Following additional crystallization, the product I came down in the form of dark red rhombic crystals, m.p. 107–108°. Yields in the order of 70% have been obtained.

Anal. Calcd. for $C_{16}H_{17}O_4Re$: C, 41.8; H, 3.69; Re, 40.5; mol. wt., 460. Found: C, 42.4; H, 3.89; Re, 40.8; mol. wt., 481 (isopiestic). Principal infrared absorptions, cm.$^{-1}$ (KBr pellet): 3150 m, 3000 m, 2930 m, 1710 s, 1785 s, 1590 s, 1440 m, 1430 s, 1390 m, 1335 s, 1220–1140 s (br), 1095 s, 1058 m, 1025 s, 1010 s, 995 m, 975 m, 955 s, 945 s, 892 s, 865 s, 832 s, 825 s, 812 m, 785 s.

Isomerization of Adduct I.—Freshly reduced platinum (60 mg.) was added to 420 mg. of complex I dissolved in approximately 20 ml. of benzene. This mixture, together with a magnetic stirring bar, was sealed in a glass ampoule. The mixture was heated at 75° for 17 hr., while maintaining rapid stirring. It was then filtered, the filtrate was reduced to dryness under reduced pressure, and the residue was crystallized twice from methanol to yield 407 mg. (95% yield) of blood-red rhombic crystals, m.p. 151–152°.

Anal. Calcd. for $C_{16}H_{19}O_4Re$: C, 41.8; H, 3.69. Found: C, 42.0; H, 3.91. Principal infrared absorptions, cm.$^{-1}$ (KBr pellet): 3120 m, 3000 m, 2940 m, 1700 s, 1675 s, 1575 s, 1440 m, 1420 s, 1385 s, 1345 s, 1290 s, 1240 m, 1200–1110 s (br), 1090 s, 1050 m, 1010 s, 995 s, 980 s, 935 s, 880 m, 862 s, 825 s, 815 s, 788 s, 772 m, 735 m, 708 m.

Hydrogenation of Adduct I.—The complex (460 mg., 1.0×10^{-3} mole) was dissolved in 30 ml. of anhydrous ethanol and hydrogenated over 70 mg. of platinum at 26° and atmospheric pressure. Following a 5.5-hr. reaction period the stirring was discontinued, and the reaction mixture was allowed to stand in the apparatus for an additional 16 hr. It was then filtered, and the filtrate was concentrated and cooled at −30° until crystallization was induced. Successive recrystallization from diethyl ether and ethanol enabled the isolation of 240 mg. (53%) of very dark red, needle-like crystals, m.p. 132–133°.

Anal. Calcd. for $C_{16}H_{18}O_4Re$: C, 41.7; H, 4.13. Found: C, 42.3; H, 4.28. Principal infrared absorptions, cm.$^{-1}$ (KBr pellet): 3140 m, 3000 m, 2950 m, 2930 m, 2860 m, 1690 s, 1550 s, 1480 m, 1450 s, 1420 s, 1370 s, 1320 m, 1255 m, 1220–1170 s (b), 1135 m, 1095 m, 1055 m, 1020 s, 990 m, 945 m, 906 m, 890 m, 892 m, 882 m, 865 m, 815 s, 795 m, 695 m.

β-Dicyclopentadienylrhenium Methyl Acrylate.—The titled adduct formed from dicyclopentadienylrhenium hydride and methyl propiolate is best prepared in the manner described for complex I, but with ethanol as the reaction medium. Recrystallization from methanol results in the isolation of orange-brown plates (40% yield), m.p. 161–162°.

Anal. Calcd. for $C_{14}H_{15}ReO_2$: C, 41.9; H, 3.77. Found: C, 42.5; H, 3.99. Principal infrared absorptions, cm.$^{-1}$ (KBr pellet): 3150 m, 2930 m, 1610 vs, 1430 s, 1390 s, 1350 m, 1345 m, 1245 s, 1215 m, 1150 vs (b), 1105 s, 1065 s, 1030 s, 970 s, 910 m, 865 m, 840 s, 835 s, 818 s, 725 s.

Attempts to either hydrogenate or isomerize IV under conditions found suitable for adduct I were unsuccessful as the complex was recovered unchanged from the reaction mixtures.

Acknowledgment.—This study was partially supported by the United States Atomic Energy Commission under Contract No. AT(11-1)-999. We are indebted to Dr. A. H. Filbey for his aid and encouragement throughout the course of this work and to Prof. N. LeBel, Wayne State University, for the n.m.r. spectra.

Contribution from Dayton Laboratory,
Monsanto Research Corporation, Dayton, Ohio

The Formation of P–N and P–N–P Bonds by Elimination of Phenol in a Basic Condensation[1]

By MORRIS L. NIELSEN

Received July 13, 1964

Displacement of phenol from a phenyl ester of phosphoric acid or a phosphoramidic acid by anions of certain amines or phosphoramidates in the presence of a base results in the formation of P–N and P–N–P bonds. From $(C_6H_5O)_3PO$ and $NaNHC_6H_5$ there was obtained $(C_6H_5O)_2P(O)NHC_6H_5$; with $NaN(C_6H_5)_2$, the product was $(C_6H_5O)_2P(O)N(C_6H_5)_2$. From $(C_6H_5O)_3PO$ and sodium amide, however, the product was $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)_2$. From $(C_6H_5O)_2P(O)NH_2$, by self-condensation, was obtained both $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)NH_2$ and $(C_6H_5O)_2(O)NHP(O)(OC_6H_5)NHP(O)(OC_6H_5)NH_2$. From $(C_6H_5O)_3PO$ and $(C_6H_5O)_2P(O)NH_2$ the principal product was $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)NHP(O)(OC_6H_5)_2$. The last three compounds have not been reported before. The properties of these compounds and their metal and amine derivatives are described.

