[Contribution from the U. S. Naval Ordnance Laboratory]

The Reactions of 1,4-Bis(diphenylphosphino)benzene with Phenyl Azide and 1,4-Diazidobenzene

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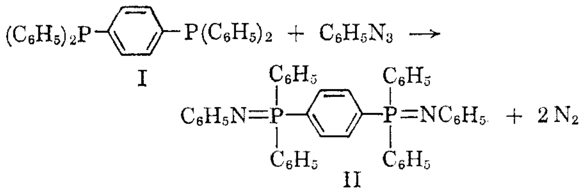
1,4-Bis(diphenylphosphino)benzene was prepared by the reaction of diphenylchlorophosphine with p-dilithiobenzene. Phenyl azide on reaction with 1,4-bis(diphenylphosphino)benzene gave the compound $C_6H_5N{=}P(C_6H_5)_2$-p-$C_6H_4P(C_6H_5)_2{=}NC_6H_5$. Its positional isomer, $(C_6H_5)_3P{=}N$$p$-$C_6H_4N{=}P(C_6H_5)_3$ was prepared by the reaction of 1,4-diazidobenzene with triphenylphosphine. When 1,4-bis(diphenylphosphino)benzene reacted with 1,4-diazidobenzene, the product that resulted was the new polymer, $[\text{—}P(C_6H_5)_2$-p-$C_6H_4P(C_6H_5)_2{=}N$-p-$C_6H_4N{=}]_x$.

As part of this laboratory's program of extending the knowledge and utility of the phosphonitrile polymers, $(R_2PN)_x$, an effort to introduce cross-linking centers into the polymeric molecules was initiated. The preparation of a molecule containing two reactive groups which can be incorporated into the phosphonitrile bonding of two different chains or rings would satisfy the requirements for a cross-linking agent. Before preparing polymers using this concept, it seemed advisable to study the reactions of simple model compounds which would presumably react in a fashion identical to the proposed polymer formation mechanism. To this end, 1,4-bis(diphenylphosphino)benzene has been prepared and its reactions with phenyl azide and 1,4-diazidobenzene are described.

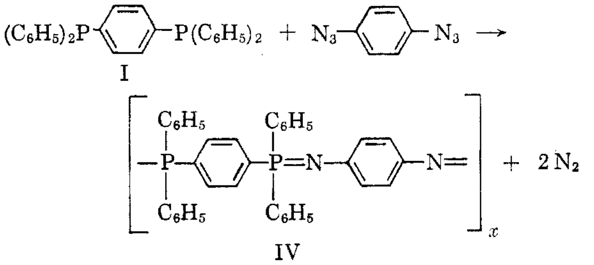
Recently, the synthesis of several aryldiphosphines has been reported.[1,2] The new compound I, 1,4-bis(diphenylphosphino)benzene was prepared by the reaction of diphenylchlorophosphine with a suspension of p-dilithiobenzene[3] in n-hexane. Confirmation of structure was obtained by the formation of the bismethiodide, $(C_6H_5)_2PC_6H_4P(C_6H_5)_2 \cdot 2CH_3I$.

In order to test the extension of the azide synthesis of phosphonitrile polymers to a difunctional phosphine, I was caused to react with phenyl azide according to the expression:



and gave the expected product, compound II. The positional isomer of II, $(C_6H_5)_3P{=}NC_6H_4N{=}P(C_6H_5)_3$, compound III was prepared from the reaction of 1,4-diazidobenzene with triphenylphosphine. The 1,4-diazidobenzene was prepared in good yield by the reaction of p-phenylenebis(diazoniumfluoborate)[4] with sodium azide.

An interesting derivative of the phosphonitrile bonding system was made from the reaction of compound I with 1,4-diazidobenzene which is described by the expression:



The product, compound IV, is the first linear polymer to be described wherein an organic moiety regularly alternates with the phosphonitrile bond and through which the conjugated unsaturation can be transmitted.

