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
Hydrazinophosphorus Compounds. I. Preparation of Some Substituted Hydrazinophosphines, Hydrazinophosphine Oxides, and Hydrazinophosphine Sulfides

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Received September 6, 1962

A series of substituted hydrazinophosphines, hydrazinophosphine oxides, and hydrazinophosphine sulfides has been synthesized by the hydrazinolysis of the appropriate chlorophosphorus compounds. The compounds prepared were characterized by elemental analysis, infrared analysis, and ¹H and ³¹P nuclear magnetic resonance studies. Nuclear magnetic resonance data indicate that the chemical shifts for phosphorus atoms in the various hydrazinophosphorus compounds increase in the series (C₆H₅)₂P(O)- < (C₆H₅)₂P- < (C₆H₅)P(S)-.

There exist, on the basis of the more common substituents for phosphorus, a great many possible classes of compounds which may contain the hydrazino-phosphorus linkage, P-N-N-, but a survey of the literature reveals that no unoxidized derivative of the hypothetical hydrazinophosphine, H₂P-NH-NH₂, has been reported. Most of the work on hydrazinophosphorus compounds has been done in the area of hydrazine derivatives of the esters of phosphorus acids²⁻⁴ and in the area of phosphazene chemistry^{5,6}; thus, little is known of the properties of systems containing the P-N-N, N-N-P-N-N,

and N-N-P  structures which, in some respects, may be looked upon as homologs of triazane and higher nitrogen chain compounds. Few hydrazinophosphorus compounds which contain the P-C bond are known.

In addition, the synthesis and study of hydrazinophosphines is a logical extension to recent studies of aminophosphines and their derivatives^{7,8} since the addition of another basic center, *i.e.*, the terminal -NR₂ group, may change the course of the reactions observed for aminophosphines.

Experimental

Materials.—Anhydrous hydrazine (97%), methylhydrazine, and 1,1'-dimethylhydrazine were obtained from the Olin Mathieson Chemical Corporation. The alkyhydrazines were distilled from calcium hydride. Methylhydrazine boiled at 87.3–88.0° at 761 mm., and 1,1-dimethylhydrazine boiled at 62.2–63.0° at 758 mm. 1,1,2-Trimethylhydrazine was prepared as reported by Class, *et al.*,⁹ and after distilling from calcium hydride boiled at 58–62° at 760 mm. 1-Ethyl-2,2-dimethylhydrazine was prepared as reported by Klages, *et al.*,¹⁰ and after distillation from LiAlH₄ boiled at 92–93°. The infrared spectra of these compounds were found to be identical with those reported in the

literature.¹¹ Reagent grade triethylamine was dried over calcium hydride and distilled, the fraction boiling at 88.5–89.5° at 759 mm. being collected. The various phosphorus compounds were obtained from the Victor Chemical Works and were vacuum distilled immediately before use to remove oxidation products which might have formed on standing.

All solvents were dried thoroughly. Commercial grade nitrogen, treated to remove oxygen and water vapor, was used to maintain an inert atmosphere in many of the syntheses.

Analyses.—Elemental analyses were carried out by the Galbraith Microanalytical Laboratories of Knoxville, Tennessee. Melting points were determined in sealed capillary tubes in a Thomas-Hoover melting point apparatus. Analytical data, melting points, and yield data are listed in Table I.

Infrared Spectra.—Infrared spectra were obtained on a Perkin-Elmer Infracord Model 137 spectrophotometer. Since most of the compounds studied are crystalline solids, the spectra were obtained from Nujol mulls. Diphenylphosphine is an exception and its spectrum was obtained in a 0.0295-cm. cell without solvent.

Assignments were made for the various bands in the infrared spectra on the basis of known absorption frequencies^{12,13} and by comparison of the various spectra in which a given frequency is observed which can be correlated with the presence of a specific group. Though the assigned formulas for the new compounds synthesized are amply supported by their method of synthesis and by analytical data, it is reassuring that a reasonable assignment of the bands in the infrared spectra can be made on the basis of these formulas. The infrared absorption frequencies and assignments encountered in the spectra of these compounds are listed in Table II. The spectra of 2,2-dimethylhydrazinodiphenylphosphine and 2,2-dimethylhydrazinodiphenylphosphine oxide are given in Fig. 1a and 1b as typical examples of the spectra obtained.

Nuclear Magnetic Resonance Spectra.—Nuclear magnetic resonance spectra for ¹H and ³¹P were obtained on a Varian High-Resolution Model V-4300-2 spectrometer. The peaks in the various n.m.r. spectra along with the chemical shifts are listed in Table III. The peaks listed in the table correspond in detail with those to be expected from the various formulas assigned to the compounds concerned in each instance. The ¹H spectrum of 2,2-dimethylhydrazinodiphenylphosphine is given in Fig. 2 as a typical example of the n.m.r. spectra obtained.

Procedures.—The general method for the synthesis of the hydrazinophosphorus compounds was the hydrazinolysis of the appropriate halophosphorus derivative with the appropriate hydrazine. In some instances the reaction was promoted by the addition of triethylamine to act (instead of the hydrazine) as

