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# gem-DIMETALLIC COMPOUNDS : ON THE METAL-METAL INTERCONVERSION BETWEEN gem-ORGANOBORON COMPOUNDS AND n-BUTYLLITHIUM.

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Methatetical reactions of the type:

$$RM + R'M' \rightleftharpoons R'M + RM'$$

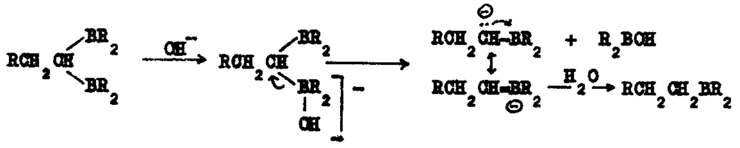
(R and R' = organic residues, M and M' = metals) have been investigated for a number of organometallic compounds. It has been demonstrated that in the equilibrium mixture the more electropositive metal becomes linked to the more electronegative organic group or, in other words, to the more stable carbanion, insofar as carbanion stability is the measure of the ability to accommodate a negative charge (1).

Transmetalation reactions of this kind, particularly those concerning the boron-lithium interconversion, have recaived relatively little attention in the organoboron chemistry.

H.Gilman and coworkers reported a few examples of exchange reactions between arylboronic acids ans n-butyllithium (2). More recently we observed an analogous interconversion for ortho-chloroboronic acid, which, on treatment with n-butyllithium, is converted in high yield in the corresponding ortho-substituted lithium derivative (3).

It is known, through the work of H.C.Brown (4), that the 1,1-diboroderivatives, which are easily obtained from acetylenic compounds on hydroboration, are exceedingly unstable to hydrolytic cleavage, being converted into the corresponding alkylborane.

This fact could be understood in terms of stability of the carbanion which is formed by attack of the base on the electrophilic boron atom, the stability being reached through the resonance with the vacant orbital of the second boron atom:



On this ground it seemed to us therefore attractive to investigate the possibility of a transmetalation reaction through gem-organoboron compounds and n-butyllithium, in the hope of obtaining other interesting organometallic compounds.

As starting materials for a first exploration in this field we have chosen 1-hexyne, 1-decyne and phenylacetylene.

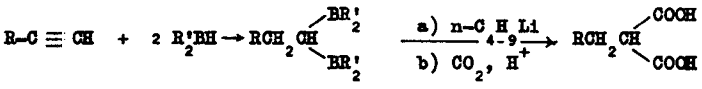
These compounds were hydroborated with two moles of dicyclohexylborane in THF. at room temperature. This hydroboration procedure is known to give the gem-dihydroboration products in practically quantitative yields (4).

To achieve the transmetalation, the solution of the organoboron compounds were treated at -78°C with a solution of n-butyllithium in heptane during 15 minutes.

In order to establish the position of the carbon-lithium bonds in the reaction products we treated the mixture with carbon dioxide to obtain lithium salts of the corresponding carboxylic acids.

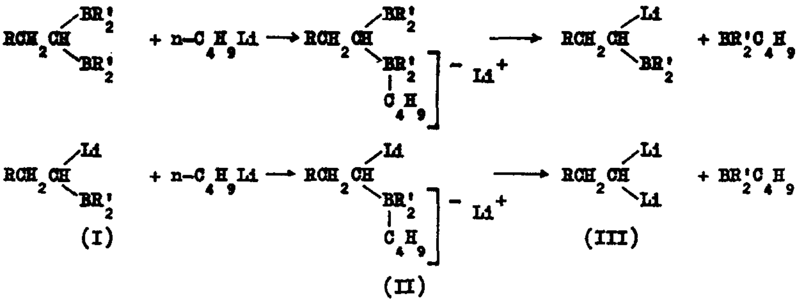
We had of course previously checked that the gem-organoboron compounds themselves do not react with carbon dioxide at least under our experimental conditions.

Using one mole of n-butyllithium per mole of gem-organoboron compounds we obtained a 35% yield of the corresponding malonic acids. The yield of the acids is raised to 65-70% when two moles of n-butyllithium are used.



R = n-$C_4H_9$, n-$C_8H_{17}$, $C_6H_5$ ; R' = Cyclohexyl

The formation of malonic acids could appear somewhat unexpected. To explain these results in a simple way one can indeed assume the existence of an intermediate organolithium compound of general formula: $RCH_2CHLi_2$ (5). An intermediate of this kind could arise from two successive metalation steps, according to the schema (6):



R = n-$C_4H_9$, n-$C_8H_{17}$, $C_6H_5$ ; R' = Cyclohexyl

However, hydrolysis followed by oxidation with alkaline hydrogen peroxide of the transmetalation product coming from 1-decyne, yielded substantial amounts of 1-decanol and only traces of the expected n-decane.

This results could be indicative of the presence in our reaction intermediate of a carbon-boron bond: this seems therefore to exclude for the actual intermediate of our reaction the structure (III) and is an element in favour of structure (I) or (II).

Work in this field is in progress in order to explore the chemistry of this new gem-organometallic compound and rigorously ascertain its structure.

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5) cfr. the formation of gem-dimercurials ( ethylidenedimercuric chloride) from gem-organoboron compounds: D.S.Matteson, J.G.Shdo - J.Org.Chem. 29 2742 (1964). Methylendilithium, as a very poorly soluble compound, has been obtained by pyrolysis of methyllithium by K.Ziegler, K.Nagel, M.Patheiger-Z.anorg.allg.Chemie 282 345 (1955)

6) According to this schema, n-butanol in significative yield has been isolated when the reaction mixture, after the separation of the malonic acids, was treated with alkaline hydrogen peroxyde.