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TRANSMETALATION REACTIONS WITH 1,1-DIALUMINOHEXANE. A NOVEL SYNTHESIS OF C_{n+1} 1-ALKENES FROM C_n 1-ALKYNES

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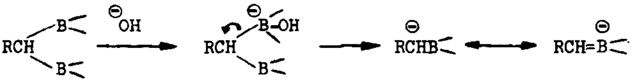
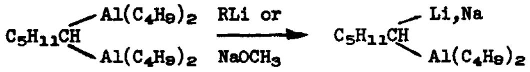
The instability of geminal diboroalkanes toward sodium hydroxide has been attributed to a stabilization of the incipient carbanion by interaction with the vacant p-orbital of boron.[1]



From a consideration of this proposed mechanism, we were encouraged to explore the feasibility of effecting the cleavage with other bases such as sodium methoxide, butyllithium and methyllithium. Thus it was observed that 1,1-diboroalkanes, derived by hydroboration of 1-alkynes with diborane, underwent transmetalation to produce intermediates containing boron and sodium or boron and lithium at the same carbon atom.[2] The synthetic potentialities of such reagents containing two ligands of different reactivities have prompted us to extend our investigations to transmetalation reactions between 1,1-dialuminohexane and various metalating agents.

Bis-1,1-(diisobutylalanyl)alkanes are readily accessible via hydroalumination of 1-alkynes.[3] Thus the reaction of 1-hexyne with 2 moles of diisobutylaluminum hydride in hydrocarbon solvents or tetrahydrofuran yielded 85% bis-1,1-(diisobutylalanyl)hexane.[4] Treatment of this 1,1-dialumino derivative with methyllithium, butyllithium or sodium methoxide in tetrahydrofuran resulted in intermediates (2) containing aluminum and sodium or aluminum and lithium substituted at the termina carbon atom.



$$C_5H_{11}CH\begin{matrix}Al(C_4H_9)_2\\Al(C_4H_9)_2\end{matrix}\xrightarrow[NaOCH_3]{RLi\ or}C_5H_{11}CH\begin{matrix}Li,Na\\Al(C_4H_9)_2\end{matrix}$$

(1) (2)

Evidence for the formation of such intermediates is based on the following results. Addition of excess methyl iodide to (2) followed by hydrolysis of the reaction mixture yielded, depending on the amount and nature of the base used, 51 to 74% n-heptane (Table I).

Table I

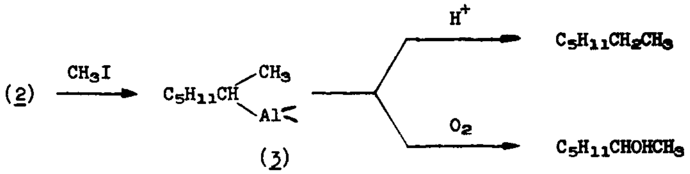
Yields of n-Heptane by Transmetalation of 1,1-Dialuminohexane followed by Addition of Methyl Iodide

Reagent	Ratio Organoaluminum/ Reagent	n-Heptane, % [a,b]
$LiCH_3$	1:1	51
	1:2	70
	1:3	74
LiC_4H_9	1:3	74
$NaOCH_3$	1:3	51

[a] Based on 1,1-dialuminohexane. [b] Determined by vpc analysis using an internal standard.

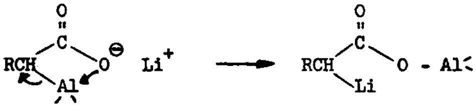
Under identical experimental conditions 1,1-dialuminohexane (1) failed to react with methyl iodide and gave only n-hexane on hydrolysis.

The fact that derivative (3) derived from the alumino-lithio derivative (2) was converted to 2-heptanol in 90% yield when reacted with oxygen indicates that



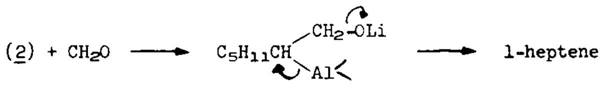
the two metal ligands in (2) are attached to the same carbon atom.[5] In order to demonstrate that a 1,1-dilithio compound is not involved in the reaction, intermediate (3) was treated with carbon dioxide in tetrahydrofuran, a reaction which converts secondary organolithium derivatives into carboxylic acids, but does not affect secondary organoaluminum compounds. Vpc examination of the hydrolyzed reaction mixture revealed only n-heptane, thus indicating that transmetalation of 1,1-dialuminohexane produces a geminal dimetallic containing both aluminum and lithium as ligands.

Besides giving the above alkylation reaction, the alumino-lithio derivative (2) yielded on carbonation 73% n-amylmalonic acid.[6] Under similar conditions 1,1-dialuminohexane (1) fails to react with CO_2. Formation of the diacid can be rationalized in terms of an intramolecular (or intermolecular) displacement of aluminum by the carboxylate group to give intermediate (4) which then undergoes further carbonation.



(4)

Finally, addition of gaseous formaldehyde or paraformaldehyde to the alumino-lithio derivative instead of giving 1-heptanol on hydrolysis resulted in the formation of 1-heptene in 70% yield. Apparently the intermediate (5) which is formed must undergo elimination with great ease.[7]



$$(2) + CH_2O \longrightarrow C_5H_{11}CH\begin{matrix}\diagup CH_2{-}OLi \\ \diagdown Al\lessdot\end{matrix} \longrightarrow \text{1-heptene}$$

(5)

It should be noted that the isobutyl groups attached to the aluminum are readily hydrolyzed to isobutane and hence do not interfer in the isolation of 1-alkenes. We are currently exploring the full scope of this and related reactions.

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2. G. Zweifel and H. Arzoumanian, Tetrahedron Letters, 2535 (1966).
3. G. Wilke and H. Müller, Ann., 629, 222 (1960).
4. The structure of the 1,1-dialumino derivative has been established by its conversion to 1,1-dideuteriohexane when treated with D_2O. E. G. Hoffmann, Ann., 618, 276 (1958).
5. In order to achieve high yields of the mixed geminal dimetallic derivative, a 100% excess of methyllithium is required. It is not yet clear if the exce reagent forms the ate- complex with the organoaluminum moiety of the 1-alumi 1-lithio compound or if the departing methyl diisobutylalane is converted to lithium dimethyl diisobutylalanate.

6. It has been reported that 1,1-diboron compounds, derived via hydroboration of 1-alkynes with dicyclohexylborane, after treatment with butyllithium and followed by carbonation, yield malonic acid derivatives. G. Cainelli, G. dal Bello, and G. Zubiani, Tetrahedron Letters, 3429 (1965).

7. The reaction of 1-boro-1-lithiohexane (ref. 2) with formaldehyde gives among other products low yields of 1-heptene. Similarly it has been reported that the reaction of 1-boro-1-lithioalkanes with various aldehydes and ketones yield 20-50% olefins. G. Cainelli, G. dal Bello, and G. Zubiani, Tetrahedron Letters, 4315 (1966).