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TABLE I

| Compound | Yield, % | M.p., °C. | Analysis | | | | |
|---|----------|------------------------------|--|--------------|----------------|----------------|----------------|
| | | | C | H | N | P | S or Cl |
| (C ₆ H ₅) ₂ PNHN(CH ₃) ₂ ^a (I) | 84.5 | 68.5–69.5 | 68.83 ^c 68.65 ^d | 7.02 7.17 | 11.47 11.29 | 12.68 12.66 | |
| (C ₆ H ₅) ₂ P(O)NHN(CH ₃) ₂ ^a (II) | 82.9 | 167.0–168.0 | 64.60 64.39 | 6.58 6.38 | 10.77 10.73 | 11.90 11.92 | |
| (C ₆ H ₅) ₂ P(S)NHN(CH ₃) ₂ (IV) | 87.5 | 95.5–97.0 | 60.85 60.67 | 6.41 6.20 | 10.26 10.14 | 11.45 11.21 | 11.41 11.60 |
| [(C ₆ H ₅) ₂ P] ₂ NN(CH ₃) ₂ ^b (III) | 93.8 | 129.5–132.5 | 72.88 72.65 | 6.12 5.98 | 6.54 6.12 | 14.46 14.56 | |
| (C ₆ H ₅) ₂ P(O)NCH ₃ N(CH ₃) ₂ ^a (VI) | 19.0 | 165.0–166.5 | 65.68 65.52 | 6.98 6.92 | 10.22 10.08 | 11.29 11.03 | |
| (C ₆ H ₅) ₂ PN(C ₂ H ₅)N(CH ₃) ₂ ^b (VII) | | | 70.57 70.38 | 7.77 7.63 | 10.29 10.14 | 11.37 11.44 | |
| (C ₆ H ₅) ₂ P(O)N(C ₂ H ₅)N(CH ₃) ₂ ^b (IX) | 46.7 | 140.0–141.0 | 66.65 66.44 | 7.34 7.24 | 9.72 9.55 | 10.74 10.89 | |
| (C ₆ H ₅) ₂ P(S)N(C ₂ H ₅)N(CH ₃) ₂ (VIII) | 81.4 | 126.5–127.5 | 63.13 63.30 | 6.95 7.09 | 9.20 9.10 | 10.18 10.34 | 10.53 10.62 |
| (C ₆ H ₅) ₂ PNHNHP(C ₆ H ₅) ₂ ^b (X) | 30.1 | 129.0–129.5 | 71.97 72.02 | 5.54 5.57 | | 15.48 15.06 | |
| [(C ₆ H ₅) ₂ P] ₂ NN(CH ₃)P(C ₆ H ₅) ₂ ^b (XIII) | 21.8 | 152.3–153.0 | 74.24 74.33 | 5.56 5.71 | 4.68 4.75 | 15.52 15.41 | |
| C ₆ H ₅ P(Cl)NHN(CH ₃) ₂ ^a (XIV) | | Viscous liq. dec. at b.p. | | | | | 24.70 24.97 |
| C ₆ H ₅ P(NHN(CH ₃) ₂) ₂ ^a (XV) | 12.0 | 61.5–63.0 | 53.08 51.79 | 8.46 8.15 | 24.77 22.01 | 13.69 14.10 | |
| C ₆ H ₅ P(O)NHN(CH ₃) ₂ ^a (XVIb) | 61.0 | 161.0–164.0 | 49.58 49.74 | 7.90 8.03 | 23.13 23.01 | 12.91 12.79 | |
| C ₆ H ₅ P(S)(NHN(CH ₃) ₂) ^a (XVIII) | 64.0 | 106.0–106.5 | 46.50 46.43 | 7.41 7.59 | 21.69 21.80 | 11.99 12.07 | 12.41 12.25 |
| P(O)(NHN(CH ₃) ₂) ₃ ^a (XX) | 76.0 | 193.5–195.0 | 32.14 31.67 | 9.44 9.57 | 37.48 37.03 | 13.81 13.56 | |
| P(S)(NHN(CH ₃) ₂) ₃ ^a (XXI) | 50.0 | 75.5–78.0 | 29.99 29.74 | 8.81 8.52 | 34.97 35.07 | 12.89 13.07 | 13.34 13.49 |

^a Same method as for product I. ^b Same method as for product III. ^c Calculated. ^d Found.

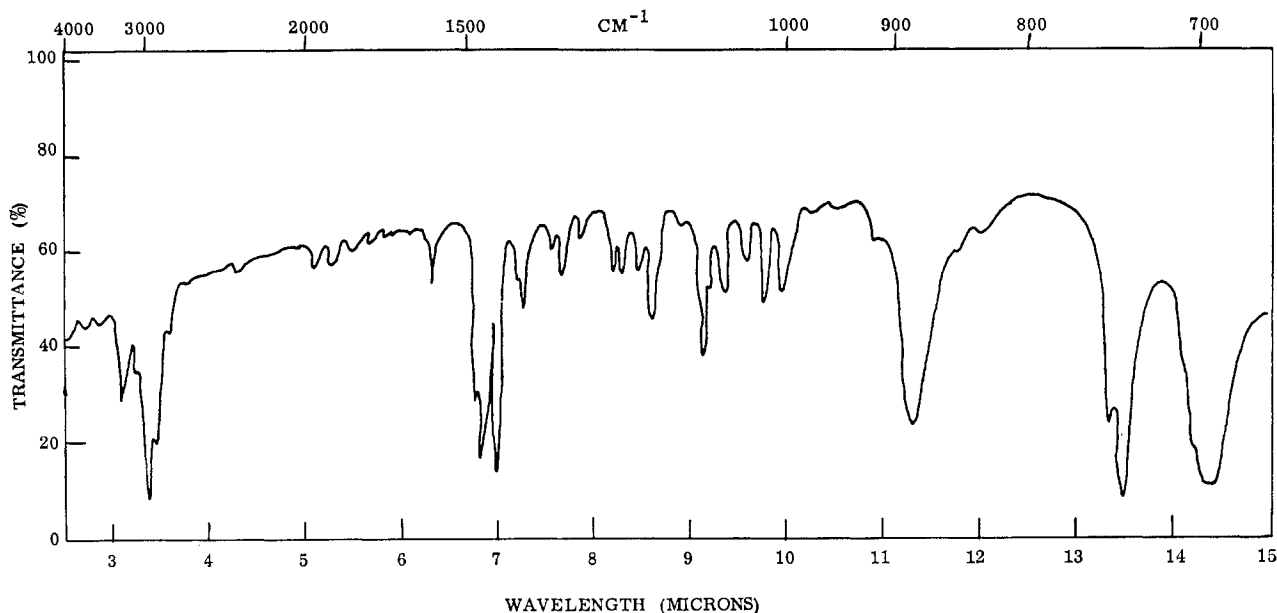


Fig. 1a.—Infrared spectrum of 2,2-dimethylhydrazinodiphenylphosphine (I) in Nujol mull.

hydrogen chloride acceptor. The hydrazinophosphines were converted to the corresponding phosphine sulfides and oxides by reaction with sulfur and activated manganese dioxide, respectively.

Preparation of 2,2-Dimethylhydrazinodiphenylphosphine (I).—Over a 2-hr. period, 55.1 g. (0.25 mole) of diphenylchlorophosphine in 25 ml. of dry benzene was added with stirring at 0–5° to a solution of 33.0 g. (0.55 mole) of 1,1-dimethylhydrazine in 25 ml. of dry benzene. This reaction was carried out under nitrogen. The mixture then was warmed to room temperature,

stirred for 1 hr., and filtered under nitrogen, yielding, after washing successively with benzene and ether, 23.99 g. (99.3% of theoretical) of 1,1-dimethylhydrazinium chloride, m.p. 79–81° (lit.¹⁴ 81–82°). The filtrate was evaporated at room temperature and reduced pressure to give 59.97 g. of a white solid, m.p. 62–66°. Recrystallization of this solid from 150 ml. of dry *n*-hexane, followed by sublimation at 60° (0.20 mm.), gave 51.5 g. (84.5% of theoretical) of a white, crystalline solid, I, m.p. 68.5–

