[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

# Triphosphonitrilic Hexahydrazide

BY R. J. A. OTTO AND L. F. AUDRIETH

RECEIVED FEBRUARY 10, 1958

Interaction of triphosphonitrilic chloride with hydrazine yields the hexahydrazide, $P_3N_3(N_2H_3)_6$, whose properties and whose reactions with benzaldehyde and salicylaldehyde are described.

The phosphonitrilic chlorides react with water, alcohols, ammonia, amines and mercaptans to undergo solvolysis with partial or complete replacement of the active chlorine atoms as illustrated by the equation

$$(PNCl_2)_x + 2XHA \longrightarrow (PNA_2)_x + 2_x\,HCl$$

(where A = OH, OR, $NH_2$, NHR, $NR_2$ and SR)

Replacement of the active chlorine atoms by azide groups has been achieved by Grundmann and Rätz[1] who allowed the trimeric chloride to react with sodium azide to give the compound $P_3N_3(N_3)_6$. Although Couldridge[2] had reported isolation of a triphosphonitrilic hexaphenylhydrazide, no unsubstituted hydrazide had been described heretofore. The triphosphonitrilic hexahydrazide, $P_3N_3(N_2H_3)_6$, has been obtained as a white crystalline solid by a solvolytic reaction entailing the interaction of an ethereal solution of the chloride with a suspension of anhydrous hydrazine in ether. This substance hydrolyzes readily in acid solution and reacts with aldehydes to give crystalline derivatives. No rupture of the six-membered triphosphonitrilic structure occurs during these reactions as is indicated (a) by the fact that the hydrazide and its aldehyde derivatives reveal, in their infrared spectra, an absorption band at 1218 cm.$^{-1}$, assigned by Daasch[3] to the $P_3N_3$ ring system and (b) that the molecular weight of the salicylaldehyde derivative corresponds to the trimeric formula, $[PN(NHN{=}CHC_6H_4OH)_2]_3$.

## Experimental

**Triphosphonitrilic Hexahydrazide (I), $P_3N_3(N_2H_3)_6$.**—A dilute ethereal solution of $(PNCl_2)_3$ (2.57 g. in 50 ml.) is added slowly to a well-stirred suspension of anhydrous $N_2H_4$ in ether (8 ml. in 30 ml.). The resulting crystalline precipitate is removed from the solution, consisting of ether and a heavy lower layer containing the excess hydrazine and reaction by-products dissolved in it, by filtration in a closed system. The crude product is purified by dissolving in water and reprecipitating the hydrazide by addition of ethanol. Yields approximating 0.9 g. (35% of theory) were obtained in a number of separate preparations.

*Anal.* Calcd. for $P_3N_{15}H_{18}$: P, 29; N, 65.5; H, 5.6. Found: P, 28.7; N, 63.5; H, 5.57.

Much of the product I together with the hydrazine hydrochloride which is formed during the reaction, appears to dissolve in the excess of hydrazine. Use of anhydrous reagents is necessary, because the solubility of the product is greatly increased when hydrazine containing appreciable amounts of water is employed.

The hexahydrazide I crystallizes in shiny platelets which are insoluble in organic solvents but soluble in water. No melting is observed up to 360°; the hydrazide deflagrates when brought into contact with a Bunsen flame.

The phosphonitrilic hydrazide hydrolyzes rapidly in acid solution. Hydrazine dihydrochloride was isolated by addition of an excess of concd. HCl. Since micro-Dumas determinations for the nitrogen content in phosphorus–nitrogen compounds frequently give low results, it was considered desirable to check this observation as a means for the quantitative determination of hydrazine in I by titration with standard iodate.[4] Samples of I (191.4 and 99.7 mg.) after treatment with concentrated hydrochloric acid required 35.5 and 18.5 ml., respectively, of 1 *M* $KIO_3$ corresponding to mole ratios of 1.97 and 2.02 for $N_2H_4{:}P$.

**Aldehyde Derivatives** of I.—When an aqueous solution of I is shaken vigorously with freshly distilled benzaldehyde (or salicylaldehyde) a white crystalline substance precipitates. Purification can be effected by solution in dioxane and reprecipitation by addition of water.

(a) **The benzaldehyde derivative,** $P_3N_3(NHN{=}CHC_6H_5)_6$, melts with decomposition at 250°. It is soluble in dioxane but insoluble in $C_2H_5OH$, $(C_2H_5)_2O$, $CCl_4$, $CHCl_3$ and $H_2O$.

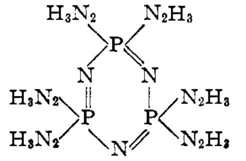
*Anal.* Calcd. for $P_3N_{15}H_{42}C_{42}$: N, 24.8; C, 59.4; H, 4.95. Found: N, 24.6; C, 59.0; H, 4.2, 5.08.

(b) **The salicylaldehyde derivative,** $P_3N_3(NHN{=}CHC_6H_4OH)_6$, melts at 225° with decomposition. It is soluble in dioxane, nitrobenzene and camphor but insoluble in ether, ethanol and water.

*Anal.* Calcd. for $P_3N_{15}H_{42}C_{42}O_6$: N, 22.2; C, 53.2; H, 4.45. Found: N, 21.08; C, 52.96; H, 4.52.

The method of Rast[5] was used for the determination of the molecular weight; calcd., 945; found, 860, 895 and 970.

**Structure.**—The infrared spectra of I and of its reaction products with benzaldehyde and salicylaldehyde reveal in each case an absorption band at 1218 cm.$^{-1}$ which has been ascribed by Daasch[3] as characteristic of the $P_3N_3$ ring system. It is evident, therefore, on the basis of the experimental observations presented above that the triphosphonitrilic hexahydrazide can be given the empirical formula $P_3N_{15}H_{18}$ and can be represented by the structural formula



**Acknowledgments.**—The authors wish to thank Mr. J. Nemeth who carried out the micro-analytical determinations. The present investigation was sponsored under a grant from the National Science Foundation (NSF G-2743) whose support is gratefully acknowledged.

URBANA, ILLINOIS

---

[1] C. Grundmann and R. Rätz, *Z. Naturforschung*, **10b**, 116 (1955).

[2] W. Couldridge, *J. Chem. Soc.*, **53**, 398 (1888).

[3] L. W. Daasch, THIS JOURNAL, **76**, 3403 (1954).

[4] R. A. Penneman and L. F. Audrieth, *Anal. Chem.*, **20**, 1058 (1948).

[5] K. Rast, *Ber.*, **55**, 1057, 3727 (1922).