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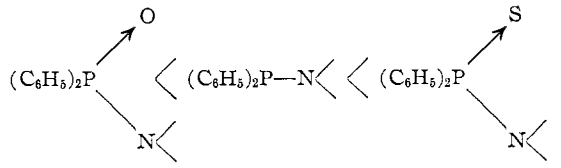


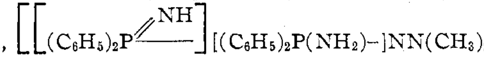
Acknowledgments.—We gratefully acknowledge the support of the Petroleum Research Fund, administered by the American Chemical Society, for the research reported in this paper; also the excellent assistance of Professor Wallace Brey, in whose laboratory the n.m.r. data were obtained.

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida

Hydrazinophosphorus Compounds. II. Reactions of Substituted Hydrazinophosphines

By ROBERT P. NIELSEN, JOSEPH F. VINCENT[1a] and HARRY H. SISLER[1b]

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 $[(C_6H_5)_2P(CH_3)NHN(CH_3)_2]I$, $[(C_6H_5)_2P(CH_3)N(CH_3)N(CH_3)_2]I$, $[(C_6H_5)_2P(NH_2)NHN(CH_3)_2]Cl$, $[(C_6H_5)_2P(NH_2)N(CH_3)N(CH_3)_2]Cl$,  $\left[\left[(C_6H_5)_2P\overset{NH}{=\!=}\right][(C_6H_5)_2P(NH_2)-]NN(CH_3)_2\right]Cl$, and $[(C_6H_5)_2P(NH_2)N(C_2H_5)N(CH_3)_2]Cl$. The hydrazinophosphine oxides studied are inert toward methyl iodide and chloramine. A compound of the empirical composition $(C_6H_5)_2PNHN(CH_3)\cdot CS_2$ was formed by reaction of 2,2-dimethylhydrazinodiphenylphosphine with carbon disulfide.

Introduction

Alkylation experiments on aminophosphines[2-4] 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 Laboratory[5] raised the question as to whether or not the same effect would obtain in the atomic grouping $>P-N-N<$ 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.

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-dimethyl hydrazinodiphenylphosphine[5] 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 $C_{15}H_{20}N_2PI$: 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 $[(C_6H_5)_2P(CH_3)[NHN(CH_3)_2]]I$ is assigned to I.

Hydrolysis of 2,2-Dimethylhydrazinomethyldiphenylphosphonium Iodide.—Two g. of sodium hydroxide was added to 3.0 g. of 2,2-dimethylhydrazinomethyldiphenylphosphonium 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-

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[1] (a) Visiting N. S. F. Science Faculty Fellow from the Woman's College of Georgia, Milledgeville, Georgia; (b) To whom communcations should be addressed.

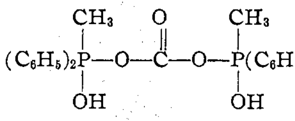
[2] A. Burg and J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).

[3] H. Sisler and N. Smith, *J. Org. Chem.*, **26**, 4733 (1961).

[4] G. Ewart, D. Payne, A. Porte, and A. Lane, *J. Chem. Soc.*, 3984 (1962).

[5] R. P. Nielsen and H. H. Sisler, *Inorg. Chem.*, **2**, 753 (1963).

terial as methyldiphenylphosphine oxide, the oil was treated with a solution of sodium carbonate. Upon evaporation of the water a white solid remained. This solid was extracted with hot benzene, filtered, and upon removal of the benzene from the filtrate, 1.8 g. of a white solid was obtained, m.p. 107–109°. This solid evolved carbon dioxide upon treatment with dilute hydrochloric acid. Methyldiphenylphosphinic hydrogen carbonate



$$(C_6H_5)_2P(CH_3)(OH)-O-C(=O)-O-P(CH_3)(OH)(C_6H_5)_2$$

is reported to be the product of the reaction of methyldiphenylphosphine oxide with carbon dioxide and has a m.p. of 109–111°.[6] The hydrolysis may, therefore, be represented by the equation

$$[(C_6H_5)_2P(CH_3)[NHN(CH_3)_2]]I + OH^- \longrightarrow (C_6H_5)_2(CH_3)PO + H_2NN(CH_3)_2 + I^-$$