Introduction

A familiar reaction for the formation of P–N bonds is the displacement of halogen on phosphorus by ammonia, azides, hydrazine, or amines. For example

$$(C_6H_5O)P(O)Cl + 2NH_3 \longrightarrow (C_6H_5O)_2P(O)NH_2 + NH_4Cl$$

Displacement of halogen by an amide in the presence of a base has, according to Debo,[2] yielded P–N–P bonds.

$$(C_2H_5O)_2P(O)Cl + (C_2H_5O)_2P(O)NHC_2H_5 + NaH \longrightarrow (C_2H_5O)_2P(O)N(C_2H_5)P(O)(OC_2H_5)_2 + NaCl + H_2$$

The present work arose from an attempt to prepare a P–N bond by displacement of phenol by amide in a reaction which would have been analogous to the hydrolysis of an ester.

$$(C_6H_5O)_2P(O)OC_6H_5 + OH^- \longrightarrow (C_6H_5O)_2P(O)O^- + C_6H_5OH$$

$$(C_6H_5O)_2P(O)OC_6H_5 + NH_2^- \longrightarrow (C_6H_5O)_2P(O)NH^- + C_6H_5OH$$

When triphenyl phosphate and sodium amide were heated together in toluene, however, there was ob-

---

[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

[2] A. Debo, German Patent 1,041,044 (to Chemische Fabrik Joh. A. Benckiser G.m.b.H., Oct. 16, 1958); *Chem. Abstr.*, **53**, 24,397e.

tained in good yield the P–N–P compound, tetraphenyl imidodiphosphate, $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)_2$ (I), instead of the anticipated diphenyl phosphoramidate, $(C_6H_5O)_2P(O)NH_2$. Further investigation showed that the anions of aniline and diphenylamine displaced phenol to yield $(C_6H_5O)_2P(O)NHC_6H_5$ and $(C_6H_5O)_2P(O)N(C_6H_5)_2$, as anticipated. In addition, the reactions of the phosphoramidate anion, $(C_6H_5O)_2P(O)NH^-$, with itself or with triphenyl phosphate to yield three new compounds were investigated. Finally, a series of metal and amine derivatives was prepared for identification and structural studies.

Experimental

All displacement reactions involving anions were run under a nitrogen atmosphere. Toluene was dried by storage over calcium hydride. Elemental analyses and molecular weights were performed by Galbraith Laboratories, Inc., and Schwarzkopf Microanalytical Laboratory. All melting points were corrected. X-Ray diffraction (X.r.d.) powder data were obtained on a General Electric XRD-3 X-ray diffraction unit, with Cu Kα radiation filtered through nickel foil (λ 1.5418 Å.). The phosphorus-31 nuclear magnetic resonance (n.m.r.) data were obtained with a Varian Model V-4311 high resolution n.m.r. spectrometer at a frequency of 16.2 Mc. The proton n.m.r. data were obtained with a Varian Model A-60 analytical n.m.r. spectrometer. All infrared spectra were recorded from 5000 to 650 cm.$^{-1}$ on a Beckman IR-4 double-beam spectrometer, using specimens prepared as Nujol and hexachlorobutadiene (HCB) mulls.

Diphenyl N-Phenylphosphoramidate.—A suspension of 0.1 mole of sodium anilide, prepared by the method of Titherly,[3] in 300 ml. of toluene together with 0.05 mole of triphenyl phosphate was heated at reflux for 2 hr., whereupon cream-colored solids formed. The mixture was cooled and shaken with water, leaving solids, m.p. 131–131.5° (lit. 129°).[4] The toluene was evaporated to give more solids, for a combined yield of 9.3 g. (57%) of $(C_6H_5O)_2P(O)NHC_6H_5$, identified by X.r.d. by comparison with product made as in ref. 4.

Diphenyl N,N-Diphenylphosphoramidate. (A) From Triphenyl Phosphate.—Sodium diphenylamide was prepared in liquid ammonia from 0.051 mole of diphenylamine and 0.05 g.-atom of sodium in the presence of a catalytic amount of ferric nitrate. The ammonia and unreacted diphenylamine were finally baked out under vacuum at 190°. The solids were heated in 300 ml. of toluene at reflux together with 0.05 mole of triphenyl phosphate for 2 hr. On cooling, the solids were separated by centrifuging, rinsed with toluene, and recrystallized from water. Careful drying gave 4.3 g. (75%) of anhydrous sodium phenoxide, identified by X.r.d. The toluene solution, on evaporation, gave 19 g. (95%) of crude $(C_6H_5O)_2P(O)N(C_6H_5)_2$, identified by X.r.d. as the same as the product obtained in B below. Recrystallization from benzene–heptane gave 10 g. (50%), m.p. 97–99° (lit. 180°,[5] see below).

(B) **From Diphenyl Phosphorochloridate.**—To a suspension of 0.05 mole of sodium diphenylamide in 400 ml. of toluene was added 0.05 mole of $(C_6H_5O)_2P(O)Cl$ dropwise in 12 min., the temperature rising to 38°. After heating at reflux for 1 hr., the mixture was cooled, and the solids were removed by centrifuging, rinsed with toluene, and identified as sodium chloride. The toluene solution was concentrated to yield crystals, 16.6 g. (83%). An analytical sample, recrystallized from heptane, melted at 103–104°.

Anal. Calcd. for $C_{24}H_{20}NO_3P$: C, 71.82; H, 5.02; N, 3.49; P, 7.72. Found: C, 71.53; H, 5.13; N, 3.56; P, 7.76.

A second modification, as shown by X.r.d., was obtained on recrystallization from either pyridine or triethylamine, m.p. 103–103.5°.

Anal. Found: C, 71.80; H, 5.04; N, 3.52; P, 7.70.

The substance is soluble in many organic solvents but not in water. It is believed that the m.p. of 180° reported by Otto[5] for a preparation from $(C_6H_5)_2NP(O)Cl_2$ and phenol is in error.

Tetraphenyl Imidodiphosphate (I).—A mixture of 0.45 mole of triphenyl phosphate and 0.68 mole of sodium amide in 1200 ml. of toluene was heated at reflux for 2 hr. Some foaming occurred because of elimination of ammonia, and solids (other than $NaNH_2$) appeared. The mixture was cooled to about 40° and water was added to dissolve the sodium phenoxide. The toluene layer was separated, acidified with dilute hydrochloric acid, and then washed with water twice and concentrated to about 200 ml. Solids were precipitated by adding hexane and were recrystallized from acetone–water and then from benzene–hexane, 82 g. (75%), m.p. 111–112° (lit. 110–112°).[6]

Triphenyl Amidoimidodiphosphate[7] (II). (A) **Using Sodium Amide.**—A mixture of 0.05 mole of diphenyl phosphoramidate and 0.05 mole of sodium amide was heated in toluene at reflux for 4 hr. The sodium phenoxide was removed by centrifuging, and some of the toluene was distilled off. Addition of dilute hydrochloric acid to the toluene solution, while cooling, gave solids, 8.6 g. (85%), m.p. 119–120°.

Anal. Calcd. for $C_{18}H_{18}N_2O_5P_2$: C, 53.47; H, 4.49; N, 6.93; P, 15.32; mol. wt., 404. Found: C, 53.39; H, 4.30; N, 7.17; P, 15.39; mol. wt. (in acetone), 415.

