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The Reaction of Copper(I) Methyltrialkylborates with Allylic Halides or 2-Propynylic Halides

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Synopsis. The reactions between copper(I) methyltrialkylborates (readily obtainable from organoboranes) and allylic halides or 2-propynylic halides were found to give corresponding alkylation products. These reactions provide novel synthetic routes to 1-alkenes or 1,2-alkadienes from organoboranes.

Recently we have reported that lithium methyltrialkylborate readily undergoes a cation exchange reaction by copper(I) halide to give copper(I) methyltrialkylborate (**1**), which successfully reacts with acrylonitrile, ethyl acrylate, 1-acyl-2-vinylcyclopropane,[1] benzylic bromides,[2] and aroyl chlorides.[3]

In an attempt to develop reaction of such borate complexes, we examined the possibility of alkylation reactions of 2-propenylic halides and 2-propynylic halides. No reaction occurs between allyl bromide and lithium methyltrialkylborates at room temperature, whereas when copper(I) borates (**1**) are used instead of lithium borates, the reaction proceeds smoothly to give corresponding products as shown in Eqs. 1. and 2.

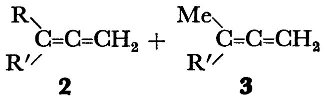
$$R_3B + MeLi \longrightarrow [R_3BMe]Li \xrightarrow{CuX} \underset{\mathbf{1}}{[R_3BMe]Cu} + LiX \qquad (1)$$

$$\mathbf{1} + CH_2{=}CHCH_2X' \longrightarrow RCH_2CH{=}CH_2 + R_2BMe + CuX' \qquad (2)$$

The yields of alkylation products are dependent upon the copper(I) halides and allyl halides employed, as revealed in the case of copper(I) methyltrihexylborate in Table 1. In general, allyl chloride gives good yields of products. This reaction is applicable to representative organoboranes and 2-propenylic chlorides. The reaction appears to proceed through an allylic rearrangement as the main path, judging from the results obtained in the reaction of copper(I) methyltripropylborate with cinnamyl chloride, and it was noted that the attack of the methyl group in the borate complex may not be involved.

In the same way, copper(I) methyltrialkylborates react with 2-propynylic halides to give corresponding 1,2-alkadienes (Eq. 3). Some of the representative results are summarized in Table 1. Although the latter reaction provides a convenient synthetic procedure of 1,2-alkadienes from organoboranes, the formation of undesirable products (**3**) by the attack of methyl groups in borates reduces yields of desired products (**2**).

$$\mathbf{1} + R'\text{-}C{\equiv}C\text{-}CH_2Br \longrightarrow$$



$$\underset{\mathbf{2}}{(R)(R')C{=}C{=}CH_2} + \underset{\mathbf{3}}{(Me)(R')C{=}C{=}CH_2} \qquad (3)$$

It is becoming increasingly evident that copper(I) methyltrialkylborates have a considerably high utility in organic synthesis. The applicability of this new alkylating agent to coupling and addition reactions is under further investigation.

Experimental

Materials. All copper(I) halides, allylic halides, and

TABLE 1. REACTION OF COPPER(I) METHYLTRIALKYLBORATES WITH ALLYLIC HALIDES AND 2-PROPYNYLIC HALIDES[a)]

R_3B	CuX	Allylic or 2-propynylic halide	Product	Yield[b)] %
Hexyl	CuI	$CH_2{=}CHCH_2Br$	1-Nonene	53
	CuBr			42
	CuCl			47
	CuCN			49
	CuBr	$CH_2{=}CHCH_2Cl$		82
Octyl	CuBr		1-Undecene	87
5-Chloropentyl	CuBr		8-Chloro-1-octene	91
Propyl	CuBr	$PhCH{=}CHCH_2Cl$	$PhCH(Pr)\text{-}CH{=}CH_2$	96
			$PhCH{=}CHCH_2Pr$	trace
Pentyl	CuBr	$HC{\equiv}CCH_2Cl$	1,2-Octadiene	32
		$HC{\equiv}CCH_2Br$		54
Octyl			1,2-Undecadiene	53
Butyl		$PhC{\equiv}CCH_2Br$	3-Phenyl-1,2-heptadiene	31
			3-Phenyl-1,2-butadiene	59

a) Reactions were carried out for 2 h by using a 20% excess of borate complexes at room temperature. b) Based on 2-propenylic or 2-propynylic halides employed.

