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# Reaction of Triethyl Phosphite with Boron Tribromide

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**Summary.** Reaction of boron tribromide with triethyl phosphite led to the formation of triethyl tribromoborophosphate **1**, a complex bearing a P→B bond.

**Keywords.** Boron tribromide; Complexes; NMR Spectroscopy; Triethyl phosphite; *Lewis* acids.

## Introduction

In 1959, *Gerrard et al.* published their results on the reaction between triphenyl phosphite and boron tribromide [1]. Contrary to their expectation, the reaction did not lead to the P→B adduct, but yielded phosphorus tribromide and triphenyl borate. Later, they reported on the reaction of tributyl phosphite with boron trichloride resulting in dibutyl phosphorchloridite and butoxyboron dichloride, stating that boron tribromide reacted with trialkyl phosphite in the same way [2]. *Binder* and *Palmtag* presented the reaction of triethyl phosphite with boron trifluoride, which did not give any compound bearing a B-P bond [3]. The reaction resulted in products of so-called 'mutual replacement'. Very recently, *Stasi* and *Just* [4] tested the reaction of triethyl phosphite with boron trichloride and boron trifluoride. They did not observe the formation of a B-P complex, but detected the corresponding diethyl phosphorhalidites instead.

We present here the results of our study on the reaction of triethyl phosphite with boron tribromide, unexpectedly leading to a complex bearing a boron-phosphorus bond.

## Results and Discussion

The reaction of triethyl phosphite with boron tribromide was carried out in chloroform for 18 hours at room temperature leading to triethyl tribromoborophosphate (**1**), ethoxybromophosphono bromoboronite (**2**), phosphorus tribromide (**3**), and triethyl borate (**4**) in a 10:5:1:1 ratio (Scheme 1).

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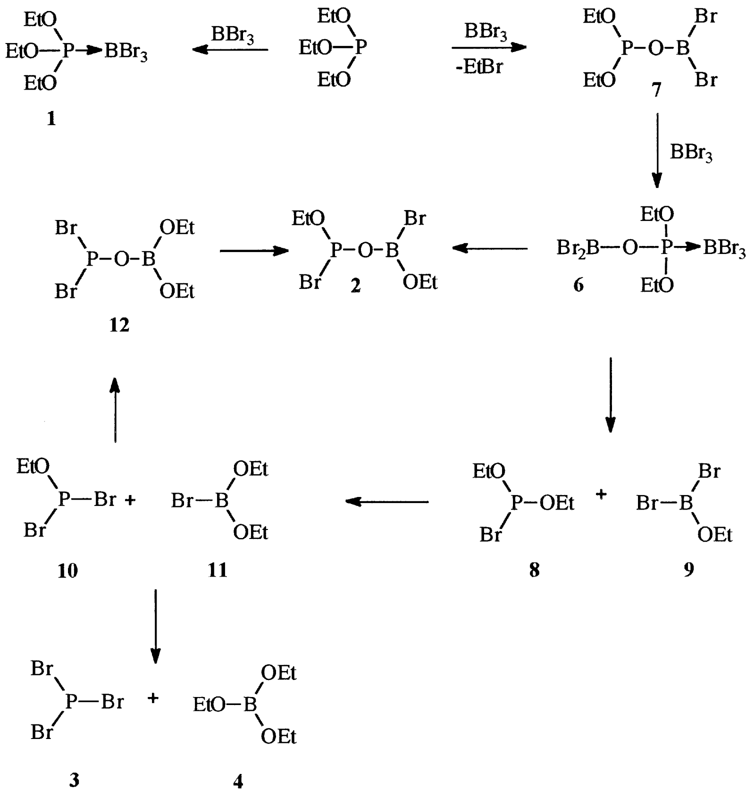

Scheme 1

Attempts to separate the products failed due to their instability. NMR and mass spectroscopic studies of the mixture, however, allowed a characterization of the components.

