**Synthesis of Dichlorophenyl-N-phenylphosphine Imine.**—The procedure is essentially that described for trichloro-N-phenylphosphine imine except that the reflux time was 24 hr. The yield was 73% of the theoretical quantity. The melting point of the product is 119–119.5° (119–120° reported).[30]

*Anal.* Calcd for $C_{12}H_{11}NCl_2P$: C, 53.36; H, 3.73; N, 5.19; Cl, 26.26; P, 11.47. Found: C, 55.48; H, 4.39; N, 5.49; Cl, 22.05; P, 12.09.

The low values for chlorine content and correspondingly high values for other elemental analyses are due to hydrolysis of this highly moisture-sensitive material.

**Synthesis of Chlorodiphenyl-N-phenylphosphine Imine.**—The procedure was essentially that described for trichloro-N-phenylphosphine imine except that the reflux time was only 2 hr. The yield of the chlorodiphenyl-N-phenylphosphine imine was 8.01 g, 69% of the theoretical value. The melting point is 89–92° (88–90° reported).[31]

*Anal.* Calcd for $C_{18}H_{15}NClP$: C, 69.36; H, 4.85; N, 4.49; Cl, 11.38; P, 9.94. Found: C, 68.79; H, 5.01; N, 4.52; Cl, 11.24; P, 9.87.

**Acknowledgment.**—The generous support of the National Science Foundation is gratefully acknowledged.

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(30) I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **31**, 3685 (1961).

(31) I. N. Zhmurova and A. V. Kirsanov, *ibid.*, **33**, 1015 (1963).

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CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE LABORATORY
CORONA, CALIFORNIA

# Beryllium Phosphonitrilates[1]

BY KAY L. PACIOREK[2] AND REINHOLD H. KRATZER

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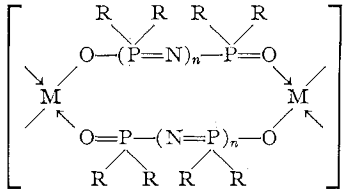
Interaction of beryllium acetylacetonate with the phosphonitrilic derivatives $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$ and $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$ yielded exclusively monomeric species. Both mono- and disubstituted products were prepared. Treatment of the monosubstituted materials $Be(C_5H_7O_2)(OP(C_6H_5)_2[NP(C_6H_5)_2]_{1,3}O)$ with diphenylphosphinic acid resulted mainly in disproportionation. Structural arrangements and reactions of these compounds are discussed.

## Introduction

Block, *et al.*,[3] successfully synthesized thermally stable polymers by interaction of beryllium and other metal acetylacetonates with diphenylphosphinic acid. However, these materials proved to be insoluble in common organic solvents and did not lend themselves to usual fabrication techniques. In view of this finding, it appeared advantageous to consider a system embodying the ladder concept, but at the same time imparting greater flexibility by having longer chains between the metal atoms. Phosphonitriles as exemplified by cyclic diphenylphosphonitrilic tetramer possess high thermal and oxidative stability. Consequently a P–N chain might be incorporated in the general structure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Two oxygen-terminated phosphonitrilic derivatives, $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$ and $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$, were chosen as candidate materials for this investigation; the latter was believed to be surely incapable of chelating to a central metal atom.

## Experimental Section

Commercial $Be(C_5H_7O_2)_2$, mp 108–109°, was purified by crystallization from heptane, then dried *in vacuo* at 50°. Compounds $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$, mp 171–172°, and $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$, mp 269–270°, obtained by hydrolysis of $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3Cl$[4] and $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$,[5] respectively, were dried *in vacuo* at 100° prior to use. Diphenylphosphinic acid, mp 196–197°, was prepared by hydrolysis of $(C_6H_5)_2POCl$ (in aqueous acetonitrile) followed by crystallization from water and drying *in vacuo* at 100°.

Reactions were carried out in evacuated sealed ampoules, each equipped with a small side-arm collection tube; the solid reagents were finely ground and thoroughly mixed.

