Percyanophospholes

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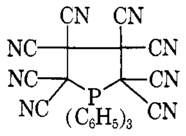
Tetracyanoethylene and dicyanoacetylene reacted with phosphines with spontaneous dimerization to give percyanophospha heterocycles or polymeric derivatives.

The reaction of acetylene dicarboxylic ester with aromatic phosphines is known to occur with the formation of a nonisolable unstable phosphole as intermediate which rearranges subsequently to a stable butadiene derivative.[1-3] Triphenylarsine and acetylene dicarboxylic ester gave a stable arsole derivative[2] and the larger size of the arsenic atom was proffered as a tentative explanation for the difference in stability between the phosphole and the arsole compounds. The present investigation suggests this to be of minor importance, however. No stable phosphole derivatives have been reported thus far which were formed from olefins or acetylenes directly.

The facile addition of triphenylphosphine to cyano-substituted ethylenic double bonds such as in tetracyano-7-oxabicyclohexa-2,5-diene which gave a stable ylid[4] invited further investigation of this type of reaction.

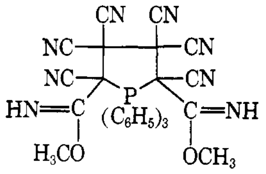
Aromatic phosphines react exothermically with two moles of tetracyanoethylene to give a stable, colorless, crystalline derivative of octacyano(triphenyl)phospholidine (I) (octacyano-P,P,P-triphenylphosphacyclopentane).



I

The reaction is best carried out in acetonitrile, but other solvents may be used successfully as long as they are unreactive toward tetracyanoethylene. The reaction also proceeded easily on diluting the two components with sodium chloride and subjecting the mixture to about 10,000 p.s.i. of external pressure. The reactants are probably brought in close contact with each other at the applied pressure, and exist in small droplets and in this state the reaction is facilitated. Different methods of preparation gave yields varying from 80 to 100%.

The structure of I as a percyanophospholidine is supported by the following results: it gave no indication of a zwitterion and failed to show the typical color test of tetracyanoethylene.[5] Decomposition occurred at about 230° with the ejection of some tetracyanoethylene and formation of a black polymeric product which still contained the triphenylphosphine unit as evidenced by the strong absorption at 9.0 μ and the three intensive absorption bands in the 13–15-μ region.



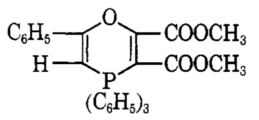
II

Reflux in methanol yielded a bisimino ether for which structure II is proposed.

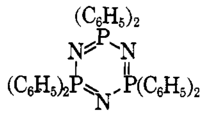
Hydrolysis with concentrated hydrochloric acid at 140–150° yielded butanetetracarboxylic acid as a mixture of the high and low melting form and triphenylphosphine oxide. The acidic component was further characterized by conversion into the tetramethyl ester whose infrared spectrum was superimposable on that of an authentic specimen. Further confirmation was obtained by conversion to its bisanhydride. These results indicated that two tetracyanoethylene units had been linked together.

Strong evidence for the phosphole structure of I was given by the nuclear magnetic resonance spectrum. The phosphorus chemical shifts in some compounds including I are given in Table I. It has been reported by several investigators[6-9] that in compounds of the general structure $-\overset{\diagdown}{\underset{\diagup}{P}}{=}O$ and $-\overset{\diagdown}{\underset{\diagup}{P}}{=}N$ the resonance of phosphorus generally lies above that of phosphoric acid. In cases where phosphorus is attached to a larger number of oxygen or nitrogen atoms somewhat lower chemical shifts have been reported.

The shift of 0.0 ± 1.0 p.p.m. for $(C_6H_5)_3P{=}N{-}C_6H_5$ is in good agreement with the previous observations in similar compounds. In III where there is little doubt about the structure[1] the chemical shift is -17.0 ± 1.0



III



IV

p.p.m. which is quite different from the others. The chemical shift in IV which is a very stable compound[10] is very much in agreement with other similar compounds of this basic structure.[11] This slightly low field shift in contrast to the compounds of the structure $-\overset{\diagdown}{\underset{\diagup}{P}}{=}N-$

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(1) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 2018 (1961).

