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# The Pyrolysis of Dimethylhydrazinophosphine Derivatives[1]

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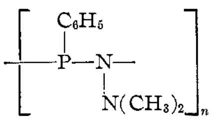
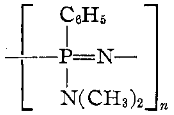
The pyrolytic decompositions of $(C_6H_5)_2PNHN(CH_3)_2$, $C_6H_5P[NHN(CH_3)_2]_2$, and $P[NHN(CH_3)_2]_3$ have been shown to yield in each instance phosphonitrilic materials whose compositions correspond to the formulations $[(C_6H_5)_2PN]_n$, $[C_6H_5P[N(CH_3)_2]N]_n$, and $[P[NHN(CH_3)_2][N(CH_3)_2]N]_n$, respectively. These rearrangements are formally analogous to the Arbuzov rearrangement.

In a recent publication[2] from this laboratory the synthesis of $(C_6H_5)_2PNHN(CH_3)_2$ and of $C_6H_5P[NHN(CH_3)_2]_2$ was reported. It was also stated that the latter compound undergoes pyrolytic condensation when heated to 200° to yield a polymer of the empirical formula $[C_6H_5PN_2(CH_3)_2]_n$ (average value of $n$ was 12 to 13). Further thought on this matter resulted in our speculating that this polymer probably does not have the structure



$$\left[-\overset{C_6H_5}{\overset{|}{P}}-\underset{\underset{N(CH_3)_2}{|}}{N}-\right]_n$$

which would result from a simple condensation reaction, but that more probably an Arbuzov-type rearrangement had occurred yielding the phosphonitrilic structure



$$\left[-\overset{C_6H_5}{\underset{\underset{N(CH_3)_2}{|}}{\overset{|}{P}}}=N-\right]_n$$

This paper reports experiments carried out to test the validity of this speculation.

In this study 2-dimethylhydrazinodiphenylphosphine, $(C_6H_5)_2PNHN(CH_3)_2$, and bis(2,2-dimethylhydrazino)phenylphosphine, $C_6H_5P[NHN(CH_3)_2]_2$, were pyrolyzed, and the resulting polymers were closely examined by elemental analysis, infrared spectroscopy, and molecular weight determination; the data thus obtained demonstrate clearly that the pyrolytic reactions do indeed yield phosphonitrilic materials. Similar but less definitive results were obtained with impure tris(2,2-dimethylhydrazino)phosphine.

## Experimental

**Materials.**—Reagent grade benzene, triethylamine, and 1,1-dimethylhydrazine were dried over calcium hydride and distilled; they were stored over calcium hydride. Phenyldichlorophosphine and diphenylchlorophosphine were obtained from the Victor Chemical Works, and reagent grade phosphorus trichloride was obtained commercially. The phosphines were vacuum distilled to remove oxidized materials and stored under nitrogen. An atmosphere of dry nitrogen was used during the experiments, and the products and purified phosphines were stored under dry nitrogen.

**Analysis.**—The Galbraith Microanalytical Laboratory of Knoxville, Tenn., conducted the elemental analyses. Molecular weights were determined in this laboratory by the cryoscopic method, using benzene as solvent.

**Infrared Spectra.**—Infrared spectra were obtained on a Perkin-Elmer Infrared Model 137 spectrometer. Because the phosphines react with oxygen and moisture, Nujol mulls were prepared in a drybox and kept in a dry nitrogen atmosphere until they were analyzed. The condensed polymers become decreasingly soluble in benzene and similar solvents as the molecular weight increases; their infrared spectra were obtained using a KBr disk.

**Pyrolysis of 2,2-Dimethylhydrazinodiphenylphosphine.**—2,2-Dimethylhydrazinodiphenylphosphine, prepared by the method of Nielsen and Sisler,[2] was heated to 148° for 18 hr. under a blanket of dry nitrogen. The purity of the starting material was established by its elemental analysis, molecular weight (Table I), and infrared spectrum. Then it was heated at 250° for 3 hr. under a reduced pressure of 0.5 mm. The residue consisted of 19.18 g. of impure diphenylphosphonitrilic trimer (89.4% yield) and was purified by crystallization from benzene three times, giving a final melting point of 229–231°. Reported values of the melting point are 228 and 230–232°. Analytical (Table I) and infrared data confirm the product as being $[(C_6H_5)_2PN]_3$.