All melting points were determined in sealed capillaries and are uncorrected. Molecular weights were determined in benzene employing a Mechrolab osmometer. The elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

The infrared absorptions of the starting materials and the products are compiled in Table I. Unfortunately, in this series of compounds, no useful correlations are apparent with the exception of the obvious features such as, for example, the presence of absorptions at about 1590 and 1525 cm$^{-1}$ in the materials containing the acetylacetonate group. Thus, infrared spectral analyses were employed merely for identification of the various products obtained.

**Preparation of $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ (II).**—A mixture of $Be(C_5H_7O_2)_2$ (1.809 g, 8.73 mmoles) and $(C_6H_6)_2P(O)NP(C_6H_5)_2OH$ (2.149 g, 5.15 mmoles) was heated at 103° for

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[1] Presented in part before the Division of Inorganic Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

[2] MHD Research, Inc., Newport Beach, Calif. 92663.

[3] B. P. Block, E. S. Roth, C. H. Schaumann, and L. R. Ocone, *Inorg. Chem.*, **1**, 860 (1962).

[4] K. L. Paciorek, *ibid.*, **3**, 96 (1964).

[5] We are indebted to D. L. Herring and C. M. Douglas of the U. S. Naval Ordnance Laboratory, Corona, Calif., for a generous sample of this material.

TABLE I

INFRARED ABSORPTION SPECTRA ($\mathrm{CM^{-1}}$) OF BERYLLIUM PHOSPHONITRILATES AND RELATED COMPOUNDS IN THE 1800–640-$\mathrm{CM^{-1}}$ REGION[a]

| | |
|---|---|
| $\mathrm{Be(C_5H_7O_2)_2}$ | 1575 s, 1525 s, 1450 s, 1375 s, 1298 m-s, 1190 m, 1035 s, 1015 sh, 960 m-s, 935 m-s, 823 s-b, 781 m, 746 m-s, 722 m, 660 s |
| $\mathrm{(C_6H_5)_2P(O){-}N{=}P(C_6H_5)_2OH}$ | 1575 w, 1460 s, 1438 m, 1378 m, 1333 w, 1310 w, 1186 m, 1124 s, 1110 s, 1064 w, 1030 m, 1000 w, 925 m, 862 w, 769 vb, 723 s, 689 s |
| $\mathrm{(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_3OH}$ | 1580 w, 1455 m, 1450 m, 1435 m, 1370 m, 1285 s, 1265 s, 1210 s, 1175 s, 1117 m, 1065 s, 1027 w, 995 w, 927 w, 843 vw, 780 w, 752 w, 744 w, 722 s, 692 s |
| $\mathrm{Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]}$ (II) | 1590 m, 1570 vw, 1525 m, 1460 s, 1450 s, 1435 m, 1378 s, 1197 s, 1173 m, 1158 w, 1133 m, 1124 m, 1100 m, 1064 m, 1048 vw, 1024 m, 997 w, 929 m, 836 mw, 800 s, 790 s-m, 761 m, 753 m, 727 s, 693 s, 671 m |
| $\mathrm{Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2}$ (III) | 1465 s, 1443 m, 1380 m, 1212 w, 1192 s, 1175 m, 1125 m, 1087 m, 1065 m, 1058 sh, 1030 w, 1000 w, 836 w, 785 m, 756 w, 727 s, 693 s, 675 m |
| $\mathrm{Be(C_5H_7O_2)[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]}$ | 1600 m, 1520 m, 1460 m, 1450 m, 1440 m, 1405 m, 1395 m, 1380 m, 1290 m, 1265 s, 1230 s, 1180 m, 1123 s, 1085 w, 1070 m, 1029 m, 1000 w, 935 m, 847 m, 813 m, 804 m, 774 m, 757 m, 752 m, 748 m, 719 s, 695 s, 673 m, 645 w |
| $\mathrm{Be[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]_2}$ | 1460 m, 1455 m, 1435 m, 1373 m, 1323 m, 1290 m, 1267 s, 1223 s, 1176 m, 1139 m, 1124 m, 1111 m, 1070 w, 1028 w, 1000 w, 845 w, 835 w, 790 w, 748 m, 743 m, 726 s, 717 sh, 695 s, 664 m |
| $\mathrm{Be[OP(C_6H_5)_2NP(C_6H_5)_2O][OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]}$ | 1470 m, 1455 m, 1440 m, 1383 m, 1275 s, 1233 w, 1210 s, 1180 m, 1130 m, 1097 w, 1072 m, 1058 w, 1030 m, 1002 w, 846 m, 800 w, 769 w, 755 m, 746 m, 727 m, 719 m, 695 s, 692 sh, 680 vw, 672 w, 666 w |
| $\mathrm{(Be[OP(C_6H_5)_2O][OP(C_6H_5)_2[NP(C_6H_5)_2]_3O])_2}$ | 1466 m, 1455 m, 1435 m, 1375 m, 1290 vw, 1233 m, 1208 m, 1177 w, 1140 m, 1080 m, 1029 m, 1000 w, 848 w, 790 w, 757 m, 725 s, 693 s, 673 mw |
| $\mathrm{(Be[OP(C_6H_5)_2O]_2)_{\mathit{n}}}$ | 1460 m, 1458 m, 1435 m, 1375 m, 1169 m, 1139 s, 1080 s, 1025 m, 999 w, 925 w, 764 s, 735 s, 694 s, 674 s |