EXPERIMENTAL[5]

Preparation of 1,4-bis(diphenylphosphino)benzene. Into a three necked, round-bottom flask fitted with a stirrer, a condenser, and a dropping funnel was added 350 ml. of a pentane-heptane solution containing 64.0 g. (1.0 mole) of butyllithium. Then, with stirring, 78.5 g. (0.33 mole) of p-dibromobenzene in 700 ml. of hexane was added dropwise over the course of an hour. After the addition was completed, the temperature was increased to 50–55° and the stirring continued for 48 hr. Next, 220.0 g. (1.0 mole) of diphenylchlorophosphine was added dropwise with stirring to the dull-yellow suspension of p-dilithiobenzene over the course of 2 hr. After the addition was completed, the resulting mixture was heated to 60–65° for 24 hr., then filtered at the boiling point. The insoluble residue was extracted with 600 ml. of boiling benzene and then filtered. By the process of recrystallization, 28.0 g. (19% yield, based on 0.33 mole of p-dibromobenzene) of 1,4-bis(diphenylphosphino)benzene was isolated from the filtrate. The material was further purified by two vacuum sublimations at a temperature of 155–160°. The pure product melted at 166–167°.

Anal. Calcd. for $C_{30}H_{24}P_2$: C, 80.6; H, 5.4; P, 13.9; mol. wt., 446. Found: C, 80.6; H, 5.4; P, 13.8; mol. wt., 458, (freezing point of benzene).

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(1) F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 3939 (1957).

(2) F. A. Hart, *J. Chem. Soc.*, 3324 (1960).

(3) R. I. Wagner, American Potash and Chemical Corp., Whittier, Calif., private communicaton.

(4) P. Ruggli and E. Caspar, *Helv. Chim. Acta*, **18**, 1416 (1935).

(5) All melting points are uncorrected.

Reaction of 1,4-bis(diphenylphosphino)benzene with methyl iodide. To 2.0 g. (0.004 mole) of 1,4-bis(diphenylphosphino) benzene dissolved in 100 ml. of hot benzene was added dropwise with stirring 3.46 g. (0.024 mole) of methyl iodide. The solution clouded immediately and the lemon yellow precipitate which rapidly formed was collected and recrystallized three times from ethanol. The yield was 2.4 g. of pure 1,4-bis(diphenylphosphino)benzene dimethiodide, which decomposed over the range 334–337°.

Anal. Calcd. for $C_{32}H_{30}P_2I_2$: I, 34.8. Found: I, 35.2.

Reaction of 1,4-bis(diphenylphosphino)benzene with phenyl azide. To 2.0 g. (0.004 mole) of pure 1,4-bis(diphenylphosphino)benzene dissolved in 100 ml. of toluene at 55–57° was added 1.1 g. (0.009 mole) of phenyl azide. After an induction period of 10 min., the evolution of nitrogen began and continued for 1 hr. The yellow precipitate which formed overnight was collected. By the process of recrystallization from toluene, 1.5 g. (54%) of compound II was isolated as glistening yellow crystals (m.p. 118–120°).

Anal. Calcd. for $C_{42}H_{34}P_2N_2$: C, 80.2; H, 5.4; P, 9.9; N, 4.4; mol. wt., 628. Found: C, 80.3; H, 5.6; P, 9.2; N, 4.3; mol. wt., 640 (freezing point of tribromomethane).

Preparation of 1,4-diazidobenzene. Into a three-necked flask fitted with thermometer, dropping funnel and mechanical stirrer was placed a solution containing 38.4 g. of sodium borofluoride dissolved in 160 ml. of water to which had been added 160 ml. of concd. hydrochloric acid. The stirrer was started and after the solution had been cooled to −20°, a solution containing 14.2 g. of *p*-phenylenediamine and 19.2 g. of sodium nitrite dissolved in 266 ml. of water was added dropwise over the course of 2.5 hr. at a rate that kept the temperature from rising above −10°. A precipitate which formed was removed by filtration, washed with 35 ml. of ethyl ether and then air dried. The dried, beige-colored $F_4BN_2C_6H_4\text{-}N_2BF_4$, weighed 23.5 g. (59.3%).

