



**Table I. Yields of Diisopropyl (Dichloromethyl)boronate (3a) from Addition of Lithium Diisopropylamide to Triisopropyl Borate and Dichloromethane at Various Temperatures**

solvent	temp, °C	yield, % <sup>b</sup>
THF	-78	55 <sup>c</sup>
THF	0	52
THF	9	33
THF	20	≤1
ether <sup>d</sup>	0	37

<sup>a</sup> Internal temperature except -78 °C, which is bath temperature. <sup>b</sup> Isolated, except the 1% figure, which is an NMR estimate. <sup>c</sup> A revised workup, not otherwise tested, led to 70% isolated yield. <sup>d</sup> In this run only, technical triisopropyl borate containing a few percent of 2-propanol was used. Pure triisopropyl borate in ether at -78 °C failed.

base. The reaction was run in an ice/salt bath (0 °C internal temperature), and the diethylamine (bp 55 °C at 760 torr) and THF were removed by vacuum distillation below room temperature. Diethyl ether was added to the residue of lithium triisopropoxy(dichloromethyl)borate, which was then acidified, and 3a was isolated by simple distillation (~69%). We have found that distillation of crude reaction mixtures at too high a temperature can result in decomposition of dihaloboronic esters, and a rapid distillation below 1 torr into a cold trap was therefore used prior to simple distillation at 5 torr. Simple distillation to remove the last few percent of triisopropyl borate (forerun) from 3a results in some loss of 3a, but we did not test fractional distillation for this purpose.

**(Diiodomethyl)boronate.** We obtained only a trace of diisopropyl (dibromomethyl)boronate by substituting dibromomethane for dichloromethane in the original procedure. However, it proved a simple matter to prepare *d,l/meso*-2,3-butanediol (diiodomethyl)boronate by treating the (dichloromethyl)boronate with sodium iodide in acetone.

**(1,1-Dichloroethyl)boronates.** 1,1-(Dichloroethyl)-lithium (1b) has been generated from 1,1-dichloroethane and lithium dialkylamides or from 1,1,1-trichloroethane and alkyllithiums.<sup>10,11</sup> It might be anticipated that yields would be low, if only because  $\beta$ -elimination of hydrogen chloride is plausible, and the literature does not contradict such pessimism. With preformed 1b and trimethyl borate, we obtained ~30% yield of dimethyl (1,1-dichloroethyl)boronate, which is poor even considering possible losses in solvent stripping. The reaction failed altogether if the internal temperature of the reaction mixture was not monitored and kept below -100 °C during addition of the 1,1-dichloroethane to the *sec*-butyllithium.

In contrast, treatment of a mixture of 1,1-dichloroethane and trimethyl borate in THF at -78 °C with lithium diisopropylamide followed by acidification efficiently yielded dimethyl (1,1-dichloroethyl)boronate (3b): 55% when the solvent was stripped; 79% when proper fractional distillation was used.

Triisopropyl borate gave only a low yield of (1,1-dichloroethyl)boronate, as if the extra steric hindrance slowed capture of the (1,1-dichloroethyl)lithium sufficiently to give it time to decompose.

**Conclusion.** The addition of lithium diisopropylamide or diethylamide to a mixture of dichloromethane and triisopropyl borate in THF at temperatures as high as 0

°C provides a useful synthesis of diisopropyl (dichloromethyl)boronate which is much easier to scale up than the previously described preparation of (dichloromethyl)lithium at -100 °C followed by addition of the trialkyl borate. Similarly, dimethyl (1,1-dichloroethyl)boronate is efficiently prepared by addition of lithium diisopropylamide to 1,1-dichloroethane and trimethyl borate in THF at -78 °C.

### Experimental Section

**General Data.** Tetrahydrofuran (THF) was Aldrich gold label and was used directly. Reactions were run under argon. Triisopropyl borate was used as purchased from Aldrich Chemical Co., trimethyl borate was from Callery Chemical Co., diethylamine was distilled from sodium, and diisopropylamine and other reagent grade chemicals were used as supplied.

