

The Preparation and X-ray Structure of $[P(C_2H_5)_4]^+[N_3]^-$ and the Attempted Preparation of $[PH_4]^+[N_3]^-$

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ABSTRACT

Tetraethylphosphonium azide, $[P(C_2H_5)_4]^+[N_3]^-$, was prepared from tetraethyl phosphonium bromide and silver azide. Single crystals of $[P(C_2H_5)_4]^+[N_3]^-$ were grown from dichloromethane/THF (10:1) solution. The structure was determined by single-crystal X-ray diffraction analysis. $[P(C_2H_5)_4]^+[N_3]^-$ crystallizes in the monoclinic space group $C 2/c$ with $Z = 4$ and unit cell dimensions $a = 12.961(6)$, $b = 6.835(3)$, $c = 12.378(6)$ Å, and $\beta = 100.57(4)^\circ$. The attempted preparation of phosphonium azide $[PH_4]^+[N_3]^-$ from phosphonium iodide and silver azide lead instead to the formation of PH_3 and HN_3 . The instability of $[PH_4]^+[N_3]^-$ with respect to PH_3 and HN_3 is in accord with thermodynamic considerations according to which the reaction $PH_3(g)$ and $HN_3(g)$ to yield $[PH_4]^+[N_3]^-$ is thermodynamically unfavorable. (Non SI units employed: kcal \approx 4.184 J, Å = 10^{-10} m.) © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:129–132, 1998

INTRODUCTION

We have recently been studying the preparation and properties of binary and ternary group 15 azides in general and phosphorus azides in particular [1a–c]. Covalently bound group 15 azides can conveniently be prepared from the corresponding halides and either sodium or silver azide [2]. For example, the following compounds were synthesized from the chloride precursors: $[PN(N_3)_2]_3$ [1b,3], $P_3N_3(N_3)_5(NC_5H_{10})_1$ [4], $P_3N_3(N_3)_4(NC_5H_{10})_2$ [5], $P_3N_3(N_3)_3(NC_5H_{10})_3$ [5], $E(N_3)_3$ ($E = P, As, Sb, Bi$) [2,6a–d], $P(N_3)_5$ [6e], and $[PCl_{6-n}(N_3)_n]^-$ [6f].

In the work presented in this article, we now want to focus on the attempted preparation of ionic azides from metathetical reactions of ionic phosphonium halide salts and silver azide.

EXPERIMENTAL

Materials and Methods

The vacuum lines, handling techniques, and spectrometers used in this study have been described

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elsewhere [4,5,7]. All solvents were commercial materials and were dried and purified by condensation prior to use (CH_2Cl_2 , Fissons, P_4O_{10} ; THF, Fissons, Na; SO_2 , BOC, CaH_2 ; SO_2ClF , Aldrich, CaH_2 ; HF, Merck, BiF_3). AgN_3 was prepared by literature methods from silver nitrate and sodium azide [8]. Commercial PH_3 (Air Products, 4.5) and $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{Br}]^-$ (Aldrich) were used without further purification.

Preparation of $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{N}_3]^-$

In a typical experiment, 0.25 g (1.10 mmol) of $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{Br}]^-$ was dissolved in 10 mL CH_2Cl_2 in a two-bulb reaction vessel [7] and reacted with 0.30 g (2.00 mmol, excess) of AgN_3 at room temperature. After 1 hour reaction time, the precipitated AgBr and unreacted AgN_3 were filtered off. After addition of 1 mL of THF to the clear solution the reaction vessel was placed into a freezer (-18°C) overnight, after which time white crystals of $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{N}_3]^-$ had formed that were suitable for a single-crystal X-ray diffraction analysis. Yield: 0.09 g (0.48 mmol), 43%. A higher yield of pure but not crystalline $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{N}_3]^-$ (0.19 g, 1.0 mmol, 91%) was obtained when, after 1 hour reaction time and filtration, the clear CH_2Cl_2 solution was evaporated to dryness.

Analytical Data of $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{N}_3]^-$