[a] All of the infrared spectra were determined as Nujol mulls.

12 hr; melting followed by partial solidification was observed. For the last 2 hr, the side arm was cooled with liquid nitrogen to collect the evolved acetylacetone. Subsequently, the tube containing the distillate was sealed off and opened to a high-vacuum system. The liquid was fractionated through −47, −63, and −196° traps. Pure acetylacetone (465 mg, 4.64 mmoles, 90% yield; vapor pressure at 0°, 2.4 mm) was collected in the −47° trap; in the −63 and −196° traps was found a more volatile unidentified material (0.60 mmole).

The solid reaction mixture was subjected to sublimation at 110°; on the cold-finger $\mathrm{Be(C_5H_7O_2)_2}$ (730 mg, 3.52 mmoles, 98% of the excess used) was recovered. The residue was crystallized from benzene followed by drying *in vacuo* at 85° giving $\mathrm{Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]}$, mp 193–193.5°. The $\mathrm{P^{31}}$ nmr spectrum showed (in benzene solution) one peak only at −28.8 ppm (referenced to 85% $\mathrm{H_3PO_4}$).

*Anal.* Calcd for $\mathrm{BeC_{29}H_{27}P_2NO_4}$: Be, 1.72; C, 66.41; H, 5.19; P, 11.81; N, 2.67; mol wt 524.48. Found: Be, 1.94; C, 66.48; H, 5.30; P, 11.70; N, 2.72; mol wt 525 (concentration, 0.021 *M*).

**Heat Treatment of $\mathrm{Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]}$ (II).**—A 361-mg sample of compound II was heated in an evacuated, sealed ampoule at 165–175° for 8 hr. The material did not change its physical appearance, and only a very small quantity of sublimate was observed. Both the sublimate and the bulk of the material were identified as unchanged $\mathrm{Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]}$ by infrared spectral analysis and mixture melting point with an authentic sample.

**Preparation of $\mathrm{Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2}$ (III).**—A mixture of $\mathrm{Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]}$ (1.222 g, 2.33 mmoles) and $\mathrm{(C_6H_5)_2P(O)NP(C_6H_5)_2OH}$ (924 mg, 2.21 mmoles) was heated at 110° for 12 hr; no change in the physical appearance was observed. Cooling the side arm with liquid nitrogen gave very little condensate. Accordingly, the solid was heated to 145°, resulting in the condensation of some yellow liquid on the upper part of the ampoule. The temperature was allowed to rise slowly to 175°, and heating at this temperature was maintained for 2 hr. During this period a yellow liquid distilled into the side-arm tube. However, the solid mixture itself did not change in appearance. The ampoule was cooled and opened to a high-vacuum system. Fractionation of the volatiles afforded pure acetylacetone (178 mg, 1.77 mmoles, 80% yield; vapor pressure at 0°, 2.4 mm) and 0.261 mmole of more volatile materials.

While the solid mixture was heated at 175° under pumping, some sublimate, 30 mg, had collected on the upper portion of the ampoule. It was identified as $\mathrm{Be(C_5H_7O_2)_2}$ by its infrared spectrum and mixture melting point with an authentic sample.

