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REACTIONS OF CUPROUS METHYLTRIALKYLBORATES OBTAINABLE FROM TRIALKYLBORANES WITH ACRYLONITRILE, ETHYL ACRYLATE AND 1-ACYL-2-VINYLCYCLOPROPANE CONVENIENT SYNTHESES OF NITRILES, CARBOXYLIC ESTERS AND γ,δ-UNSATURATED KETONES

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Previously, we have reported that organoboranes undergo a spontaneous 1,4-addition reaction in the presence of oxygen to numerous α,β-unsaturated carbonyl compounds including methyl vinyl ketone,[1] *acetylacetylene,*[2] *1,3-butadiene monoxide,*[3] *3,4-epoxy-1-butyne,*[4] *and crotonaldimine,*[5] and that these reactions proceed through a radical chain mechanism In an attempt to develope the reaction, we have also examined the possibility of such an addition reaction of organoboranes to acrylonitrile and ethyl acrylate which should provide convenient synthetic procedures of nitriles and carboxylic esters. It was, however, shown that neither acrylonitrile nor ethyl acrylate reacts with organoboranes under the usual conditions, because of polymerization of substrates, or because unstable intermediates initially formed undergo other reactions [6] In the present paper, we wish to report that when cuprous methyltrialkylborates readily obtainable from trialkylboranes are used as alkylating agents, this difficulty is overcome

Addition of a solution of lithium methyltrialkylborates prepared from trialkylboranes and methyllithium to cuprous halides in tetrahydrofuran at 0°C resulted in the immediate disappearance of precipitate and a clear solution was obtained Although we have not undertaken a detailed study of these complexes, cuprous methyltrialkylborates (II) are considered to be possibly formed via cation exchange reaction (eq 1) [7]

$$\mathrm{R_3B} \quad + \quad \mathrm{MeLi} \longrightarrow \underset{\text{I}}{[\mathrm{R_3BMe}]\mathrm{Li}} \xrightarrow{+\ \mathrm{CuX}} \underset{\text{II}}{[\mathrm{R_3BMe}]\mathrm{Cu}} \quad + \quad \mathrm{LiX} \qquad (1)$$

The reaction of acrylonitrile with cuprous methyltrialkylborates thus obtained, gave corresponding 1,4-adducts which were converted into alkyl cyanides in good yields by hydrolysis (eq 2)

$$[\mathrm{R_3BMe}]\mathrm{Cu} \quad + \quad \mathrm{CH_2{=}CH{-}CN} \longrightarrow \xrightarrow{+\ \mathrm{H_2O}} \mathrm{RCH_2CH_2{-}CN} \qquad (2)$$

Yields of nitriles were markedly depended on cuprous halides used For example, cuprous methyltri-n-propylborate prepared from cuprous iodide gave hexanenitrile in a yield of only 19% On the other hand, when such a complex formed from cuprous bromide instead of the iodide was used as an alkylating agent, hexanenitrile was obtained in a 84% yield In the reaction, as the amount of butanenitrile was negligibly small, attack of methyl group in the complex may not be involved.

The following procedure for the preparation of octanenitrile is representative A dry 25-ml flask equipped with a magnetic stirring bar, septum inlet and reflux condenser was flushed with nitrogen The flask was charged under nitrogen with 0 358 g (2 5 mmol) of anhydrous cuprous bromide and 2 ml of dry tetrahydrofuran Lithium methyltri-n-pentylborate (2 5 mmol) prepared from an equimolar amount of tri-n-pentylborane in tetrahydrofuran and methyllithium in ether, was added to the solution at 0°C, and stirred for 5 min To the mixture was then added 0 137 ml (2 08 mmol) of acrylonitrile The reaction mixture was stirred at room temperature for 2 hr Then the residual organoborane was oxidized by the addition of 3N aqueous sodium hydroxide (1 ml), followed by the dropwise addition of 30%-hydrogen peroxide (1 ml) The solution was stirred for 2 hr at room temperature, and the organic layer separated by saturation with potassium carbonate was analyzed by glpc Analysis indicated that 1 85 mmol (89%) of octanenitrile had been formed

The results of representative reactions are summarized in Table 1

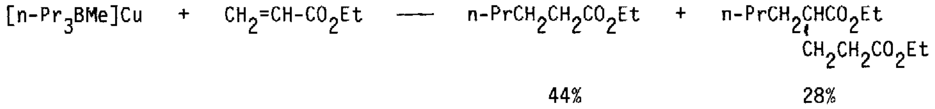
Table 1. Synthesis of Nitriles by the Reaction of Cuprous Methyltrialkylborates with Acrylonitrile