^1H NMR (297 K, CD_2Cl_2 , 81.015 MHz, TMS, δ in ppm): 1.20 (3) td [$^3J_{\text{HH}} = 7.7$ Hz, $^3J_{\text{HP}} = 18.0$ Hz], 2.40 (2) qd [$^3J_{\text{HH}} = 7.7$ Hz, $^2J_{\text{HP}} = 13.1$ Hz]. ^{14}N NMR (297 K, CD_2Cl_2 , 14.462 MHz, MeNO_2 , δ in ppm): -132.8 (1), -283.1 (2). $^{31}\text{P}\{^1\text{H}\}$ NMR (297 K, CD_2Cl_2 , 81.015 MHz, H_3PO_4 85% in water, δ in ppm): 40.3. IR (298 K, KBr disc, ν in cm^{-1}): 2970–2890 s ($\nu\text{-CH}$, C_2H_5); 2040 vs ($\nu_{\text{as}} - \text{N}_3$); 1465, 1415, 1390 ($\delta\text{-HCH}$, C_2H_5); 1050 m ($\nu\text{-CC}$, C_2H_5); 795 s ($\nu\text{-PC}$, $\text{P}(\text{C}_2\text{H}_5)_4^+$). MS (EI, 70 eV, 298 K, $I \geq 5\%$ of PHEt_2^+ (basis peak), m/z): 146 PEt_4^+ , 118 PEt_3^+ , 90 HPet_2^+ , 75 $\text{HPet}(\text{CH}_2)^+$, 62 H_2PEt^+ , 61 $\text{H}_2\text{P}(\text{CH}_2)^+$, 60 HPet^+ , 59 PEt^+ , 43 HN_3^+ , 29 Et^+ , 28 C_2H_4^+ , 27 C_2H_3^+ , 18 H_2O^+ , 15 CH_3^+ .

X-ray Structure Determination of $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{N}_3]^-$

Crystal Data. Tetraethylphosphonium azide, $\text{C}_8\text{H}_{20}\text{N}_3\text{P}$, $M = 189.24$, monoclinic, $a = 12.961(6)$, $b = 6.835(3)$, $c = 12.378(6)$ Å, and $\beta = 100.57(4)^\circ$; $U = 1077.9(9)$ Å³, space group C 2/c, $Z = 4$, $D_c = 1.166$ g cm⁻³. Crystal dimensions $0.30 \times 0.20 \times 0.20$ mm. $\mu(\text{Mo-K}\alpha) = 0.21$ mm⁻¹, $\lambda = 0.71073$ Å, $F(000) = 416$.

Data Collection and Processing. Rigaku AFC6S diffractometer, -100°C , ω scan mode, $2\theta_{\text{max}} = 60.0^\circ$,

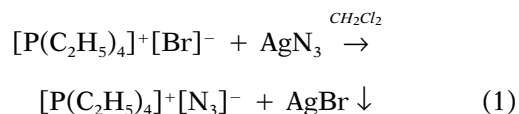
graphite monochromated Mo- K_α radiation, 2519 independent measured reflections, 1572 unique reflections, 1207 reflections with $[I_{\text{net}} > 2.5 \sigma I_{\text{net}}]$. Absorption corrections were made using ψ scans.

Structure Analysis and Refinement. The structure was solved by direct methods, and all nonhydrogen atoms were refined anisotropically. Refinement was by block matrix least-squares to $R_F = 0.037$, ($R_F = \Sigma[F_0 - F_c]/\Sigma[F_0]$), $R_w = 0.039$, ($R_w = \text{Sqrt}[\Sigma\{w[F_0 - F_c]^2\}/\Sigma\{wF_0^2\}]$); for all reflections: $R_F = 0.062$, $R_w = 0.041$. In the last D-map, the deepest hole was -0.38 e Å⁻³, and the highest peak was 0.39 e Å⁻³. Computations were carried out using the NRCVAX program system and published scattering factors [9–11].

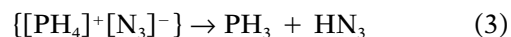
Further details of the crystal structure determinations are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-406973, the names of the authors, and the journal citation.

RESULTS AND DISCUSSION

Tetraethylphosphonium azide, $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{N}_3]^-$, was prepared in high yield according to Equation 1. The structures of $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{N}_3]^-$ was determined experimentally by X-ray diffraction analysis. Figures 1 and 2 show a formula unit and the packing diagram. Table 1 summarizes the most important experimentally obtained structural parameters for $[\text{P}(\text{C}_2\text{H}_5)_4]^+[\text{N}_3]^-$.



Phosphonium iodide, $[\text{PH}_4]^+[\text{I}]^-$, was reacted with silver azide at -60°C , and the precipitation of yellowish AgI immediately indicated the occurrence of a reaction (cf. Equation 2). However, the desired phosphonium azide, $[\text{PH}_4]^+[\text{N}_3]^-$, which was likely formed as an intermediate, is not stable at -60°C or higher temperatures but spontaneously decomposes into PH_3 and HN_3 (Equation 3), which were both identified by multinuclear NMR (^1H , ^{14}N , ^{31}P) and gas IR spectroscopy [12].



