Short Communication

Borazine derivatives

V. Phosphorus-substituted borazines*

We have described previously the synthesis and properties of silicon[1-3]-, tin[3]- and sulfur[4]-containing borazines. In this note we report the synthesis of *B*-tris[β-(diphenylphosphino)ethyl]-N-triphenylborazine by the reaction:

$$3(C_6H_5)_2PH + [CH_2{=}CHBNC_6H_5]_3 \xrightarrow[\text{peroxide}]{tert\text{-butyl}} (C_6H_5)_2PCH_2CH_2BNC_6H_5]_3$$

The structure of the product was assumed to be as written, since previous studies[4] of radical additions to *B*-trivinyl-N-triphenylborazine had demonstrated that terminal addition to the vinyl group takes place. Two derivatives, the tris(phosphine sulfide) and the mercuric chloride adduct, were prepared.

Incidental to these studies the feasibility of the preparation of diphenylphosphine by the reaction:

$$(C_6H_5)_3SnH + (C_6H_5)_2PCl \longrightarrow (C_6H_5)_2PH + (C_6H_5)_3SnCl$$

was investigated. When it was carried out in hexane, this reaction gave diphenylphosphine in 54% yield. Very likely this procedure can be improved, but there was little motivation to do so in view of the several simple preparative routes to diphenylphosphine[5]. The tin hydride route to phosphines may, however, be of value in cases where the organophosphorus compound to be reduced contains functional groups sensitive to lithium aluminum hydride or sodium, the reagents used in the simpler syntheses[5].

Experimental

B-Tris[β-(diphenylphosphino)ethyl]-N-triphenylborazine and its derivatives. A solution of 2.0 g (5.2. mmoles) of $[CH_2{=}CHBNC_6H_5]_3$ (ref. 6), 4.7 g (25.2 mmoles) of diphenylphosphine and 0.05 g of *tert*-butyl peroxide in 30 ml of toluene under nitrogen was heated at reflux for 4.5 h. The solvent then was removed under reduced pressure, *n*-hexane was added, and the mixture was allowed to stand. After 2 days crystalline material, 4.2 g (86%), m.p. 154.5–158°, formed. Recrystallization from toluene–ligroin gave pure $[(C_6H_5)_2PCH_2CH_2BNC_6H_5]_3$, m.p. 160–162.5°. (Found: C, 75.90; H, 6.19; N, 4.39. $C_{60}H_{57}B_3N_3P_3$ calcd.: C, 76.20; H, 6.09; N, 4.44%.)

This product was converted to $[(C_6H_5)_2P(S)CH_2CH_2BNC_6H_5]_3$ as follows: To a refluxing solution of 1.15 g (1.21 mmoles) of $[(C_6H_5)_2PCH_2CH_2BNC_6H_5]_3$ in 10 ml of toluene was added 0.25 g (10.9 mg-atom) of sulfur. The sulfur dissolved, and the mix-

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* For Part IV, see ref. 4.

ture was heated at reflux for 5 h. During this time it changed in color from yellow to dark reddish-brown. When the mixture was cooled to room temperature, 0.87 g (69 %) of product crystallized. Recrystallization from toluene gave pure material, m.p. 217–219°. (Found: C, 69.04; H, 5.66; N, 4.22. $C_{63}H_{57}B_3N_3P_3S_3$ calcd.: C, 69.17; H, 5.52; N, 4.03 %.)

The mercuric chloride adduct, $[(C_6H_5)_2P(HgCl_2)CH_2CH_2BNC_6H_5]_3$, was prepared by adding 2.72 g of mercuric chloride in tetrahydrofuran to the crude $[(C_6H_5)_2PCH_2CH_2BNC_6H_5]_3$ obtained from 1.0 g of $[CH_2{=}CHBNC_6H_5]_3$. A white solid precipitated which was washed with methanol to give 4.16 g of adduct, m.p. 267–269°. (Found: C, 40.47; H, 3.70; Hg, 34.02. $C_{60}H_{57}B_3Cl_6Hg_3N_3P_3$: C, 40.94; H, 3.26; Hg, 34.19 %.)

Preparation of diphenylphosphine via triphenyltin hydride. To a solution of 35 g (0.1 mole) of triphenyltin hydride[7] in 50 ml of hexane at 0° under an atmosphere of nitrogen was added dropwise 18.7 g (0.085 mole) of diphenylchlorophosphine (Victor Chemical Works). A vigorous, exothermic reaction ensued, and a white precipitate formed. Fifty ml of hexane was added. The mixture was stirred at room temperature for 2 h, then was filtered to remove 29.8 g of triphenyltin chloride, m.p. 100° (105° after recrystallization), lit.[8] m.p. 105–107°. The filtrate was distilled to give 8.57 g (54.4 %) of diphenylphosphine, b.p. 108–110°/1 mm, n_D^{25} 1.6240 (lit.[5c] b.p. 150–151°/12 mm, n_D^{20} 1.6269). The small residue solidified at room temperature. It was washed with methanol to give white solid, m.p. 215–223°, and was identified as crude hexaphenylditin.

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