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Addition Reaction of Copper(I) Methyltrialkylborates with Ethyl Propiolate. Stereospecific Synthesis of (*E*)-α,β-Unsaturated Acid Esters

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Synopsis. The reaction between ethyl propiolate and copper(I) methyltrialkylborates was found to give the corresponding addition products which are converted by hydrolysis into the α,β-unsaturated acid esters in relatively good yields. The α,β-unsaturated esters thus obtained are selectively *E*-isomers.

Previously, we have reported that copper(I) methyltrialkylborates readily available by the reaction between lithium methyltrialkylborates and copper(I) halides undergo addition reactions to acrylonitrile, ethyl acrylate, and 1-acyl-2-vinylcyclopropanes.[1] These borates also react with alkyl halides such as benzylic,[2] allylic and propargylic halides,[3] and aroyl halides.[4] In the present paper, we wish to report the stereospecific synthesis of (*E*)-α,β-unsaturated carboxylic esters *via* the reaction of copper(I) methyltrialkylborates with ethyl propiolate.

No reaction occurs between ethyl propiolate and lithium methyltrialkylborates at room temperature. However, when copper(I) methyltrialkylborates prepared from lithium methyltrialkylborates and copper(I) halides are used, the reaction proceeds smoothly to give α,β-unsaturated esters together with ethyl 2-butenoate (Eqs. 1 and 2).

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

$$\mathrm{[R_3BMe]Cu + HC{\equiv}C\text{-}CO_2Et \longrightarrow RCH{=}CHCO_2Et + CH_3CH{=}CHCO_2Et} \qquad (2)$$

When copper(I) methyltripropylborate obtained from copper(I) bromide and lithium methyltripropylborate was treated with ethyl propiolate at 0 °C in tetrahydrofuran under nitrogen atmosphere, ethyl (*E*)-2-butenoate, ethyl (*E*)-2-hexenoate, and ethyl (*Z*)-2-hexenoate were formed in 32, 37, and 2% yields, respectively. Ethyl 2-butenoate, an undesirable by-product, is considered to be formed by the addition of methyl group of the methyltripropylborate as an alkylating group. It was found that yields and product ratios of the *E*-isomer depend markedly on the copper(I) halides and solvents employed. The reaction using copper(I) iodide as a halide and 1,2-dimethoxyethane (DME) as a solvent was effective for the prevention of formation of a by-product. Under such reaction conditions, the desired (*E*)-α,β-unsaturated acid esters were obtained in good yields from representative organoboranes. The results are summarized in Table 1. The new reaction is applicable to representative primary trialkylboranes such as propyl, butyl, isobutyl, and hexylboranes. Although the reaction mechanism is still unknown, the formation of (*E*)-α,β-unsaturated acid esters as main products seems to suggest that the reaction proceeds through the *cis*-addition process.[5]

TABLE 1. (*E*)-α, β-UNSATURATED ACID ESTERS FROM COPPER(I) METHYLTRIALKYLBORATES AND ETHYL PROPIOLATE[a)]

Organo-borane R_3B, R=	CuX X=	Sol-vent	Reac-tion time (h)	Yield of products (%)[b)]	
				$MeCH{=}CHCO_2Et$	$RCH{=}CHCO_2Et$ (Ratio of *E*-isomer, %)
Propyl	Br	THF	0.5	32	39 (95)
	I	THF	0.5	36	36 (97)
	Br	DME	0.5	18	44 (98)
	Cl	DME	0.5	19	32 (94)
	I	DME	0.5	5	63 (>99)
Butyl	I	DME	0.5	—	61 (>99)
Isobutyl	I	DME	0.5	—	53 (99)
Hexyl	I	DME	1.0	—	42 (98)

a) All the reactions were carried out by using 20% excess borate complexes. b) Based on ethyl propiolate used. Analyzed by VPC.

The preparation of α,β-unsaturated esters from ethyl propiolate and dialkylboranes was reported by Negishi *et al.*[6] The present reaction, however, provides a more general synthetic method for (*E*)-α,β-unsaturated acid esters from organoboranes.