Although dichloromethane and not water was used as the solvent for the reaction of phosphonium

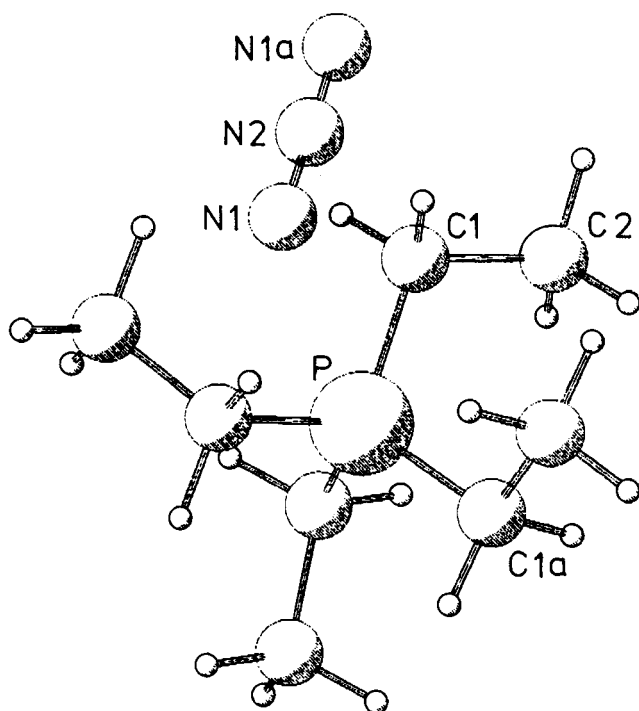


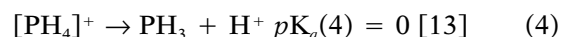
FIGURE 1 Structure of a formula unit of $[P(C_2H_5)_4]^+[N_3]^-$ in the crystal (Pluto representation [11]).

TABLE 1 Selected Measured (X-ray) Bond Lengths (Å) and Angles (°) of $[P(C_2H_5)_4]^+[N_3]^-$

	d (Å)		\angle (°)
P–C(1)	1.797(2)	C(1)–P–C(1) _a	109.7 (1)
C(1)–C(2)	1.518(2)	N(1)–N(2)–N(3)	180.0
N(1)–N(2)	1.178(2)		
N(2)–N(3)	1.178(2)		

^aAtomic labeling in analogy to Figure 1.

iodide with silver azide (qualitatively similar results were obtained in $CFCl_3$, anhydrous HF, SO_2 , and SO_2ClF solution), the equilibrium constants for aqueous solutions according to Equations 4 and 5 nicely account for the instability of $[PH_4]^+[N_3]^-$ with respect to HN_3 and PH_3 (cf. Equations 3 and 6).



$$K(3) = \frac{K(4)}{K(5)} = \frac{[PH_3][HN_3]}{[PH_4^+][N_3^-]} \\ = \frac{1}{2.14 \times 10^{-5}} = 4.7 \times 10^4 \quad (6)$$

In conclusion, the reaction of phosphonium halide salts with silver azide provides a convenient methods for the preparation of ionic phosphonium azide salts of the type $[PR_4]^+[N_3]^-$. Whereas tetraethylphosphonium azide $[P(C_2H_5)_4]^+[N_3]^-$ was prepared and structurally characterized for the first time, the parent compound phosphonium azide, $[PH_4]^+[N_3]^-$, is unstable at $-60^\circ C$ or higher temperatures and decomposes into PH_3 and HN_3 .

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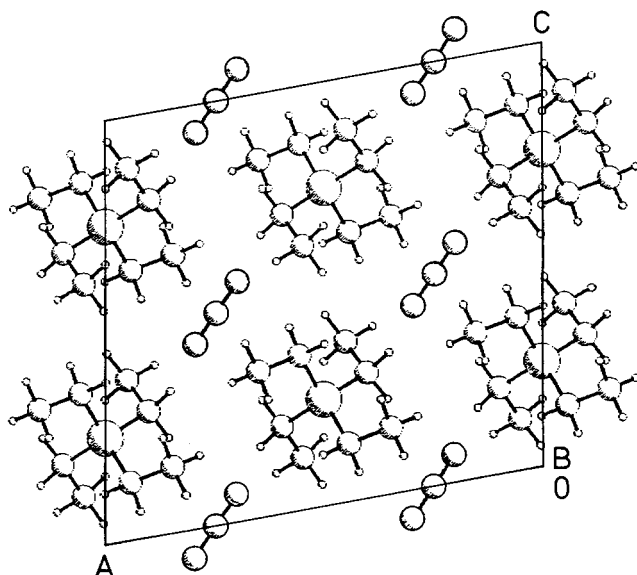


FIGURE 2 Packing diagram of $[P(C_2H_5)_4]^+[N_3]^-$ (Pluto representation [11]).

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