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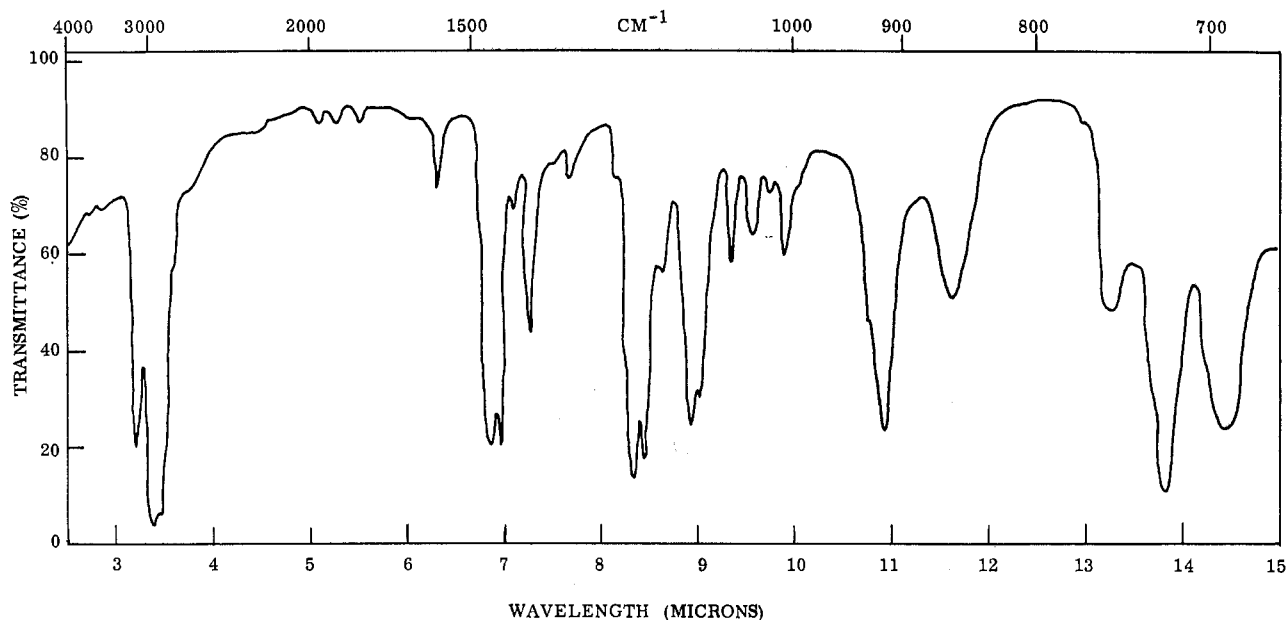


Fig. 1b.—Infrared spectrum of 2,2-dimethylhydrazinophosphine oxide (II) in Nujol mull.

TABLE II
INFRARED ABSORPTION FREQUENCIES AND ASSIGNMENTS

| Group | Range, cm. ⁻¹ |
|---|--------------------------------|
| N-H (free) | 3450-3590 (w) |
| N-H (associated) | 3175-3320 (w-m) |
| C-H (stretch, aromatic) | 3030-3100 (s) |
| C-H (stretch, aliphatic) | 2880-3000 (s), 2610-2800 (w-m) |
| P-H | 2280 (m) |
| Phenyl, monosubstituted | 1900-1975 |
| | 1835-1900 (w-triplet) |
| | 1790-1880 |
| N-H (deformation) | 1625-1700 (w) |
| Phenyl, skeletal in-plane vibrations | 1565-1590 (w) |
| C-H (deformation, aromatic) | 1475-1487 (w-m) |
| C-H (deformation, aliphatic) | 1451-1470 (m) |
| | 1370-1380 (w) (doublet) |
| P-phenyl | 1430-1440 (s) |
| -NR ₂ , N-CH ₃ | 1390-1430 (w-m) |
| C-CH ₃ | 1373-1380 (w-m) |
| Phenyl | 1318-1358 (w) |
| P=O | 1175-1188 (m-s) |
| Phenyl (near P=O or P=S), monosubstituted | 1109-1220 (m-s) |
| N-CH ₃ | 1040-1050 (w-m) |
| N-N | 950-996 (w) |
| N-H | 880-917 (m-s) |
| P-N | 743-773 (m-s) |
| C-H chains, P=S | 700-727 (m-s) |
| Phenyl (C-H, out-of-plane deformations) | 690-697 (m-s), 671-688 (m) |

69.5°. Contact of the product with the atmosphere was avoided in all steps of the procedure. Analytical data (Table I), hydrolytic products (see below), infrared data (Fig. 1a), and ¹H and ³¹P n.m.r. data all confirm the identity of the product as (C₆H₅)₂-PNHN(CH₃)₂.

Hydrolysis of 2,2-Dimethylhydrazinodiphenylphosphine.—A sample of I was dissolved in warm, aqueous 6 M sodium hydroxide. The vapor above the solution was tested for free hydrazine with a drop of potassium permanganate on a strip of filter paper. The purple color of the MnO₄⁻ ion was decolorized immediately as the vapor from the hydrolysis mixture contacted the filter paper. Upon acidification of the hydrolysis mixture, which had been allowed to boil in the presence of atmospheric oxygen until

Fig. 2.—Proton n.m.r. spectrum of 2,2-dimethylhydrazinodiphenylphosphine (I) in CDCl₃ solvent at 56.4 Mc.

| Peak | Area | Position, p.p.m. | Type |
|------|------|------------------|--------------------------------|
| A | 10.2 | -0.88 | -C ₆ H ₅ |
| B | 1.0 | 3.29 | -NH |
| C | 6.2 | 4.07 | -CH ₃ |

all the 1,1-dimethylhydrazine was removed, a white precipitate formed and was collected. This material was identified as diphenylphosphinic acid by its melting point (191-192°) and infrared spectrum, which contained a very prominent absorption band at 1200 cm.⁻¹ assigned to the P→O bond.¹⁸ No other hydrolysis products were observed.