(B) **Using Sodium Hydride.**—A mixture of 0.05 mole of diphenyl phosphoramidate and 0.05 mole of sodium hydride was heated in benzene at reflux for 4 hr. Work-up as above gave 7.5 g. (74%) of II, identified by X.r.d.

(C) **Using the Sodium Derivative of Diphenyl Phosphoramidate.**—To 0.05 mole of diphenyl phosphoramidate in about 1 l. of toluene at 110° was added a solution of what was presumably the sodium derivative of diphenyl phosphoramidate prepared separately from 0.05 mole of diphenyl phosphoramidate and 0.05 mole of sodium hydride in about 1.5 l. of toluene at 50°. After heating for 4 hr. at reflux, during which no sodium phenoxide appeared, the mixture was cooled and shaken with 0.5 l. of water. Acidification of the water solution yielded solids, 18.5 g. (92%) of II, identified by X.r.d.

(D) **Using Sodium in Liquid Ammonia.**—Sodium (0.025 g.-atom) was added to 0.025 mole of diphenyl phosphoramidate in about 250 ml. of liquid ammonia and stirred until the initial blue color disappeared. Removal of the ammonia left a solid which was dissolved in water and reprecipitated with hydrochloric acid. Recrystallization from benzene–heptane yielded 1.4 g. (28%) of II as identified by X.r.d.

(E) **Using Sodium Phenoxide.**—A mixture of 0.025 mole of diphenyl phosphoramidate and 0.025 mole of sodium phenoxide was heated in toluene at reflux for 4 hr. Work-up gave 4.35 g. (86%) of II, identified by X.r.d.

Three crystalline forms were observed by X.r.d. Form II was obtained from crystallization from benzene, m.p. 120°.

Anal. Found: C, 53.63; H, 4.49; N, 6.81; P, 15.10. It was converted to form I either by melting or by recrystallization from boiling benzene–heptane. Form III resulted after recrystallization from ethanol–heptane, m.p. 144–145°.

The substance is soluble in ethanol, acetone, dioxane, acetonitrile, dimethoxyethane, ethyl acetate, dimethyl sulfoxide, chloroform, or benzene; it is insoluble or only slightly soluble in water, hexane, or cyclohexane; it is readily soluble in dilute sodium hydroxide.

Tetraphenyl Amidodiimidotriphosphate (III). (A) **From II.**—Triphenyl amidoimidodiphosphate (0.02 mole) and 0.02 mole of sodium hydride were mixed in toluene at 50°, then heated to 105° while adding alternate portions of diphenyl phosphoramidate

---

[3] A. W. Titherly, *J. Chem. Soc.*, **71**, 464 (1897).

[4] A. Michaelis and G. Schulze, *Ber.*, **27**, 2572 (1894).

[5] P. Otto, *ibid.*, **28**, 613 (1895).

[6] A. V. Kirsanov and I. N. Zhmurova, *Zh. Obshch. Khim.*, **28**, 2478 (1958); *Chem. Abstr.*, **53**, 3118*i*.

[7] The name "amidoimidodiphosphate" has been accepted by Leonard T. Capell, Nomenclature Department, Chemical Abstracts.

(0.02 mole) and sodium hydride (0.04 mole). After heating at reflux for 3 hr., the mixture was cooled, shaken with water, and the water layer acidified. The waxy solids were recrystallized from methanol–water, with the first fraction consisting of 2.6 g. (23%) of crude III, m.p. 127–135°; the remaining fractions consisted of 2.8 g. of II. The analytical sample, obtained by recrystallization from dioxane–acetone, melted at 158–161°.

Anal. Calcd. for $C_{24}H_{24}N_3O_7P_3$: C, 51.53; H, 4.32; N, 7.51; P, 16.61; mol. wt., 559. Found: C, 51.29; H, 4.43; N, 7.52; P, 16.90; mol. wt. (in 95% ethanol), 548.

(B) **From Diphenyl Phosphoramidate.**—Diphenyl phosphoramidate (0.1 mole) and 0.067 mole of sodium hydride reacted in 500 ml. of toluene at 45° within 10 min. to yield a solution, presumably of the sodium derivative, $(C_6H_5O)_2P(O)NHNa$. There was then added 0.083 mole of coarse-grained commercial sodium amide, and stirring was continued at 45° for 1 hr. The temperature was then increased over a period of 1.5 hr. until reflux occurred, and refluxing was continued for 2.5 hr. Nearly all the sodium amide had disappeared, and a finely divided solid had formed. This was centrifuged off, rinsed with toluene, and identified as sodium phenoxide, 7.0 g. (91%). The toluene solution was extracted with water, and the water layer was cooled and acidified while stirring with benzene. The crude precipitated solids were recrystallized by dissolving in acetone–pyridine (7:1), neutralizing the solution with dilute HCl, and adding water as a nonsolvent, yielding 7.1 g. (38%) of III, m.p. 151–151.5°. The X.r.d. powder pattern differed from that of the sample above and was designated form II.

Anal. Found: C, 50.85; H, 4.86; N, 7.64; P, 17.06.

Four crystalline forms were observed by X.r.d. In addition to forms I and II above, form III, m.p. 139–141°, resulted after recrystallization from acetone.

Anal. Found: C, 51.28; H, 4.25; N, 7.62; P, 16.48.

Form IV, m.p. 150–150.5°, resulted from decomposition of a 1:1 adduct with acetonitrile either on standing several hours in air or on heating at 56° for 0.5 hr. under vacuum.

Anal. Found: C, 51.15; H, 4.33; N, 7.56; P, 16.31.

The substance is soluble in methanol, ethanol, dioxane, acetonitrile, pyridine, dimethylformamide, or dimethyl sulfoxide; it is insoluble or only slightly soluble in water, acetone, ether, carbon tetrachloride, benzene, or hexane. Separation of III from II was achieved by differences in solubility, III being less soluble.

Pentaphenyl Diimidotriphosphate (IV).—A mixture of 0.05 mole of diphenyl phosphoramidate, 0.10 mole of sodium hydride, and 0.05 mole of triphenyl phosphate in 500 ml. of toluene was heated at reflux for 4 hr., then cooled and extracted with water. The aqueous solution was acidified to yield a noncrystallizable liquid. After this had been stirred repeatedly with cyclohexane to remove phenol and unreacted triphenyl phosphate, crystals formed. Recrystallization from acetone–water gave 9.6 g. (60%) of IV, m.p. 126–127°.

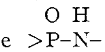
Anal. Calcd. for $C_{30}H_{27}N_2O_8P_3$: C, 56.61; H, 4.28; N, 4.40; P, 14.60; mol. wt., 636. Found: C, 57.31; H, 4.67; N, 4.41; P, 14.90; mol. wt. (in acetone), 629.