The residue was boiled with benzene, and only a small portion (45 mg) failed to dissolve. This was identified as unreacted $\mathrm{(C_6H_5)_2P(O)NP(C_6H_5)_2OH}$. The product $\mathrm{Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2}$ crystallized from benzene as glistening needles, mp 222–223°; its infrared spectrum exhibited a sharp band at 676 $\mathrm{cm^{-1}}$ indicative of benzene. Drying *in vacuo* resulted in dull needles, mp 237–238°.

*Anal.* Calcd for $\mathrm{BeC_{48}H_{40}P_4N_2O_4}$: Be, 1.07; C, 68.49; H, 4.79; P, 14.72; N, 3.32; mol wt 841.78. Found: Be, 1.33; C, 68.56; H, 4.82; P, 14.85; N, 3.23; mol wt 805 (concentration, 0.030 *M*). The $\mathrm{P^{31}}$ nmr spectrum (in benzene solution) showed one peak only at −27.2 ppm.

**Heat Treatment of $\mathrm{Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2}$ (III).**—A 483-mg sample of compound III was heated in an evacuated ampoule at 330° for 48 hr. On cooling, the material solidified into a slightly straw-discolored glass. This substance exhibited an infrared spectrum identical with that of the starting material; however, it melted at 90–93°, then partially solidified at 140°, and finally melted again at 196–215°. It had a molecular weight of 975. One crystallization from benzene (followed by drying at 90° *in vacuo*) gave a material with mp 233–235°, mol wt 787 (concentration, 0.040 *M*), mixture melting point with authentic $\mathrm{Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2}$ 235–237°.

**Preparation of $\mathrm{Be(C_5H_7O_2)[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]}$.**—A mixture of $\mathrm{Be(C_5H_7O_2)_2}$ (2.556 g, 12.33 mmoles) and $\mathrm{(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH}$ (4.189 g, 5.13 mmoles) was heated overnight at 103°. A yellow-discolored liquid resulted. Subsequently the side arm was cooled to −196° while the reaction mixture was heated at 100°. After 4 hr the heated material solidified. The side arm was sealed off and opened to the high-vacuum system. Fractionation gave 459 mg (4.58 mmoles, 89% yield) of pure acetylacetone (vapor pressure at 0°, 2.4 mm) and 0.26 mmole of a more volatile substance.

The solid residue was sublimed at 115° resulting in the recovery of $\mathrm{Be(C_5H_7O_2)_2}$ (1.29 g, 6.23 mmoles, 87% of excess). Crystallization of the sublimation residue from heptane afforded $\mathrm{Be(C_5H_7O_2)[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]}$, mp 188–189° (after drying at 90° *in vacuo*). The $\mathrm{P^{31}}$ nmr spectrum (in benzene) showed two equal-area peaks at −10.6 and 0 ppm. The starting material $\mathrm{(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH}$ exhibited in its $\mathrm{P^{31}}$ nmr spectrum two equal-area peaks at −15.4 and −2.4 ppm.

*Anal.* Calcd for $BeC_{53}H_{47}P_4N_3O_4$: Be, 0.98; C, 68.97; H, 5.13; N, 4.55; mol wt 922.85. Found: Be, 0.94; C, 69.36; H, 5.48; N, 4.77; mol wt 884 (concentration, 0.029 *M*).

**Preparation of $Be[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]_2$.**—A mixture of $Be(C_5H_7O_2)[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$ (1.684 g, 1.82 mmoles) and $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$ (1.510 g, 1.85 mmoles) was heated at 164–173° for 3 hr. It started to melt at 120° and was completely molten at 162°. Cooling the side arm gave very little condensate. The ampoule was cooled and opened to a high-vacuum system. It was then heated at 170–185° for 18 hr *in vacuo* under pumping. During this treatment, the contents of the ampoule solidified. Fractionation of the volatiles, collected in a −196° trap, using the procedure described previously, afforded 114 mg (1.14 mmoles, 63% yield) of pure acetylacetone (vapor pressure at 0°, 2.3 mm) and 0.06 mmole of a more volatile fraction. The solid was boiled with three 30-ml portions of heptane, and the mixture was filtered hot. The heptane solution on concentration deposited unreacted $Be(C_5H_7O_2)[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$. The heptane-insoluble material was crystallized from a 1:1 benzene–heptane mixture giving $Be[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]_2$, mp 359–361° (after drying at 120° *in vacuo*). The $P^{31}$ nmr spectrum (in benzene) showed two equal-area peaks at −6.3 and +2.6 ppm.

