# SHORT COMMUNICATIONS

## *Synthesis of Trimethylboron from Boric Anhydride or Borate**

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(Received November 26, 1958)

Many organoboron compounds have been prepared by the action of Grignard reagents⁽¹⁾ on boron trihalides or esters of boric acid. But so far as is known, there is no report** on the synthesis of organoboron compounds from naturally occuring materials such as boric anhydride or sodium borate directly. Related reactions are concerned only with sodium hydride⁽²⁾ at a temperature as high as 330°C in an autoclave. Recently, with progress in the study of organoaluminum compounds, many attempts have been made to utilize organoaluminum compounds in related reactions in place of Grignard reagents⁽³,⁴⁾. Previously we⁽⁵⁾ found that the silicon-oxygen bond in polymeric form was cleaved and alkylated simultaneously with organoaluminum compounds. In the present communication, this reaction was applied to boron-oxygen compounds and it was found that organoboron compound was obtained directly from inorganic boric anhydride or its salts in a good yield.

The reaction was carried out as follows. Methylaluminum sesquichloride⁽⁶⁾ $(CH_3)_3Al_2Cl_3$ was added to a boron compound in an inert atmosphere and the reactant was refluxed at 150 to 170°C for several hours, and trimethylboron (b. p. −21.8°C) generated was caught by a dry-ice acetone trap.

The results obtained are shown in Table I. In the case of boric anhydride the yield of trimethylboron is especially good and almost quantitative but it is somewhat low in the case of borate. It is interesting to note that when the reaction was carried out in isoamyl ether solution, no trimethylboron was produced. Also, by the use of methylmagnesium chloride in the same ethereal solution, no methyl-boron

TABLE I

REACTION OF METHYLALUMINUM SESQUICHLORIDE WITH BORON COMPOUNDS

| B compd. | $Me_3Al_2Cl_3$ | | | | Reacn. temp. | Reacn. time | $BMe_3$ | Yield |
|---|---|---|---|---|---|---|---|---|
| | (g.) | (m. mole) | (g.) | (m. mol.) | (°C) | (hr.) | (g.) | (%) |
| $B(OBu)_3$ | 40 | (172) | 25.5 | (124) | room temp. | over night | 6.5 | 93.6 |
| $B_2O_3$ | 10.5 | (151) | 54 | (251) | 100～170 | 6 | 14 | 68.8 |
| $Na_2B_4O_7$ | 12 | ( 60) | 50 | (244) | 140～160 | 4 | 5.5 | |
| | | | | | 170* | 3 | 4.0 | 71.2 |
| $B_2O_3$ | 6 | ( 87) | MeMgCl**/400 cc. $i$-$Am_2O$ | | 150～160 | 6 | — | |
| $B_2O_3$ | 6 | ( 87) | 42/50 g. $i$-$Am_2O$ | | 150 | 5 | — | |

* after eight days.

** from 12 g. (0.5 mole) of Mg.

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* Presnted before the Symposium of Organosilicon and Organometallic Compounds at Osaka, October 18, 1958.

1) M. S. Kharasch and O. Reinmth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall Inc., New York (1954). pp. 1335; M. F. Lappert, *Chew. Rev.*, **56**, 959 (1956).

** Recently, R. Köster reported briefly that trialkylborons were synthesized by the reaction of trialkylaluminum with trialkylboroxole $[RBO]_3$, but not obtained from boric anhydride directly because of the decomposition of the trialkylaluminum compounds. See ref. 4.

2) H. I. Schlesinger and H. C. Brown, U. S. Patent. 2534533 (1950); H. I. Schlesinger, H. C. Brown and A. E. Finholt, *J. Am. Chem. Soc.*, **75**, 208 (1953).

3) For examples, Kali-Chemie A. -G., Brit. P., 768, 765 (1957).
R. Köster and K. Ziegler, *Angew. Chem.*, **69**, 94 (1957).
*Chem. and Ind. News*, **36**, No. 17, 66 (1958).

4) R. Köster, *Angew. Chem.*, **70**, 371 (1958).

5) I. Shiihara, H. Takahashi and J. Iyoda, the 11th Annual Meetings of Chemical Society of Japan in Tokyo, April 1958.

6) J. Iyoda and I. Shiihara, the Symposium of Organosilicon and Organometallic Compounds at Osaka, October 15, 1957.

compounds were obtained. These results are explained as follows: both organometallic compounds are stabilized by the etherate formation with ether, and consequently their affinity toward the oxygen of the boron-oxygen bond are lowered.

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