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Preparation of Diphenylphosphinous Azide and Syntheses of Phosphonitriles

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Diphenylphosphinous azide has been isolated from the low-temperature reaction of diphenylphosphinous chloride and lithium azide as a colorless solid which decomposed at 13.6–13.8° to yield 25% of diphenylphosphonitrilic trimer. Decomposition in the presence of chain-terminating P(III) compounds resulted in linear materials only.

In view of the isolation and thermal decomposition of bis(trifluoromethyl)phosphinous azide[1] and diphenylarsinous azide,[2] and the statements[2-4] that the reactions of halophosphines with alkali metal azides resulting in phosphonitrilic materials[5] proceed *via* a phosphinous azide intermediate, the preparation and identification of such an intermediate was attempted and is reported here.

Diphenylphosphinous azide was isolated from the low-temperature reaction of diphenylphosphinous chloride with lithium azide in acetonitrile. It is a colorless solid, which in the pure state decomposes sharply at 13.6–13.8°. The infrared spectral studies revealed that during decomposition of diphenylphosphinous azide the absorption at 4.78 μ due to the azido group attached to P(III) shifts with time to 4.70 μ; the latter band is attributed[6] to the azido group on P(V). Simultaneously, the disappearance of a medium to strong band at 9.15 μ associated with the P(III) compound and the development of new bands at 8.95 and 13.85 μ were observed. The decomposition of diphenylphosphinous azide at room temperature affords a spectrum of products. In addition to a 25% yield of diphenylphosphonitrilic trimer, hydrolytically unstable, azido-terminated chains of varying lengths are produced. On heating the linear materials to between 100 and 185°, one equivalent of molecular nitrogen is evolved.

When the reaction of diphenylphosphinous chloride with an excess of lithium azide is conducted in benzene, at room temperature diphenylphosphinous azide is detectable by infrared analysis. Carrying the reaction to completion at a temperature considerably above the decomposition point of the phosphinous azide intermediate (at 70°) results in a 34% yield of diphenylphosphonitrilic trimer, in analogy to the decomposition of preformed diphenylphosphinous azide in acetonitrile.

In an attempt to prepare $(C_6H_5)_2PN{=}P(C_6H_5)_2Cl$ and $(C_6H_5)_2PN{=}P(C_6H_5)_3$, diphenylphosphinous azide was decomposed in the presence of a substantial molar excess of diphenylphosphinous chloride and triphenylphosphine, respectively. Under these conditions neither the expected products nor cyclic phosphonitriles were produced; only relatively long-chain compounds were formed, implying that the attack of diphenylphosphinous azide upon these chain-terminating agents proceeds less readily than other processes. This behavior is in agreement with previous investigations where the reaction between molar quantities of diphenylphosphinyl azide gave $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_3Cl$.[6] The fact that Baldwin and Washburn[7] found no evidence of reaction in the attempted preparation of $(C_6H_5)_2PN{=}P(C_6H_5)_3$ is rather surprising. Interestingly, triphenylphosphine appears to be oxidized more readily than diphenylphosphinous chloride by diphenylphosphinous azide, inasmuch as the ratios of $(C_6H_5)_2P{=}N$ units to the chain-terminating agent are much higher in the case of diphenylphosphinous chloride. The chloro-terminated chains are easily hydrolyzed and at the same time are very probably oxidized (by atmospheric oxygen) at the P(III) end of the chain.

Experimental

Reagent grade chemicals were used after additional purification. The purification procedures employed here were described previously.[6] Infrared spectra were recorded on a Beckman IR-5 infrared spectrophotometer; for solutions 0.1-mm. liquid cells were employed; otherwise spectra were run as mineral oil mulls.