The material is soluble in methanol, ethanol, tetrahydrofuran, dioxane, acetone, chloroform, or benzene; it is insoluble or only slightly soluble in water, ether, or hexane.

Saponification of IV with NaOH in sodium phenoxide at 135° for 1.25 hr. gave $Na_5P_3O_8(NH)_2 \cdot 6H_2O$ in about 25% yield, identified by X.r.d.

Triphenyl Imidodiphosphoric Acid.—Hydrolysis of IV with a trace of hydrochloric acid in moist air at room temperature for several days gave a new compound, triphenyl imidodiphosphoric acid, $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)OH$. The resulting viscous liquid was stirred with cyclohexane and ether to yield a solid which was recrystallized from ethyl acetate–cyclohexane; m.p. 159–161°.

Anal. Calcd. for $C_{18}H_{17}NO_6P_2$: C, 53.34; H, 4.23; N, 3.46; P, 15.28. Found: C, 54.41; H, 4.16; N, 4.27; P, 14.51.

Titratable Acidic Hydrogens.—The imido phosphorus compounds, I, II and III, presumably containing the  $>\overset{O}{P}-\overset{H}{N}-$ structure, are characteristically acidic in water and can be titrated as strong acids in acetone–water or dioxane–water solution. The number of titratable acidic hydrogens found per mole were, respectively, 1.01, 0.92, and 1.57. Inspection of the formulas suggests: 1.0, 1.0, and 2.0. While the titration of III was unexpectedly (and reproducibly) low, there were two breaks in the titration curve, the first corresponding to 0.78 equivalent of H^+.

X.r.d. Powder Data.—Considerable use was made of X.r.d. analysis for identifying the above compounds. The task was complicated by the occurrence of polymorphic forms, but these could be obtained reproducibly by recrystallization from specific solvent systems. It is possible that some of these forms may result from isomerism. For identification and a test of purity, reliance was placed much more on X.r.d. analysis than upon melting points, since melting points often varied as transitions between the forms occurred, and published melting points were found unreliable. A summary of the X.r.d. powder data and melting points is given in Table I. Complete X.r.d. data have been reported elsewhere.[8]

Metal and Amine Derivatives.—Table II lists the metal and amine derivatives of I and II, prepared for identification and structure studies. In general, the products were obtained on mixing I or II with the metal hydroxide or other suitable salt (or an amine) in solution, from which the crystalline products were isolated on evaporation of the solvent, with added assistance of a nonsolvent if necessary. The metal derivatives are soluble in organic solvents; *e.g.*, the iron derivative dissolves readily in ethanol, acetone, ether, or benzene, but it is insoluble in water or hexane; the sodium derivative is soluble in either benzene or water.

The metal derivatives underwent expected chemical reactions: the sodium derivative of I, when acidified, yielded the original ester; the silver derivative of I, with HCl, H_2S, or H_2SO_4, yielded I; with D_2SO_4, the silver derivative yielded partially deuterated I.

With methyl iodide, the silver derivative of I yielded tetraphenyl N-methylimidodiphosphate. The reaction occurred readily at 95–100° in a sealed ampoule, and the product was isolated from benzene solution by adding hexane, yield 42%, m.p. 91–93° (lit. 68°),[2] identical by X.r.d. with tetraphenyl N-methylimidodiphosphate prepared by Debo's method (see below).

Anal. Calcd. for $C_{25}H_{23}NO_6P_2$: C, 60.61; H, 4.68; N, 2.83; P, 12.50. Found: C, 60.51; H, 4.38; N, 3.13; P, 12.59.

Tetraphenyl N-Methylimidodiphosphate (V).[2]—Diphenyl phosphorochloridate (0.05 mole) was added slowly to 0.05 mole of diphenyl N-methylphosphoramidate and 0.05 mole of sodium hydride in benzene. After heating at reflux, the mixture was filtered and the solvent was removed. Crystals formed slowly, 6.2 g. (25%), m.p. 92–92.5°. It is believed that the m.p. of 68° reported by Debo is in error unless this compound is polymorphic. The structure was confirmed by proton n.m.r. (see below).

N.m.r. Chemical Shifts.—The P^{31} n.m.r. data, summarized in Table III, have been discussed elsewhere.[9,10] They have been useful for identification and for confirmation of structure. The H^1 n.m.r. data are summarized in Table IV.

Infrared Absorption Spectra.—All compounds were examined by infrared spectroscopy.[11] In general, the N–H stretching vibrations are found as strong bands in the 3400–3000 cm.$^{-1}$ region. Additional bands or broadening of the above bands in

---

[8] The X-ray powder data have been submitted to J. V. Smith, Ed., "A.S.T.M. X-Ray Powder Data File," Department of Geology, University of Chicago, Chicago, 37, Ill.

[9] M. L. Nielsen and J. V. Pustinger, Jr., *J. Phys. Chem.*, **68**, 152 (1964).

[10] M. L. Nielsen, J. V. Pustinger, Jr., and J. Strobel, *J. Chem. Eng. Data*, **9**, 167 (1964).

[11] Complete data have been deposited as Document No. 8090 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting $3.75 for photoprints, or $2.00 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I