*Anal.* Calcd for $BeC_{96}H_{80}P_8N_6O_4$: Be, 0.55; C, 70.37; H, 4.92; P, 15.12; N, 5.13; mol wt 1638.56. Found: Be, 0.84; C, 70.85; H, 5.07; P, 15.45; N, 5.31; mol wt 1573 (concentration, 0.012 *M*).

**Preparation of $Be[OP(C_6H_5)_2NP(C_6H_5)_2O][OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$.**—A mixture of $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ (1.6468 g, 3.314 mmoles) and $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$ (2.5653 g, 3.145 mmoles) was heated overnight at 130° with the side arm immersed in a Dry Ice bath. Very little distillate was collected. The ampoule was then opened to a high-vacuum system and heated at 165° for 6 hr. Acetylacetone (307 mg, 3.07 mmoles, 98% yield) was collected in a −196° trap. The solid residue was boiled with three 50-ml portions of heptane, and the mixture was filtered hot. The heptane-insoluble material crystallized from benzene, mp 357–359°.

*Anal.* Calcd for $BeC_{72}H_{60}P_6N_4O_4$: Be, 0.74; C, 69.74; H, 4.88; N, 4.52; mol wt 1240.00. Found: Be, 0.95; C, 69.43; H, 5.14; N, 4.44; mol wt 1185 (concentration, 0.017 *M*).

**Reaction of $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ with $(C_6H_5)_2POOH$.**—A mixture of $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ (1.470 g, 2.80 mmoles) and $(C_6H_5)_2POOH$ (595 mg, 2.72 mmoles) was heated initially at 110° for 15 hr, then at 160–165° for an additional 4 hr. The mixture discolored yellow, a sublimate deposited on the upper part of the ampoule, and in the side arm a distillate was collected. The ampoule was opened to the high-vacuum system, and the solid was heated for 3 hr at 150° under pumping. Acetylacetone (233 mg, 2.33 mmoles, 86% yield) was collected in a −196° trap.

The sublimate (45 mg, 0.217 mmole) was identified as $Be(C_5H_7O_2)_2$. The solid residue (1.78 g) was boiled with benzene, and the mixture was filtered hot; 1.00 g of material failed to dissolve. No solvent could be found for this compound, mp *ca.* 436–470°. The benzene filtrate on evaporation afforded pure $Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2$, identified by its infrared spectrum and mixture melting point with an authentic sample. On the basis of the $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ originally employed, 66% disproportionation to $Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2$ occurred.

**Reaction of $Be(C_5H_7O_2)[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$ with $(C_6H_5)_2POOH$.**—Heating of a mixture of $Be(C_5H_7O_2)[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$ (1.826 g, 1.98 mmoles) and $(C_6H_5)_2POOH$ (476 mg, 2.18 mmoles) in a sealed ampoule at 165° for 6 hr resulted in partial melting. Subsequently, the ampoule was opened to a high-vacuum system, and heating was continued for an additional 6 hr under pumping. Acetylacetone (174 mg, 1.73 mmoles, 88% yield) was collected in a −196° trap.

The solidified reaction mixture was boiled with benzene; all of the materials dissolved except for a 160-mg portion. This benzene-insoluble material, mp softening at *ca.* 474°, appeared to be pure $[Be[OP(C_6H_5)_2O]_2]_n$.

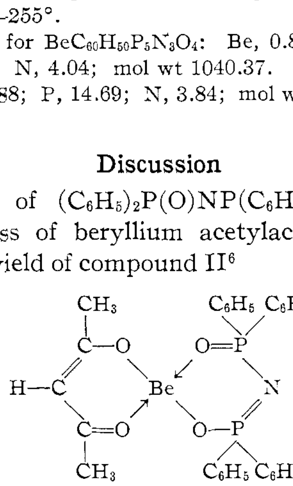
*Anal.* Calcd for $BeC_{24}H_{20}P_2O_4$: Be, 2.03; C, 65.01; H, 4.54, P, 13.97. Found: Be, 1.97; C, 66.15; H, 4.69; P, 14.48. It exhibited an infrared spectrum almost identical with that observed for the benzene-insoluble product obtained from the interaction of $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ with $(C_6H_5)_2POOH$.