TABLE III
 NUCLEAR MAGNETIC RESONANCE DATA^{a,b}

| Formula | Pattern splitting | Chem. shift | Assignment |
|--|--|--------------|---|
| (C ₆ H ₅) ₂ PNHN(CH ₃) ₂ ^c | Complex | 1.9 τ | H (C ₆ H ₅) |
| | Doublet | 6.0 τ | H (NH) |
| | Singlet | 6.8 τ | H (CH ₃) |
| | Broad | -37.6 p.p.m. | P |
| [(C ₆ H ₅) ₂ P] ₂ NN(CH ₃) ₂ ^{d,e} | | (obscured) | H (C ₆ H ₅) |
| | Singlet | 7.52 τ | H (CH ₃) |
| | Broad | -47.4 p.p.m. | P |
| | | 2.07 τ | H (-C ₆ H ₅) |
| (C ₆ H ₅) ₂ P(O)NHN(CH ₃) ₂ ^e | | 2.55 τ | H (<i>p</i> -C ₆ H ₅ , <i>m</i> -C ₆ H ₅) |
| | | 5.53 τ | H (NH) |
| | Doublet (18.8 c.p.s.) | 7.42 τ | H (CH ₃) |
| | Singlet | -22.0 p.p.m. | P |
| | Broad | 1.97 τ | H (<i>o</i> -C ₆ H ₅) |
| (C ₆ H ₅) ₂ P(S)NHN(CH ₃) ₂ ^e | | 2.68 τ | H (<i>p</i> -C ₆ H ₅ , <i>m</i> -C ₆ H ₅) |
| | | 6.21 τ | H (NH) |
| | Doublet (21.5 c.p.s.) | 7.61 τ | H (CH ₃) |
| | Singlet | -57.3 p.p.m. | P |
| | Broad | 2.12 τ | H (<i>o</i> -C ₆ H ₅) |
| (C ₆ H ₅) ₂ P(O)N(CH ₃)N(CH ₃) ₂ ^e | | 2.61 τ | H (<i>p</i> -C ₆ H ₅ , <i>m</i> -C ₆ H ₅) |
| | | 7.45 τ | H (N-CH ₃) |
| | Doublet (10.5 c.p.s.) | 7.61 τ | H (N(CH ₃) ₂) |
| | Singlet | -28.2 p.p.m. | P |
| | Broad | 2.06 τ | H (<i>o</i> -C ₆ H ₅) |
| | | 2.54 τ | H (<i>p</i> -C ₆ H ₅ , <i>m</i> -C ₆ H ₅) |
| (C ₆ H ₅) ₂ P(O)N(C ₂ H ₅)N(CH ₃) ₂ ^e | | 6.75 τ | H (-CH ₃ -) |
| | Quadruplet (7 c.p.s.) | 7.48 τ | H (N-CH ₃) |
| | | 8.83 τ | H (CH ₃ -CH ₂ -) |
| | Doublet (ca. 7 c.p.s.) | -26.2 p.p.m. | P |
| | Singlet | 1.82 τ | H (<i>o</i> -C ₆ H ₅) |
| | Triplet (7 c.p.s.) | 2.46 τ | H (<i>p</i> -C ₆ H ₅ , <i>m</i> -C ₆ H ₅) |
| | Broad | 6.67 τ | H (-CH ₃ -) |
| (C ₆ H ₅) ₂ P(S)N(C ₂ H ₅)N(CH ₃) ₂ ^f | | 7.48 τ | H (N-CH ₃) |
| | | 8.76 τ | H (CH ₃ -CH ₂ -) |
| | Quadruplet (7 c.p.s.) | -66.4 p.p.m. | P |
| | | 1.84 τ | H (<i>o</i> -C ₆ H ₅) |
| | Doublet (8 c.p.s.) | 2.56 τ | H (<i>p</i> -C ₆ H ₅ , <i>m</i> -C ₆ H ₅) |
| | Singlet | 6.33 τ | H (NH) |
| C ₆ H ₅ P(S)(NHN(CH ₃) ₂) ₂ ^e | | 7.51 τ | H (CH ₃) |
| | | -61.1 p.p.m. | P |
| | Doublet (27.3 c.p.s.) | 6.05 τ | H (NH) |
| | Singlet | 7.43 τ | H (CH ₃) |
| | Broad, perhaps a septuplet (12 c.p.s.) | -12.5 p.p.m. | P |
| P(O)(NHN(CH ₃) ₂) ₃ ^e | | 6.05 τ | H (NH) |
| | | 7.43 τ | H (CH ₃) |
| | Doublet (2.37 c.p.s.) | -12.5 p.p.m. | P |
| | Quadruplet (23 c.p.s.) | | |

^a Solvent CDCl₃ except where otherwise noted. ^b All phosphorus resonance spectra at 19.3 Mc. with H₃PO₄ as replaceable standard. ^c Proton resonance spectra at 56.4 Mc. with benzene as external standard. ^d Benzene solvent. ^e Proton resonance spectra at 60.0 Mc. with (CH₃)₄Si as internal standard. ^f Proton resonance spectra at 60.0 Mc. with CH₃CHO as replaceable standard.

Preparation of 2,2-Dimethylhydrazinodiphenylphosphine Oxide (II).—The reaction of 23.7 g. (0.10 mole) of diphenylphosphinic

chloride ((C₆H₅)₂P—Cl) with 13.0 g. (0.21 mole) of 1,1-dimethylhydrazine at 70° by the method used for I yielded a theoretical amount of 1,1-dimethylhydrazinium chloride. After evaporation of the filtrate and recrystallization of the crude material from a 1:3 *n*-hexane–benzene mixture followed by sublimation at 140° (0.20 mm.), 21.6 g. of a white, crystalline solid, II, was obtained. This product melted at 167.0–168.0°. Aqueous, basic hydrolysis of II with 6 *M* NaOH gave 1,1-dimethylhydrazine, and acidification of the resulting solution precipitated diphenylphosphinic acid, m.p. 191–192°. Analytical data, method of synthesis, and n.m.r. data all confirm the formula (C₆H₅)₂P(O)NHN(CH₃)₂. The infrared spectrum of II (Fig. 1b) shows the strong P→O absorption at 1200 cm.⁻¹, whereas the N–H stretch absorption observed for I at 3230 cm.⁻¹

has shifted to 3080 cm.⁻¹ in the spectrum of II, presumably a result of the formation of the P→O bond.

Oxidation of 2,2-Dimethylhydrazinodiphenylphosphine with Atmospheric Oxygen.—A solution of 2.94 g. of I in 50 ml. of dry benzene was warmed to 50° in a stream of dry air for 12 hr. As the benzene evaporated there appeared a white, crystalline solid and a dark gum. The crystals were collected, recrystallized from benzene, and sublimed at 160° (0.33 mm.). The yield, 0.94 g., represents a 45% conversion to the oxide, which melted at 167.5–168.0°. A mixture melting point of this product with compound II was 166–168°; their infrared spectra were identical.

Oxidation of 2,2-Dimethylhydrazinodiphenylphosphine with Activated Manganese Dioxide.¹⁵—A benzene solution of 2.94 g. of I was heated to 50° in contact with 4.1 g. (0.72 mole) of acti-

(15) Beacon Chemical Industries, Inc., 33 Richdale Avenue, Cambridge 40, Massachusetts.

vated manganese dioxide for 12 hr. Upon filtration and evaporation of the filtrate a crop of white crystals was obtained which was recrystallized from benzene and sublimed at 160° (0.30 mm.) to give 1.60 g. of a white, crystalline solid, m.p. 166.5–168.5° (45% conversion to the oxide, based on the amount of I used). A mixture melting point of this product with II was 166–168°; their infrared spectra were identical.

Preparation of 1,1-Bis-(diphenylphosphino)-2,2-dimethylhydrazine (III).—Diphenylchlorophosphine (3.54 g., 0.0161 mole) and 3.62 g. (0.0358 mole) of triethylamine were dissolved in 50 ml. of dry toluene and to this was added a solution of 3.84 g. (0.0161 mole) of 2,2-dimethylhydrazinodiphenylphosphine in 50 ml. of dry toluene. The addition and subsequent steps were performed under a nitrogen atmosphere. There was no immediate evidence of reaction. However, as the mixture was warmed to 110° a precipitate formed in the solution. The mixture was stirred at 110° for 1 hr. and filtered hot to yield on the filter 2.13 g. (95.6% of theoretical) of triethylammonium chloride, m.p. 251–253° (lit.¹⁶ 253–254°). Evaporation of the filtrate gave 6.51 g. (93.8% of theoretical) of a white solid, III, which, after recrystallization from *n*-heptane, melted at 129.5–132.5°. All the data confirm the structural formula for III as [(C₆H₅)₂P]₂NN(CH₃)₂.

Oxidation of 2,2-Dimethylhydrazinodiphenylphosphine with Sulfur.—A benzene solution of 3.47 g. (0.015 mole) of I was warmed to 60° in contact with 0.48 g. (0.015 mole) of finely divided sulfur. When the sulfur had dissolved completely the benzene was evaporated to yield a white, crystalline mass. Recrystallization of this material from a 1:1 mixture of *n*-hexane and benzene gave 3.59 g. (92% of theoretical) of a white crystalline solid, IV, which melted at 95.5–97.0°. Analytical data, method of preparation, and infrared and n.m.r. data all confirm the formula (C₆H₅)₂P(S)NHN(CH₃)₂ for IV.