CONDENSATION PRODUCTS AND RELATED COMPOUNDS

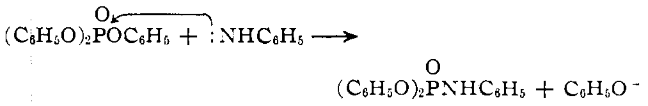
Name	Formula	M.p., °C.	—X.r.d. powder data, three strongest lines, *d*, Å.— (intensity basis 100)		
Diphenyl phosphoramidate	$(C_6H_5O)_2\overset{O}{P}NH_2$	151–151.5	13.1 (100)	4.364 (18)	4.484 (8)
Tetraphenyl imidodiphosphate	$(C_6H_5O)_2\overset{O}{P}NH\overset{O}{P}(OC_6H_5)_2$	111–112	9.88 (100)	4.541 (60)	9.16 (36)
Triphenyl amidoimidodiphosphate	$(C_6H_5O)_2\overset{O}{P}NH\underset{\underset{C_6H_5}{O}}{\overset{O}{P}}NH_2$				
Form I		119–120	11.6 (100)	4.31 (40)	4.91 (25)
Form II		120	25.6 (100)	12.6 (14)	4.997 (6)
Form III		144–145	10.1 (100)	16.8 (65)	4.861 (63)
Triphenyl imidodiphosphoric acid	$(C_6H_5O)_2\overset{O}{P}NH\underset{\underset{C_6H_5}{O}}{\overset{O}{P}}OH$	159–161	13.0 (vvs)	4.72 (m)	4.60 (m)
Tetraphenyl amidodiimidotriphosphate	$(C_6H_5O)_2\overset{O}{P}NH\underset{\underset{C_6H_5}{O}}{\overset{O}{P}}\text{-}NH\text{-}\underset{\underset{C_6H_5}{O}}{\overset{O}{P}}NH_2$				
Form I		158–161	11.3 (100)	11.9 (51)	12.5 (11)
Form II		151–151.5	10.7 (100)	12.6 (60)	21.4 (33)
Form III		139–141	11.4 (100)	12.5 (79)	4.66 (47)
Form IV		150–150.5	13.0 (100)	10.9 (85)	4.720 (35)
Acetonitrile adduct of tetraphenyl amidodiimidotriphosphate	$CH_3CN\cdot(C_6H_5O)_2\overset{O}{P}NH\underset{\underset{C_6H_5}{O}}{\overset{O}{P}}\text{-}NH\text{-}\underset{\underset{C_6H_5}{O}}{\overset{O}{P}}NH_2$	Dec.	11.1 (100)	17.7 (95)	13.8 (40)
Pentaphenyl diimidotriphosphate	$(C_6H_5O)_2\overset{O}{P}NH\underset{\underset{C_6H_5}{O}}{\overset{O}{P}}NH\overset{O}{P}(OC_6H_5)_2$	126–127	12.5 (100)	11.1 (16)	13.3 (12)
Diphenyl N-phenylphosphoramidate	$(C_6H_5O)_2\overset{O}{P}NHC_6H_5$	131–131.5	5.039 (100)	4.201 (100)	8.15 (87)
Diphenyl N,N-diphenylphosphoramidate	$(C_6H_5O)_2\overset{O}{P}N(C_6H_5)_2$				
Form I		103–104	8.0 (100)	4.66 (60)	16.2 (40)
Form II		103.5	4.58 (100)	8.3 (80)	4.31 (65)
Tetraphenyl N-methylimidodiphosphate	$(C_6H_5O)_2\overset{O}{P}\text{-}\underset{\underset{CH_3}{\vert}}{N}\text{-}\overset{O}{P}(OC_6H_5)_2$	92–92.5	5.644 (100)	5.082 (100)	4.322 (94)

the 3000–2500 cm.$^{-1}$ region for the imido compounds, such as $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)_2$, is attributable to hydrogen-bonded N–H. These disappear with N-substitution (of methyl for hydrogen) or in the metal derivatives such as $Ag[(C_6H_5O)_2P(O)NP(O)(OC_6H_5)_2]$. The internal N–H deformation absorptions of (P)–NH_2 compounds are shown in the 1580–1550 cm.$^{-1}$ region. A sharp band at 1425–1400 cm.$^{-1}$ is tentatively assigned to N–H deformation absorption rather than P=N as reported for $(C_2H_5O)_2P(O)NHP(O)(OC_2H_5)_2$, alternately $(C_2H_5O)_2P(O)\text{-}N{=}P(OC_2H_5)_2OH$.[12]

Portions of the spectra of four related compounds are shown in Fig. 1. Attention is directed to the relative intensities of the bands at 1425–1400 cm.$^{-1}$ as compared with that of the aromatic C=C skeletal in-plane vibrations at about 1520 cm.$^{-1}$.

Discussion

The reaction which is common to the above condensations appears to be the elimination of phenol from a phenyl ester of phosphorus through nucleophilic displacement by an anion. Thus, with $NaNHC_6H_5$



$$(C_6H_5O)_2\overset{O}{P}OC_6H_5 + :NHC_6H_5 \longrightarrow (C_6H_5O)_2\overset{O}{P}NHC_6H_5 + C_6H_5O^-$$

Since sodium phenoxide is insoluble in toluene, it is precipitated during the reaction. The displacement reaction with $NaN(C_6H_5)_2$ also goes smoothly.

$$(C_6H_5O)_3PO + NaN(C_6H_5)_2 \longrightarrow (C_6H_5O)_2P(O)N(C_6H_5)_2 + NaOC_6H_5$$

The reaction of $NaNH_2$, however, surprisingly gives a high yield of tetraphenyl imidodiphosphate (I), instead of the anticipated diphenyl phosphoramidate.

$$2(C_6H_5O)_3PO + 3NaNH_2 \longrightarrow Na[(C_6H_5O)_2P(O)NP(O)(OC_6H_5)_2] + 2NH_3 + 2NaOC_6H_5$$

$$\Big\downarrow \text{acidification}$$

$$(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)_2$$

The formation of the P–N–P compound most probably involves a P–N intermediate. One could theorize that the phosphoramidate is formed in small

---

[12] M. I. Kabachnik, V. A. Gilyarov, and E. M. Popov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1022 (1961); *Chem. Abstr.*, **55**, 27,014*f*.

TABLE II

	Prepared in	M.p., °C.	Analysis		X.r.d. powder data, three principal lines, d, Å.		
			Calcd.	Found			
			Metal Derivatives				
I. Tetraphenyl imidodiphosphate							
$Na[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]$	Ethanol				13.5 (100)	4.518 (67)	4.955 (46)
$Na[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]\cdot 0.5H_2O$	(Anhydrous, above, exposed to air)		N, 2.73; P, 12.09	N, 2.76; P, 12.08	13.2 (100)	4.587 (50)	4.343 (28)
$Na[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]\cdot 3H_2O$	Acetone–water		N, 2.51; P, 11.11	N, 2.49; P, 11.12	14.3 (100)	4.181 (25)	4.484 (16)
$Ba_{0.5}[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]\cdot 8H_2O$	Ethanol–water		Ba, 9.89; N, 2.02; P, 8.92	Ba, 9.73; N, 2.16; P, 8.60	14.6 (100)	4.24 (15)	9.9 (10)
$Na_{0.5}Tl_{0.5}[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]\cdot 0.5H_2O$	Ethanol–water	155–157	Na, 1.90; N, 2.32; P, 10.27; Tl, 16.95	Na, 1.80; N, 2.43; P, 10.10; Tl, 18.81	12.1 (100)	4.031 (24)	5.83 (17)
$Cu_{0.5}[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]$	Ethanol	120	Cu, 6.20; N, 2.74; P, 12.10	Cu, 6.24; N, 2.90; P, 11.79	11.4 (100)	10.8 (80)	6.86 (30)
$Fe_{0.33}[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]$	Ethanol	*ca.* 320	Fe, 3.73; N, 2.81; P, 12.41	Fe, 4.08; N, 2.58; P, 12.39	10.9 (100)	12.2 (37)	9.0 (26)
$[Co(NH_3)_6][(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]_3$	(Drying hydrate below)		Co, 3.68; N, 7.87; P, 11.60	Co, 3.66; N, 7.50; P, 11.72	15.9 (100)	4.355 (24)	5.96 (15)
$[Co(NH_3)_6][(C_6H_5)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]\cdot H_2O$ (?)	Formamide–water		Co, 3.63; N, 7.76; P, 11.45	Co, 3.57; N, 7.49; P, 11.60	15.6 (100)	4.688 (56)	4.266 (32)
$Ag[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]$							
Form I	Dioxane from $AgNO_3$		Ag, 18.3; N, 2.38; P, 10.53	Ag, 18.0; N, 2.25; P, 10.61	8.84 (100)	9.26 (68)	3.909 (23)
Form II	Benzene from excess Ag_2O	185–186		Ag, 18.1; N, 2.14; P, 9.88	9.88 (100)	9.46 (50)	9.2 (30) 8.9 (20)
Form III	Benzene from Ag_2O			N, 2.03; P, 10.52	9.16 (100)	8.89 (70)	4.575 (20)
II. Triphenyl amidoimidodiphosphate							
$Ba_{0.5}[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)NH_2]\cdot H_2O$	Ethanol–water		Ba, 14.01; N, 5.72	Ba, 14.04; N, 5.58	16.4 (100)	10.7 (10)	5.68 (6) 5.59 (6)
$Ag[(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)NH_2]$	Dioxane with silver acetate		Ag, 21.10; N, 5.48	Ag, 22.52; N, 4.96	12.7 (100)	11.9 (95)	15.0 (35)