(2) J. B. Hendrickson, R. E. Spenger, and J. J. Sims, *Tetrahedron Letters*, 477 (1961).

(3) A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, 2126 (1961).

(4) C. D. Weis, *J. Org. Chem.*, **27**, 3520 (1962).

(5) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

(6) J. R. Van Wazer, C. F. Callis, J. N. Shovlery, and R. C. Jones, *ibid.*, **78**, 5715 (1956).

(7) K. John, T. Moeller, and L. F. Audrieth, *ibid.*, **82**, 5616 (1960).

(8) K. John, T. Moeller, and L. F. Audrieth, *ibid.*, **83**, 2608 (1961).

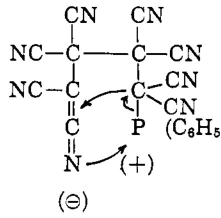
(9) E. Fluck, *Chem. Ber.*, **94**, 1388 (1961).

(10) K. Freudenberg and H. Richtzenhain, *Ann.*, **552**, 126 (1942). We are indebted to G. Nichols for a sample of this compound.

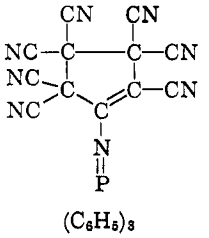
(11) M. Becke-Goehring, K. Kohn, and E. Fluck, *Z. anorg. allgem. Chem.*, **302**, 103 (1959).

could be due to either the second nitrogen or anisotropy effect of the phosphonitrile ring.[12-14] The two possible structures for the product are I and VI. In I the phosphorus atom is bonded as in III and in VI it is like $(C_6H_5)_3P{=}N{-}C_6H_5$. The vast difference in the chemical shifts of these compounds (see Table I) arises from the nature of the bonding rather than from the substituents. The chemical shift of I is −22.0 p.p.m. and is close to that of III in which the phosphorus is attached to five carbon atoms. To the extent the phosphorus chemical shifts are invariably positive in compounds of the type $-\overset{\diagdown}{\underset{\diagup}{P}}{=}N$ this low chemical shift suggests the structure to be I rather than VI. It was thought that n.m.r. studies of C^{13} nuclei should give an unambiguous assignment of I based on its symmetry, but solubility did not permit observance of C^{13} resonance in natural abundance.

Structure VI conceivably might have been formed by migration of triphenylphosphine from carbon to the nitrogen on the other end of the percyanoalkane chain. (V–VI). Acidic cleavage of the P–N bond of VI, followed by hydrolysis of the imino compound formed to give a β-ketone and its subsequent cleavage would also afford butanetetracarboxylic acid.



V



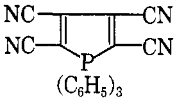
VI

Triphenylarsine or stibine did not react with tetracyanoethylene, as was observed previously for the oxabicycloderivative.

A possible explanation is that the *d*-orbital of the phosphorus overlaps partially the π-electron field of the alpha cyano substituents and contributes thus to the stability of I while the arsine atom is large enough to frustrate this interaction. The stability of IX compared with the corresponding tetraester[2,3] derived from it is attributed to the same effect.

ortho- and *para*-methyl-substituted triphenylphosphines (VII, VIII) underwent the same type of reaction. Tris(*p*-methoxyphenylphosphine), however, gave a tarry product only. Tributylphosphine gave a dark-colored polymeric product of low molecular weight. The 2:1 ratio of tetracyanoethylene to phosphine indicates that the same type of reaction occurred as with aromatic phosphines with the formation of an unstable phospholidine. Analysis suggested that the product, apparently during the work-up procedure, lost two cyano groups which were given off as hydrogen cyanide. No reaction was observed with fumaronitrile.