If alkylation had occurred on the end nitrogen atom to yield $[(C_6H_5)_2PNHN(CH_3)_3]I$, diphenylphosphinic acid, $(C_6H_5)_2P(O)OH$, would have been produced in the hydrolysis.

Reaction of 2,2-Dimethylhydrazinodiphenylphosphine with Chloramine.—2,2-Dimethylhydrazinodiphenylphosphine[5] (4.5 g., 0.0184 mole) in 50 ml. of dry ether was treated for 15 min. with the effluent gases from a chloramine generator[7] which produces a 1:10 mixture of chloramine and ammonia at a rate of 0.10 mole of chloramine per hour. The reaction was run at 0°, and a white solid was observed forming in the ether as the reaction proceeded. The crude product (4.7 g.), m.p. 186–189°, was collected (86% of theory) and recrystallized from absolute ethanol at room temperature to give a white, crystalline solid, II, m.p. 195.0°.

Anal. Calcd. for $C_{14}H_{17}N_3PCl$: C, 56.85; H, 6.47; N, 14.21; P, 10.47. Found: C, 56.92; H, 6.69; N, 14.21; P, 10.41.

An aqueous solution of this salt gives a positive chloride test, and a warmed basic solution evolves ammonia and 1,1-dimethylhydrazine. Acidification of this solution precipitates diphenylphosphinic acid. On the basis of these reactions, the analytical data, and the presence in the infrared spectra of a strong, sharp band at 1130 cm.$^{-1}$, the structure $[(C_6H_5)_2P(NH_2)[NHN(CH_3)_2]]Cl$ is assigned to II.

An alcohol solution of this salt was allowed to react with a Dowex-50 ion-exchange column in the acetate form with the result that the chloride was quantitatively removed from the solution, but upon crystallization serious decomposition of the resulting amino-(2,2-dimethylhydrazino)-diphenylphosphonium acetate occurred. Similar results were encountered with attempts to prepare the hydroxide; this is not unexpected in view of the known[5] tendency for the compound to undergo basic hydrolysis.

Attempted Reaction of 2,2-Dimethylhydrazinodiphenylphosphine Oxide with Methyl Iodide and Chloramine.—No reaction was observed when 2,2-dimethylhydrazinodiphenylphosphine oxide was treated with methyl iodide in ether at 25°, benzene at 50°, or toluene at 110°, and quantitative recovery of the starting materials was accomplished. Similar negative results were encountered when 2,2-dimethylhydrazinodiphenylphosphine oxide was treated with great excesses of chloramine in benzene at 25° and toluene at 90°.

Reaction of 1,2,2-Trimethylhydrazinodiphenylphosphine with Methyl Iodide.—Ten ml. (22.79 g., 0.196 mole) of methyl iodide was added to 5.0 g. (0.0194 mole) of 1,2,2-trimethylhydrazinodiphenylphosphine[5] in 50 ml. of anhydrous ether at 25°. Considerable heat was evolved and a white solid appeared in the solution. The mixture was stirred overnight and upon removing the ether by filtration, 7.3 g. (94% of theory) of a yellow semisolid was obtained. This material was dissolved in hot ethanol, but no crystallization occurred upon reducing the volume and cooling the solution. Ether was added and caused the separation of a clear oil which crystallized on standing to give clusters of clear, colorless solid, III, m.p. 134.0–136.0°.

