Synthesis and Reactions of Phosphine-Methylsulfonyloxyborane Complexes

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Functionalizations of the boranato group of phosphine-boranes have been investigated. Trimethylphosphine-borane readily reacted with methanesulfonic acid in dichloromethane with evolution of hydrogen. The resulting trimethylphosphine-methylsulfonyloxyborane was subjected to nucleophilic substitution reaction on the boron atom with arenethiols or secondary phosphine-boranes in the presence of NaH. The reactivities of the substitution products obtained were also investigated. A new phosphine-borane having a P-B-P-B-P-B-P-B bond linkage was synthesized.

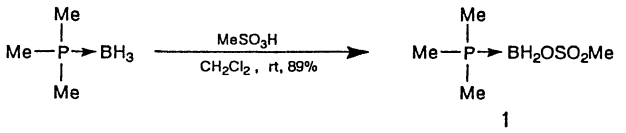
Phosphine-boranes, adducts of phosphines with boranes, exhibit unique chemical properties, and they have intriguing potential for use as hydroboration agents or as precursors to useful organophosphorus compounds.[1,2] We have been interested in the peculiar properties of phosphine-boranes and have investigated syntheses and reactions of these compounds.

In the previous papers we reported that a variety of phosphine-borane derivatives, including optically active ones, was prepared by chemical transformation of phosphine moieties.[3] Based on these results, we then sought to explore a new method for the functionalization of the boranato group of phosphine-boranes. This paper describes the synthesis and reactions of methanesulfonate derivatives of phosphine-boranes as well as the reactions of the new classes of organophosphorus compounds having a P-B-S or a P-B-P bond linkage.

Results and Discussion

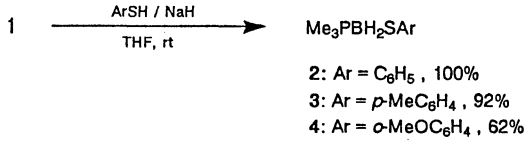
In seeking functionalizations of the boranato group, we came to examine the synthesis of sulfonate derivatives of phosphine-boranes, since the sulfonates are anticipated to undergo substitution reaction on the boron atom to lead to various kinds of phosphine-boranes.[4] Our initial trial was undertaken to investigate the reaction of phosphine-boranes with sulfonic acid. Several phosphine-boranes {Ph_3PBH_3, $Ph_2(CH_3)PBH_3$, $Ph(CH_3)_2PBH_3$, $Ph_2(H)PBH_3$, $(t\text{-Bu})_3PBH_3$, $[2,4,6\text{-}(MeO)_3C_6H_2]_3PBH_3$} were treated with an excess amount of methanesulfonic acid or trifluoromethanesulfonic acid. The reactions proceeded at 0—25 °C with evolution of hydrogen in an aprotic solvent such as dichloromethane or diethyl ether. Unfortunately, however, many attempts for the isolation of the products by chromatography or recrystallization were unsuccessful in these cases.

Next, we tried the reaction of trimethylphosphine-borane with methanesulfonic acid in dichloromethane. In contrast to the unsuccessful results mentioned above, the product trimethylphosphine-methylsulfonyloxyborane (**1**) was isolated as a crystalline solid in 89% yield. This compound, although it was highly sensitive to moisture and it was difficult to be purified by recrystallization, was practically pure and could be used for further reactions.[5]



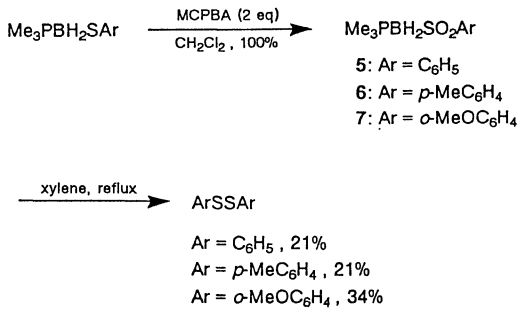
1 (1)

The methanesulfonate **1** was allowed to react with thiols. The reaction with arenethiols in the presence of sodium hydride proceeded smoothly at room temperature to afford the corresponding substitution products possessing a P-B-S bond in 62—100% yield. Alkanethiols such as α-toluenethiol or 2-methyl-2-propanethiol also reacted readily under the same conditions. However, these products were labile at room temperature and were not isolated as a pure form.