Reaction of Trimethylhydrazine with Diphenylchlorophosphine.—Using the method used for I, 11.0 g. (0.05 mole) of diphenylchlorophosphine was allowed to react with 7.5 g. (0.10 mole) of trimethylhydrazine. The yield of 1,1,2-trimethylhydrazinium chloride was essentially quantitative and upon evaporation of the filtrate at room temperature and reduced pressure there was left 12.8 g. of a light yellow, viscous liquid, V. This material undergoes decomposition upon distillation at its boiling point at pressures below 0.2 mm. No method for purification was found. Because of the conversion in good yields of this product to the corresponding phosphine oxide we are sure that the product contains as its major component 1,2,2-trimethylhydrazinodiphenylphosphine, (C₆H₅)₂PN(CH₃)N(CH₃)₂.

Oxidation of 1,2,2-Trimethylhydrazinodiphenylphosphine.—A benzene solution of 4.3 g. of V from the above reaction was warmed in a stream of dry air for 24 hr. Upon evaporation of the benzene a crop of long crystals was formed within a yellow, viscous mass. The crystals were collected and recrystallized from a 1:1 mixture of *n*-hexane and benzene. Further purification by sublimation at 169° (0.17 mm.) yielded 2.9 g. of a crystalline solid, VI, m.p. 165.0–166.5°. The yield represents a 63% conversion of 1,2,2-trimethylhydrazinodiphenylphosphine, V, to its oxide, VI. The analytical results, method of synthesis, and the infrared and n.m.r. spectra confirm the formula (C₆H₅)₂P(O)N(CH₃)N(CH₃)₂.

Preparation of 1,2,2-Trimethylhydrazinodiphenylphosphine Oxide.—Using the method used for I, 8.15 g. (0.11 mole) of trimethylhydrazine was allowed to react with 11.83 g. (0.05 mole) of diphenylphosphinic chloride at 60°. Filtration of the reaction mixture gave 5.4 g. of 1,1,2-trimethylhydrazinium chloride, m.p. 54–56°, on the filter and a gum upon evaporation of the filtrate. The gum was dissolved in boiling cyclohexane and the resulting solution was filtered and allowed to cool, at which point a crop of crystals formed. The solid (6.2 g.) was collected, washed, and dried; it melted at 165.0–165.5°. The infrared spectrum of this material is identical with that of product VI, and helps to confirm the assigned formula for VI.

Reaction of 1-Ethyl-2,2-dimethylhydrazine with Diphenylchlorophosphine.—Using the method used for III, 6.17 g. (0.07 mole) of 1-ethyl-2,2-dimethylhydrazine was allowed to react with 15.44 g. (0.07 mole) of diphenylchlorophosphine and 7.23 g. (0.0715 mole) of triethylamine in 70 ml. of benzene at 40°. Triethylammonium chloride (9.15 g., 95% of theoretical) was collected on the filter and evaporation of the filtrate at 25° (1.0 mm.) left a straw-colored, viscous liquid, VII.

A benzene solution of VII was exposed to a stream of dry, undiluted oxygen at room temperature for 3 hr. Upon evaporation of the benzene a dark gum was observed from which no pure product could be isolated. However, conversion of product VII to the corresponding sulfide which is described in the following paragraph leads to the conclusion that 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine, (C₆H₅)₂PN(C₂H₅)N(CH₃)₂, is the major constituent of product VII.

Reaction of 1-Ethyl-2,2-dimethylhydrazinodiphenylphosphine with Sulfur.—A benzene solution of 4.24 g. of VII was warmed to 80° and 0.513 g. (0.0156 mole) of finely divided sulfur was added. The sulfur dissolved and the resulting solution was boiled for 3 hr. and then allowed to evaporate to dryness, yielding 3.87 g. of a white crystalline mass which was recrystallized from acetone to give long, highly refractive crystals, m.p. 126.5–127.5°, VIII. The yield observed corresponds to an 81.4% conversion of 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine to its sulfide, VIII. The analytical data, method of synthesis, infrared, and n.m.r. data confirm the formula (C₆H₅)₂P(S)N(C₂H₅)N(CH₃)₂ for VIII.

Preparation of 1-Ethyl-2,2-dimethylhydrazinodiphenylphosphine Oxide.—Using the method used for III, 6.17 g. (0.07 mole) of 1-ethyl-2,2-dimethylhydrazine was allowed to react with 16.56 g. (0.07 mole) of diphenylphosphinic chloride and 7.23 g. (0.0715 mole) of triethylamine in 50 ml. of benzene at 20°. The reaction was allowed to proceed over a 2-week period after which the mixture was filtered to yield 8.97 g. of triethylammonium chloride on the filter and 5.36 g. of a white, crystalline solid upon evaporation of the filtrate. (In another run the reaction was essentially complete in 1 hr. at 80°.) Sublimation of the solid gave a product, IX, with m.p. 140.0–141.0°. The analytical data, method of synthesis, and the infrared and n.m.r. spectra of IX confirm the formula (C₆H₅)₂P(O)N(C₂H₅)N(CH₃)₂.

Preparation of 1,2-Bis-(diphenylphosphino)-hydrazine.—Using the method used for III, 1.08 g. (0.0337 mole) of anhydrous hydrazine was treated with 29.73 g. (0.1348 mole) of diphenylchlorophosphine and 18.2 g. (0.1796 mole) of triethylamine in 150 ml. of chloroform. A deep yellow color developed upon mixing the reactants at 20° and no precipitate appeared on heating to 65°. After warming for 1 hr. at 65° the solution was evaporated to a solid residue which was extracted with 300 ml. of benzene. Upon filtration of the benzene solution, 16.64 g. of triethylammonium chloride (86% of theoretical) was obtained on the filter, while evaporation of the filtrate at reduced pressure left a white paste, to which 300 ml. of dry ether was added. A white solid separated upon the ether addition; this solid was collected, washed three times with 50-ml. portions of ether, and recrystallized from acetone to yield 3.60 g. of a white, crystalline solid, m.p. 129.0–129.5°, X.

Inasmuch as this material was obtained from acetone solution, it is highly probable that it possesses the symmetrical configuration, and, therefore, does not contain a free –NH₂ group, since such a group would be expected to lead to reaction with a ketone to produce a hydrazone.¹⁷ The apparent structure, therefore, is (C₆H₅)₂PNHNHP(C₆H₅)₂.