Anal. Calcd. for $C_{16}H_{22}N_2PI$: C, 48.01; H, 5.54; N, 7.00; P, 7.74; I, 31.71. Found: C, 47.65; H, 5.62; N, 6.81; P (by difference), 7.63; I, 32.29. The analytical data, the method of synthesis, and the presence in the infrared spectrum of a strong, sharp band at 1120 cm.$^{-1}$ are consistent with the following structure for compound III: $[(C_6H_5)_2P(CH_3)[N(CH_3)N(CH_3)_2]]I$.

Reaction of 1,2,2-Trimethylhydrazinodiphenylphosphine with Chloramine.—1,2,2-Trimethylhydrazinodiphenylphosphine[5] (5.4 g., 0.21 mole) in 50 ml. of anhydrous ether was treated at 0° with a gaseous ammonia–chloramine mixture which contained 0.021 mole of chloramine.[7] A white solid appeared in the ether upon reaction, and when the reaction was complete the mixture was filtered and the solid residue was washed twice with 10-ml. portions of ether and dried to give 5.5 g. of crude product (85% of theory). This was dissolved in a minimum amount of chloroform and the volume reduced until crystallization occurred. The product, IV, melts at 174.0–175.0°.

Anal. Calcd. for $C_{15}H_{21}N_3PCl$: C, 58.15; H, 6.83; N, 13.56; P, 10.00; Cl, 11.45. Found: C, 58.04; H, 6.98; N, 13.20; P, 9.86; Cl, 11.60.

The analytical data, method of synthesis, and the presence in the infrared spectrum of a strong, sharp band at 1120 cm.$^{-1}$ are consistent with the following structure for compound IV: $[(C_6H_5)_2P(NH)_2[N(CH_3)N(CH_2)_3]]Cl$.

Reaction of 1-Ethyl-2,2-dimethylhydrazinodiphenylphosphine with Chloramine.—Seven g. (0.026 mole) of 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine[5] in 50 ml. of anhydrous ether was allowed to react with 0.026 mole of gaseous chloramine[7] at 0°. The reaction was rapid and produced 6.1 g. of crude product, m.p. 176–183°. This material was recrystallized from an absolute ethanol–ether mixture to give 2.5 g. of a white, crystalline solid, m.p. 195.5–196.0°, V.

Anal. Calcd. for $C_{16}H_{23}N_3PCl$: C, 59.35; H, 7.16; N, 12.98; P, 9.57. Found: C, 59.29; H, 7.27; N, 12.94; P, 9.72.

The analytical data, the method of synthesis, and the presence in the infrared spectrum of a strong, sharp band at 1125 cm.$^{-1}$ are consistent with the following structure for compound V: $[(C_6H_5)_2P(NH)_2[N(C_2H_5)N(CH_3)_2]]Cl$.

Attempted Reaction of 1-Ethyl-2,2-dimethylhydrazinodiphenylphosphine Oxide with Chloramine and with Methyl Iodide.—1-Ethyl-2,2-dimethylhydrazinodiphenylphosphine oxide was treated with excess chloramine in benzene at 50° and in toluene at 90°. In each case the only product was recovered starting material. Similar negative results were encountered when 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine oxide was treated with methyl iodide.

Reaction of 1,1-Bis-(diphenylphosphino)-2,2-dimethylhydrazine with Chloramine.—1,1-Bis-(diphenylphosphino)-2,2-dimethylhydrazine[5] (3.4 g., 0.0079 mole) in 50 ml. of anhydrous ether was treated with a 10:1 mixture of gaseous ammonia and chloramine[7] (0.20 mole) at room temperature. The product was 3.2 g. of a white solid, part of which was identified as ammonium chloride. The product was recrystallized from a mixture of chloroform and ligroin to give 1.3 g. of white, crystalline solid, m.p. 199–201°. A nitrogen analysis showed that this solid was contaminated with ammonium chloride which was not completely removed by recrystallization. Making use of the principle of ion-exclusion chromatography,[8] a dilute ethanol solution of the product was passed through a 20–50 mesh Dowex-50 8X ion-exchange column (ammonium form) and the eluent was monitored with a conductivity bridge. The ammonium chloride was adsorbed on the column and the first fraction, upon evaporation of the ethanol, contained the desired product, VI, m.p. 204.0–205.0°.