(2)

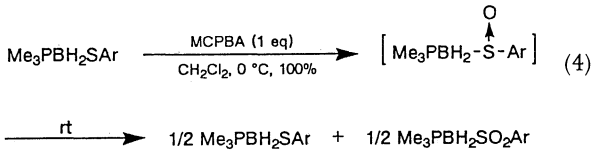
The reactivities of the substitution products were examined. Treatment of compounds **2**, **3**, and **4** with 2 equivalents of *m*-chloroperbenzoic acid (MCPBA) afforded the corresponding oxidation products **5**, **6**, and **7** in essentially quantitative yield. These compounds, which are regarded as sulfone analogues, were stable at ordinary temperature. They decom-



(3)

posed in a xylene solution at reflux to result in the formation of the respective disulfides in 21—34% yield.

We attempted the preparation of sulfoxide analogues by the reaction of **2**, **3**, and **4** with 1 equivalent of MCPBA. Thin layer chromatography of the reaction mixtures indicated that the expected products were produced at 0 °C for 10 min. The subsequent work-up involving flash chromatography on silica gel provided the solution that contained the expected sulfoxide analogues. However, the evaporation of the solvent under reduced pressure resulted in the disproportionation of the products to sulfide and sulfone analogues. It is noted that this disproportionation proceeded rapidly without any catalyst such as an acid.

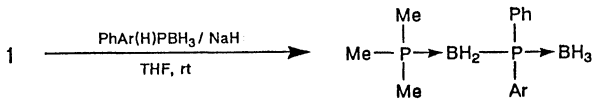


(4)

Our attention next turned to the synthesis of a new kind of phosphine-boranes that contains a linear P-B bond chain.[6] Some charge alternation (+−+−+−+−) may exist in these molecules, since phosphine-boranes possess +1 and −1 formal charges on phosphorus and boron atoms. These characteristic bond sequences might account for the peculiar properties of the compounds.

We envisioned that these compounds could be synthesized by the substitution reactions at boranato moieties. Thus, sequential treatments of phosphine-boranes with methanesulfonic acid and a secondary phosphine-borane may, in principle, enable homologation of the P-B bond unit.

First, compound **1** was allowed to react with $Ph_2(H)PBH_3$ or $Ph(o\text{-}MeOC_6H_4)(H)PBH_3$ in the presence of NaH. The nucleophilic substitution reaction on the boron atom proceeded under ordinary conditions, and the expected products **8** and **9** were isolated in 100% and 91% yields, respectively.

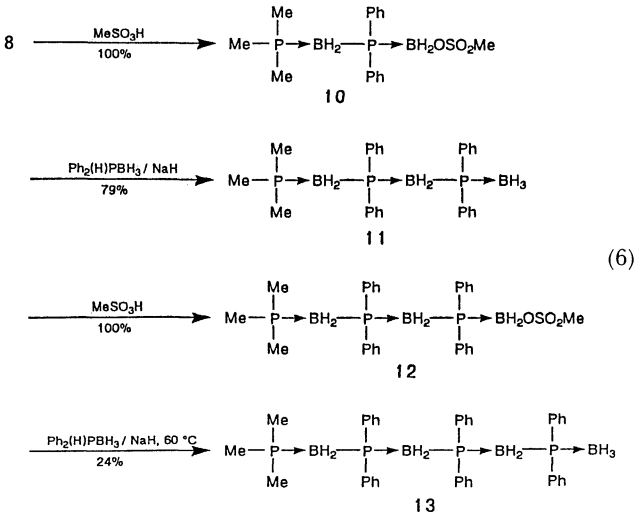


(5)

8: Ar = C_6H_5, 100%

9: Ar = o-$MeOC_6H_5$, 91%

Compound **8** was treated with methanesulfonic acid to afford methanesulfonate derivative **10** in quantitative yield. It is noted that the BH_3 group was selectively subjected to substitution reaction. The reaction of compound **10** with $Ph_2(H)PBH_3$ provided compound **11** in high yield. Further treatment of **11** with methanesulfonic acid afforded compound **12**,



(6)

which was allowed to react with $Ph_2(H)PBH_3$ to furnish compound **13** possessing a P-B-P-B-P-B-P-B bond linkage.