**Diisopropyl (Dichloromethyl)boronate (3a). Method A (LDA, -78 °C).** *n*-Butyllithium (64 mL of 1.56 M, 0.1 mol) was added dropwise to 17 mL (0.12 mol) of diisopropylamine in 200 mL of THF cooled in a dry ice/acetone bath. The resulting cold solution of lithium diisopropylamide (LDA) was transferred with slight argon pressure through a cannula dropwise to a solution of 25.4 mL (0.11 mol) of triisopropyl borate and 40 mL (0.55 mol) of dichloromethane in 200 mL of THF in a 1-L three-neck flask equipped with a Teflon paddle stirrer and cooled with a dry ice/acetone bath. The mixture was stirred at -78 °C for 15 min, and then gaseous hydrogen chloride was bubbled into the cooled, stirred mixture until the methyl orange endpoint was reached. A thick slurry of diisopropylamine hydrochloride forms during this acidification and may be thinned with diethyl ether if necessary. The mixture was filtered (suction), the solid was washed thoroughly with several portions of ether, and the solvents were distilled from the combined filtrate through a 30-cm column packed with glass helices, with the distillation temperature kept below 45 °C by application of vacuum as necessary. The residue of diisopropyl (dichloromethyl)boronate (3a) was distilled: bp 50–52 °C (5 torr); 14.9 g (70%); NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  1.23 (d, 12, CH<sub>3</sub>), 4.63 (m, 2, Me<sub>2</sub>CH), 5.29 (s, 1, CHCl<sub>2</sub>).

**3a. Method B (LDA, 0 °C).** The foregoing procedure was followed except that 0.5 mol of LDA was prepared in 500 mL of THF at 0 to -5 °C and added dropwise to a stirred solution of 127 mL (0.55 mol) of triisopropyl borate and 320 mL (5 mol) of dichloromethane in 500 mL of THF in a 2-L three-neck flask maintained at an internal temperature of 0 °C with a cooling bath at -5 °C over a period of ~30 min. The mixture darkened only slightly to yellow-brown, indicating insignificant decomposition of the unstable intermediate (dichloromethyl)lithium (1a). Workup was similar to that described in method A, except that the filtered salts were washed with THF and the filtrate was concentrated with a rotary evaporator, evidently with some loss of product. (All of the data in Table I are based on this type of workup, with reactions usually run on a 0.1-mol scale.) Distillation yielded a small forerun of triisopropyl borate followed by 55 g (52%) of diisopropyl (dichloromethyl)boronate (3a): bp 50–52 °C (5 torr), which contained ~3% triisopropyl borate as the only evident impurity by NMR analysis.

**3a. Method C (Lithium Diethylamide, 0 °C).** Lithium diethylamide was prepared from 7.50 g (0.103 mol) of diethylamine and 77 mL (0.10 mol) of 1.30 M butyllithium in hexane plus 25 mL of THF to prevent precipitation at 0 °C. A solution of 10 mL (0.156 mol) of dichloromethane and 19.3 g (0.105 mol) of triisopropyl borate in 80 mL of THF was cooled to -5 °C with an ice/salt bath, and the cold lithium diethylamide solution was dropwise to the stirred solution slowly enough that the internal temperature remained at 0 to +5 °C. The cooling bath was left in place during distillation of the solvents at pressures down to 0.1 torr into a -78 °C trap. The residue of borate salts was treated with 100 mL of diethyl ether followed by gaseous hydrogen chloride. The brown color of the precipitate obscured the methyl orange endpoint, and excess hydrogen chloride was used. The precipitate (mostly lithium chloride) was filtered and washed with ~30 mL more ether, and the combined ether solutions were concentrated. Rapid distillation below room temperature into a -78 °C trap was followed by simple redistillation: bp 42–56 °C (5 torr); 16.1 g estimated by NMR to contain 91% 3a (14.7 g, 69%)

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with the remainder triisopropyl borate.