Anal. Calcd. for $C_{26}H_{29}N_4P_2Cl$: C, 63.09; H, 5.91; N, 11.32; P, 12.52; Cl, 7.16. Found: C, 63.58; H, 5.92; N, 11.17; P, 12.42; Cl, 6.91.

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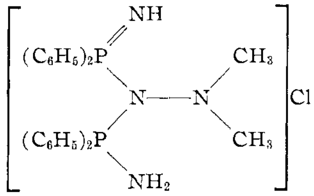
[6] D. D. Coffman and S. S. Marvel, *J. Am. Chem. Soc.*, **51**, 3496 (1929).

[7] H. Sisler, F. Neth, R. S. Drago, and D. Yaney, *ibid.*, **76**, 3906 (1954).

[8] R. Wheaton and W. Bauman, *Ind. Eng. Chem.*, **45**, (1) 228 (1953).

The analytical data, the method of synthesis, and the infrared spectrum of VI (see Discussion) are consistent with the structure



Reaction of 2,2-Dimethylhydrazinodiphenylphosphine with Carbon Disulfide.—Five ml. (6.3 g., 0.084 mole) of reagent grade carbon disulfide was added to 1.97 g. (0.0807 mole) of 2,2-dimethylhydrazinodiphenylphosphine[6] in 10 ml. of anhydrous ether. A deep red color developed immediately and slowly faded as the solution was warmed at 40° over a 5-hr. period. Upon standing overnight the volume of the solution decreased to half its original volume and large, white crystals, VII, appeared in the solution. These were collected and washed with *n*-hexane; m.p. 140.5–141.5°. The yield was 82% of theory, assuming a 1:1 reaction of carbon disulfide with 2,2-dimethylhydrazinodiphenylphosphine. The infrared spectrum of VII shows no NH absorption near 3250 cm.$^{-1}$ nor any P–H absorption near 2300 cm.$^{-1}$, but does contain a very weak absorption near 2600 cm.$^{-1}$, which is the region where S–H absorption is expected.[9]

Anal. Calcd. for $(C_6H_5)_2PNHN(CH_3)_2\cdot CS_2$: C, 56.23, H; 5.35; N, 8.74; P, 9.67; S, 20.01. Found: C, 56.09; H, 5.55; N, 8.69; P, 9.46; S, 20.17.

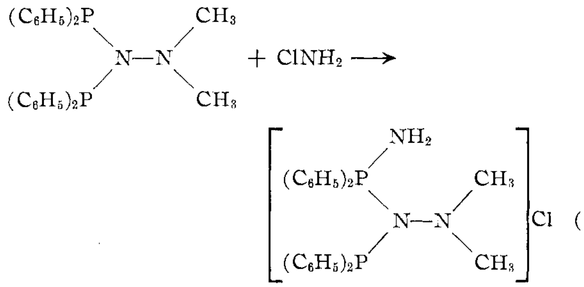
A red color develops upon dissolving VII in carbon disulfide.