Dicyanoacetylene and triphenylphosphine reacted in acetonitrile with the formation of tetracyano(triphenyl)phosphole (IX) (tetracyano-P,P,P-triphenylphosphacyclopentadiene). The orange-colored compound is rather insoluble in organic solvents. The assignment of its structure is based on analytical results and the similarity of the pattern of its infrared spectrum with the spectrum of I. Thermal decomposition at 245° gave carbonized product and triphenylphosphine. There was no indication of a zwitterionic structure such as was proposed for the analogous methylphosphole tetracarboxylate[2,3] or any rearranged product thereof.[2]



IX

Experimental[15]

Octacyano-P,P,P-triphenylphospholidine. A.—Triphenylphosphine (5.8 g., 0.022 mole) was added slowly to a slurry of tetracyanoethylene (5.2 g., 0.04 mole) in acetonitrile (15 ml.). The temperature was maintained at 25–35° by external cooling. After the addition was completed stirring was continued for 10 min. and then the crystalline product (8.4 g., 80%) filtered from the ice-cold solution. Recrystallization of the buff-colored material from benzene yielded colorless crystals, m.p. 168.5–170°. The compound turned slightly red on melting.

Anal. Calcd. for $C_{30}H_{15}N_8P$: C, 69.50; H, 2.92; N, 21.61; P, 5.97. Found: C, 69.78; H, 3.15; N, 21.52; P, 5.89.

Mol. wt. (benzene) calcd.: 518; found: 512, 527. The infrared spectrum showed characteristic absorptions for CN at 4.41 μ (w) and 4.52 μ (w) with a ratio of the size of the bands about 1:2. The aromatic vibration bands were at 6.22 μ (vs), 6.32 μ (m), 6.92 μ (m), 7.20 μ (m). The absorption at 8.93 μ (s) was found to be characteristic of all aromatic phosphine compounds usually ranging from 8.9 to 9.2 μ. Further characteristic absorptions are at 9.98 μ (w); 10.95 μ (m); 13.12 μ (m); 13.31 μ (w); 13.72 μ (s); 14.40 μ (s). The triple sequence of medium to strong sized absorption bands in the 13.3–14.5-μ region was found to be very characteristic of five bonded phosphorus compounds and aromatic phosphonium compounds in general. The ultraviolet spectrum showed absorptions at $\lambda_{max}^{dioxane}$, 300 mμ (ε 15,700); shoulder at 276 mμ (ε 10,480); shoulder at 269 mμ (ε 9960).

N.m.r. Spectra. All the spectra were obtained on a Varian Associates high resolution spectrometer operating at 15.1 Mc./sec. The solvent was dioxane in all cases and saturated solutions were used. Calibrations were carried out by superposition technique with 85% orthophosphoric acid in a capillary as reference. All the chemical shifts are expressed in parts per million with respect to 85% orthophosphoric acid.

B.—Tetracyanoethylene (2.56 g., 0.002 mole) and triphenylphosphine (2.71 g., 0.001 mole) were well mixed with sodium chloride (5 g.) and the mixture placed in a die and subjected to 10,000-p.s.i. pressure. The pellet obtained was powdered and added to water (30 ml.). Buff-colored crystals (5.1 g., 97%) were filtered off, m.p. 168°, whose infrared spectrum was superimposable to the spectrum of the previously obtained sample.

Octacyano-P,P,P-tri-*o*-tolylphospholidine (VII).—Tri-*o*-tolylphosphine (3.04 g., 0.01 mole) was added to a suspension of tetracyanoethylene (.256 g., 0.02 mole) in acetonitrile (15 ml.). The slurry was heated to 50° whereupon a sudden change in color occurred. Subsequent filtration of the ice-cold solution gave buff-colored crystals (4.37 g., 78%). Recrystallization from benzene afforded colorless crystals, m.p. 235–237°.

Anal. Calcd. for $C_{33}H_{21}N_8P$: C, 70.70; H, 3.78; N, 19.98; P, 5.50. Found: C, 70.65; H, 3.88; N, 19.85; P, 5.49.

