

THE REACTION OF COPPER(I) METHYLTRIALKYLBORATES WITH ETHYL β -BROMOACRYLATES. STEREOSPECIFIC SYNTHESSES OF (E)- AND (Z)- α,β -UNSATURATED ACID ESTERS FROM ORGANOBORANES

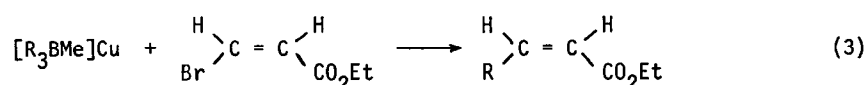
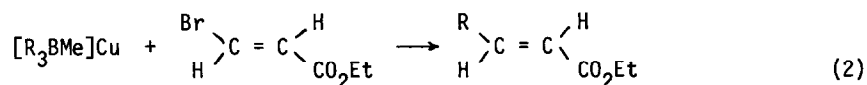
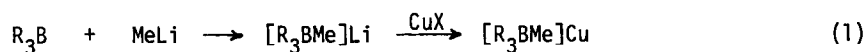
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Recently, we have reported that lithium methyltrialkylborates readily undergo cation exchange reactions by copper(I) halides to give copper(I) methyltrialkylborates (eq. 1), which in turn successfully react with acrylonitrile, ethyl acrylate, 1-acyl-2-vinylcyclopropane,¹ benzylic bromides,² allylic chlorides, propargylic bromides,³ and aroyl chlorides.⁴ In an attempt to explore the possibility of utilizing the reaction of such borates, we examined the synthesis of α,β -unsaturated carboxylic esters via the reaction with ethyl β -bromoacrylates.

An addition of a solution of ethyl (E)- β -bromoacrylate in tetrahydrofuran to a solution of the copper(I) methyltripropylborate obtained from lithium methyltripropylborate and copper(I) iodide at 0°C resulted in a gradual formation of a dark solution. After the reaction was completed, the residual organoborane was oxidized under the usual conditions. Gipc analysis showed the formation of ethyl (E)-2-hexenoate in a yield of 80% (eq. 2). The yields of ethyl



2-hexenoate are highly dependent upon the copper(I) halides employed, as shown in Table 1. When copper(I) iodide was used, it was found that the most favorable result is obtained. This new reaction is applicable to representative primary trialkylboranes, including organoboranes with functionalized alkyl group such as tris(10-carbomethoxydodecyl)borane.⁵ The α,β -unsaturated esters thus obtained from ethyl (E)- β -bromoacrylate are selectively E-isomers.

On the other hand, the (Z)- β -alkylacrylate is selectively produced from the corresponding (Z)- β -bromoacrylate (eq. 3). In Table 2, we showed such an example in the reaction of ethyl β -bromoacrylates with copper(I) methyltripropylborate to give corresponding ethyl 2-hexenoates. Although the reaction mechanism is still unknown, this evidence seems to suggest that the reaction proceeds through the cis-addition and trans-elimination process.

The following procedure for the preparation of ethyl (E)-2-heptenoate is representative. A dry 25 ml-flask was charged under nitrogen atmosphere with 1.425 g (7.5 mmol) of copper(I) iodide and 5 ml of anhydrous THF. To this solution was added lithium methyltributylborate (7.5 mmol in THF) at 0°C, and reacted for 5 min. Then ethyl (E)- β -bromoacrylate (0.895 g, 5 mmol)

Table 1. Synthesis of α,β -Unsaturated Acid Esters by the Reaction of Copper(I) Methyltrialkylborates with Ethyl (E)- β -Bromoacrylate

Organoborane R_3B , R=	CuX	Product	Yield ^a (E:Z) %
n-Propyl	CuCl	Ethyl 2-hexenoate	42 (100 : 0)
	CuBr		60 (100 : 0)
	CuI		80 (100 : 0)
n-Butyl	CuI	Ethyl 2-heptenoate	98 (100 : 0)
iso-Butyl	CuI	Ethyl 5-methyl-2-hexenoate	65 (100 : 0)
n-Octyl	CuI	Ethyl 2-undecenoate	81 (100 : 0)
$MeO_2C-(CH_2)_{10}$	CuI	Ethyl 13-carbomethoxy-2-tridecenoate	55 (100 : 0)

a) Based on ethyl β -bromoacrylate used.

Table 2. Stereoselectivity of the Reaction of Copper(I) Methyltripropylborate with Ethyl β -Bromoacrylate

Organoborane R_3B , R=	Ethyl β -bromoacrylate E : Z	Yield of ethyl 2-hexenoate ^a % (E : Z)
n-Propyl	100 : 0	96 (100 : 0)
	92 : 8	95 (90 : 10)
	43 : 57	95 (44 : 56)
	32 : 68	95 (34 : 66)
	14 : 86	95 (14 : 86)

a) Ethyl (E), and (Z)-2-hexenoate were readily separated by preparative glpc (20%-Silicone SE-30 on Uniport-B, 2m) and characterized by nmr, ir, and mass spectra, refractive index, and elemental analysis.

was gradually added and the reaction mixture was stirred for 2 h at 0°C. The residual organoborane was oxidized by alkaline hydrogen peroxide under the usual conditions. The product was extracted with ether, and the extracts thus obtained were analyzed by glpc, revealing the formation of ethyl (E)-2-heptenoate (4.9 mmol, 98%). An analytically pure sample was obtained by preparative glpc (20%-Silicone SE-30 on Uniport-B, 2 m), n_D^{23} 1.4382 (lit.⁶ n_D^{25} 1.4355).

Conjugate addition reactions of organocopper reagents to α,β -acetylenic esters are convenient methods for preparing the α,β -unsaturated acid esters.⁷ The present reaction, however, provides novel stereospecific synthetic procedures of (E), and (Z)- α,β -unsaturated acid esters from organoboranes.

References

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5. In this case, copper(I) methyltris(10-carbomethoxydodecyl)borate was prepared from methylcopper(I) and tris(10-carbomethoxydodecyl)borane in THF at 0°C.
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