**Dimethyl (1,1-Dichloroethyl)boronate (3b).** A solution of 285 mmol of LDA in 300 mL of THF prepared as described in the preceding paragraph was cooled with a dry ice/acetone bath ( $-78^{\circ}\text{C}$ ) and added dropwise through a cannula over a period of 1 h to a stirred solution of 25 mL (0.3 mol) of 1,1-dichloroethane and 30 mL (0.265 mol) of trimethyl borate in 300 mL of THF in a 2-L three-neck flask cooled with dry ice/acetone. The mixture was allowed to warm to  $-50^{\circ}\text{C}$ , then cooled again to  $-78^{\circ}\text{C}$ , and treated with gaseous hydrogen chloride to the methyl orange endpoint. The slurry became too thick for efficient stirring and was diluted with sufficient diethyl ether to fluidize it. Filtration, washing the salts with ether, and distillation of the solvents through a packed column was carried out as described in part A of the preceding paragraph. The residue of dimethyl (1,1-dichloroethyl)boronate (**3b**) was distilled; 26.8 g (79%). It is essential that overheating of this compound ( $\sim 100^{\circ}\text{C}$ ) be avoided in order to prevent loss of hydrogen chloride and polymerization. NMR (90 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.08 (s, 3,  $\text{CCH}_3$ ), 3.79 (s, 6,  $\text{OCH}_3$ ). Anal. Calcd for  $\text{C}_4\text{H}_9\text{BCl}_2\text{O}_2$ : C, 28.12; H, 5.31; B, 6.33; Cl, 41.51. Found: C, 27.80; H, 5.15; B, 6.36; Cl, 41.49.

**Dimethyl (1,1-Dichloroethyl)boronate (3b) from Preformed (1,1-Dichloroethyl)lithium.** A solution of 42 mL (0.5 mol) of 1,1-dichloroethane in 300 mL of ether and 300 mL of THF was cooled to  $-110^{\circ}\text{C}$  (internal temperature), and a solution of 0.53 mol of *sec*-butyllithium in cyclohexane was added dropwise slowly enough that the internal temperature of the reaction mixture remained below  $-100^{\circ}\text{C}$ . The mixture was allowed to warm to  $-90^{\circ}\text{C}$ , stirred 1 h, and then cooled to  $-110^{\circ}\text{C}$ . A tan slurry of (1,1-dichloroethyl)lithium resulted. A solution of 66 mL (0.58 mol) of trimethyl borate was added dropwise, maintaining the temperature below  $-100^{\circ}\text{C}$ , and the mixture was then allowed

to warm to  $-50^{\circ}\text{C}$ . The mixture was then cooled with a  $-78^{\circ}\text{C}$  bath, and gaseous hydrogens chloride was bubbled into the mixture to the methyl orange endpoint. The mixture was allowed to warm to room temperature and concentrated on a rotary evaporator. The product was distilled rapidly under high vacuum into a  $-78^{\circ}\text{C}$  trap and then redistilled; bp  $48^{\circ}\text{C}$  (40 torr); 25.6 g (30%).

**2,3-Butanediol (Diiodomethyl)boronate.** Diisopropyl (dichloromethyl)boronate (**3a**) was transesterified with *d,l*/*meso*-2,3-butanediol as previously described for the *R,R* isomer.<sup>3</sup> Addition of 0.785 mL (5 mmol) of the resulting butanediol (dichloromethyl)boronate to a solution of 1.65 g (11 mmol) of sodium iodide in 15 mL of acetone, stirring 1 h at  $20$ – $25^{\circ}\text{C}$ , concentration, separation of the organic product from the sodium iodide with the aid of petroleum ether, and again concentrating yielded 1.68 g (92%) of butanediol (diiodomethyl)boronate as an oil, which was crystallized from petroleum ether; mp  $30$ – $31^{\circ}\text{C}$ . The *d,l*/*meso* ratio as estimated by proton NMR was originally  $\sim 88/12$  and shifted to  $\sim 82/18$  after three recrystallizations. NMR (90 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.35 (d, 6,  $\text{CH}_3$ ), 4.18 (m, 1.6, *d,l*-OCH), 4.35 (s, 1,  $\text{CHI}_2$ ), 4.72 (m, 0.4, *meso*-OCH). Anal. Calcd for  $\text{C}_5\text{H}_9\text{BI}_2\text{O}_2$ : C, 16.42; H, 2.48; B, 2.96; I, 69.39. Found: C, 16.35; H, 2.56; B, 3.12; I, 69.09.