To the benzene solution, from which $Be[OP(C_6H_5)_2O]_2$ was removed by filtration, was added heptane and after prolonged standing at room temperature an amorphous precipitate was formed, mp 230–255°.

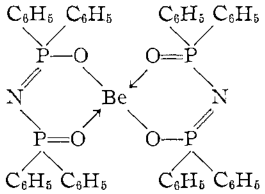
*Anal.* Calcd for $BeC_{60}H_{50}P_5N_3O_4$: Be, 0.87; C, 69.21; H, 4.84; P, 14.89; N, 4.04; mol wt 1040.37. Found: Be, 1.10; C, 68.70; H, 4.88; P, 14.69; N, 3.84; mol wt 2016 (concentration, 0.012 *M*).

## Discussion

Interaction of $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$ at 103° with an excess of beryllium acetylacetonate gave a quantitative yield of compound II[6]



II



III

This material failed to disproportionate into III and beryllium acetylacetonate on heating at 165–175°. Interestingly, however, treatment of $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ (II) with another mole of $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$ at 175° gave, in addition to the desired product III, a very small, nevertheless significant, amount of beryllium acetylacetonate. Thus, it can be inferred that at these higher temperatures, necessary for the synthesis of the disubstituted materials, the presence of proton-containing moieties promotes disproportionation.

Following the procedure employed in the preparation of compounds II and III, interaction of beryllium acetylacetonate and $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$ afforded the products $Be(C_5H_7O_2)[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$ and $Be[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]_2$. Both of these were monomeric, as was also the mixed-substituted derivative $Be[OP(C_6H_5)_2NP(C_6H_5)_2O][OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$.

Two possible structural arrangements can be postulated for all of these compounds: (1) beryllium bonded to the phosphonitrilate chain *via* oxygen bonds, as proposed in structures II and III; (2) beryllium bonded

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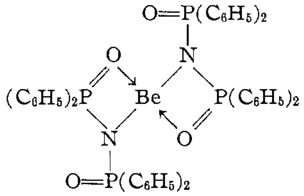
[6] Recently, A. Schmidpeter, R. Boehm, and H. Groeger, *Angew. Chem.*, **76**, 860 (1964), obtained from $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$ a monomeric compound with Zn in the center of the spirane.

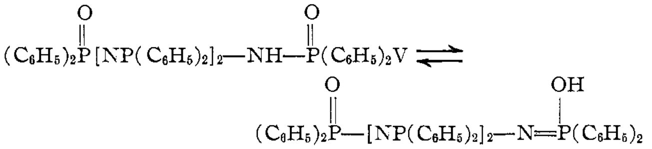
to the phosphonitrilate chain *via* oxygen and nitrogen bonds, as represented by IV.



IV

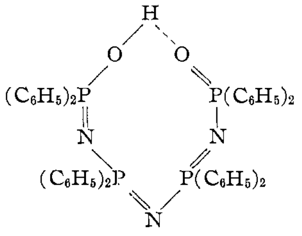
$P^{31}$ nmr spectral investigations of $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ and $Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2$ showed the presence of one type of phosphorus only, proving the correctness of II and III. Likewise, $Be(C_5H_7O_2)[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$ and $Be[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]_2$ exhibited in their $P^{31}$ nmr spectra two equal-intensity peaks in accordance with structural arrangements analogous to II and III.[7]

For each of the phosphonitrilic starting materials a keto–enol relationship can be readily visualized, *i.e.*

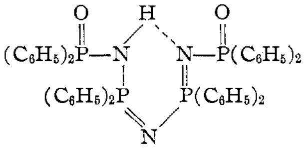


$$(C_6H_5)_2\overset{O}{\overset{\|}{P}}[NP(C_6H_5)_2]_2{-}NH{-}\overset{O}{\overset{\|}{P}}(C_6H_5)_2V \rightleftharpoons (C_6H_5)_2\overset{O}{\overset{\|}{P}}{-}[NP(C_6H_5)_2]_2{-}N{=}\overset{OH}{\overset{|}{P}}(C_6H_5)_2$$

However, the $P^{31}$ nmr spectrum of the above compound showed just two equal-area peaks, indicating the presence of only two different kinds of phosphorus atoms. This result is in agreement with structures VI and VII. The smaller ring size would favor VII; however, if one considers the chelating ability of the P=O group as compared to the —P=N— moiety, the form VI becomes more probable.

