Dialkylthioboronates

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Many organo boron compounds are known to be effective catalysts for vinylpolymerization[1-3]. Accordingly, several dialkylthioboronates have been prepared for testing the catalytic activity. It was found that though the activites of the compounds as polymerization catalysts were low, they reacted in a characteristic manner with ammonia. These compounds are new substances, and the synthetic method and some properties of them are described in this paper.

The only known dialkylthioboronate is dimethylthioboronate[4], $(CH_3)_2BSCH_3$, which was prepared by the interaction of methylmercaptan and tetramethyl diborane.

$$2CH_3SH + B_2H_2(CH_3)_4 = 2(CH_3)_2BSCH_3 + 2H_2$$

In the present studies, the dialkylthioboronates have been prepared by reaction between dialkylboron chloride and the sodium salt of mercaptan. While alcohols react readily with dialkylboron chloride to produce dialkylboronous esters[3], mercaptans do not react at least at room temperature. Dialkylthioboronate reacts readily with ammonia to produce a white solid at about −60°C, which appears to be an unstable 1 : 1 addition product. This product easily decomposes to dialkylamino borine, R_2BNH_2, on distillation. The reaction is considered to be as follows:

$$R_2BSR' \xrightarrow{\text{liq. } NH_3} R_2BSR' : NH_3$$
$$\xrightarrow{\text{distill.}} R_2BNH_2 + R'SH$$

The details of this aspect will be reported in the near future.

TABLE I. YIELDS OF R_2BSR'

R in R_2BCl	Wt., g.	R in $R'SH$[a]	Na, g.	Product, g.	Yield, %[b]
iso-C_3H_7	33	C_2H_5	10	18	30.0
n-C_4H_9	45	C_2H_5	10	30	40.0
n-C_4H_9	30	*iso*-C_3H	7	16	36.6
n-C_4H_9	31	*n*-C_4H_9	6	34	38.0

a) The amount of R'SH is 25 g. in each experiment.

b) The yield was calculated from R'SH employed.

Experimental and Results. — In a 300 cc. three necked round-bottomed flask, fitted with a mechanical stirrer with a mercury seal, a reflux condenser, and a dropping funnel, were placed about 100 cc. of anhydrous ether and the various amonts of sodium shown in Table I. To the mixture, 25 g. of mercaptan was dropped slowly, with stirring. After completion of addition, the system was heated for about three hours, and the mixture was cooled to room temerature. The unchanged sodium was removed, and about 100 cc. of ethereal solution containing a certain amount of dialkylboron chloride (shown in Table I) was added slowly from the dropping funnel. The reaction proceeds as follows:

$$R_2BCl + R'SNa = R_2BSR' + NaCl$$

After the dropping had been completed, the mixture was heated for about four hours. The solvent was distilled off, and further distillation was carried out under reduced pressure. The products were redistilled for measurements of physical constants. The results are shown in Table II.

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[1] G. S. Kolesnikov and L. S. Fedorova, *Izv. AN. USSR*, No. 2, 236 (1957).

[2] J. Furukawa et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 728 (1958).

[3] N. Ashikari, *J. Polymer Sci.*, **28**, 641 (1958).

[4] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

TABLE II. PHYSICAL CONSTANTS OF R_2BSR'

R_2BSR'	b.p., °C	d_4^{20}	Calcd. B%	Found B%[c]
$(iso\text{-}C_3H_7)_2BSC_2H_5$	80/20 mm.	0.8490	6.96	7.04
$(n\text{-}C_4H_9)_2BSC_2H_5$	142/60 mm.	0.8400	5.91	6.11
$(n\text{-}C_4H_9)_2BS(iso\text{-}C_3H_7)$	74/4 mm.	0.8525	5.50	5.58
$(n\text{-}C_4H_9)_2BS(n\text{-}C_4H_9)$	78/3 mm.	0.8318	5.14	5.42

c) Quantitative analysis of boron was carried out by Synder's method[5].

Dialkylthioboronate is a colorless liquid having an unpleasant odor and is oxidized slowly in air. It seems, however, to be stable in cold water.

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[5] H. R. Synder, J. A. Kuck and J. R. Johnson, ibid., **60**, 110 (1938).