**Pyrolysis of Bis(2,2-Dimethylhydrazino)phenylphosphine.**—Bis(2,2-dimethylhydrazino)phenylphosphine, prepared by the method of Nielsen and Sisler,[2] was heated under a blanket of dry nitrogen for 3 days as the temperature was raised slowly from 115 to 145°. The purity of the starting compound was established by its elemental analysis, molecular weight (Table I), and infrared spectrum. The temperature was raised to 220° for 3 hr. and then lowered to 160° under a reduced pressure of 0.5 mm. for 18 hr. This gave 8.6 g. (70.5% yield) of a reddish brown glass. Analytical (Table I) and infrared data confirm the identity of the product as $[C_6H_5P(N(CH_3)_2)N]_n$. The infrared spectrum of the liquid removed from the cold trap showed it to be impure 1,1-dimethylhydrazine, which agrees with the following proposed equation for the reaction.

$$nC_6H_5P[NHN(CH_3)_2]_2 \xrightarrow{\Delta} [C_6H_5P[N(CH_3)_2]N]_n + nH_2NN(CH_3)_2$$

**Pyrolysis of Tris(2,2-dimethylhydrazino)phosphine.**—Over a period of 3 hr. 7.9 g. (0.0574 mole) of phosphorus trichloride dissolved in 25 ml. of benzene was added to 11.9 g. (0.198 mole) of 1,1-dimethylhydrazine and 18.1 g. (0.179 mole) of triethylamine dissolved in 25 ml. of benzene. The solution was held at 0–5° by an ice bath, and the atmosphere was excluded by a blanket of dry nitrogen. The triethylamine hydrochloride was removed by filtration at 0° under a blanket of dry nitrogen. The filter cake was washed with 50 ml. of benzene and the wash liquid was added to the filtrate; 20.7 g. of triethylamine hydrochloride was recovered (85.6% of theory). After recrystallization it melted at 247–252°. Pure triethylamine hydrochloride melts at 254°. The solvent and remaining reactants were removed by evaporation below 0° and at 1 mm. pressure. At this point 8.6 g. of product was recovered (72% yield based on $P[NHN(CH_3)_2]_3$. The

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[1] From a thesis presented in partial fulfillment of the requirements of the M.S. degree, Aug. 1964.

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

TABLE I

ANALYTICAL AND MELTING POINT DATA

| Compound | M.p., °C. | Mol. wt.[a] |  | C, % |  | H, % |  | N, % |  | P, % |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd |
| $(C_6H_5)_2PNHN(CH_3)_2$ | 69–70 | 255 | 244 | 68.96 | 69.13 | 6.90 | 6.62 | 11.28 | 11.52 | 12.68 | 12.73 |
| $(C_6H_5)P[NHN(CH_3)_2]_2$ | 68–69.5 | 228 | 226 | 53.01 | 53.08 | 8.35 | 8.46 | 24.58 | 24.76 | 13.92 | 13.69 |
| $[(C_6H_5)PN]_3$ | 229–231 | ... |  | 72.64 | 72.36 | 5.28 | 5.06 | 6.73 | 7.03 | 15.74 | 15.55 |
| $[(C_6H_5)P(N(CH_3)_2)N]_n$ | 85.5–88.5 | 1840 |  | 57.59 | 57.83 | 6.45 | 6.57 | 16.57 | 16.86 | 18.91 | 18.64 |
| $[((CH_3)_2NHN)P(N(CH_3)_2)N]_n$ | 103–130 | 1085 |  | 30.32 | 32.42 | 8.40 | 8.84 | 34.58 | 37.82 | 22.08 | 20.91 |

[a] Determined in benzene. Solute concentrations in the range of 0.1 to 0.6 g. in 25 ml. of benzene.

sample was then heated to 180° at 3.0 mm.; 1,1-dimethylhydrazine was recovered from the cold trap after this step. Analytical (Table I) and infrared data indicate that the product is impure $[P[N(CH_3)_2][NHN(CH_3)_2]N]_n$ and contains a slight excess of an impurity compound of hydrogen, phosphorus, and oxygen. These analytical data may be rationalized if we assume that the product contains about 10% $H_3PO_3$ impurity, indicating that the sample may have become slightly contaminated with moisture from the atmosphere while attempts were being made to sublime it.

**Infrared Spectra.**—Infrared spectra of 2,2-dimethylhydrazinophosphine[2] and diphenylphosphonitrilic trimer[3] have been published. The spectra obtained in this study confirm that these samples are indeed these compounds. Figures 1 and 2 show the infrared spectra of bis(2,2-dimethylhydrazino)phenylphosphine and dimethylaminophenylphosphonitrile, respectively. Tetracoordinated phosphorus containing a P-phenyl bond[4,5] gives a strong absorption at 1110–1130 cm.$^{-1}$. This can be seen in the spectrum of dimethylaminophenylphosphonitrile. It is present as a slight hump in the spectrum of bis(2,2-dimethylhydrazino)phenylphosphine, indicating a slight degree of oxidation of tricoordinated phosphorus. The broad band between 1160 and 1340 cm.$^{-1}$ is characteristic of phosphonitrilic polymers. Since the position of this band is affected by both the substitution on the phosphorus atom and the size of the ring,[6] the breadth of the band for this sample indicates that this sample is a mixture of different size rings. Many of the infrared absorption frequencies of these compounds can be assigned from general infrared data.[5,7,8]