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2-propynylic halides are commercially available. The organic compounds used in the experiments were purified by distillation before use. Trialkylboranes were prepared by the usual procedure.[5)]

The IR and NMR spectra were taken on a Hitachi-Perkin-Elmer Model 125 spectrophotometer and a Hitachi R-22 spectrometer at 90 MHz using tetramethylsilane as the internal standard, respectively.

General Procedure. The following procedure for the preparation of 8-chloro-1-octene is representative. A dry 50 ml-flask was charged under dry nitrogen atmosphere with 1.72 g (12 mmol) of copper(I) bromide and 6 ml of dry tetrahydrofuran. To this mixture was added lithium methyltris(5-chloropentyl)borate[2,4)] (12 mmol in THF) at 0 °C, and the mixture was stirred for 5 min. Then allyl chloride (0.815 ml, 10 mmol) was gradually added and the mixture was stirred for further 2 h at room temperature. The residual organoborane was oxidized with 5.4 ml of 3 M NaOH and 5.4 ml of 30% H_2O_2 at room temperature for 2 h. The product was extracted with ether. The combined extract was washed with water and then dried over anhydrous sodium sulfate. The ether solution thus obtained was analyzed by VPC, revealing the formation of 8-chloro-1-octene (9.1 mmol, 91%). An analytically pure sample was obtained by preparative VPC with Varian autoprep Model-2800.

Identification of the Products. 1-Nonene and 1-undecene were identified by direct comparison with authentic samples which were commercially available from Tokyo Kasei Kogyo Co., Ltd. 1,2-Octadiene and 1,2-undecadiene were characterized by comparison with samples prepared by the methods reported by Meisters[6)] and Moore,[7)] respectively.

8-Chloro-1-octene: n_D^{24} 1.4508. Found: C, 65.31; H, 10.15%. Calcd for $C_8H_{15}Cl$: C, 65.52; H, 10.31%. Mass; m/e=146, 148 (M^+). IR (neat): 3055, 1630, 910 cm^{-1}. NMR (CCl_4); τ, 8.6 (8H, s), 7.99 (2H, t, J=7.0 Hz), 6.51 (2H, t, J=6.5 Hz), 4.85—5.15 (2H, m), 4.0—4.45 (1H, m).

3-Phenyl-1-hexene: n_D^{24} 1.4999. Found: C, 89.75; H, 9.91%. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06%. Mass: m/e=158 (M^+). IR (neat): 1630, 1600, 915 cm^{-1}. NMR (CCl_4); τ, 9.10 (3H, t, J=6.3 Hz), 8.50—8.95 (2H, m), 8.15—8.45 (2H, m), 6.78 (1H, q), 4.90—5.15 (2H, m), 3.85—4.25 (1H, m), 2.82 (5H, s).

3-Phenyl-1,2-heptadiene: n_D^{24} 1.5637. Found: C, 90.77; H, 9.42%. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36%. Mass: m/e=172 (M^+). IR (neat): 1945, 1600, 1496, 695 cm^{-1}. NMR (CCl_4): τ, 9.05 (3H, t, J=6.5 Hz), 8.3—8.8 (4H, m), 7.40—7.70 (2H, m), 4.96 (2H, m). 2.5—2.9 (5H, m).

3-Phenyl-1,2-butadiene: n_D^{24} 1.5612. Found: C, 92.35; H, 7.68%. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74%. Mass; m/e=130 (M^+). IR (neat): 1945; 1600, 1500, 965, 695 cm^{-1}. NMR (CCl_4): τ, 7.93 (3H, t, J=2.6 Hz), 4.90—5.50 (2H, m), 2.55—2.90 (5H, m).

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