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Synthesis and Characterization of 2-Formoxy- and 2-Acetoxy-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes[2]

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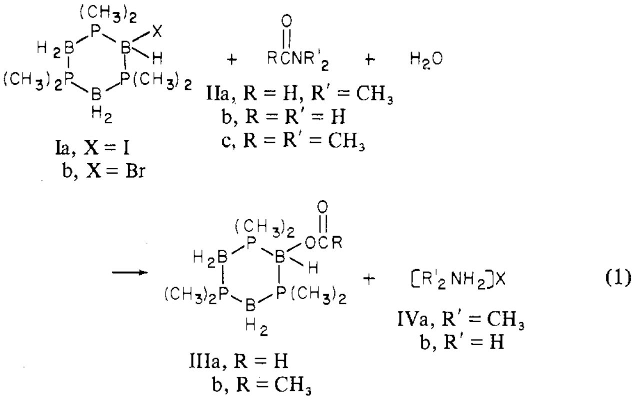
2-Halo-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes undergo nucleophilic attack either by formamide or dimethylformamide or by dimethylacetamide in the presence of water to yield the corresponding formoxy or acetoxy derivatives. Alternatively these carbalkoxy derivatives were prepared using silver carboxylate salts in lieu of the carboxamide derivatives.

During the course of an investigation of nucleophilic displacement reactions on B-halogenated 1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes[4] using dimethylformamide (DMF) as the reaction medium, an unanticipated peak was observed on gas–liquid chromatographic (GLC) analysis of the crude products. A detailed investigation of the reaction showed that when DMF dried by azeotropic distillation with benzene was used, the spurious material constituted a very small portion (<3%) of the product, whereas it was the major component when untreated DMF was employed. Infrared analyses of the crude products and the apparent role of water as a reactant inferred that DMF acted as an unintended nucleophile leading to reaction as indicated by eq 1.

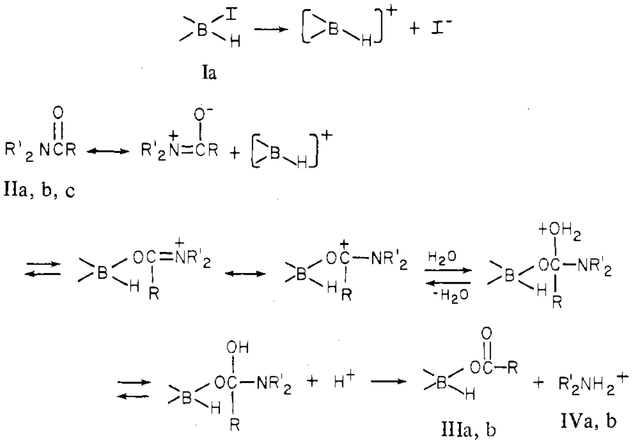


Using the same reaction conditions as were employed initially but omitting the intended nucleophile (e.g., cyanide ion), 1,2,3,4,5,6-hexahydro-2-iodo-1,1,3,3,5,5-hexamethylcyclotriboraphosphane (Ia), heated at 100 °C for 5 h with 90% aqueous DMF (IIa) or formamide (IIb), produced 2-formoxy-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane (IIIa) in yields of 67% and 63%, respectively. Compound IIIa was proved to be the spurious material in the cyanide reaction by comparison of infrared spectra and GLC retention times. The presence of coproduct ammonium iodide (IVb) was confirmed in the aqueous filtrate from the formamide reaction by positive silver iodide and Nessler's reagent[5] tests as well as by liberation of ammonia on basification.

Aqueous formic acid under the same conditions failed to give IIIa and resulted in extensive degradation of the ring as evidenced by the formation of hydrogen, boric acid, and the characteristic odor of phosphines.

Compound Ia reacted with aqueous *N*,*N*-dimethylacetamide (IIc), in a manner similar to its reaction with aqueous DMF, at 100 °C during 4 h to provide the 2-acetoxy compound IIIb in low yields (21–22%). The reason for the low yields was not apparent since reaction conditions and workup procedures were essentially the same as in the preparation of IIIa. In one experiment, conducted in a sealed tube under vacuum, the moderate quantity of hydrogen obtained as by-product suggested that decomposition of the triboraphosphane ring had occurred.