Octacyano-P,P,P-tri-*p*-tolylphospholidine (VIII).—*p*-Tolylphosphine (3.04 g., 0.01 mole) and tetracyanoethylene (2.56 g., 0.02 mole) were added to acetonitrile (15 ml.). The crystals went into solution with moderate evolution of heat, and crystals deposited after a few minutes. Further cooling of the solution furnished buff-colored crystals (3.7 g., 66.5%). Recrystallization from acetonitrile and subsequently from benzene gave colorless crystals, m.p. 205–206°.

Anal. Calcd. for $C_{33}H_{21}N_8P$: C, 70.70; H, 3.78; N, 19.98; P, 5.53. Found: C, 71.01; H, 4.02; N, 19.73; P, 5.38.

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(12) J. H. Goldstein and G. S. Reddy, *J. Chem. Phys.*, **36**, 2644 (1962).

(13) K. Ito, *J. Am. Chem. Soc.*, **80**, 3502 (1958).

(14) J. S. Waugh and R. W. Fessenden, *ibid.*, **79**, 846 (1957).

(15) Melting points are uncorrected.

The infrared spectrum exhibited the same absorption pattern as I, except for the additional CH_3 bands.

Hexacyanobis(imidic Acid, Methyl Ester)-P,P,P-triphenylphospholidine (II).—A solution of octacyano-P,P,P-triphenylphospholidine (5 g., 0.096 mole) in methanol (40 ml.) was refluxed for 10 min. Filtration of the ice-cold mixture gave off-colored crystals (2 g., 35.5%). Recrystallization from acetonitrile gave colorless crystals, m.p. 215–220° dec. The compound turned slightly brown at about 180°.

Anal. Calcd. for $C_{32}H_{23}N_8O_2P$: C, 65.98; H, 3.98; N, 19.23; P, 5.32. Found: C, 65.70; H, 4.37; N, 19.78; P, 5.36.

The infrared spectrum exhibited principal absorption bands at 3.01 μ (m); 4.63 μ (w); 6.03 μ (s); 6.35 μ (s); 6.43 μ (s).

Hydrolysis of I.—Octacyano-P,P,P-triphenylphospholidine (50 g., 0.0965 mole) was suspended in concentrated hydrochloric acid (210 ml.) and the mixture heated in an autoclave to 140° for 3 hr. The product was diluted with 500 ml. of water and allowed to stand for 12 hr. Filtration gave impure triphenylphosphine oxide (30.3 g., theoretical yield 25 g.), identified by the superimposability of the infrared spectrum of a recrystallized sample on that of a known specimen. The filtrate was evaporated to dryness on a steam bath. The residue (55.7 g.) was extracted with ether in a Soxhlet for 24 hr. Concentration of the ethereal extract (50 ml.) yielded a white crystalline precipitate (11.9 g., 53%) of crude 1.2.3.4 butanetetracarboxylic acid as a mixture of the low and high melting forms. It was filtered and washed with a few milliliters of cold ether. An analytical sample was recrystallized from water, m.p. 235°.[16] (It melted at 192°, resolidified, and melted finally at 235°.) Crude butanetetracarboxylic acid (1.5 g., 0.0064 mole) was treated with an excess of diazomethane in ether. Recrystallization of the tetramethyl ester from petroleum ether gave a mixture of the low and high melting form, m.p. 45–62°.

Anal. Calcd. for $C_{21}H_{188}O$: C, 49.68; H, 6.25. Found: C, 49.88; H, 6.35.

The infrared spectrum was superimposable with the one of an authentic sample of methyl 1.2.3.4-butanetetracarboxylate. The mixture of the butanetetracarboxylic acids (1 g., 0.0043 mole) was refluxed in acetic anhydride (8 ml.) for 3 min. The precipitate of butanetetracarboxylic acid dianhydride was filtered and identified by the superimposability of the infrared spectrum and the m.p. 248°, with a specimen which was prepared according to the literature.[17]

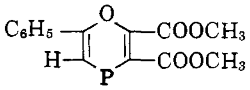
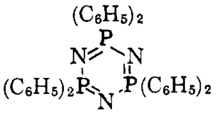
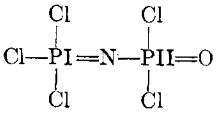
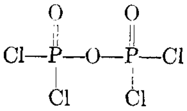
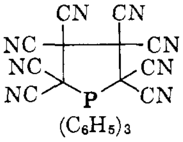
Thermal Decomposition of I.—Octacyano-P,P,P-triphenylphospholidine (1 g., 0.0019 mole) was heated in a test tube to 220–250° for 8 min. Tetracyanoethylene sublimed to the cold part of the tube and was identified by its infrared spectrum. The dark-colored residue showed still the typical absorption pattern of the triphenylphosphine unit as shown by its absorption at 9.1 μ and the three strong bands between 13 and 15 μ.