To 5.2 g. (0.08 mole) of sodium azide dissolved in 400 ml. of ice water was added with stirring over a 30-min. period, 10.0 g. (0.032 mole) of $F_4BN_2C_6H_4\text{-}N_2BF_4$. Nitrogen was evolved during the course of the reaction. The precipitate which formed was collected and by the process of recrystallization from ether using 0.3 g. of decolorizing charcoal to remove impurities, 3.1 g. (59%) of the cream-colored, crystalline product, 1,4-diazidobenzene, m.p. 81.2–82.2° (lit.[6] 83°), was isolated.

Anal. Calcd. for $C_6H_4N_6$: N, 52.5. Found: N, 52.9.

Reaction of triphenylphosphine with 1,4-diazidobenzene. To 1.0 g. (0.006 mole) of 1,4-diazidobenzene dissolved in 50 ml. of benzene was added 35 ml. of a benzene solution containing 3.2 g. (0.012 mole) of triphenylphosphine. Nitrogen was evolved during the 3-hr. reaction period. The product was precipitated from solution by the dropwise addition of the benzene solution to 300 ml. of petroleum ether (b.p. 30–65°). Then by the process of recrystallization from benzene, 2.2 g. (60%) of yellow crystalline product, $(C_6H_5)_3\text{-}C_6H_4NP{=}N\text{-}P(C_6H_5)_3$, m.p. 255–257° was isolated.

Anal. Calcd. for $C_{42}H_{34}P_2N_2$: C, 80.2; H, 5.4; P, 9.9; N, 4.4; mol. wt., 628. Found: C, 80.3; H, 5.6; P, 9.7; N, 4.2; mol. wt., 615 (freezing point of tribromomethane).

Reaction of 1,4-bis(diphenylphosphino)benzene with 1,4-diazidobenzene. To 1.50 g. (0.003 mole) of 1,4-bis(diphenylphosphino)benzene dissolved in 75 ml. of benzene was added at room temperature, a solution containing 0.50 g. (0.003 mole) of 1,4-diazidobenzene dissolved in 25 ml. of benzene. Nitrogen was slowly evolved and the solution gradually turned pink in color during the 4-hr. course of the reaction. The precipitate which formed was collected and extracted with 100 ml. of boiling benzene to remove any unchanged starting material. The product IV, a red-orange solid, after drying in vacuum weighed 1.3 g. (70%) and on heating softened over the range 150–200°, yielding on cooling, a brittle, amber-colored glass. (The molecular weight of this material could not be determined by cryoscopic techniques.)

Anal. Calcd. for $(C_{36}H_{28}P_2N_2)_x$: C, 78.6; H, 5.1; P, 11.2; N, 5.1. Found: C, 78.7; H, 5.1; P, 11.2; N, 4.8.

Weighed samples of compound IV were pyrolyzed under vacuum. In a typical experiment, a 192.6-mg. sample (previously dried under vacuum for 24 hr. at 100–102°) was heated under vacuum at a rate of increase in temperature of 2 degrees per min. Over the range of 230–250°, 99.5 mg. of light yellow decomposition products sublimed from the heated zone.

Anal. Calcd. for $C_{36}H_{28}P_2N_2$: N, 5.1. Found: N, 2.2.

In a second experiment using the procedure described above for the synthesis of compound IV, 1.50 g. (0.003 mole) of (I) reacted with 1.00 g. (0.006 mole) of 1,4-diazidobenzene and yielded a polymeric mixture which melted at 120–140°, lost nitrogen during the process, finally resolidified and yielded a porous solid which did not melt at 325°.

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[6] O. Silberrad and B. J. Smart, *J. Chem. Soc.*, 170 (1906).