Ammonia and Amine Derivatives

I. Tetraphenyl imidodiphosphate							
$NH_3\cdot(C_6H_5O)_2\overset{O}{P}NH\overset{O}{P}(OC_6H_5)_2$	Dioxane	116–117	N, 5.62; P, 12.43	N, 5.71; P, 12.28	12.4 (100)	4.914 (63)	14.1 (52)
$C_6H_{11}NH_2\cdot(C_6H_5O)_2\overset{O}{P}NH\overset{O}{P}(OC_6H_5)_2$	Dioxane–water	118	N, 4.82; P, 10.67	N, 4.78; P, 10.56	10.8 (100)	4.385 (12)	5.73 (12)
$C_5H_{10}NH\cdot(C_6H_5O)_2\overset{O}{P}NH\overset{O}{P}(OC_6H_5)_2$							
Form I	Benzene–hexane	100–102	N, 4.95; P, 10.95	N, 4.90; P, 11.19	3.73 (100)	12.5 (75)	4.24 (75)
Form II	Piperidine	97–102		N, 5.09; P, 10.76	4.36 (100)	3.65 (50)	9.9 (45)
$NH_2(CH_2)_2NH_2\cdot 2(C_6H_5O)_2\overset{O}{P}NH\overset{O}{P}(OC_6H_5)_2$	Dioxane–water	90–100	N, 5.48; P, 12.09	N, 5.31; P, 11.80	17.2 (100)	13.4 (100)	4.646 (47)
II. Triphenyl amidoimidodiphosphate							
$C_6H_{11}NH_2\cdot(C_6H_5O)_2\overset{O}{P}NH\overset{O}{P}(OC_6H_5)NH_2$	Dioxane		N, 8.35; P, 12.30	N, 8.22; P, 12.17	14.9 (100)	11.9 (60)	4.587 (45) 4.646 (35)

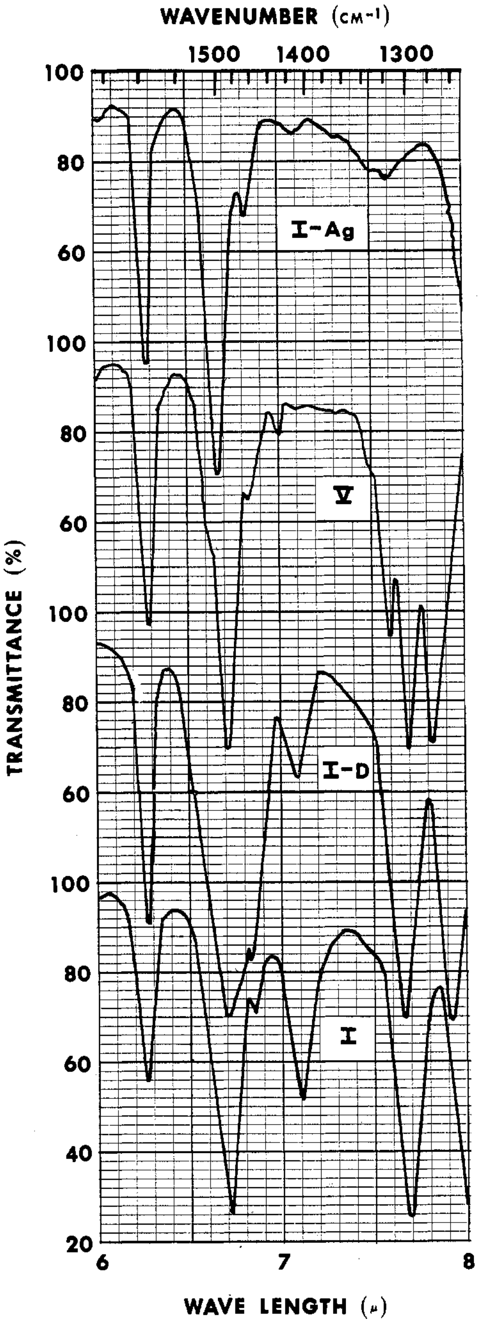


Fig. 1.—Infrared absorption spectra: I, tetraphenyl imidodiphosphate; I-D, partially deuterated tetraphenyl imidodiphosphate; V, tetraphenyl N-methylimidodiphosphate; I-Ag, silver derivative of tetraphenyl imidodiphosphate.

amounts, and, once formed, perhaps eliminates ammonia in a self-condensation such as reported by Klement and Biberacher[13] for the sodium salt.

$$2(NaO)_2\overset{O}{P}NH_2 \longrightarrow (NaO)_2\overset{O}{P}NH\overset{O}{P}(ONa)_2 + NH_3$$

It was found, however, that diphenyl phosphoramidate, in refluxing toluene over a course of several hours, lost only trace amounts of ammonia and could be recovered.

A more likely mechanism is the reaction of traces of the phosphoramidate anions, as they are formed, with

---

[13] R. Klement and G. Biberacher, *Z. anorg. allgem. Chem.*, **283**, 246 (1956).