Experimental

Spectra were measured with the following instruments; ^{1}H NMR: JEOL-MH100 (100 MHz), ^{11}B and ^{31}P NMR: JEOL GX270 (86.5 MHz and 110 MHz), IR: Hitachi-IR2I5 Spectrophotometer, MS: JEOL JMS-HX110. ^{11}B and ^{31}P NMR spectra were obtained in $CDCl_3$ with $(CH_3O)_3B$ and 85% H_3PO_4 as external standards, respectively. Microanalyses were performed at the Chemical Analysis Center of Chiba University.

All experiments were carried out under an argon atmosphere. The products were isolated by preparative thin-layer chromatography (TLC) on silica gel (Wakogel B-5F) or column chromatography on silica gel (Wakogel C-200).

Trimethylphosphine-Methylsulfonyloxyborane (1). Methanesulfonic acid (0.45 cm^3, 7 mmol) was added to a solution of trimethylphosphine-borane[7] (0.45 g, 5 mmol) in dry dichloromethane (3 cm^3), whereupon hydrogen gas evolved. After 30 min, finely powdered potassium hydrogencarbonate (0.20 g, 2 mmol) was added with stirring. The reaction mixture was passed through a short column of silica gel by using ethyl acetate as an eluent. The filtrate was concentrated in vacuo to give practically pure methanesulfonate **1** as a white powder (0.81 g, 89%). Mp 87—93 °C; IR (KBr) 3010, 2400, 1400, and 1310 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.35 (d, J=12 Hz, 9H) and 2.81 (s, 3H); ^{11}B NMR ($CDCl_3$) δ=−28.8 (d, $J_{B\text{-}P}$=90.8 Hz); ^{31}P NMR ($CDCl_3$) δ=−13.89 (d, $J_{P\text{-}B}$=90.8 Hz); FABMS m/z 183 (M^+−1); MS m/z 183 (M^+−1).

Reaction of 1 with Thiols (General Procedure). Sodium hydride (40% oil dispersion, 2 mmol) was washed with hexane and suspended in dry THF (3 cm^3). Thiol (1 mmol) and trimethylphosphine-methylsulfonyloxyborane (1 mmol) were added at 0 °C, and the mixture was stirred for 2 h at room temperature. The reaction mixture was treated with hydrochloric acid (1 mol dm^{-3}) and extracted with $CHCl_3$. The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residual oil was chromatographed on silica gel (AcOEt/hexane) to give the product as a white powder.

2: Mp 83—84 °C; IR (KBr) 2400, 1580, 1470, 1290, and 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (d, J=12 Hz, 9H) and 6.60—7.70 (m, 5H); MS m/z 198 (M^+).

3: Mp 79—82 °C; IR (KBr) 2400, 1490, 1290, 1090, 950, and 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.24 (d, J=11 Hz, 9H), 2.19 (s, 3H), and 6.68—7.31 (m, 4H); MS m/z 212 (M^+).

4: Mp 104—105 °C; IR (KBr) 2350, 1560, 1470, 1240, and 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.34 (d, J=10 Hz, 9H), 3.88 (s, 3H), and 6.70—7.70 (m, 4H); MS m/z 228 (M^+).

Synthesis of Sulfone Analogues 5, 6, and 7. *m*-Chloroperbenzoic acid (2 mmol) was added to substrate (1 mmol) in dichloromethane (3 cm^3) at 0 °C. After stirring for 10 min, the reaction mixture was subjected to flash column chromatography on silica gel (AcOEt and acetone) to give the product as a colorless crystal.

5: Mp 103—104 °C; IR (KBr) 2990, 2450, 2400, 1440, 1210, 1100, 960, and 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.56 (d, J=12 Hz, 9H) and 7.10—8.00 (m, 5H); MS m/z 218 (M^+-BH_3). Anal. Found: C, 46.96; H, 6.69%. Calcd for $C_9H_{16}O_2BPS$: C, 46.99; H, 7.01%.

6: Mp 79—80 °C; IR (KBr) 3000, 2450, 2400, 1300, 1210, 1100, 1080, and 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.51 (d, J=12 Hz, 9H), 2.34 (s, 3H), and 7.22—7.73 (m, 4H); MS m/z 246 (M^++2). Anal. Found: C, 49.18; H, 7.24%. Calcd for $C_{10}H_{19}O_2BPS$: C, 49.20; H, 7.43%.

7: Mp 132—133 °C; IR (KBr) 2990, 2480, 2410, 1590, 1480, 1210, 1100, and 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.53 (d, J=12 Hz, 9H), 3.85 (s, 3H), and 6.60—8.00 (m, 4H). Anal. Found: C, 46.15; H, 6.91%. Calcd for $C_9H_{19}O_3BPS$: C, 46.18; H, 6.98%.