Results and Discussion

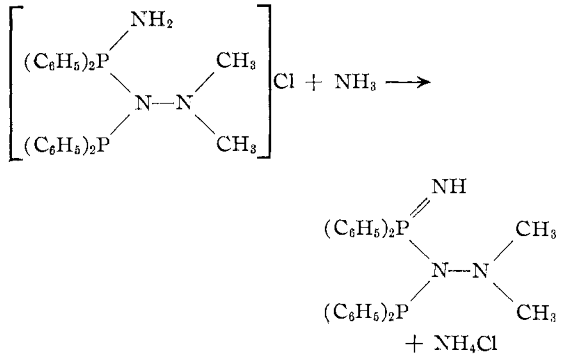
The data obtained in this study indicate that substituted hydrazinophosphines are best regarded as N-substituted phosphines and in most cases behave in a manner similar to aminophosphines. Alkylation with methyl iodide invariably occurs on the phosphorus to give hydrazinophosphonium salts which do not undergo further alkylation even if treated with as much as a tenfold excess of alkylating agent. Further evidence that the hydrazino group is deactivated toward alkylation lies in the observation that hydrazinophosphine oxides cannot be alkylated under conditions which will immediately alkylate hydrazinophosphines or hydrazines. Similar results were encountered in chloramination reactions where aminohydrazinophosphonium salts were obtained exclusively in high yields and very little, if any, oxidation of the hydrazine linkage, as determined by the appearance of ammonium chloride in the product mixture, was observed. It thus appears that not only is the nitrogen atom attached to the phosphorus deactivated toward electron acceptor species but also the second nitrogen atom in the hydrazino group has little tendency to act as an electron donor.

A sharp, strong absorption between 1100 and 1150 cm.$^{-1}$ was found in the infrared spectrum of all the compounds in this series which contain tetracoördinate phosphorus, including both the phosphonium type compounds formed by the chloramination or alkylation of hydrazinophosphines, and the various hydrazino phosphine oxides and sulfides. The consistency of the presence of this band in these compounds and its absence in the spectra of the hydrazinophosphines, combined with the establishment by chemical means (as, *e.g.*, hydrolysis) in some instances of the fact that the phosphorus atom rather than a nitrogen atom is the point of chloramination or alkylation, lends a great deal of support to the above conclusion that it is indeed the phosphorus atom in all cases which is alkylated or aminated.

The double chloramination of bis-1,1-(diphenylphosphino)-2,2-dimethylhydrazine is the first example of attack of two chloramine molecules on another species without causing complete decomposition. Since the chloramination reagent contains, in addition to chloramine, a large excess of ammonia gas, the following equations represent a reasonable path for the reaction.



(1)



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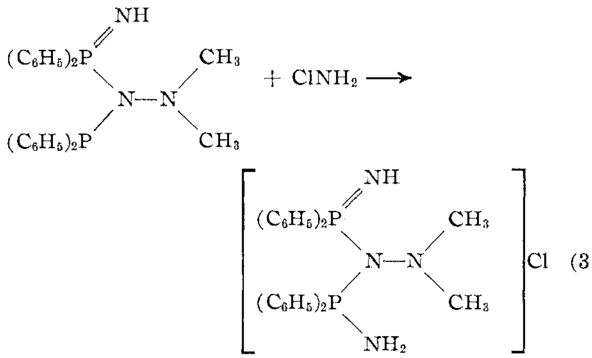

(3)

The ammonia in this case acts as a dehydrohalogenation agent. It is thought that the insolubility of the final product in ether prevents further dehydrohalogenation from occurring. The final product, VI, contains a very intense absorption in the infrared at 1250 cm.$^{-1}$ which has been assigned previously to the P=N bond[10] and also a strong, sharp band at 1120 cm.$^{-1}$.

It is a reasonable presumption, in view of the known tendency of tertiary phosphines to form brightly colored 1:1 complexes with carbon disulfide,[11] that the initial

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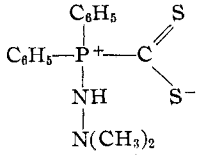
[9] L. J. Bellamy, "The Infrared-Red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1958.

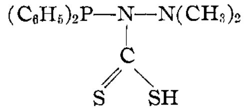
[10] H. S. Ahuja, Dissertation, University of Florida, 1961, p. 78.

[11] K. Issleib and W. Seidel, *Ber.*, **92**, 2681 (1959).

