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19. (2,2-DIMETHYLHYDRAZINO)-DIPHENYLPHOSPHINE

$$2(CH_3)_2NNH_2 + ClP(C_6H_5)_2 \rightarrow (CH_3)_2NNHP(C_6H_5)_2 + (CH_3)_2NNH_2 \cdot HCl$$

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(2,2-Dimethylhydrazino)diphenylphosphine may be prepared by the action of *unsym*-dimethylhydrazine‡ on diphenylphosphinous chloride‡ in benzene at temperatures just below room temperature. A 2:1 mol ratio provides an extra mol of the free base to act as a hydrogen chloride acceptor. The *unsym*-dimethylhydrazinium chloride, which is only very slightly soluble in benzene, may be easily removed by filtration. The hydrazinophosphine may then be recovered from the filtrate in good yield by evaporation of the solvent at room temperature under reduced pressure.

Procedure

A 500-ml. three-necked flask is fitted with a pressure-equalizing dropping funnel of about 200 ml. capacity, a glass-joint-type mechanical stirrer, and a desiccant-filled

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‡ Both reactants are commercially available. Diphenylphosphinous chloride was obtained from the Victor Chemical Division, Stauffer Chemical Company, Chicago Heights, Ill. *Unsym*-dimethylhydrazine was obtained from the Eastman Kodak Company, Rochester, N.Y., but may be obtained from several sources.

drying tube. [Appropriate drying agents include, among others, Drierite (10 to 20 mesh), silica gel, and Linde Molecular Sieve Type 4a.] (*Caution. Desiccants which are strong oxidizing agents should be avoided.*) The apparatus is flushed with dry nitrogen and flamed to ensure dryness. In the flask are placed 100 ml. of anhydrous benzene and 50 ml. (39.2 g.; 0.653 mol) of *unsym*-dimethylhydrazine (dried over calcium hydride). (*Caution. Unsym-dimethylhydrazine is flammable and toxic.*) In the dropping funnel are placed 100 ml. of benzene (dried over calcium hydride) and 50 ml. (59.5 g.; 0.269 mol) of chlorodiphenylphosphine.

Stirring is begun and the flask is cooled in an ice bath. The contents of the addition funnel are added dropwise over a 90-minute period with constant stirring and cooling. When addition is complete, the ice bath is removed and the mixture is stirred for an additional 30 minutes at 40 to 50°. During this period, the crystals of *unsym*-dimethylhydrazinium chloride increase in size and thus become easier to remove by filtration.

After being cooled, the mixture is filtered into a 500-ml. round-bottomed flask through a fritted-glass funnel of medium porosity, using a vacuum-adapter take-off to speed filtration and avoid extended exposure to the atmosphere. The filtrate is evaporated on a rotating vacuum evaporator at room temperature. The yield of dried crude product is 61 g. (92%). The transfer of the solid product should be conducted in a dry-box, or under a flow of dry nitrogen gas, or be carried out very rapidly. The crude product is crystallized by dissolving it in 150 ml. of cyclohexane or *n*-hexane (dried over calcium hydride) at a temperature just below the boiling point and filtering the resulting solution rapidly through coarse filter paper into an Erlenmeyer flask which can be kept closed with a glass stopper. As the solution cools, (2,2-dimethylhydrazino)diphenylphosphine crystallizes. After the solution has stood overnight in a refrigerator, the crystals may be collected and washed with cold hexane. The yield is about 70%; m.p. 66 to 68°.

Additional lower-melting product of 85 to 90% purity can be recovered by evaporation of the hexane mother liquor.

Further purification can be effected by sublimation at 60° at 0.1 mm. of Hg. About 55 g. of purified product melting at 68.5 to 69.5° is normally obtained (84% yield).

Properties

The (2,2-dimethylhydrazino)diphenylphosphine forms colorless needle-like or prismatic crystals. It is soluble in benzene, ether, chloroform, and alcohol. Hydrolysis occurs in water to yield free *unsym*-dimethylhydrazine and diphenylphosphinous acid, which is readily oxidized to diphenylphosphinic acid upon contact with air.

Boiling a solution of (2,2-dimethylhydrazino)diphenylphosphine in benzene overnight in contact with dry air causes precipitation of the oxide, $(C_6H_5)_2P(O)NHN(CH_3)_2$ (m.p. 167 to 168°). Addition of a stoichiometric amount of sulfur to a boiling benzene solution of (2,2-dimethylhydrazino)diphenylphosphine yields, on cooling, the sulfide, $(C_6H_5)_2P(S)NHN(CH_3)_2$ (m.p. 95.5 to 97.0°). Alkylation to $[(C_6H_5)_2(CH_3)PNHN(CH_3)_2]I$ (m.p. 156 to 158°) occurs upon reaction with methyl iodide in ether. Reaction with chloramine in ether yields the aminophosphonium salt, $[(C_6H_5)_2P(NH_2)NHN(CH_3)_2]Cl$ (m.p. 195°). All of the above-described derivatives are colorless solids.

Storage in sealed glass ampuls or in air-tight bottles is recommended.

References

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