Molecular weights were determined in benzene using a Mechrolab osmometer. The nitrogen evolved was measured by high vacuum techniques using a Sprengel pump and was analyzed by mass spectrometry. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Reaction of $(C_6H_5)_2PCl$ with Excess LiN_3. (a) Isolation of $(C_6H_5)_2PN_3$.—Diphenylphosphinous chloride (3.036 mmoles) was treated in acetonitrile (50 ml.) with LiN_3 (6.12 mmoles) on the high vacuum line. The addition took *ca.* 30 min.; subsequently the mixture was stirred at −15–20° for 10 hr. After conclusion of the reaction and cooling the mixture to −196° no noncondensable gas was present. The solution obtained after filtration (on the line, at −30°) was divided into two portions. The bulk of the filtrate was warmed to room temperature; it yielded 2.386 mmoles of N_2. Heating at 180° for 4 hr. (after removal of the solvent) gave an additional 0.199 mmole of N_2. Further heating with $(C_6H_5)_3P$ for 48 hr. at 100° failed to produce more nitrogen. Total N_2, 2.585 mmoles; total phosphorus in residue, 2.386 mmoles; ratio of N_2:P, 1.09:1.

From the other portion of the filtrate, acetonitrile was removed at −20° *in vacuo*. *n*-Pentane was distilled onto the colorless

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(2) W. T. Reichle, *Tetrahedron Letters*, 51 (1962).

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(4) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).

(5) D. L. Herring, *Chem. Ind.* (London), 717 (1960).

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(7) R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961).

residue at −196°; the mixture was warmed to −20°, filtered, and when cooled to −78°, $(C_6H_5)_2PN_3$ crystallized out from the filtrate. The molecular weight of the residue, obtained by vapor pressure lowering of a *n*-butane solution, was found to be 275 (calcd. for $(C_6H_5)_2PN_3$, 227). The amount of substance used was determined by measuring the amount of N_2 given off on decomposition. This purified material (after removal of butane) decomposed sharply at 13.6–13.8° becoming yellow in color. At this stage only *ca.* 90% of the total nitrogen was evolved; the remaining 10% was obtained by heating to 180°, at which temperature the material became white. *Anal.* Calcd. for $[(C_6H_5)_2PN]_n$: P, 15.55; N 7.03. Found: P, 14.63; N, 6.89; Cl, 0.07; N_3^-, <0.1; ratio of P:N, 1:1.042.

(b) **Thermal Decomposition of $(C_6H_5)_2PN_3$.**—Diphenylphosphinous chloride (33.51 mmoles) was treated in an inert atmosphere with LiN_3 (81.69 mmoles) in acetonitrile (70 ml.), following the procedure outlined in (a). After filtration the solution was stirred overnight at room temperature while attached to a mercury bubbler. The precipitate formed (1.75 g.), filtered under dry nitrogen, exhibited in its infrared spectrum a medium to weak band at 4.70 μ. Extraction with ligroin afforded 0.893 g. of $[(C_6H_5)_2PN]_3$, identified by its infrared spectrum and mixture melting point with an authentic sample. The residue melted at 95–110°. *Anal.* Found: C, 70.64; H, 5.83; P, 14.27; N, 7.35; Cl, 0.

The filtrate, on removal of acetonitrile, gave 2.313 g. of material, which on extraction with ligroin yielded an additional 0.190 g. of $[(C_6H_5)_2PN]_3$. Thus the total amount of cyclic trimer obtained was 1.033 g., which corresponds to 25% of the total reaction products. The ligroin-insoluble material melted at 97–108° *Anal.* Calcd. for $[(C_6H_5)_2PN]_7(C_6H_5)_2PN_3$: C, 71.10; H, 4.97; P, 15.28; N, 8.64; mol. wt., 1621. Found: C, 71.00; H, 5.09; P, 14.55; N, 8.93; mol. wt., 1560. Heating 0.279 mmole (based on the above molecular weight determination) of this material at 185° for 2 hr. gave 0.286 mmole of N_2.

Treatment of $(C_6H_5)_2PCl$ with LiN_3 in Benzene.—Treatment of 227 mmoles of $(C_6H_5)_2PCl$ with 274 mmoles of LiN_3 in benzene (500 ml.) at room temperature yielded transient phosphinous azide (detected by infrared spectral analysis); however, under these conditions LiN_3 became quickly coated, preventing further reaction. Heating the stirred mixture at 65–75° for 5 days afforded a tacky precipitate (34 g.) containing 2.2 g. (4.8% yield) of a mixture of $[(C_6H_5)_2PN]_3$ and $[(C_6H_5)_2PN]_4$ (extracted with benzene), lithium salts (removed by extraction with water), and 16.4 g. (38% yield) of phosphonitrilic compounds insoluble in common organic solvents. *Anal.* Found: C, 71.28; H, 5.23; P, 15.25; N, 7. 10; O, 0.99.