The $^{11}B$ NMR signal of **1** occurred at $-18.8$ ppm as a doublet ($^{1}J_{PB} = 268$ Hz), its $^{31}P$ NMR signal at 38.5 ppm as a quartet ($^{1}J_{PB} = 270$ Hz), thus clearly indicating the formation of a phosphorus-boron bond. EI-MS showed the molecular ion peak at $m/z = 417$. The $^{11}B$ and $^{31}P$ NMR signals of **2** were observed at 18.3 and 198.4 ppm as singlets. Its $^{1}H$ NMR spectrum showed the presence of ethoxy groups linked to phosphorus and to boron atoms, the character of the $^{11}B$ and $^{31}P$ NMR signals suggesting tricoordination of boron and phosphorus. The molecular ion peak (EI-MS) was found at $m/z = 228$. Phosphorus tribromide (**3**) gave a $^{31}P$ NMR signal at 228.3 ppm; the $^{11}B$ NMR resonance of triethyl borate (**4**) occurred at 18.0 ppm.

In order to disclose the mechanism of this reaction, it was performed under NMR monitoring. Several minutes after mixing the reagents, formation of **1** ($\delta_P = 38.5$ and $-18.8$ ppm), **6** ($\delta_P = 69.0$ ppm, $\delta_B = -15.6$ 25.7 ppm), and **7** ($\delta_P = 141.3$ ppm, $\delta_B = 27.6$ ppm) in a 10:1:1 ratio was observed. $^{1}H$ NMR measurements showed the signals of the evolving bromoethane. One hour later, the signals of compound **7** had disappeared.

Within the next six hours, the intensities of the signals of **6** decreased, and formation of compounds **2** ($\delta_P = 198.3$ ppm, $\delta_B = 18.3$ ppm) and **3**

($\delta_P = 228.2$ ppm) was observed. Three new signals appeared in the $^{31}$P NMR spectrum of the mixture, and we suggest the formation of the following intermediates: **8** ($\delta_P = 184.2$ ppm), **10** ($\delta_P = 209.7$ ppm), and **12** ($\delta_P = 217.1$ ppm). They were identified by their $^{31}$P NMR signals which were in accordance with literature data [5, 6]. However, attempts of their isolation failed. After 12 more hours, only the signals of the end products were observed.

The mechanism of the reaction remains unclear. Nevertheless, we suggest that first triethyl phosphite reacts with boron tribromide, formating **1** and intermediate **7**. **7** in turn immediately reacts with one molecule of boron tribromide to yield complex **6**. Reaction of **6** triethyl phosphite leads to two molecules of ethyl ethoxybromophosphono bromoboronite (**2**).

The mechanism of the formation of **3** and **4** is even less clear. Most probably, fragmentation of **6** leads to the formation of diethyl phosphorbromidite (**8**) and ethoxyboron dibromide (**9**). These two compounds undergo the mutual replacement to give ethyl phosphordibromidite (**10**) and diethoxyboron bromide (**11**) which, in the course an intermolecular rearrangement, afford phosphorus tribromide (**3**) and triethyl borate (**4**). We also suppose that compounds **10** and **11** react with each other to give compound **12** which rearranges subsequently to the end product **2** (Scheme 1).

Repetition of the reaction employing boron trichloride under the same experimental conditions did not give rise to any compound bearing a B-P bond. Diethyl phosphorochloridite ($\delta_P = 167.4$ ppm) and ethyl dichloroboronite ($\delta_B = 31.6$ ppm) were obtained as products which is in accordance with literature data [1–4].

It is difficult to explain why the reaction of boron tribromide with phosphite leads to the formation of a P-B bond whereas the reaction of boron trichloride with phosphites does not. It is possible that the complex $(RO)_3P \rightarrow BCl_3$ occurs as an intermediate but is so unstable that its detection is beyond our technological possibilities. The problem is still under investigation.

## Experimental

All NMR spectra were recorded on a Bruker AC 300 spectrometer ($^1$H: internal *TMS*; $^{11}$B: external $Et_2O \cdot BF_3$ $^{31}$P: external $H_3PO_4$); electron impact mass spectra were measured on a Varian MAT 311 instrument.

### *Reaction of triethyl phosphite with boron tribromide*

Boron tribromide (0.68 g, 2.72 mmol) was dissolved in $CHCl_3$ under argon, cooled to −20°C, and triethyl phosphite (0.45 g, 2.72 mmol) was added. The mixture was allowed to warm up to room temperature and was stirred for 12 h. The precipitate was collected by filtration to give 0.08 g of a white solid. The filtrate was evaporated to give 0.73 g of a mixture of products.

