Tetrahedron Letters No. 2, pp 173 - 174, 1977. Pergamon Press. Printed in Great Britain.

THE COUPLING REACTION OF COPPER(I) METHYLTRIALKYLBORATES WITH AROYL CHLORIDES. A CONVENIENT SYNTHESIS OF ALKYL ARYL KETONES FROM ORGANOBORANES

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(Received in Japan 18 November 1976; received in UK for publication 2 December 1976)

Recently, we have reported that copper(I) methyltrialkylborates readily undergo addition reactions to acrylonitrile, ethyl acrylate, and 1-acyl-2-vinylcyclopropane.[1] These reagents also react with relatively active halides such as benzyl,[2] allyl, and propargyl halides.[3] In an attempt to develop the reaction of such borates, we examined the possibility of a coupling reaction with aroyl chlorides.

To the solution of copper(I) methyltripropylborate obtained from lithium methyltripropylborate and copper(I) halides (eq. 1), benzoyl chloride was added at 0°C and stirred at room temperature. After the reaction was complete, the residual organoborane was oxidized under the usual conditions. G.l.c. analysis showed the formation of 1-phenyl-1-butanone with a small amount of 1-phenylethanone (eq. 2).

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

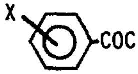
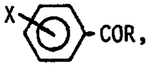
(2)

Yields of 1-phenyl-1-butanone and 1-phenylethanone remarkably depended on the copper(I) halides used, as shown in Table 1. When cyclooctadiene-copper(I) chloride complex[4] was used, the reactions proved far more favorable. The reaction is applicable to representative organoboranes and aroyl chlorides such as 4-methyl-, 4-chloro, and 2-chlorobenzoyl chlorides.

Although the reaction mechanism is still unknown, copper(I) ion seems to play an important role, because when lithium methyltrialkylborates were used under the same reaction conditions instead of corresponding copper(I) borates, satisfactory results could not be obtained. For example, treatment of lithium methyltripropylborates with benzoyl chloride provided 1-phenyl-1-butanone and 1-phenylethanone only in yields of 2% and 15%, respectively.[5]

The following procedure for the preparation of 1-phenyl-1-pentanone is representative. A dry 25 ml-flask was charged under nitrogen atmosphere with 2.45 g (12 mmol) of cyclooctadiene-copper chloride complex[4] and 12 ml of dry ethyl ether. To this solution was added lithium methyltri-n-butylborate[2] (12 mmol in THF) at 0°C, and stirred for 5 min. Then benzoyl chloride (1.25 ml, 10 mmol) was added, and the mixture was stirred for 2 h at room temperature. The residual organoborane was oxidized by alkaline hydrogen peroxide under the usual conditions. The product was extracted with ether, and the extract thus obtained was analyzed by g.l.c., revealing the formation of 1-phenyl-1-pentanone (10.2 mmol, 85%). Analytically pure sample was obtained by preparative g.l.c. (20%-Silicone SE-30 on Uniport-B, 2 m), n_D^{20} =1.5163 (lit.[6] n_D^{20} = 1.5150).

Table 1. Synthesis of Alkyl Aryl Ketones by the Reaction of Copper(I) Methyltrialkylborates with Aroyl Chlorides

Organoborane, R_3B, R =	CuX	Aroyl chloride	Product Yield[a], (%)	
		 , X=		
n-Propyl	CuCl	H	62	12
	CuBr	H	62	22
	CuI	H	36	12
	CuCN	H	53	26
	CuCl·COD	H	83	12
n-Butyl	CuCl·COD	H	85	
iso-Butyl	CuCl·COD	H	92	
n-Hexyl	CuCl·COD	H	45	
	CuBr	H	75	
n-Propyl	CuCl·COD	4-Me	81	
n-Propyl	CuCl·COD	4-Cl	90	
n-Propyl	CuCl·COD	2-Cl	80	

[a] Based on the aroyl chloride used.

Organic syntheses of alkyl aryl ketones by the use of organoboranes have been already reported by Brown et al.,[7] and Negishi et al..[5,8] We have also reported a synthetic procedure of such ketones via the reaction of organoboranes with α-azidostyrene, recently.[9] The present reaction, however, provides another synthetic method for alkyl aryl ketones by using readily available reagents and organoboranes under mild reaction conditions.

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5. Recently, it has been reported that lithium tetraalkylborates react smoothly with acyl halides to produce the corresponding ketones in high yields. For instance, the reaction of lithium tetra-n-butylborate with benzoyl chloride at 0°C for 1 h, and then at 40-45°C for 24 h, was reported to give 1-phenyl-1-pentanone in a yield of 80% [E. Negishi, K. W. Chiu, and T. Yoshida, J. Org. Chem., 40, 1676 (1975)].
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