**Acknowledgment.** We thank the National Science Foundation for Grant CHE8400715.

**Registry No.** **3a**, 62260-99-5; **3b**, 101772-81-0; triisopropyl borate, 5419-55-6; dichloromethane, 75-09-2; 1,1-dichloroethane, 75-34-3; trimethyl borate, 121-43-7; *d,l*-2,3-butanediol (diiodomethyl)boronate, 101772-82-1; *meso*-2,3-butanediol (diiodomethyl)boronate, 101772-83-2; *d,l*-2,3-butanediol, 6982-25-8; *meso*-2,3-butanediol, 5341-95-7.

## Comparative Trapping Kinetics of Silylene. 1. Silylene Reactions with 1,3-Butadiene and Acetylene and with 1,3-Butadiene and Methanol

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Received October 23, 1985

Relative rate studies of silylene trapping by butadiene, methanol, and acetylene are reported. For the reactions:  $\text{SiH}_2 + \text{H}_2\text{C}=\text{CHC}(\text{H})=\text{CH}_2 \xrightarrow{2} \text{CH}_2\text{C}(\text{H})=\text{CHCH}_2\text{SiH}_2$  vs.  $\text{SiH}_2 + \text{CH}_3\text{OH} \xrightarrow{1} \text{CH}_3\text{OSiH}_3$ ,  $\ln(k_3/k_7) = (5.91 \pm 0.91) - (5846 \pm 1540) \text{ cal}/RT$  ( $696$ – $1016 \text{ K}$ ), and reaction 3 vs.  $\text{SiH}_2 + \text{HC}\equiv\text{CH} \xrightarrow{6} \text{HC}\equiv\text{CSiH}_3$ ,  $\ln(k_3/k_6) = (1.51 \pm 0.32) - (712 \pm 520) \text{ cal}/RT$  ( $603$ – $102 \text{ K}$ ). Relative rates, extrapolated to room temperature, are favorably compared to existing absolute rate constant measurements. On the basis of estimated Arrhenius parameters for the reaction 7, tentative absolute Arrhenius parameters with temperature dependencies for a number of silylene-substrate reactions are calculated.

### Introduction

1,3-Butadiene and other 1,3-dienes are known to be efficient trapping agents for both silylenes<sup>1</sup> and disilenes.<sup>2,3</sup> The former reaction is complex in that the initial addition of the silylene has been shown to be 1,2 to form an allylsilacyclopropane.<sup>4</sup> Allylic resonance assisted openings of this ring followed by 5-membered ring closing of the intermediate biradicals produces silacyclopentene trapping

products. This is illustrated for silylene and 1,3-butadiene in Scheme I. [The minor product (sila-2-cyclopentene) has not been reported for this exact reaction, but is a product in a number of other 1,3-diene trapping reactions.]

Silacyclopentenenes are thermally stable products: hence 1,3-dienes are often the silylene trapping agents of choice for quenching studies of organosilicon compound reactions at elevated temperatures.

Dienes are also used as trapping agents for disilenes and silenes. These reactions are probably concerted Diels-Alder processes as shown in Scheme II.

Unfortunately little kinetic data, either absolute or comparative, are available for these reactions. Thus to our knowledge, only one absolute rate measurement has been reported for a silylene-1,3-diene reaction:<sup>5</sup>  $\text{PhMeSi:}$  reacts

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