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5. PHOSPHORUS(III) ISOCYANATE (Phosphorus Triisocyanate)

 $PCl_3 + 3AgNCO \rightarrow P(NCO)_3 + 3AgCl$

Submitted by ROBERT E. ZOBEL* and ROBERT P. PINNELL* Checked by MARY F. SWINIARSKI† and ROBERT R. HOLMES†

Phosphorus(III) isocyanate was first prepared by the reaction of phosphorus(III) chloride with silver isocyanate in warm benzene.¹ A later modification utilized phosphorus(III) iodide as a starting material with nitromethane as solvent.²

Less-expensive preparations, in terms of materials, have involved reactions between phosphorus(III) chloride and lithium cyanate, in benzene,³ or sodium and potassium cyanates in polar solvents such as nitriles, ketones, nitroparaffins, and esters.⁴ Liquid sulfur dioxide has also been found useful as a solvent for reaction between phosphorus(III) chloride and sodium cyanate.⁵

The synthesis from silver isocyanate and phosphorus(III) chloride has proved the most dependable and gives the highest

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yield of product. The preparation requires ca. 4 hours; no substantial modifications are necessary in order to scale the synthesis for larger quantities of product other than allowance for a slightly extended period of filtration and solvent evaporation.

Procedure

■ Caution. Phosphorus(III) isocyanate is quite toxic and all operations should be carried out in an efficient hood.

Silver isocyanate is prepared by the method of Neville and McGee.⁶ The material obtained from this preparation should be thoroughly dried in a vacuum desiccator over P_4O_{10} for at least 2 days before use.

A 500-ml., three-necked flask is equipped with a Teflon blade stirrer, a reflux condenser, and an equilibrating dropping funnel. The top of the condenser is fitted with a gas inlet tube and provision made for maintaining an inert atmosphere throughout the preparation. The assembled apparatus should be carefully dried before use.

Into the flask is placed 100 g. (0.66 mole) of silver isocyanate and 100 ml. of dry benzene. A mixture of 30 g. (0.22 mole) of phosphorus(III) chloride and 20 ml. of dry benzene is placed in the dropping funnel. The entire system is then flushed once more with nitrogen. The mixture of phosphorus(III) chloridebenzene is allowed to flow in dropwise, with stirring, over a period of half an hour.*

The rate of addition should be regulated to avoid excessive generation of heat during the initial reaction. After addition is complete, the resulting mixture is refluxed for a period of $1\frac{1}{2}$ hours.

The cooled slurry is vacuum-filtered through a fritted tube assembly. Provision should be made for admitting nitrogen into the apparatus upon completion of the filtration. The sol-

^{*} Rapid darkening of the silver isocyanate at this point indicates incomplete drying, and a significantly lower yield of product can be expected.

vent is removed at room temperature using a solvent stripper. The residual liquid is transferred, under nitrogen, to a semimicro distillation apparatus and the product distilled through a short column at $81^{\circ}/20$ mm. pressure to yield 18-21 g. of phosphorus(III) isocyanate (52-60% based on silver isocyanate). *Anal.** Calcd. for P(NCO)₃: C, 22.93%; N, 26.76%; P, 19.73%. Found: C, 22.90%; N, 26.70%; P, 19.65%.

Properties

Phosphorus(III) isocyanate boils at 169.3° (760 mm.), and melts at $-2.0^{\circ.1}$ Upon standing for 2–3 days polymerization occurs to yield a white material of m.p. 80–95°. The rate of polymerization is retarded by the presence of contaminants and serves as an indication of product purity. Distillation of the polymer melt results in nearly quantitative yields of the monomer.

The product has $n_{\rm p}^{25^{\circ}} = 1.525$ and $d_{26^{\circ}} = 1.450$ g./cc. The specific conductivity is $1.89 \times 10^{-5} \Omega^{-1}$ at 25° C.⁷ The infrared spectrum of phosphorus(III) isocyanate reveals fundamental absorptions at 316, 365, 388, 577, 603, 681, 1421, 2239, and 2293 cm.⁻¹. The band at 1421 cm.⁻¹ is the principal evidence cited for the isocyanate formulation in bonding to phosphorus.⁸ Contamination by phosphoryl isocyanate can be detected by infrared absorption at 1282 cm.⁻¹, attributed to the P==O stretching frequency. The phosphine also exhibits ³¹P n.m.r., absorption at -97.0 p.p.m. relative to 85% H₃PO₄.⁹

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6. PHOSPHORAMIDIC ACID AND ITS SALTS

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The classical Stokes' method¹ for the preparation of phosphoramidic acid and its salts entails a three-step procedure with the use of organic intermediates. Ammonium hydrogen phosphoramidate, $NH_4HPO_3NH_2$, however, is prepared more conveniently and in higher yield by the simple reaction of phosphoryl chloride with aqueous ammonia. The acid salt is stable and nonhygroscopic, and it is readily converted to the free acid or to other salts of the acid.

A. AMMONIUM HYDROGEN PHOSPHORAMIDATE

 $POCl_3 + 5NH_3 + 2H_2O \rightarrow NH_4HPO_3NH_2 + 3NH_4Cl$

Procedure

Reagent-grade phosphoryl chloride (18.3 ml., 0.2 mole) is added, dropwise and with vigorous stirring, for about 5 minutes to 300 ml. of an ice-cold 10% aqueous ammonia solution (1.5 moles NH_3). There is some fuming and evolution of heat, after

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