The Novel Synthesis of Alkyl Cyanides by the Reaction of Sodium Trialkylcyanoborate with Sodium Cyanide and Lead(IV) Acetate

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Sodium trialkylcyanoborates gave good yields of the corresponding alkyl cyanides in the reactions with sodium cyanide and lead(IV) acetate.

In studies on the combination of alkyl groups of trialkylboranes with the ligand of metal complexes,[1] the authors found that in the reaction of stoicheiometric amounts of sodium trialkylcyanoborate (prepared as in equation 1) and lead(IV) acetate in tetrahydrofuran (THF) a certain amount of alkyl cyanide was formed accompanied by a small amount of alkyl acetate. The presence of a large excess of sodium cyanide increased the yield of RCN and decreased the amount of ROAc markedly. The trialkylboranes derived from internal alkenes gave better results than those derived from terminal alkenes. However it was difficult to obtain >50% yields of RCN based on the alkenes employed, even in the case of tricyclohexylborane (the best result among the trialkylboranes examined).

$$R_3B \xrightarrow[20\,^{\circ}C,\,3\,h]{NaCN} [R_3\overset{-}{B}CN]Na^+ \xrightarrow[20\,^{\circ}C,\,5\,min]{NaCN} \xrightarrow[-20\,^{\circ}C,\,12\,h]{Pb(OAc)_4} RCN \qquad (1)$$

Fortunately, this situation was improved considerably by using 9-borabicyclo[3.3.1]nonane (9-BBN) as the hydroborating agent for alkenes, because the reactions of sodium cyanoborate complexes of 9-alkyl-9-BBN gave appreciable yields of RCN without any difficulty. Thus, cyclohexene,

Table 1. Synthesis of alkyl cyanides from sodium trialkylcyanoborates.[a]

R_3B of $R_3\bar{B}CN$	Product RCN[b]	Yield[c]
$(c\text{-}C_6H_{11})_3B$	$c\text{-}C_6H_{11}CN$	45
$(n\text{-}C_6H_{13})_3B$	$n\text{-}C_6H_{13}CN$	27
	$n\text{-}C_4H_9CH(Me)CN$	4
$(Me_2CHCHMe)_3B$	$Me_2CHCH(Me)CN$	40
9-$(c\text{-}C_6H_{11})$-9-BBN	$c\text{-}C_6H_{11}CN$	88
9-$(Me_2CHCHMe)$-9-BBN	$Me_2CHCH(Me)CN$	82
9-(2-norbornyl)-9-BBN	2-norbornyl cyanide	70

[a] The reactions were carried out using NaR_3BCN (20 mmol), NaCN (100 mmol), Pb^{IV} acetate (60 mmol), and THF (80 ml). [b] Isolated by column chromatography. [c] Based on alkenes employed.

2-methyl-2-butene, and norbornene were converted to the corresponding alkyl cyanides in 88, 82, and 70% yields respectively based on the alkenes employed. These experimental results are shown in Table 1.

In these reactions the formation of sodium trialkylcyanoborates before the reaction with $Pb(OAc)_4$ is necessary, otherwise the yields of RCN become negligible.

Although a few methods for the synthesis of alkyl cyanides using trialkylboranes have been reported, all of them are carbon–carbon bond formations of the alkyl group of trialkylboranes with such species as bromoacetonitrile,[2] diazoacetonitrile,[3] acetonitrile,[4] and acrylonitrile.[5] The present reaction is, to our knowledge, the first case in which an alkyl group of the trialkylboranes is directly combined with the cyano group. Moreover it is synthetically interesting that in the present reaction the secondary alkyl cyanides were obtained from the internal alkenes by a simple procedure and under mild reaction conditions, and they were easily isolated from the reaction mixtures.

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