Experimental

Materials. Commercial copper(I) halides and ethyl propiolate were used. The solvents were purified by distillation before use. Trialkylboranes were prepared by the usual procedure.[7]

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 an internal standard.

General Procedure. The following procedure for the preparation of ethyl (*E*)-2-hexenoate is representative. A dry 100 ml-flask equipped with a septum inlet and a magnetic stirring bar was flushed with dry nitrogen. The flask was charged with copper(I) iodide (4.68 g, 24 mmol) and dry DME (40 ml). Lithium methyltripropylborate[2] (24 mmol, prepared from equimolar amount of tripropylborane in THF and methyllithium in ether) was added to the solution at 0 °C with stirring. After 5 min, ethyl propiolate (1.9 ml, 20 mmol) was added and the reaction mixture was stirred at 0 °C for 30 min. The residual organoborane was then oxidized with 3 M-aqueous sodium hydroxide (8 ml) and 30% hydrogen peroxide (8 ml) at room temperature for 2 h. The products were extracted with ether and analyzed by VPC. Analysis indicated the presence of 12.6 mmol (63%) of ethyl (*E*)-2-hexenoate and 1.0 mmol (5%) of ethyl (*E*)-2-butenoate. Analytically pure materials were obtained by preparative

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VPC. (15% SE-30 on Uniport B, 1.2 m) with Varian autoprep Model-2800.

Identification of the Products. *Ethyl (*E*)-2-Hexenoate*: n_D^{23} 1.4371. Found: C, 67.48; H, 9.78%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93%. Mass: m/e=142 (M^+). IR (CCl_4); 1720, 1650, 985 cm^{-1}. NMR (CCl_4); τ, 9.02 (3H, t, J=7.0 Hz), 8.71 (3H, t, J=7.0 Hz), 8.47 (2H, m), 7.80 (2H, q), 5.84 (2H, q), 4.20 (1H, d, J_{vinyl}=16.0 Hz), 3.08 (1H, dt, J=7.0 and 7.0 Hz).

*Ethyl (*E*)-2-Heptenoate*: n_D^{23} 1.4393 (lit,[8] n_D^{25} 1.4355). Found: C, 69.36; H, 10.38%. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32%. Mass; m/e=156 (M^+). IR (CCl_4); 1720, 1650, 985 cm^{-1}. NMR (CCl_4); τ, 9.06 (3H, t, J=7.0 Hz), 8.75 (3H, t, J=7.0 Hz), 8.57 (4H, m), 7.78 (2H, q), 5.87 (2H, q), 4.23 (1H, d, J_{vinyl}=16.0 Hz), 3.10 (1H, dt, J=7.0 and 7.0 Hz).

*Ethyl (*E*)-5-Methyl-2-hexenoate*: n_D^{21} 1.4362. Found: C, 69.07; H, 10.29%. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32%. Mass; m/e=156 (M^+). IR (CCl_4); 1725, 1655, 990 cm^{-1}. NMR (CCl_4); τ, 9.03 (6H, d, J=6.5 Hz), 8.82 (3H, t, J=7.0 Hz), 8.21 (1H, m), 7.93 (2H, t, J=7.0 Hz), 5.86 (2H, q), 4.25 (1H, d, J_{vinyl}=16.0 Hz), 3.16 (1H, dt, J=7.0 and 7.0 Hz).

*Ethyl (*E*)-2-Nonenoate*: n_D^{22} 1.4417. Found: C, 71.50; H, 11.07%. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94%. Mass; m/e=184 (M^+). IR (CCl_4); 1725, 1655, 985 cm^{-1}. NMR (CCl_4); τ, 9.09 (3H, t, J=6.0 Hz), 8.72 (3H, t, J=6.0 Hz), 8.64 (8H, s), 7.79 (2H, q), 5.86 (2H, q), 4.43 (1H, d, J_{vinyl}=16.0 Hz), 3.10 (1H, dt, J=6.5 and 6.5 Hz).

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