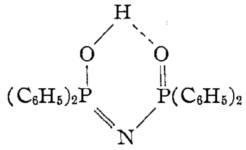


VI



VII

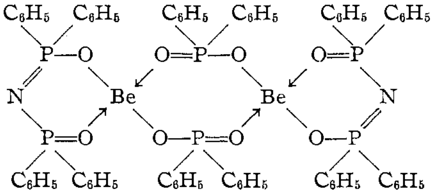
The hydrogen bridge arrangement VIII was suggested by Fluck[8] for $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$; similar cyclic configuration was put forward by Sisler[9] for the acid's precursor, $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$. On the basis of infrared spectral assignments, in particular the absorption at 925 $cm^{-1}$, it was believed[4] that $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$ exists predominantly in the keto form, $(C_6H_5)_2P(O){-}NH{-}P(O)(C_6H_5)_2$. Subsequent findings revealed that some P–OH compounds also exhibit absorption in this region.[10] Thus, in conjunction with the nmr data for $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_3OH$ the hydrogen-bridged enol form of Fluck[4] appears more likely than the above keto form.



VIII

The rearrangement of the monomeric species III to a polymeric system represented by I appeared feasible at elevated temperatures. Yet, heating of $Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2$ at 330° for 48 hr resulted in only a slight increase in the molecular weight, and the bulk of the material consisted of unchanged III.

Since diphenylphosphinic acid forms polymeric systems with beryllium acetylacetonate, it was expected that with $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ it would yield dimer IX.



IX

From this interaction, however, 66% of the disproportionation product III, together with a small quantity (8%) of beryllium acetylacetonate, was isolated. The remainder was insoluble in common organic solvents. On the basis of the 66% yield of $Be[OP(C_6H_5)_2NP(C_6H_5)_2O]_2$ this insoluble material can be assumed to consist of $[Be[OP(C_6H_5)_2O]_2]_n$ admixed chemically (as end groups) or physically with $Be[OP(C_6H_5)_2NP(C_6H_5)_2O][OP(C_6H_5)_2O]$.

Heating a mixture of $Be[C_5H_7O_2][OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$ and diphenylphosphinic acid gave some of the desired dimer $\{Be[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O][OP(C_6H_5)_2O]\}_2$; however, pure $[Be[OP(C_6H_5)_2O]_2]_n$ (33%) was also obtained, pointing clearly to a high degree of disproportionation.

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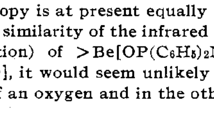
[7] $P^{31}$ nmr spectroscopy, however, is not sufficient proof of structures analogous to II and III in the case of the Be derivatives of $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$. We are indebted to one referee for pointing out that a structure comprised of a six-membered ring would be more likely. This structure



is in agreement with present data, inasmuch as the $P^{31}$ nmr spectrum contains two equal-area peaks. The detection of the $(C_6H_5)_2P(O)$ moiety by infrared analysis is virtually impossible owing to the strong P=N— absorptions in the same region. A differentiation between Be–O and Be–N bonds on the basis of infrared spectroscopy is at present equally difficult owing to lack of data. Yet, in view of the similarity of the infrared spectra and the chemical behavior (disproportionation) of $>Be[OP(C_6H_5)_2NP(C_6H_5)_2O]$ and $>Be[OP(C_6H_5)_2[NP(C_6H_5)_2]_3O]$, it would seem unlikely that the beryllium atom in one case is the center of an oxygen and in the other case is the center of a nitrogen tetrahedron.

[8] E. Fluck and F. L. Goldmann, *Chem. Ber.*, **96**, 3091 (1963).

[9] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

[10] C. M. Douglas, private communication.