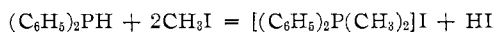
Reaction of Methylhydrazine with Diphenylchlorophosphine.—The method used for I was used to carry out the reaction of 10.4 g. (0.0472 mole) of diphenylchlorophosphine with 4.35 g. (0.0945 mole) of methylhydrazine in 75 ml. of dry ether at 25°. On filtration, 3.71 g. of methylhydrazinium chloride was obtained on the filter and evaporation of the filtrate gave 9.57 g. (86.7% of theoretical) of a yellow, viscous liquid, XI, which was free of

(16) A. U. Hofmann, *Ann.*, **73**, 91 (1850).(17) R. Klement and K. Knollmüller, *Ber.*, **93**, 834 (1960).

chlorine, as evidenced by the absence of a precipitate upon adding silver nitrate solution to a dilute nitric acid solution of a few drops of XI. Decomposition occurs upon distillation at reduced pressures and no way was found to effect purification.

Anal. Calcd. for $C_{13}H_{15}N_2P$: C, 67.81; H, 6.57; N, 12.17; P, 13.45. Found: C, 67.55; H, 6.46; N, 11.96; P, 14.34.

The product did not appear to be a pure substance, but in view of the analytical results, it appears that it might consist of a mixture of the isomers $(C_6H_5)_2PNHNH(CH_3)$ and $(C_6H_5)_2PN-(CH_3)NH_2$. No method was found to separate the mixture. Upon distillation, thermal decomposition occurs resulting in a volatile fraction, XII, and a resinous residue. The volatile fraction, b.p. 98–99° (0.36 mm.), was identified as diphenylphosphine, b.p. 280° (760 mm.).¹⁸ *Anal.* Calcd. for $(C_6H_5)_2PH$: C, 77.41; H, 6.95; P, 16.64. Found: C, 77.42; H, 6.22; P, 15.88. Cryoscopic estimation of the molecular weight of XII in benzene gave the value 185; the molecular weight of $(C_6H_5)_2PH$ is 186.2. A methyl iodide derivative of XII was prepared and had a m.p. of 243°. A m.p. of 241° is given for the methyl iodide derivative of diphenylphosphine¹⁸ produced in the reaction



An intense absorption at 2280 cm^{-1} in the infrared spectrum of XII indicates the presence of the P–H bond.¹² The resinous residue from the distillation was not identified.

Preparation of 1,1,2-Tris-(diphenylphosphino)-2-methylhydrazine.—The method used for III was used to carry out the reaction of 11.90 g. (0.054 mole) of diphenylchlorophosphine and 7.24 g. (0.0732 mole) of trimethylamine with 0.82 g. (0.018 mole) of methylhydrazine at 100° in dry toluene. The initial addition had to be made at 0° to remove the heat generated, after which the mixture was stirred at 100° for 1 hr. and filtered, to yield triethylammonium chloride on the filter and a yellow gum upon evaporation of the filtrate. Ether (300 ml.) was added to the gum and a white solid separated which was washed with three 150-ml. portions of ether and dried *in vacuo*. The amount obtained was 2.55 g. (21.8% yield, based on the amount of diphenylchlorophosphine used) and the m.p. was 151° dec. Recrystallization of the solid from acetone gave a white, crystalline product, XIII, with a melting point of 152.3–153.0° dec. Analytical data, method of synthesis, and infrared and n.m.r. data all confirm the formula for XIII to be $[(C_6H_5)_2P]_2NN[P(C_6H_5)_2](CH_3)$.

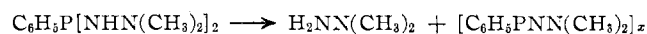
Preparation of 2,2-Dimethylhydrazinophenylchlorophosphine.—The method used for I was used to carry out the reaction of 17.9 g. (0.10 mole) of phenyldichlorophosphine with 12.0 g. (0.20 mole) of 1,1-dimethylhydrazine in 40 ml. of benzene at 25°. After 1 hr. of stirring at 25° the mixture was filtered to yield 9.2 g. (95% of theoretical) of 1,1-dimethylhydrazinium chloride on the filter, and a clear, viscous liquid, XIV, upon evaporation of the filtrate at room temperature and reduced pressure. An attempt to distil the product XIV resulted in the evolution of hydrogen chloride and left a resinous material in the pot. No further purification of XIV was attempted. This material is extremely sensitive to oxygen and moisture, and fumes in moist air. The chloride analysis and method of preparation are in agreement with the formula $(C_6H_5)_2P(Cl)NHN(CH_3)_2$.

Preparation of Bis-(2,2-dimethylhydrazino)-phenylphosphine.—Phenyldichlorophosphine (13.15 g., 0.0735 mole) was allowed to react with 23.0 g. (0.384 mole) of 1,1-dimethylhydrazine in 45 ml. of benzene at room temperature according to the method used for I. The mixture was stirred at 25° for 1 hr. and then filtered to give 15.28 g. (99.4% of theoretical) of 1,1-dimethylhydrazinium chloride. A yellow paste was obtained upon evaporation of the filtrate at room temperature and reduced pressure. The paste from the filtrate was dissolved in a minimum amount of hot benzene and the resulting solution was filtered under nitrogen. Upon cooling the filtrate, a crop of white crystals formed and was collected, dried, and sublimed at 50° (0.20 mm.) to yield a small amount (12% of theoretical) of a white crystalline

solid, XV, m.p. 61.5–63.0°. The product, XV, contains no chlorine and is very sensitive to oxygen and moisture. A sample exposed to the atmosphere for a few seconds may increase its weight by several per cent, which is partly responsible for the relatively poor analytical data. These data plus the method of preparation and the infrared data support the postulated formula $C_6H_5P-[NHN(CH_3)_2]_2$, though the presence of a small band in the infrared spectrum corresponding to the range commonly assigned to P=O indicates the probable presence of some oxide impurity in the sample.

Thermal Condensation of Bis-(2,2-dimethylhydrazino)-phenylphosphine.—During the sublimation of XV it was observed that appreciable quantities of 1,1-dimethylhydrazine collected in the –78° trap used to protect the vacuum pump. It also was found that after an initial small amount of XV had collected on the cold finger of the sublimation apparatus no further sublimation occurred. Instead, the white solid in the pot gradually became an amber-colored, viscous liquid as the temperature was raised from 50° up to 200°. When no additional 1,1-dimethylhydrazine collected in the cold trap the sublimation pot was cooled to room temperature and it was observed that the residue had solidified to a brittle, resin-like solid, XVI, with melting point 105–115°.

Anal. Calcd. for $C_8H_{11}N_2P$: C, 57.83; H, 6.67; N, 16.86; P, 18.64. Found: C, 56.79; H, 5.54; N, 15.84; P, 21.12. A molecular weight determination in benzene gave the value 2076. We believe that XVI is a polymer formed in accordance with the following equation, in which x has an average value of 12.5.



The fact that this condensation occurs indicates that only small yields of bis-(2,2-dimethylhydrazino)-phenylphosphine are to be expected from the reaction of phenyldichlorophosphine with dimethylhydrazine in a system which has been heated.

Oxidation of Bis-(2,2-dimethylhydrazino)-phenylphosphine.—A solution of 3.6 g. of bis-(2,2-dimethylhydrazino)-phenylphosphine in 100 ml. of dry benzene was warmed for 12 hr. in contact with dry air. Upon cooling the solution, crystals formed which were collected and sublimed at 160° (0.20 mm.) to give a white, crystalline product, XVIIa, m.p. 161.0–163.0° in 40% yield, based on the amount of XV originally present. Infrared data and method of synthesis of XVIIa are consistent with the formula $(C_6H_5)_2P(O)[NHN(CH_3)_2]_2$. This formulation also is supported by the fact that the physical properties of XVIIb (see below) are identical with those of XVIIa.

