $C_6H_5PCl_4$ solution was added at the rate of 2.28 mmoles/min. for 12 hr., at the end of which time the reaction was 97% complete as evidenced by the amount of HCl evolved. The solution was kept at reflux an additional 12 hr., at which time no more HCl was evolved. At the end of the reaction 99% of the HCl expected on the basis of reaction 1 had been titrated.

For the separation of the reaction products, the crude mixture was first filtered hot to remove the excess NH_4Cl (110 g., 2.02 moles). The filtrate was then concentrated to about 25% of its original volume and allowed to stand at room temperature. Slow coprecipitation of tetramers and trimers occurred under these conditions. A well-defined solid product (fraction A), 75 g., m.p. 200–250°, rich in tetramer, was recovered from the solution by filtering after 24 hr. A second fraction (fraction B), 70 g., m.p. 180–200°, was recovered when the filtrate was allowed to stand an additional 24 hr. Dilution of the filtrate with *n*-pentane than gave 56 g. of crude trimer (fraction C), m.p. 120–150°. Further concentration of the solution resulted in the separation of a hydrolytically unstable oil, which probably consisted of linear and higher cyclic isomers.

Fractions A and B were combined and extracted with *n*-pentane. Infrared spectral analysis of the *n*-pentane-insoluble fraction indicated that it consisted mostly of tetramers, but also contained a small amount of trimer. The *n*-pentane-insoluble fraction was crystallized from benzene. Several tetrameric fractions, identified by their infrared spectra, totaling 44 g., with melting ranges from 200–205° to 240–254°, were recovered.

The cyclic trimer can be distinguished from the cyclic tetramer by the very strong characteristic infrared absorption at 1180 cm.$^{-1}$ for the trimer and a very strong absorption at 1300 cm.$^{-1}$

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[1] F. S. Humiec and I. I. Bezman, *J. Am. Chem. Soc.*, **83**, 210 (1961).

[2] (a) R. A. Shaw and C. Stratton, *Chem. Ind.* (London), 52 (1959); (b) *J. Chem. Soc.*, 5004 (1962).

[3] (a) T. Moeller and P. Nannelli, *Inorg. Chem.*, **1**, 721 (1962); (b) *ibid.*, **2**, 659 (1963); (c) *ibid.*, **2**, 896 (1963).

TABLE I

REACTION OF $C_6H_5PCl_4$ WITH NH_4Cl IN SEVERAL SOLVENTS

Expt.	Solvent	Temp., °C.	Concn. of $C_6H_5PCl_4$, *M*	HCl evolved, % theor.	Rate of addn. of $C_6H_5PCl_4$	% trimer	% tetramer
A	*s*-TCE	144	1.15	126	Fast	None isolated	31.2
B	*s*-TCE	144	1.2	125	Fast	2.4	24.7
C	*s*-TCE	144	0.7[a]	165	Slow	18.3	32.0
D	Chlorobenzene	131	0.5	99	Fast	29.4	45.6
E	Chlorobenzene	131	0.05	98	Fast	45.0	22.0
F	Chlorobenzene	131	0.2[a]	99	Slow	45.5	16.0
G	Pentachloroethane	158	0.41[a]	440	Slow	None isolated	None isolated
H	1,2,4-Trichlorobenzene	211	2.46	83.5	Fast	None isolated	None isolated

[a] This represents the concentration if the $C_6H_5PCl_4$ had been added rapidly at the start of the reaction.

for the tetramer. In addition, absorptions at 850 cm.$^{-1}$ for the trimer and 800 cm.$^{-1}$ for the tetramer can be used to distinguish the two homologs.

Two trimeric compounds, melting at 158–159° and 191–192°, were isolated from the reaction mixture. In all cases, the higher melting compound was obtained in very small yields of 2 to 3%. Both compounds were characterized as trimeric by their infrared spectra and molecular weights. Infrared spectra from 3500 to 675 cm.$^{-1}$ are nearly identical for the two compounds. The only apparent difference is a weak absorption occurring at 1130 cm.$^{-1}$ (m.p. 191–192°) and 1117 cm.$^{-1}$ (m.p. 158–159°). This might be attributed to slight differences in ring stretching vibrations resulting from different arrangements of substituents about the ring.