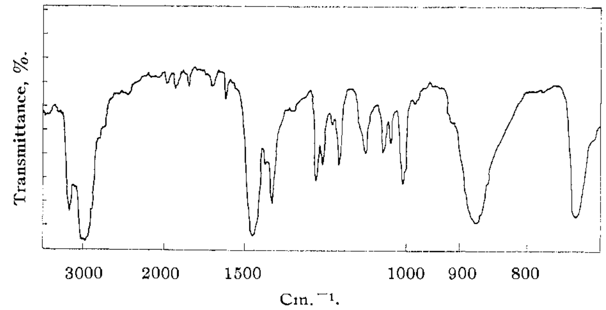


Figure 1.—Infrared spectrum of bis(2,2-dimethylhydrazino)phenylphosphine (Nujol mull).

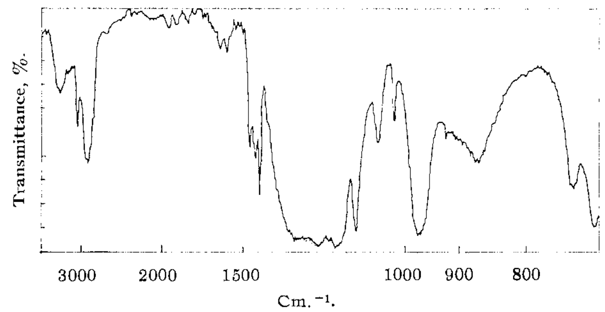
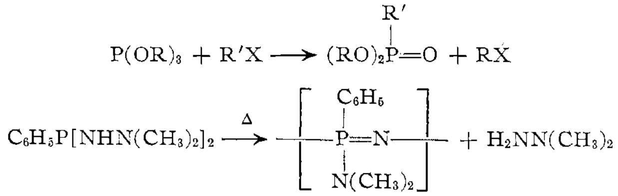


Figure 2.—Infrared spectrum of dimethylaminophenylphosphonitrile.

## Discussion

The pyrolytic conversion of $C_6H_5P[NHN(CH_3)_2]_2$ to $[C_6H_5P[N(CH_3)_2]N]_n$ and $P[NHN(CH_3)_2]_3$ to $[[(CH_3)_2NNH]P[N(CH_3)_2]N]_x$ involves removal of one 1,1-dimethylhydrazine molecule and the shifting of a dimethylamine radical from the nitrogen to the phosphorus atom with the formation of a double bond between the phosphorus and nitrogen atoms. As this occurs the phosphorus atom changes from the tricoordinated to the tetra-coordinated state. This may be considered to be formally analogous to the Arbuzov rearrangement



$$P(OR)_3 + R'X \longrightarrow (RO)_2\overset{\overset{\displaystyle R'}{|}}{P}{=}O + RX$$

$$C_6H_5P[NHN(CH_3)_2]_2 \xrightarrow{\Delta} \left[ \underset{\underset{\displaystyle N(CH_3)_2}{|}}{\overset{\overset{\displaystyle C_6H_5}{|}}{-P}}{=}N- \right] + H_2NN(CH_3)_2$$

In the purification of $(C_6H_5)_2PNHN(CH_3)_2$, practically all the material sublimes to the cold finger, while only 10–15% of the $C_6H_5P[NHN(CH_3)_2]_2$ can usually be recovered by sublimation. Under similar conditions, $P[NHN(CH_3)_2]_3$ does not sublime at all. However, all three of these hydrazinophosphines, either crude or pure, give high yields of phosphonitrilic materials when pyrolyzed. The increasing difficulty of obtaining pure monomers by sublimation in the series $(C_6H_5)_2P[NHN(CH_3)_2] < C_6H_5P[NHN(CH_3)_2]_2 < P[NHN(CH_3)_2]_3$ may reflect increasing tendency toward condensation in this series, or possibly increasing degree of intermolecular association through hydrogen bonding. Thus, the data show that phosphonitrilic polymers are produced when compounds containing a tricoordinated phosphorus atom attached to a hydrazine radical are heated over 150°. If two or more hydrazine radicals are attached to the phosphorus atom the phosphonitrilic polymer will contain one $-NR_2$ radical on each phosphorus atom.

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(8) R. A. McIvor and C. E. Hubley, *Can. J. Chem.*, **37**, 869 (1959).