Scheme I



An initial attempt to prepare IIIb by an independent route using Ib and sodium acetate in refluxing ethanol failed to replace the bromine; a 91% recovery of starting material was obtained. Compounds IIIa and IIIb were, however, synthesized from Ia using silver formate and silver acetate, respectively, in refluxing benzene. Mixture melting points of IIIa and IIIb from the two sources were undepressed; infrared spectra were identical. In addition to absorption bands of $[(CH_3)_2PBH_2]_3$[6,7] and those characteristic of C=O stretching at 1725–1700 cm^{-1}, the spectra of IIIa and IIIb showed C–O stretching at 1208 and 1279 cm^{-1}, respectively, and B–O–C at 1073 and 1050 cm^{-1}, respectively.[8] The spectrum of IIIa contained a C–H stretching band characteristic of the –CHO group at 2840 cm^{-1}; the IIIb spectrum displayed an absorption at 1368 cm^{-1} characteristic of the CH$_3$–C function. The single formoxy proton of IIIa appeared in the ^{1}H NMR spectrum at 8.22 ppm downfield from TMS.

Although purely speculative, the sequence of equations in Scheme I appears suitable to explain the experimentally observed replacement of halogen by a carbalkoxy group on tetracoordinate boron. Similar types of acylamide displacement reactions have been observed on carbon[9,10] and on closely related tetracoordinate boron compounds, e.g., $(CH_3)_3NBH_2I$ with IIa or IIc.[11]. Recent evidence[12,13] supports the initial boron–halogen bond cleavage as the rate-determining step, with the formation of a borenium ion. Such a dissociative mechanism would be especially favorable in structures such as I which, in analogy with neopentyl halides, exhibit severe steric inhibition to displacement via back-side attack.

Experimental Section

All melting points were taken in sealed capillary tubes under dry nitrogen and are uncorrected. Molecular weights were determined in ca. 0.05 M benzene solution by the vapor pressure osmometric method.[14] Infrared spectra (KBr disks) were determined using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Proton magnetic spectra were obtained using a Varian Model A-60 spectrometer (δ relative to TMS internal reference). Gas–liquid chromatographic analyses (GLC) were done employing a Perkin-Elmer 154B vapor fractometer equipped with a 2-m silicone oil–Celite column. Analytical data were obtained in this laboratory.

2-Halo-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes (Ia, b). These compounds were prepared from $[(CH_3)_2PBH_2]_3$ and the appropriate *N*-halosuccinimide as previously described.[6]

2-Formoxy-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane (IIIa). (a) Using Aqueous DMF. A solution of 0.2013 g (0.579 mmol) of Ia in 9.0 ml of DMF (IIa) and 1.0 ml of water was heated at 100–105 °C for 5 h. Dilution with 25 ml of water produced a white microcrystalline material which, when thoroughly washed with water and dried, gave 0.1033 g (0.389 mmol, 67%) of IIIa, mp 45.5–46.5 °C, and assayed 99.8% by GLC. The impurity was identified as Ia. An analytical sample was prepared by high-vacuum sublimation at a bath temperature of 25–40 °C. ^1H NMR (C_6D_6): δ 8.22 (s, 1, –CHO), 1.28–0.78 (m, 18, $P(CH_3)_2$). Anal. Calcd for $C_7H_{24}B_3O_2P_3$: C, 31.65; H, 9.11; mol wt 265.6. Found: C, 31.47, H, 9.20; mol wt 266.

(b) Using Aqueous Formamide. A solution of 0.1500 g (0.432 mmol) of Ia, 1.50 ml of formamide (IIb), and 0.30 ml of water in a 5-ml tube, after degassing and sealing under vacuum, was heated at 100 °C for 19 h. On opening, 2.99 cm^3 of a noncondensable gas, presumably hydrogen, was found. The contents of the tube was diluted with 10 ml of water and cooled, and 0.0793 g of IIIa precipitated as microcrystalline needles, mp 45.5–47.0 °C, assaying 92.3% IIIa, 1.7% Ia, and 5.9% unknown by GLC. The yield of product was thus approximately 0.073 g (0.27 mmol, 63%). An investigation of the aqueous filtrate confirmed the presence of the coproduct, ammonium iodide (IVb). On treatment of an aliquot with 5% alcoholic silver nitrate a voluminous precipitate of silver iodide was formed instantaneously. On treatment with concentrated sodium hydroxide a volatile basic gas (presumably ammonia) was detected by litmus paper. Conclusive evidence for the presence of NH_4^+ ion was obtained from a positive Nessler's reagent[5] test.

(c) Using Silver Formate. A heterogeneous mixture of 0.2422 g (0.697 mmol) of Ia, 0.2116 g (1.38 mmol) of silver formate, and 5 ml of benzene was heated under reflux for 9 h. Filtration and evaporation of the solvent left 0.2213 g of a solid, mp 56.5–69 °C. Crystallization from ethanol–water (5:4) gave a 0.1568-g mixture consisting of 20.8% IIIa and 79.1% Ia as determined by GLC and infrared analyses. Further dilution of the filtrate with water provided 0.0342 g (0.013 mmol, 18%) of IIIa, mp 46.0–47.5 °C, as fine white needles assaying 93.1% IIIa, 6.6% Ia, and 0.3% unknown. The infrared spectrum was nearly identical with spectra from the former preparations.