The last fraction (1.5 g.) to be recovered from the benzene filtrate proved to be a 1:1 benzene adduct of the *cis* trimer. This started to melt at 40° but resolidified above 80° and finally melted sharply at 185–188.5°.

A 1-g. sample o the crystalline benzene adduct was heated over 2 hr. to 120° in a vacuum apparatus at 10^{-4} mm. The volatile component was collected in a liquid N_2 trap. Based on *PVT* measurements, it was established that 1.82 mmoles of gas had collected in the liquid N_2 trap. This volatile component was identified as benzene by its infrared spectrum.

The white powder which remained after removal of the benzene melted at 185–188°. Recrystallization from chloroform–pentane gave an analytical sample of *cis*-$[NP(C_6H_5)Cl]_3$, m.p. 191–192°.

Anal. Calcd. for $[NP(C_6H_5)Cl]_3$: C, 45.70; H, 3.20; N, 8.88; P, 19.66; Cl, 22.53; mol. wt., 472. Found: C, 46.32; H, 3.17; N, 8.85; P, 19.5; Cl, 22.94; mol. wt., 429 (ebullioscopic, $CHCl_3$).

By careful fractional crystallization of the *n*-pentane-soluble fraction from a benzene–pentane mixture, 4 g. of tetramer, m.p. 200–230°, and 88 g. of trimer, m.p. 130–151°, were isolated. This trimer was combined with fraction C and recrystallized three times from benzene to give 140 g. of *trans*-$[NP(C_6H_5)Cl]_3$.

Anal. Calcd. for $[NP(C_6H_5)Cl]_3$: C, 45.70; H, 3.20; N, 8.88; P, 19.66; Cl, 22.53; mol. wt., 472. Found: C, 45.51; H, 3.11; N, 8.81; P, 19.0; Cl, 22.59; mol. wt., 458 (ebullioscopic, $CHCl_3$).

(B) Slow Addition of $C_6H_5PCl_4$ to NH_4Cl in *sym*-Tetrachloroethane (*s*-TCE) (Experiment C of Table I).—A solution of 1.05 moles of $C_6H_5PCl_4$ in 500 ml. of *s*-TCE was prepared as described previously. This was added at the rate of 0.02 mole/min. to 2.1 moles of NH_4Cl suspended in 1.0 l. of refluxing *s*-TCE (b.p. 144°). The reaction was carried out in an atmosphere of dry N_2. During the course of the addition of $C_6H_5PCl_4$, it became apparent that more than the expected amount of HCl was being evolved. It was also noted that the reflux temperature had dropped to 135° by the end of the reaction time.

Prior to separation of NH_4Cl, the reaction mixture was distilled to remove any lower boiling fractions. About 200 ml. of liquid first fraction distilled from the solution before pure *s*-TCE began to distil. Redistillation of this lower boiling fraction gave 189 ml. of liquid, b.p. 86°, which was identified as trichloroethylene by vapor phase chromatography and its infrared spectrum. Formation of this volume of trichloroethylene accounts for all of the HCl titrated in excess of that expected on the basis of eq. 1.

After filtering off the NH_4Cl, the *s*-TCE solution was flash evaporated to dryness, whereupon 126 g. of an oil remained. This oil was dissolved in benzene and, by slow preciptation with pentane, 53 g. (32% yield) of cyclic tetramer, m.p. 220–223°, was recovered. Further precipitation of solid from the benzene gave 30 g. (18.3% yield) of cyclic trimer, m.p. 113–131°. The remaining products separated from the benzene as oils which were readily hydrolyzable. The crude trimer was recrystallized from benzene five times to give 23.7 g. of pure *trans*-$[NP(C_6H_5)Cl]_3$, m.p. 158–159°.

Data of the other experiments listed in Table I were obtained similarly.