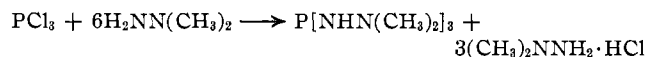
Preparation of Bis-(2,2-dimethylhydrazino)-phenylphosphine Oxide.—Using the method used for I, 19.5 g. (0.10 mole) of phenylphosphonic dichloride $(C_6H_5P(O)Cl_2)$ was allowed to react with 25.0 g. (0.42 mole) of 1,1-dimethylhydrazine in 40 ml. of chloroform at 5°. After 1 hr. of stirring at 60° the mixture was filtered hot to give a non-quantitative yield of 1,1-dimethylhydrazinium chloride on the filter and a filtrate which gave a positive test for chlorine. This results from the fact that 1,1-dimethylhydrazinium chloride is somewhat soluble in chloroform. The filtrate was evaporated to dryness and was extracted twice with boiling benzene. The resulting benzene solution deposited 17.0 g. of solid upon cooling to room temperature. Sublimation of this solid at 160° (0.18 mm.) gave 14.5 g. (61% of theoretical) of a white crystalline solid, m.p. 161.0–165.0°. A mixture melting point of this product with XVIIa gave 160–162°, and their infrared spectra are identical.

Preparation of Bis-(2,2-dimethylhydrazino)-phenylphosphine Sulfide.—The method used for I was used to carry out the reaction of 16.89 g. (0.08 mole) of phenylphosphonothioic dichloride $(C_6H_5P(S)Cl_2)$ with 19.6 g. (0.326 mole) of 1,1-dimethylhydrazine in 50 ml. of benzene at 25°. After stirring at 25° for 1 hr. the mixture was filtered to yield 14.70 g. of 1,1-dimethylhydrazinium chloride on the filter and 20.10 g. of a white solid upon evaporation of the solvent from the filtrate. The latter material was recrystallized from 1:1 *n*-hexane–benzene and then sublimed at 100° (0.20 mm.) to give 12.8 g. (64% of theoretical) of a white crystalline solid, XVIII, m.p. 106.0–106.5°. Analytical data, method of preparation, as well as infrared and

(18) A. Michaelis and A. Link, *Ann.*, **207**, 193 (1881).

n.m.r. data support the formula $C_6H_5P(S)[NHN(CH_3)_2]_2$ for XVIII.

Reaction of Phosphorus Trichloride with 1,1-Dimethylhydrazine.—The method used for I was used to carry out the reaction of 6.87 g. (0.05 mole) of phosphorus trichloride with 24.06 g. (0.4 mole) of 1,1-dimethylhydrazine in 50 ml. of benzene. Formation of solid in the solution was observed at 25°, and after 1 hr. of stirring at this temperature the mixture was filtered to yield 13.8 g., 95% of theoretical based on the equation



of 1,1-dimethylhydrazinium chloride on the filter and a yellow, viscous liquid upon evaporation of the filtrate at room temperature and reduced pressure. The latter product, XIX, gave a negative test for chlorine and decomposed upon distillation at reduced pressure. It was observed that XIX absorbs moisture rapidly upon exposure to the atmosphere.

Preparation of Phosphoryl Tri-(2,2-dimethylhydrazide).—The method used for I was used to carry out the reaction of 8.21 g. (0.0535 mole) of phosphoryl chloride with 20.0 g. (0.33 mole) of 1,1-dimethylhydrazine in 50 ml. of chloroform at 0°. After 1 hr. of stirring at 30° the mixture was filtered to give a non-quantitative yield of 1,1-dimethylhydrazinium chloride on the filter. The filtrate was evaporated to dryness at reduced pressure and extracted twice with hot benzene. After filtration of the combined benzene extractions the solution was evaporated to yield a white solid which was collected, dried, and sublimed at 105° (0.10 mm.). The sublimate was a white, crystalline mass weighing 3.79 g. (76% of theoretical) and which melted at 193.5–195.0°, XX. Analytical data, the method of preparation, and infrared and n.m.r. spectra are consistent with the formula $OP[NHN(CH_3)_2]_3$ for XX.

Preparation of Thiophosphoryl Tri-(2,2-dimethylhydrazide).—The method used for I was used to carry out the reaction of 37.0 g. (0.62 mole) of 1,1-dimethylhydrazine with 10.64 g. (0.063 mole) of thiophosphoryl chloride in 40 ml. of benzene at 0°. After 1 hr. of stirring at 45°, the mixture was filtered to give 18.6 g. of 1,1-dimethylhydrazinium chloride and 15.0 g. of a solid upon evaporation of the filtrate. Sublimation of the solid gave 7.5 g. (50% of theoretical) of a white crystalline product, XXI, with m.p. 75.5–78.0°. The analytical data, method of synthesis, and infrared and n.m.r. spectra are consistent with the formula $SP[NHN(CH_3)_2]_3$ for XXI.

Attempted Preparation of Thiophosphoryl Tri-(1,2,2-trimethylhydrazide and Thiophosphoryl Tri-(1-ethyl-2,2-dimethylhydrazide).—Thiophosphoryl chloride was allowed to react with 1,1,2-trimethylhydrazine and 1-ethyl-2,2-dimethylhydrazine in various solvents according to the method used for I. The products invariably were gums and always were contaminated with the respective substituted hydrazinium salt. No method of separation of the desired products from the contaminants was found.

Discussion

The results reported above demonstrate the general applicability of the hydrazinolysis reaction to the conversion of mono-, di-, and trihalophosphines, phosphinyl halides, phosphoryl halides, and thiophosphoryl halides to the corresponding hydrazino derivatives. In some instances the method is rendered somewhat inconvenient by the solubility of certain hydrazinium chlorides in many organic solvents, thus preventing the separation of such chlorides by precipitation from the solution containing the hydrazinophosphorus derivative. This difficulty may commonly be overcome by providing an independent hydrogen halide acceptor such as triethylamine. The provision of such an independent strongly basic hydrogen halide acceptor will in a number of cases promote hydrazinolysis reactions

which would otherwise be difficult to carry out.

It has been found to be possible to substitute more than one proton in a hydrazine with diphenylphosphino groups. Examples are 1,1-bis-(diphenylphosphino)-2,2-dimethylhydrazine and 1,1,2-tris-(diphenylphosphino)-2-methylhydrazine. The first proton usually may be substituted at low temperatures (usually no higher than 35° is required); however, to substitute additional protons, higher temperatures, as high as 110°, are required. Apparently the protons in the N–H bonds of the partially phosphorus-substituted hydrazines are less labile than those in the parent hydrazines themselves. This is in spite of the well established fact^{19–21} that attaching a phosphorus atom to a nitrogen atom reduces the electron density and basic character of the latter and thus should promote its proton-donor character. The fact that this transfer of electron density from nitrogen to phosphorus does occur is further supported by recent studies²² in our Laboratory of the chloramination and alkylation of hydrazinophosphines which show that the amination and alkylation occur exclusively on the phosphorus atom and that both of the hydrazino nitrogens are inactive toward these reactions. A possible explanation of the apparent paradox lies in the steric interference of the bulky diphenylphosphino group, but this is mere speculation and the question must at present be considered to be unresolved.