Organoborane R	CuX	Product[a]	Yield, %[b]
n-Propyl	CuI	Hexanenitrile	19
n-Porpyl	CuBr	Hexanenitrile	84
n-Propyl	CuCl	Hexanenitrile	65
n-Butyl	CuBr	Heptanenitrile	88
iso-Butyl	CuBr	5-Methylhexanenitrile	88
n-Pentyl	CuBr	Octanenitrile	89
n-Hexyl	CuBr	Nonanenitrile	93

[a] All products were either compared with authentic samples or exhibited analytical data and spectra in accordance with the assigned structures [b] By glpc analysis, based on acrylonitrile

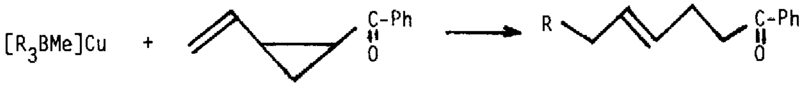
Although we have recently reported another synthetic procedure of aliphatic nitriles by electrochemical reaction,[8] the present reaction also provides a novel synthetic method of nitriles from organoboranes

Similarly, it was found that the reaction of such cuprous methyltrialkylborates with ethyl acrylate proceeds readily under the same reaction conditions (eq 3) When tri-n-propylborane was used, ethyl hexanoate and diethyl 2-butylpentanedioate were produced in yields of 44% and 28%, respectively



$$[n\text{-}Pr_3BMe]Cu \;+\; CH_2{=}CH\text{-}CO_2Et \;\text{——}\; \underset{44\%}{n\text{-}PrCH_2CH_2CO_2Et} \;+\; \underset{28\%}{\underset{CH_2CH_2CO_2Et}{n\text{-}PrCH_2CHCO_2Et}} \qquad (3)$$

Cuprous methyltrialkylborates also react with 1-acyl-2-vinylcyclopropane to form 1,6-adducts which are hydrolyzed to correponding γ,δ-unsaturated ketones in good yields (eq 4) The γ,δ-unsaturated ketones thus obtained were shown to be selectively trans-isomers This reaction should be useful as a synthetic route to trans-γ,δ-unsaturated ketones via organoboranes As we have recently pointed out, organoboranes react sluggishly with 1-acyl-2-vinylcyclopropane in the presence of oxygen to give corresponding γ,δ-unsaturated ketones, but the yields were too low for practical purposes[9] Representative results of the reaction of cuprous methyltrialkylborates with 1-benzoyl-2-vinylcyclopropane are summarized in Table 2



(4)

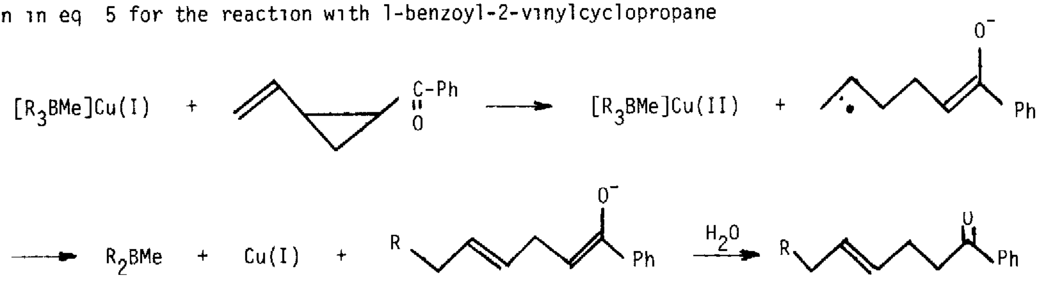
Table 2 Synthesis of trans-γ,δ-Unsaturated Ketones by the Reaction of Cuprous Methyltrialkylborates with 1-Benzoyl-2-vinylcyclopropane

Organoborane, R	CuX	Product[a]	Yield, %[b]
n-Propyl	CuI	3-Octenyl phenyl ketone	84
n-Propyl	CuBr	3-Octenyl phenyl ketone	48
n-Propyl	CuCl	3-Octenyl phenyl ketone	38
n-Butyl	CuI	3-Nonenyl phenyl ketone	81
iso-Butyl	CuI	7-Methyl-3-octenyl phenyl ketone	75

[a] All products were either compared with authentic samples or exhibited analytical data and spectra in accordance with the assigned structures [b] By glpc analysis, based on 1-benzoyl-2-vinylcyclopropane

Contrary to the reaction with acrylonitrile, cuprous methyltrialkylborate formed from cuprous iodide gave a good yield in the reaction with 1-benzoyl-2-vinylcyclopropane, as shown in Table 2 No reaction occurs between lithium methyltrialkylborates and reagents reported in this paper Consequently, cuprous and halide ions seem to play important roles in these reactions[10]

Since our efforts were mainly directed toward the practical application of the reactions, we have not undertaken mechanistic investigation of these reactions. However, as one of possible reaction pathways, the following mechanism involving an electron-transfer[11] may be proposed, as shown in eq 5 for the reaction with 1-benzoyl-2-vinylcyclopropane



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