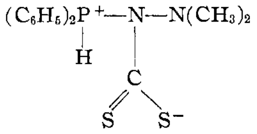
step in the formation of VII by the reaction of carbon disulfide with 2,2-dimethylhydrazinodiphenylphosphine is to form the 1:1 adduct



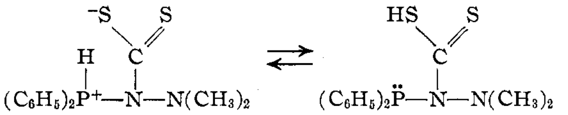
which accounts for the initial red color. The fading of the red color, the disappearance of the NH band in the regions of 1600 or 3400 cm.$^{-1}$ in the infrared spectrum of the white product, the absence of the P–H absorption (*ca.* 2300 cm.$^{-1}$) as well as the appearance of a weak absorption in the S–H region indicate that rearrangement has occurred and give support to the postulated structure



It would, of course, be expected that there would be a tendency for the proton to transfer from the SH group to one of the more basic centers in the molecule, probably the phosphorus, thus giving



This is supported by the presence of a sharp absorption band at 1100 cm.$^{-1}$ in the infrared. All the tetracoördinate phosphorus compounds in this series including the phosphonium salts, phosphine oxides, and phosphine sulfides exhibit this band. The absence of the standard P–H absorption at about 2300 cm.$^{-1}$ argues against this structure; however, the formal charge on the phosphorus may, of course, have greatly shifted this band. The proton magnetic resonance spectrum shows that the molecule contains phenyl and methyl protons in a 10:6 ratio. There is in addition a pair of proton peaks which may be variously interpreted. It is quite reasonable to speculate concerning equilibria involving shifting the proton among the various basic centers on the molecule giving structures which may be partially stabilized by weak hydrogen bonding. One attractive possibility[12] which is in accordance with the present information is



There are, however, other possibilities.

The red color obtained when additional carbon disulfide is added to VII may involve the addition of a second molecule of carbon disulfide to VII (probably through the phosphorus atom) or it may involve only the shifting of the equilibrium back toward the original red species.

Acknowledgments.—Infrared spectra were obtained with the aid of Mr. Leo Pijanowski and Mr. Howard Latz of the University of Florida. Elemental analyses were performed by Mr. Wade Renn of the University of Florida, and Galbraith Microanalytical Laboratories, Knoxville, Tennessee. The assistance afforded by a grant from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[12] This suggestion by one of the referees is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNSYLVANIA

A Study of the Thermal Decomposition of Calcium Dihydrogen Phosphide[1]

BY LOUIS L. PYTLEWSKI AND EUGENE R. NIXON

Received February 12, 1963

The thermal decomposition of $Ca(PH_2)_2$, prepared in liquid ammonia, is described for various conditions. Evidence primarily from chemical analysis and X-ray powder diffraction demonstrates that at 600 to 700° the decomposition yields as residue a brick-red crystalline phosphide of formula CaP and that beginning at about 800° the CaP loses phosphorus and is converted to black-violet crystalline Ca_3P_2. The latter compound in turn can be converted to CaP by heating with excess phosphorus at 700°.

Introduction

In connection with a study of the hydrolysis of commercially available "calcium phosphide," we decided to investigate the thermal decomposition of $Ca(PH_2)_2$ as a method of obtaining pure calcium phosphide. Legoux,[2] many years ago, prepared $Ca(PH_2)_2$ in liquid ammonia and reported that gradual heating of the ammoniates to temperatures in the vicinity of 100° produced the over-all decomposition reaction

$$Ca(PH_2)_2 \cdot xNH_3 \longrightarrow (Ca + P) + PH_3 + {}^1/_2H_2 + xNH_3 \quad (1)$$

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[1] This work was supported in part by Naval Ordnance Laboratory Contract No. N60921s-3346.

[2] C. Legoux, *Ann. chim.*, **17**, 100 (1942); see also W. O. Haas, M.S. Thesis, University of Chicago, 1941.