### *Triethyl tribromoborophosphate* (**1**; $C_6H_{15}O_3PBBr_3$)

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 4.47$ (dq, $^3J_{PH} = 7.0$ Hz, $^3J_{HH} = 7.0$ Hz, $CH_2$), 1.46 (dt, $^3J_{PH} = 0.8$ Hz, $^3J_{HH} = 7.0$ Hz, $CH_3$) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 38.39$ (q, $^1J_{PB} = 270.0$ Hz) ppm; $^{11}$B NMR (96 MHz, $CDCl_3$): $\delta = -18.8$ ($^1J_{PB} = 270.0$ Hz) ppm; EI-MS: $m/z = 417$ ($M^+$).

*Ethoxybromophosphono bromoboronate* (**2**; $C_4H_{10}O_3PBBr_2$)

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 4.31$ (dq, $^3J_{PH} = 8.8$ Hz, $^3J_{HH} = 7.1$ Hz, P-$OCH_2CH_3$), 4.01 (q, $J = 7.1$ Hz, B-$OCH_2CH_3$), 1.40 (dt, $^3J_{PH} = 0.5$ Hz, $^3J_{HH} = 7.1$ Hz, P-$OCH_2CH_3$), 1.25 (t, $J = 7.1$ Hz, B-$OCH_2CH_3$) ppm; $^{31}$P NMR (121 Mhz, $CDCl_3$): $\delta = 198.4$ (s) ppm; $^{11}$B NMR (96 MHz, $CDCL_3$): $\delta = 18.9$ (broad s) ppm; EI-MS $m/z = 308$ ($M^+$).

*Phosphorus tribromide* (**3**; $PBr_3$)

$^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 228.3$ (s) ppm; EI-MS: $m/z = 271$ ($M^+$).

*Triethyl borate* (*4*; $C_6H_{15}O_3B$)

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 4.25$ (q, $J = 7.1$ Hz, $CH_2$, 1.23 (t, $J = 7.1$ Hz, $CH_3$) ppm; H), $^{11}$B NMR (96 MHz, $CDCl_3$): $\delta = 18.0$ (s) ppm; EI-MS: $m/z = 146$ ($M^+$)

*Complex* **6** ($C_4H_{10}O_3PB_2Br_5$)

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 4.40$ (dq, $^3J_{PH} = 7.1$ Hz, $^3J_{HH} = 7.1$ Hz, $CH_2$, 1.46 (dt, $^3J_{PH} = 0.8$ Hz, $^3J_{HH} = 7.1$ Hz, $CH_3$) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 68.70$ (q, $^1J_{PB} = 218.7$ Hz) ppm; $^{11}$B NMR (96 MHz, $CDCl_3$): $\delta = 25.7$ (s), $-15.6$ (d, $^1J_{PB} = 218.7$ Hz) ppm.

*Intermediate* **7** ($C_4H_{10}O_3PBBr_2$)

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 4.08$ (dq, $^3J_{PH} = 7.1$ Hz, $^3J_{HH} = 7.1$ Hz, $CH_2$), 1.08 (dt, $^3J_{PH} = 0.5$ Hz, $^3J_{HH} = 7.1$ Hz, $CH_3$) ppm, $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 141.3$ (s) ppm; $^{11}$B NMR (96 MHz, $CDCl_3$): $\delta = 27.6$ (s) ppm.

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## References

[1] Frazer MJ, Gerrard W, Patel JK (1959) Chem Ind 728
[2] Gerrard W, Lindsay M (1960) Chem Ind 152
[3] Binder H, Palmtag J (1972) Z Naturforsch B: Anorg Chem, Org Chem **27B**: 753
[4] Stasi L, Just G (1999) Tetrahedron Lett **40**: 2283
[5] Gorenstein DG, Shah DO (1984) In: Gorenstein DG (ed) Phosphorus-31 NMR. Principles and Applications. Academic Press, New York
[6] Emsley JW, Feeney J, Sutcliffe LH (1967) High Resolution Nuclear Magnetic Resonance Spectroscopy, vol 2. Pergamon Press, Oxford

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