The formation in good yields of hydrazinophosphine oxides by reactions of the corresponding hydrazinophosphines with oxygen or activated manganese dioxide, and the formation of the hydrazinophosphine sulfides by reaction of the corresponding hydrazinophosphine with sulfur, show clearly the fact that the phosphorus atom is more readily oxidizable than either of the hydrazino nitrogen atoms.

The observed infrared absorption frequencies for the various hydrazinophosphorus compounds which were most useful in establishing the structures of these compounds⁹ are: P–C₆H₅, 1430–1440 cm.⁻¹; P=O, 1175–1188 cm.⁻¹; P=S, 700–727 cm.⁻¹; P–N, 743–773 cm.⁻¹; N–N, 950–996 cm.⁻¹. The N–N absorption frequencies usually are very weak and sometimes are difficult to locate.

The n.m.r. data tabulated in Table III are in strict and detailed agreement with reasonable predictions based on the formulas assigned to the various compounds. In almost every instance these formulas are well supported by the analytical data, methods of preparation, and, in some cases, correlation of physical constants with similar products prepared by alternative syntheses. Nevertheless, the excellent agreement of n.m.r. and infrared data is reassuring and worth noting. From the data in Table III, it is interesting to observe that the chemical shifts for ³¹P in the compounds in

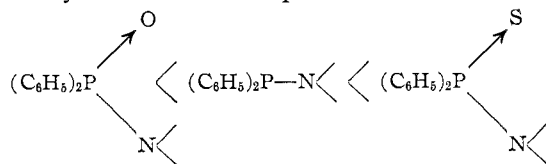
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this study increase in the sequence



Acknowledgments.—We gratefully acknowledge the support of the Petroleum Research Fund, administered by the American Chemical Society, for the research reported in this paper; also the excellent assistance of Professor Wallace Brey, in whose laboratory the n.m.r. data were obtained.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Hydrazinophosphorus Compounds. II. Reactions of Substituted Hydrazinophosphines

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Received September 7, 1962

A series of reactions of various substituted hydrazinodiphenylphosphines has demonstrated that in the hydrazinophosphines the phosphorus atom is much more basic than either of the nitrogen atoms. Reactions tried include chloramination and alkylation with methyl iodide and in each case the electrophilic reagent attaches itself to the phosphorus atom. Compounds synthesized include $[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_3)\text{NHN}(\text{CH}_3)_2]\text{I}$, $[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_3)\text{N}(\text{CH}_3)\text{N}(\text{CH}_3)_2]\text{I}$, $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)\text{NHN}(\text{CH}_3)_2]\text{Cl}$, $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)\text{N}(\text{CH}_3)\text{N}(\text{CH}_3)_2]\text{Cl}$, $[[(\text{C}_6\text{H}_5)_2\text{P}=\text{NH}][(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)-]\text{NN}(\text{CH}_3)_2]\text{Cl}$, and $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)\text{N}(\text{C}_2\text{H}_5)\text{N}(\text{CH}_3)_2]\text{Cl}$. The hydrazinophosphine oxides studied are inert toward methyl iodide and chloramine. A compound of the empirical composition $(\text{C}_6\text{H}_5)_2\text{PNHN}(\text{CH}_3)\cdot\text{CS}_2$ was formed by reaction of 2,2-dimethylhydrazinodiphenylphosphine with carbon disulfide.

Introduction

Alkylation experiments on aminophosphines²⁻⁴ have established clearly that in these compounds electron density on the phosphorus atom is increased at the expense of the amino nitrogen atom to which the phosphorus atom is attached, presumably through the mechanism of $p\pi-d\pi$ bonding. Synthesis of a series of hydrazinophosphines in our Laboratory⁵ raised the question as to whether or not the same effect would obtain in the atomic grouping $>\text{P}-\text{N}-\text{N}<$ and, if so, would it affect only the vicinal nitrogen atom or would it affect both nitrogen atoms. For this reason it was decided to investigate the reactions of methyl iodide, and also of chloramine, with a series of hydrazinophosphine derivatives, including one which contained two phosphorus atoms. In addition the reaction of 2,2-dimethylhydrazinodiphenylphosphine with carbon disulfide was carried out.

Experimental

Materials.—All non-aqueous solvents were thoroughly dried. Commercial grade nitrogen treated to remove oxygen and water vapor was used in some of the reactions. The hydrazinophosphorus derivatives and the chloramine were prepared in accordance with previously published procedures to which references are given at appropriate points.

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Analyses.—Elemental analyses were carried out by the Galbraith Microanalytical Laboratories of Knoxville, Tennessee. Melting points were determined in sealed capillary tubes in a Thomas-Hoover melting point apparatus.

Infrared Spectra.—Infrared spectra were taken on a Perkin-Elmer Infracord Model 137 spectrophotometer. Since most of the compounds studied are crystalline solids, the spectra were obtained from Nujol mulls.

Reaction of 2,2-Dimethylhydrazinodiphenylphosphine with Methyl Iodide.—A 1.72-g. (0.00704 mole) sample of 2,2-dimethylhydrazinodiphenylphosphine⁶ was dissolved in 15 ml. of dry ether and to this was added a solution of 1.0 g. (0.00704 mole) of methyl iodide in 10 ml. of dry ether. The addition was performed under a nitrogen atmosphere and took 5 min. The solution was stirred at room temperature overnight and at the end of this time was filtered to yield 2.71 g. of a white solid, I, which melted at 156.0–158.0°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{PI}$: C, 46.65; H, 5.22; N, 7.25; P, 8.02. Found: C, 46.85; H, 5.47; N, 7.10; P, 7.85.

This salt is soluble in absolute ethanol and an aqueous ethanol solution gives a positive iodide ion test; iodine is liberated by the addition of nitric acid. On the basis of the analytical data and the hydrolytic results reported below, and the presence of a strong, sharp band in the infrared spectrum at 1120 cm^{-1} , the formula $[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_3)[\text{NHN}(\text{CH}_3)_2]]\text{I}$ is assigned to I.

Hydrolysis of 2,2-Dimethylhydrazinodiphenylphosphonium Iodide.—Two g. of sodium hydroxide was added to 3.0 g. of 2,2-dimethylhydrazinodiphenylphosphonium iodide in 25 ml. of a 1:1 ethanol and water mixture and the mixture was boiled for 1 hr. As the alcohol evaporated it was replaced with water. The vapor above the solution was tested for free 1,1-dimethylhydrazine with (1) damp red litmus and (2) a drop of potassium permanganate solution on a strip of filter paper. The litmus turned blue and the permanganate ion was decolorized and reduced to Mn^{2+} .

An oil separated from the solution, but the amount was too small for distillation. In order to positively identify this ma-