TABLE III

P^{31} N.M.R. CHEMICAL SHIFTS

Compound	Chemical shift, p.p.m. (ref. H_3PO_4)	No. of peaks
$(C_6H_5O)_2P(O)NH_2$	−2.8	3
$(C_6H_5O)_2P(O)NHC_6H_5$	+6.3	2
$(C_6H_5O)_2P(O)N(C_6H_5)_2$	+8.8	1
$(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)_2$	+10.7	1
$(C_6H_5O)_2P_\alpha(O)NHP_\beta(O)(OC_6H_5)NH_2$	α +8.4	2
	β −3.8	2
$(C_6H_5O)_2P_\alpha(O)NHP_\beta(O)(OC_6H_5)$-$NHP_\gamma(O)(OC_6H_5)NH_2$	α +8.4	4
	β +6.3	Multiple
	γ −0.8	
$(C_6H_5O)_2P_\alpha(O)NHP_\beta(O)(OC_6H_5)$-$NHP(O)(OC_6H_5)_2$	α +12.5	2
	β +5.9	3
$(C_6H_5O)_2P(O)_2N(CH_3)P(O)(OC_6H_5)_2$	+7.3	1

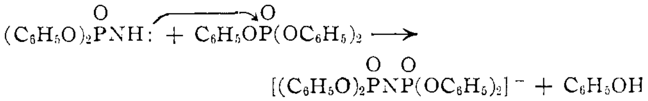
TABLE IV

H^1 N.M.R. CHEMICAL SHIFTS

	Chemical shift, p.p.m. (ref. TMS)		Ratio	
Compound	Aromatic	Imido and amido	Calcd.	Found
$(C_6H_5O)_2P(O)NH_2$	7.5–7.1	5.45[a]	10:2	5.7:1
$(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)_2$	7.34	*ca.* 9.2	20:1	20:1
$(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)NH_2$	*ca.* 7.0	*ca.* 4.2	15:3	4:1
$(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)NHP(O)(OC_6H_5)NH_2$	7.35	6.9–5.7	20:4	4.7:1
$(C_6H_5O)_2P(O)N(CH_3)P(O)(OC_6H_5)_2$	7.63	3.47[b] (C–H)	20:3	6:1

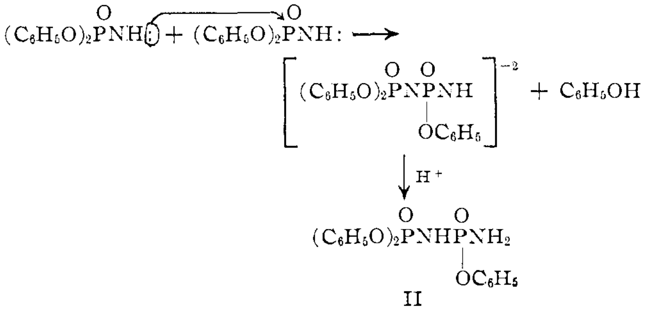
[a] Doublet. [b] Triplet.

triphenyl phosphate in a nucleophilic displacement.


$$(C_6H_5O)_2\overset{O}{P}NH\!: + C_6H_5O\overset{O}{P}(OC_6H_5)_2 \longrightarrow [(C_6H_5O)_2\overset{O}{P}N\overset{O}{P}(OC_6H_5)_2]^- + C_6H_5OH$$

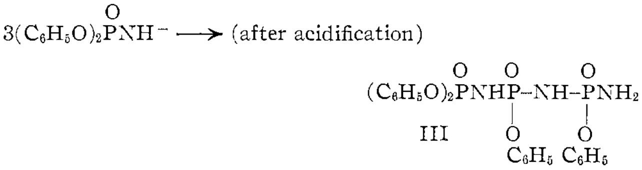
Whether or not free phenol is formed depends upon the relative acidity of the condensation product and, of course, the amount of basic condensing agent present. Compounds I, II, III, and IV are more acidic than phenol. By comparison, neither $(C_6H_5O)_2P(O)NH_2$ nor $(C_6H_5O)_2P(O)NHC_6H_5$ is acidic enough to dissolve in dilute sodium hydroxide.

The displacement reaction above brings to mind the familiar Claisen (acetoacetic ester) condensation which has been investigated by McElvain and co-workers[14] and Hauser, *et al.*[15] When diphenyl phosphoramidate was heated alone under conditions in which anions would be present, as with the stronger bases $NaNH_2$, NaH, Na, or $NaOC_6H_5$, the result was a head-to-tail self-condensation yielding II.


$$(C_6H_5O)_2\overset{O}{P}NH\!: + (C_6H_5O)_2\overset{O}{P}NH\!: \longrightarrow \left[(C_6H_5O)_2\overset{O}{P}N\overset{O}{\underset{OC_6H_5}{P}}NH\right]^{-2} + C_6H_5OH \xrightarrow{H^+} (C_6H_5O)_2\overset{O}{P}NH\overset{O}{\underset{OC_6H_5}{P}}NH_2$$

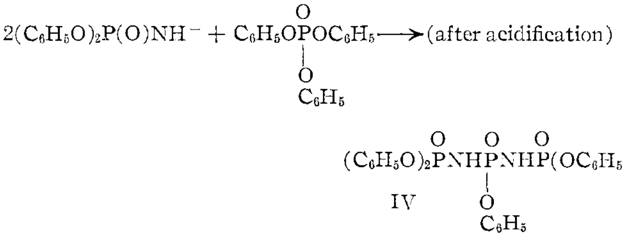
II

Either by allowing II (anion) to react with more diphenyl phosphoramidate or by starting with diphenyl phosphoramidate (anion) and gradually increasing the concentration of base (as by slow solution of relatively coarse-grained commercial sodium amide) the next member of the series, the P–N–P–N–P compound III was formed.


$$3(C_6H_5O)_2\overset{O}{P}NH^- \longrightarrow \text{(after acidification)} \quad (C_6H_5O)_2\overset{O}{P}NH\overset{O}{\underset{OC_6H_5}{P}}\text{–}NH\text{–}\overset{O}{\underset{OC_6H_5}{P}}NH_2$$

III

As a further demonstration of this condensation, the diimidotriphosphate ester, IV, was obtained by reaction of the phosphoramidate with triphenyl phosphate.


$$2(C_6H_5O)_2P(O)NH^- + C_6H_5O\overset{O}{\underset{OC_6H_5}{P}}OC_6H_5 \longrightarrow \text{(after acidification)} \quad (C_6H_5O)_2\overset{O}{P}NH\overset{O}{\underset{OC_6H_5}{P}}NH\overset{O}{P}(OC_6H_5)_2$$

IV

These new compounds have been identified with certainty on the basis of elemental analyses, molecular weight, and phosphorus-31 and proton n.m.r.