Tetracyanoethylene and Tributylphosphine.—Tributylphosphine (10 g., 0.05 mole) was added slowly to a suspension of tetracyanoethylene (12.5 g., 0.1 mole) in acetonitrile (30 ml.) which was immersed in an ice bath. The dark-colored solution was allowed to stand at room temperature for 30 min. and then the solvent was removed under reduced pressure. The dry, dark-colored residue (20 g., 88%) was extracted with ether in a Soxhlet for 8 hr. The product (insoluble in ether) softened at 190–230°.

Anal. Calcd. for $C_{22}H_{29}N_6PO_2$: C, 59.98; H, 6.63; N, 19.08; P, 7.03. Found: C, 60.43; H, 6.71; N, 18.52; P, 7.22.

TABLE I

P^{31} N.M.R. CHEMICAL SHIFTS IN SOME ORGANO-PHOSPHOROUS COMPOUNDS

Compound	Lit.	P^{31} chemical shift, p.p.m.
$(C_6H_5)_3P{=}N{-}C_6H_5$		0.0 ± 1.0
	1	−17.0 ± 1.0
$(C_6H_5)_4PBr$		−22.0 ± 1.0
	10	−9.0 ± 2.0
	9	(PI) + 0.1 ± 1.0 (PII) + 14.3 ± 1.0
	9	+10.0 ± 1.0
		−22.0 ± 1.0

Mol. wt. in dimethyl sulfoxide: 4953, 5084. The only characteristic absorption in the infrared spectrum was the CN absorption at 4.50 μ.

Tetracyano-P,P,P-triphenylphosphole (IX).—All reactants were carefully purified and kept under nitrogen during the experiment. A solution of dicyanoacetylene[18] (3.0 g., 0.040 mole) in acetonitrile (6 ml.) was added to a solution of triphenylphosphine (5.2 g., 0.02 mole) in acetonitrile (50 ml.) at 25–30°. The deep purple-colored solution was allowed to stand for 12 hr. Filtration gave light brown crystals (1.12 g., 13.6%). Several recrystallizations from pyridine gave orange-colored crystals, m.p. 237–239° (dec.).

Anal. Calcd. for $C_{26}H_{15}N_4P$: C, 75.35; H, 3.65; N, 13.52; P, 7.48. Found: C, 75.52; H, 4.00; N, 12.52, 13.10; P, 7.47.

The infrared spectrum showed absorption at 4.50 μ (w); 4.56 μ (m); 4.62 μ (m); 6.73 μ; 6.80 μ; 6.98 μ; 7.33 μ; 7.60 μ; 9.30 μ; 13.30 μ; 13.82 μ; 14.45 μ. Absorption in the ultraviolet occurred at $\lambda_{\max}^{\text{dioxane}}$, 485 mμ and 378 mμ. The deep blue mother liquor yielded upon evaporation a blue-colored, apparently polymeric residue.

Thermal Decomposition of IX.—Tetracyano-P,P,P-triphenylphosphole (0.2 g., 0.00048 mole) was heated in a sublimation apparatus to 250–260° at 0.5 mm. for 4 hr. The sublimed triphenylphosphine (0.095 g., 75%) was identified by comparison of its infrared spectrum with that of an authentic sample. The carbonaceous residue weighed 0.70 g.

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[16] W. Bertram, *Ber.*, **36**, 3295 (1903).

[17] A. J. Viorlew and W. J. Mur, "Syntheses of Organic Compounds," Ved Verlat Technik, Berlin, 1959, p. 29.

[18] E. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).