

REACTION OF LITHIUM LITHIOETHYNYLTRIALKYLBORATES WITH ALKYL HALIDES.

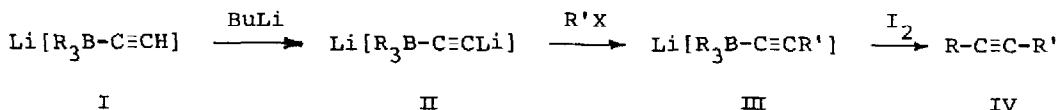
A FACILE ROUTE TO LITHIUM TRIALKYL-1-ALKYNYLBORATES

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This paper describes the preparation of lithium lithioethynyltrialkylborates (II) from easily accessible lithium trialkylethynylborates (I)¹ and the reaction with alkyl halides affording lithium trialkyl-1-alkynylborates (III) which have been known as useful intermediates in organic syntheses.²

According to the reported procedure¹ a hexane-THF solution of lithium trihexylethynylborate was prepared from butyllithium (5.25 mmol in 5 ml of hexane solution), 130 ml of acetylene, 5.0 mmol of trihexylborane and 10 ml of THF. A hexane solution of butyllithium (5.25 mmol in 5 ml solution) was added at -78° and the mixture was stirred for 20 min resulting a clear solution of lithium lithioethynyltriethylborate [II, R = CH₃(CH₂)₅]. This bifunctional intermediate could be alkylated selectively on acetylenic carbon. A solution of 1-bromobutane (0.719 g, 5.25 mmol in 3 ml of hexamethylphosphoric triamide and 3 ml of THF) was added to the solution of II at -78° and the whole was stirred for 30 min at room temperature.³ The product was determined to be lithium trihexyl-1-hexynylborate [III, R = CH₃(CH₂)₅, R' = CH₃(CH₂)₃] by transformation into 5-dodecyne¹ [IV, R = CH₃(CH₂)₅, R' = CH₃(CH₂)₃, 0.60 g, 3.6 mmol, yield 72%] by the well-determined procedure.⁴



Other halides gave analogous results; R, R'X, yield of acetylene (%) [ref.]; $\text{CH}_3(\text{CH}_2)_5$, $\text{H}_2\text{C}=\text{CHCH}_2\text{Br}$, 79 [5]; $\text{CH}_3(\text{CH}_2)_5$, (E)- $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br}$, 60 [6]; $\text{CH}_3(\text{CH}_2)_5$, $(\text{CH}_3)_3\text{SiCl}$, 83 [7]; $\text{CH}_3(\text{CH}_2)_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, 87 [8].

Judging from the yield of acetylenes, lithium lithioethynyltrialkylborates (II) were obtained in more than 90% yield from trialkylboranes. A novel functionalized boron ate complex II will be a useful intermediate leading to various type of boron ate complex and organoboron compounds. Further efforts along this line are going on.

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