It is probable, by choice of reaction conditions, rate and order of addition, and ratio of base to phosphoramidate, that one could prepare additional compounds containing longer –P–N–P– chains and even cyclic structures.

Referring to the condensation of Klement and Biberacher,[13] it is now suggested, as an aside, that the improvement this author and co-workers[16] observed when disodium phosphoramidate was heated in an alkaline "flux" such as potassium formate or phenoxide may have resulted in part from formation of an anion O_3PNH^{-3} which could displace ammonia with greater facility in forming the imidodiphosphate.

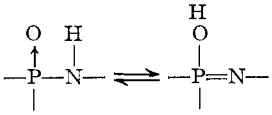
A provoking question bearing further investigation is whether the imidophosphorus compounds exist in tautomeric forms

---

[14] J. M. Snell and S. M. McElvain, *J. Am. Chem. Soc.*, **53**, 2310 (1931).

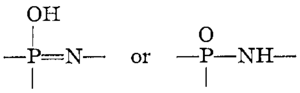
[15] C. R. Hauser and B. E. Hudson, Jr., *Org. Reactions*, **1**, 266 (1942).

[16] M. L. Nielsen, R. R. Ferguson, and W. S. Coakley, *J. Am. Chem. Soc.*, **83**, 99 (1961).



$$-\overset{\overset{\displaystyle O}{\uparrow}}{\underset{|}{P}}-\overset{\overset{\displaystyle H}{|}}{N}- \rightleftharpoons -\overset{\overset{\overset{\displaystyle H}{O}}{|}}{\underset{|}{P}}=N-$$

Certainly the hydrogen is readily replaceable and is ionic in solution. In the solid state, however, it is possible one could observe one or the other of the tautomers or perhaps their equilibrium mixture. Inspection of Fig. 1, containing portions of the infrared absorption spectra of tetraphenyl imidodiphosphate (I), of partially deuterated tetraphenyl imidodiphosphate (I-D), of the silver derivative of tetraphenyl imidodiphosphate (I-Ag), and of tetraphenyl N-methyl imidodiphosphate (V), shows that, first, in I there is a sharp band at 1420 cm.$^{-1}$ which is not present in V and is thus related to the system containing hydrogen, either as



$$-\overset{\overset{\displaystyle OH}{|}}{\underset{|}{P}}=N- \quad\text{or}\quad -\overset{\overset{\displaystyle O}{|}}{\underset{|}{P}}-NH-$$

secondly, this band is considerably weaker in I-D than in I, and thus can be attributed to N—H rather than P=N. If the P=N structure were present, one would expect this band to be as strong in I-D as in I. Finally, this band is missing from the spectrum of the silver derivative and the N-methyl derivative of I.

The formation of the N-methyl derivative by replacement of silver by methyl iodide is probably not proof for the location of the silver atom on nitrogen, since methyl could attack nitrogen to form the activated complex or transient intermediate even if silver were on oxygen. The structure of the tetraphenyl N-methylimidodiphosphate was established unequivocably by the proton n.m.r. where a triplet was found for the methyl hydrogens because of splitting with the two phosphorus nuclei.

Acknowledgments.—Instrumental analytical services were performed by Ralph R. Ferguson in X-ray diffraction analysis, John E. Strobel in nuclear magnetic resonance spectroscopy, and J. V. Pustinger, Jr., in infrared spectroscopy.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
OF THE FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA

The Donor Properties of N,N-Dimethylethylenediamine N-Oxide

BY J. T. SUMMERS AND J. V. QUAGLIANO

Received March 30, 1964

The reaction of N,N-dimethylethylenediamine N-oxide (DMEO) with a number of transition and post transition metal salts has been investigated. Coordination compounds were obtained of the types: [M(DMEO)X_2] (M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II); X = Cl, I); [M$(DMEO)_2$]$(ClO_4)_2$ (M = Cu(II), Zn(II)); and [$M^n$$(DMEO)_3$]$(ClO_4)_n$ (M = Ni(II), Fe(III), Co(III)). Their structures were investigated by thermogravimetric analysis, conductivity, magnetism, and visible and infrared spectral measurements and were found to be in agreement with those expected for a chelating ligand with one oxygen and one nitrogen donor atom. The ligand dihydrochloride, DMEO·2HCl, also formed compounds with metal halides, formulated as $[H_2DMEO]^{2+}[MCl_4]^{2-}$ (M = Mn(II), Cd(II), Pd(II)). The pK_a values of the ligand dihydrochloride were also determined.

Introduction

A number of stable coordination compounds of transition metal ions with aromatic N-oxides, such as pyridine N-oxides,[1-3] 2,2′-bipyridine N,N′-dioxide,[4,5] and pyridine N-oxide α-carboxylic acid,[6] have been prepared recently and studied in some detail. Among the aliphatic N-oxides, only trimethylamine N-oxide[7,8] has so far been investigated in regard to its donor properties, and its metal complexes seem to be much more difficult to form and less stable than those of the aromatic N-oxides. Different coordinating ability can be expected for aromatic and aliphatic N-oxides simply on the basis of their electronic structures, and we thought it worthwhile, in connection with previous work on aromatic N-oxide complexes, to collect more experimental evidence on the donor properties of aliphatic N-oxides. For this purpose we chose the ligand N,N-dimethylethylenediamine N-oxide, $(CH_3)_2N(O)CH_2CH_2NH_2$ (DMEO), which in addition to the amine N-oxide functional group has a primary amino group capable of coordination and can form a six-membered chelate ring with metal ions. Because of chelation, the metal complexes of this ligand would be expected to be reasonably stable even if the oxygen atom of the amine oxide group forms relatively weak coordinate bonds.

Experimental

Conductivity measurements at 25° were made on freshly prepared solutions as soon as thermal equilibrium had been reached (about 25 min.). In a few cases more time was required to dis-

---

[1] J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).

[2] R. L. Carlin, *ibid.*, **83**, 3773 (1961).

[3] R. L. Carlin, J. Roitman, M. Dankleff, and J. O. Edwards, *Inorg. Chem.*, **1**, 182 (1962).

[4] P. G. Simpson, A. Vinciguerra, and J. V. Quagliano, *ibid.*, **2**, 282 (1963).

[5] R. S. Nyholm and A. Truce, *J. Chem. Soc.*, 1121 (1962).

[6] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *ibid.*, 5262 (1962).

[7] K. Isslieb and A. Kreibich, *Z. anorg. allgem. Chem.*, **313**, 338 (1961).

[8] S. Kida, *Bull. Chem. Soc. Japan*, **36**, 712 (1963).