Discussion

The relative amounts of the various products of reaction 1 are greatly affected by the choice of solvent, rate of addition of $C_6H_5PCl_4$ to NH_4Cl, concentration of reactants, and temperature of the reaction (Table I). Yields of cyclic trimer are significantly higher in chlorobenzene than in tetrachloroethane.

Maximum yields of trimer are realized when the rate of addition of $C_6H_5PCl_4$ in chlorobenzene is regulated so that there is only a minimum of unreacted $C_6H_5PCl_4$ present in the reaction mixture at any time.

The data summarized in Table I now explain the apparently conflicting results obtained by previous investigators using *sym*-tetrachloroethane as the solvent.[1,2] The conditions and results of experiments A and B (rapid addition) are similar to those of Shaw and Stratton,[2] who obtained low yields of *cis* isomer as the only trimeric product isolated. On the other hand, the conditions and results of experiment C are similar to those of Humiec and Bezman,[1] who isolated 26% of the crude *trans* trimer.

Assignment of the *cis* configuration to the higher melting trimer and of *trans* to the lower melting trimer was deduced from the work of Moeller and Nannelli.[3b] However, unequivocal assignment of the *cis* and *trans* configurations was made from phosphorus-31 nuclear magnetic resonance spectra of the two isomers at 15.1 Mc. The spectrum of the higher melting isomer has a single peak at −29.4 p.p.m., whereas that of the lower

TABLE II

COMPARISON OF BROMO- AND CHLOROPHENYLPHOSPHONITRILES

	Trimeric bromo compounds		Trimeric chloro compounds	
	cis	*trans*	*cis*	*trans*
M.p., °C.	194–195	152–153 and 162–163	191–192	158–159
Crystal habit	Monoclinic	Triclinic and unidentified	Undetermined	Monoclinic
Crystallizes from heptane	First	Second	First	Second
Crystal size	Large[4]	Small[4]	Large	Small
Dipole moment	High	Low	High	Low
Infrared spectra	Identical		Identical except for weak absorption at	
			1130 cm.$^{-1}$	1117 cm.$^{-1}$
P-31 n.m.r. peaks	1	2	1	2

melting isomer has two peaks, in a 2:1 ratio, at −30.3 and −32.7 p.p.m.

During the present investigation, it was found that the melting point of the *cis* isomer (191–192°) was lowered to 160–180° when the bottled samples were stored several weeks at room temperature. This occurred without any change in elemental analysis. However, in the infrared spectrum a weak shoulder appeared at about 1117 cm.$^{-1}$. It is believed, therefore, that a solid state isomerization to the *trans* configuration occurs. Since the rate of such an isomerization would be expected to increase in solution, the unusually low yield of *cis*-$[NP(C_6H_5)Cl]_3$ can be explained. This phenomenon presently is under investigation by means of phosphorus-31 nuclear magnetic resonance techniques.

Some interesting comparisons now can be made between the existing trimeric isomers of the phenylchloro- and phenylbromophosphonitriles. These are listed in Table II.

Unlike the great difference in melting points between $(PNBr_2)_3$ (192°) and $(PNCl_2)_3$ (114°), the melting points of the triphenyl compounds are quite close for both the *cis* and *trans* isomers.

Other apparent differences between the two series include the formation of a 1:1 benzene adduct by the *cis*-trichloro isomer and the very low yield of *cis*-trichloro isomer isolated by the described synthesis. It is also noteworthy that the melting points of all reported[3c] *cis*-trisubstituted derivatives of the tribromo compound are higher than those of the corresponding *trans* derivatives.

Finally, there appears to be a tendency toward isomerization in both series. We have already discussed the apparent rearrangement of the *cis*-trichloro isomer to the *trans*. This same phenomenon also was observed in the tribromo system.[4] On the other hand, Moeller and Nannelli[3c] also suggest partial isomerization of the *trans*-tribromo compound to the *cis* isomer on recrystallization from acetonitrile, if the initial substance is impure. We have not yet observed any tendency of the *trans*-trichloro material to be converted to the *cis* isomer.

Isomerism in the trichloro compounds and other reactions will be discussed in a future communication.

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(4) T. Moeller, private communication.