The solid (15.5 g., 34% yield) left on removal of the benzene from the original filtrate consisted of $[(C_6H_5)_2PN]_3$.

Reaction of Excess $(C_6H_5)_2PCl$ with LiN_3 and Decomposition of $(C_6H_5)_2PN_3$ in the Presence of $(C_6H_5)_2PCl$.—Diphenylphosphinous chloride (55.7 mmoles) in acetonitrile (50 ml.) was treated with LiN_3 (14.3 mmoles). After filtration the solution was allowed to stand overnight at room temperature. Subsequently, the solvent was removed *in vacuo*; on standing the viscous solution deposited 0.07 g. (2% yield) of $[(C_6H_5)_2PN]_4$. The filtrate from the tetramer was treated with *n*-pentane, resulting in precipitation of a colorless grease. Repeated extraction by decantation with pentane and heptane afforded 8.73 g. (39.5 mmoles) of $(C_6H_5)_2PCl$, recovered from the combined washings. Assuming all the LiN_3 to form $(C_6H_5)_2PN_3$, the ratio of $(C_6H_5)_2PN$ to $(C_6H_5)_2PCl$ units in the product is 7.5:1, calculated from the amount of $(C_6H_5)_2PCl$ consumed. Of the total amount of 2.0 g. of pentane–heptane-insoluble material, 0.86 g. was benzene-insoluble. The benzene-soluble material was analyzed. *Anal.* Calcd. for $[(C_6H_5)_2PN]_4P(C_6H_5)_2Cl$: Cl, 3.48; mol. wt., 1017.5. Found: Cl, 3.88; mol. wt., 1048. The infrared spectra of this material and the benzene-insoluble fraction were identical and typical of phosphonitrilic derivatives, suggesting the benzene-insoluble fraction to contain higher homologs. Neither material exhibited absorption in the N_3 region. Hydrolysis of the benzene-soluble fraction with 95% ethanol deposited a product, m.p. 215–218° (softening at 198°) which was free of Cl. *Anal.* Calcd. for $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_6NHP(O)(C_6H_5)_2$: C, 71.50; H, 5.06; P, 15.39; N, 6.08; mol. wt., 1612. Found: C, 69.18; H, 5.34; P, 15.00; N, 6.34; mol. wt., 1628. The infrared spectrum of this material had a weak band at 10.75 μ, indicative of a P–NH–P linkage.[8] The ethanolic solution was evaporated to dryness; the chlorine-free residue had an average molecular weight of 800.

Decomposition of $(C_6H_5)_2PN_3$ in the Presence of $(C_6H_5)_3P$.—Diphenylphosphinous chloride (8.36 mmoles) in acetonitrile (25 ml.) was treated with LiN_3 (12.3 mmoles). The reaction mixture was filtered into a solution of $(C_6H_5)_3P$ (12.2 mmoles) in acetonitrile (40 ml.) at −25°. The resulting solution was stirred overnight at room temperature in a nitrogen atmosphere. The infrared spectrum of the product (4.86 g.), obtained after removal of the solvent *in vacuo*, pointed to the presence of phosphonitrilic derivative admixed with $(C_6H_5)_3P$; no absorption at 4.6–4.8 μ was observed. From a 0.60-g. sample of this material, 0.31 g. of $(C_6H_5)_3P$ was obtained on repeated refluxing with ligroin. On the basis of the recovered $(C_6H_5)_3P$, the ratio of $(C_6H_5)_2PN$ units to $(C_6H_5)_3P$ is 3.2:1. *Anal.* Calcd. for $[(C_6H_5)_2PN]_3P(C_6H_5)_3$: C, 75.43; H, 5.29; P, 14.40; N, 4.89; mol. wt., 860. Calcd. for $[(C_6H_5)_2PN]_2P(C_6H_5)_3$: C, 76.35; H, 5.34; P, 14.06; N, 4.24; mol. wt., 661. Found: C, 74.0; H, 5.42; P, 14.08; N, 4.90; mol. wt., 785.

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