The Reaction of Trialkylboron and α-Lithiobenzyl-2-pyridyl or Phenylsulfide. A Convenient Method for the Preparation of Alkylbenzenes

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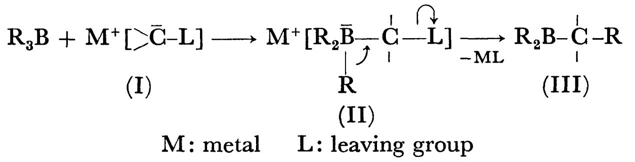
Recently it was shown[1] that benzyl-2-pyridylsulfide is easily metalated at −75°C in tetrahydrofuran by *n*-butyllithium or phenyllithium to give α-lithiobenzyl-2-pyridylsulfide, which in turn successfully reacts with various carbonyl compounds and halides.

Now we wish to report a new synthetic method for the preparation of alkylbenzenes by the use of the α-lithio derivatives of sulfides and trialkylborons.

It is well known[2] that trialkylboron reacts with the carbanion (I) to form the quaternary salt (II), in which subsequently one alkyl group migrates to a carbon atom from a boron atom to produce a new trialkylboron (III) accompanied with the elimination of ML as shown in Scheme 1.



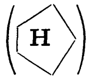
M: metal L: leaving group
Scheme 1

When the α-lithio derivative of benzyl-2-pyridylsufide or benzylphenylsulfide was treated at −75°C in tetrahydrofuran under argon atmosphere with tri-*n*-butylboron, the formation of the quaternary salt was observed. The salt was converted into two alkylbenzenes, *n*-amylbenzene and 1,2-diphenylhexane in 63% and 24% yields, respectively, after refluxing for 3 hr and alkaline hydrolysis. The products were identified on the basis of NMR spectra and gas chromatographical data.

In a similar way, various trialkylborons reacted with the α-lithio derivatives to give the corresponding alkylbenzenes. But tricyclohexyl and tricyclopentylboron failed to react with α-lithiobenzylphenylsulfide. The results are summarized in Table 1.

An undesirable by-product, diphenylethane derivative is considered to be formed by the further reaction of the new trialkylboron (III) and the α-lithio derivative.

Table 1. Yields of two alkylbenzenes

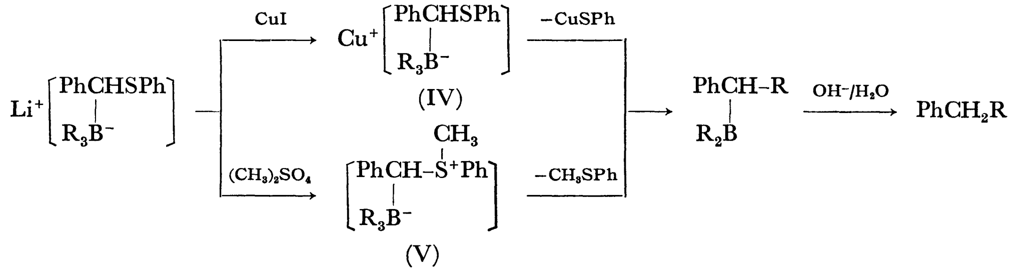
	Isolated yield %			
R_3B	$PhCH_2S$- 		$PhCH_2SPh$	
	$PhCH_2R$	$PhCH_2$-CHPhR	$PhCH_2R$	$PhCH_2$-CHPhR
$(n\text{-}C_4H_9)_3B$	63	24	71	16
$(n\text{-}C_6H_{13})_3B$	70	23	75	20
$(n\text{-}C_8H_{17})_3B$	73	trace	61	12
 $_3$B	85	0	0	0
 $_3$B	83	0	0	0

In order to minimize the formation of the by-products, the reactions were tried in the presence of the additives which would facilitate the elimination of the mercapto group from the quaternary salt.

It was found that the addition of cuprous iodide at −75°C or dimethylsulfate at room temperature was effective for the prevention of the formation of the by-products in the reaction between trialkylboron and α-lithiobenzylphenylsulfide. In each case, the desired alkylbenzene was obtained in good yield without accompanying the formation of the by-product. The results are summarized in Table 2. The reaction is considered to proceed involving cuprous quaternary salt (IV) or sulfonium betaine (V) as shown in Scheme 2.

Table 2. Yields of alkylbenzenes

R_3B	Isolated Yield % $PhCH_2R$	
	CuI	$(CH_3)_2SO_4$
$(n\text{-}C_4H_9)_3B$	92	78
$(n\text{-}C_6H_{13})_3B$	80	75
$(n\text{-}C_8H_{17})_3B$	69	63



Scheme 2

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[1] T. Mukaiyama, K. Narasaka, K. Maekawa, and M. Furusato, This Bulletin, **44**, 2285 (1971).

[2] J. J. Tufariello and L. T. Lee, *J. Amer. Chem. Soc.*, **88**, 4757 (1966); W. K. Musker and R. R. Stevens, *Tetrahedron Lett.*, **1967**, 995; J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 5936 (1968); H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **90**, 6218 (1968).