Thermal Decomposition of Sulfone Analogues. Substrate was dissolved in xylene, and the solution was kept at 140 °C for 5 h. The solvent was removed and the residue was subjected to preparative TLC on silica gel (AcOEt/hexane=1 : 10) to give corresponding disulfide.

Oxidation of Sulfide Analogues with 1 Equivalent of MCPBA. *m*-Chloroperbenzoic acid (1.0 equiv) was added to thiol (1.0 equiv) in dichloromethane at 0 °C. After stirring for 10 min,[8] the reaction mixture was passed through a short column using AcOEt/CH_3OH (5:1) as an eluent. The solvent was removed under reduced pressure. The residue was subjected to preparative TLC to give the corresponding sulfide and sulfoxide analogues in quantitative yield.

Synthesis of Phosphine-Borane Containing a Linear P-B Bond Linkage (General Procedure). Sodium hydride (40% oil dispersion, 2.0 equiv) was washed with hexane and suspended in dry THF. Secondary phosphine-borane (1.0 equiv) and phosphine-borane methanesulfonate (1.0 equiv) were added at 0 °C, and the mixture was stirred at room temperature. After the reaction was complete, the reaction mixture was quenched with hydrochloric acid (1 mol dm^{-3}). The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residual oil was chromatographed on silica gel (AcOEt/hexane). The product, which was obtained as a pasty mass, was triturated with ether to give the desired product as a white powder.

Compound **10** or **12** was synthesized from **8** or **11** in a similar procedure as the preparation of **1**.

8: Mp 122—123 °C; IR (KBr) 3040, 2350, 1480, 1430, and 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (d, J=12 Hz, 9H) and 6.90—7.90 (m, 10H); FABMS m/z 287 (M^+); MS m/z 274 (M^+-BH_3). Anal. Found: C, 62.30; H, 8.37%. Calcd for $C_{15}H_{24}B_2P_2$: C, 62.57; H, 8.40%.

9: Mp 138.0—139.5 °C; IR (KBr) 2950, 2450, 1580, 1470, 1270, and 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (d, J=12 Hz, 9H), 3.41 (s, 3H), and 6.30—8.00 (m, 9H); MS m/z 317 (M^+) and 304 (M^+-BH_3). Anal. Found: C, 60.26; H, 8.10%. Calcd for $C_{16}H_{26}B_2OP_2$: C, 60.44; H, 8.24%.

10: Mp 82—85 °C; IR (KBr) 3000, 2400, 1440, and 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (d, J=12Hz, 9H), 2.68 (s, 3H), and 7.15—7.90 (m, 10H); MS m/z 274 ($M^+-BH_2OSO_2Me$).

11: Mp 143—144 °C; IR (KBr) 3040, 2320, 1480, 1430, and 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22 (d, J=12 Hz, 9H) and 6.80—7.80 (m, 20H); MS m/z 472 (M^+-BH_3). Anal. Found: C, 66.56; H, 7.30%. Calcd for $C_{27}H_{36}B_3P_3$: C, 66.74; H, 7.47%.

12: Mp 148—153 °C; IR (KBr) 2400, 1440, 1150, and 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.19 (d, J=12 Hz, 9H), 2.34 (s, 3H), and 6.55—7.30 (m, 20H); MS m/z 274 ($Me_3PBH_2PPh_2$).

13: Mp 170—171 °C; IR (KBr) 3030, 2320, 1480, 1430, and 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (d, J=10 Hz, 9H) and 6.00—7.60 (m, 20H); MS m/z 409 ($BH_2P(Ph_2)BH_2P(Ph_2)BH_3$) and 274 ($Me_3PBH_2PPh_2$). Anal. Found: C, 68.21; H, 6.88%. Calcd for $C_{39}H_{48}B_4P_4$: C, 68.49; H, 7.07.

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6) Cyclic trimers and tetramers of phosphinoboranes were previously reported. A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953); A. B. Burg and G. Brendel, *ibid.*, **80**, 3198 (1958); A. B. Burg, *ibid.*, **83**, 2226 (1961).

7) H. Schmidbaur, E. Weiss, and G. Müller, *Synth. React. Inorg. Met.-Org. Chem.*, **15**, 401 (1985).

8) The thin-layer chromatography of the reaction mixture indicated that the sulfoxide analogue was produced in quantitative yield at this stage.