2-Acetoxy-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane (IIIb). (a) Using *N*,*N*-Dimethylacetamide. Compound Ia (0.2055 g, 0.591 mmol), 9.0 ml of DMAC, and 1.0 ml of water were heated at 100–105 °C in an open vessel for 4 h. On cooling and dilution of the mixture with 25 ml of water, 0.0401 g of crude IIIb, mp 45–47 °C, was obtained. Fractional vacuum sublimation, retaining only that material which sublimed at a bath temperature of 30–55 °C, provided 0.0345 g (0.123 mmol, 21%) of pure IIIb, mp 43.5–45.5 °C. The mixture melting point with material prepared from Ia and silver acetate was undepressed at 43.5–46.0 °C.

A second experiment was performed in a closed system enabling volatile products to be analyzed. A degassed mixture of 0.3131 g (0.901 mmol) of Ia, 2.0 ml of DMAC, and 0.3 ml of water was sealed under vacuum in a 5-ml tube and heated at 100 °C for 4 h. On opening the tube under vacuum, the noncondensable gas was measured and identified as 0.07 cm^3 of methane and 15.63 cm^3 (0.697 mmol) of hydrogen by combustion over cupric oxide. Dilution of the tube contents with 10 ml of water and cooling provided 0.0566 g (0.202 mmol, 22%) of IIIb, mp 42.5–44.5 °C.

(b) Using Silver Acetate. A heterogenous mixture of 0.1050 g (0.302 mmol) of Ia, 0.1015 g (0.608 mmol) of silver acetate, and 3 ml of benzene was heated under reflux for 12 h, after which the mixture was filtered and the filtrate evaporated to dryness under a stream of nitrogen. The brown solid was crystallized once from ethanol–water (1:1) and sublimed under vacuum at a bath temperature of 30–55 °C to obtain 0.0599 g (0.214 mmol, 73%) of IIIb, mp 42–45 °C. Two recrystallizations from ethanol–water (1:1) followed by sublimation provided an analytical sample, mp 44.0–45.0 °C. Anal. Calcd for $C_8H_{26}B_3O_2P_3$: C, 34.35; H, 9.37. Found: C, 34.09; H, 9.06.

Ia and Aqueous Formic Acid. In a 5-ml heavy-wall tube was placed 0.1400 g (0.403 mmol) of Ia and 1.50 ml of aqueous 90.7% formic acid. The evacuated, sealed tube was heated at 100 °C for 18 h. On cooling, colorless crystals were deposited on the side of the tube. The tube was opened on the vacuum line and 1.94 cm^3 (0.087 mmol) of noncondensable gas (presumably hydrogen) was obtained. Dilution of the tube contents with 10 ml of water, further dilution, cooling, and/or seeding with IIIa failed to provide a solid product. Concentration of the solution in a nitrogen stream left a white crystalline solid wet with a viscous oil. The characteristic odor of phosphine was quite apparent. An infrared spectrum confirmed the presence of boric acid contaminated with other ill-defined products; no suggestion of the presence of IIIa was evident.

Ib and Sodium Acetate. A mixture of 0.1508 g (0.502 mmol) of Ib and 0.0826 g (1.01 mmol) of anhydrous sodium acetate in 8 ml of absolute ethanol was heated under reflux for 7 h in a nitrogen atmosphere. Dilution of the cooled reaction mixture with 10 ml of water deposited 0.1371 g (91% recovery) of Ib, mp 75–77 °C. The infrared spectrum was similar to that for authentic Ib with no detectable carbonyl absorption band; the mixture melting point with Ib was undepressed.

Registry No. Ia, 59830-80-7; Ib, 59830-75-0; IIa, 68-12-2; IIb, 75-12-7; IIc, 127-19-5; IIIa, 59831-52-6; IIIb, 59831-53-7; silver acetate, 563-63-3; silver formate, 13126-70-0.

References and Notes

(1) Now a part of Kerr-McGee Corp., Oklahoma City, Okla.

(2) (a) This work was supported in part by the United States Air Force under Contract No. AF 33(616)-7810 monitored by the Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. (b) The nomenclature used in this report is that proposed by the International Union of Pure and Applied Chemistry Commission on Nomenclature of Inorganic and Organic Chemistry ("Information Bulletin—Appendices on Tentative Nomenclature, Symbols, Units, and Standards", No. 31, Section D, Aug 1973).

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(4) An article is in preparation describing other displacement reactions of these compounds.

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