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gem-DIMETALLIC COMPOUNDS:A NOVEL APPROACH TO OLEFINS STARTING FROM CARBONYL COMPOUNDS AND ACETYLENIC DERIVATIVES.

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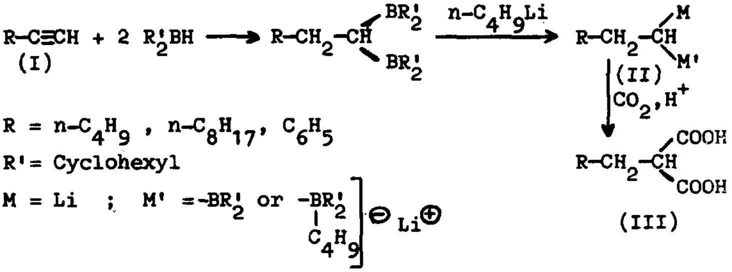
We recently reported that the reaction between n-butyllithium and gem-organodiboron compounds easily available by dihydroboration of monosubstituted acetylenes (I) (1) leads to the formation of new, highly reactive gem-organodimetallic compounds(II),reacting with carbon dioxide to the corresponding malonic acids derivatives (III) (2):



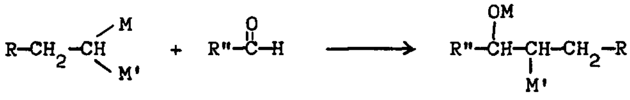
$R = n\text{-}C_4H_9$, $n\text{-}C_8H_{17}$, C_6H_5
$R' =$ Cyclohexyl
$M = Li$; $M' = -BR'_2$ or $\left[-\underset{\displaystyle C_4H_9}{\overset{|}{B}}R'_2\right]^{\ominus} Li^{\oplus}$

Concerning the real nature of our gem-organodimetallic intermediate we proposed the structure of a 1-boro-1-lithio-derivative (II, M=Li, $M'=BR'_2$) or of the corresponding ate-complex with n-butyllithium (M=Li, $M' = \left[-\underset{\displaystyle C_4H_9}{\overset{|}{B}}R'_2\right]^{\ominus} Li^{\oplus}$) (3) .

Very recently G.Zweifel and H.Arzoumanian (4) repeating the essential part of our work,drew to the same conclusions(5).

We wish to report on the reaction of this new type of gem-dimetallic compound with carbonyl derivatives.

On the basis of its facile reaction with carbon dioxide(2) one can assume confidently that, whatever can be the real nature of the two metallic rests M and M', the first step of the reaction would be a nucleophilic attack to the carbonyl double bond, leading to a organometallic intermediate of the general formula (IV):



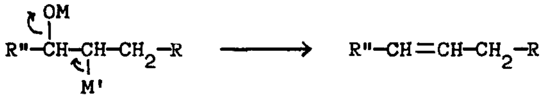
$$R{-}CH_2{-}CH\begin{matrix}\diagup M\\ \diagdown M'\end{matrix} + R''{-}\overset{O}{\overset{\|}{C}}{-}H \longrightarrow R''{-}\overset{OM}{\overset{|}{C}}H{-}\underset{M'}{\underset{|}{C}}H{-}CH_2{-}R$$

(IV)

$R = n\text{-}C_4H_9$; $R' = \text{Cyclohexyl}$

$M = Li$; $M' = -BR'_2$ or $\left[-\underset{C_4H_9}{\underset{|}{B}}R'_2\right]^{\ominus} Li^{\oplus}$

An organometallic compoud of this kind could successively undergo an 1:2 elimination to the corresponding olefins:



$$R''{-}\overset{OM}{\overset{|}{C}}H{-}\underset{M'}{\underset{|}{C}}H{-}CH_2{-}R \longrightarrow R''{-}CH{=}CH{-}CH_2{-}R$$

This possibility could be of synthetic interest as a new approach to olefins starting from ketones and terminal acetylenes.

We found that benzaldehyde and aliphatic, aromatic and alicyclic ketones, including steroidal ones, can be effectively converted to the corresponding olefins by reaction with the gem-dimetal compound arising from 1-hexyne.

A choice of experimental results are summarized in Table I.

TABLE I

Olefins obtained starting from 1-hexyne .

Starting Carbonyl Compounds	Olefins obtained	Temp. C°	Yield %	trans-cis ratio
1. Benzaldehyde	1-Phenyl-ept-1-ene	40°	45-50	96-4
2. "	"	18°	-	86-14
3. "	"	0°	-	57-43
4. "	"	-23°	-	50-50
5. "	"	-78°	-	30-70
6. Benzophenone	1,1-Diphenyl-ept-1-ene	25°	45-50	--
7. Di-n-amyl-ketone	6-n-amyl-undec-6-ene	25°	30-35	--
8. Cyclohexanone	n-hexylidencyclohexane	25°	20-25	--
9. Cholestanone	3-n-hexyliden-5α cholestane	25°	20-25	not det.

The general procedure was as follows. To the solution in THF of a mole of the dihydroboration product of 1-hexyne and dicyclohexylborane at -78° two moles of n-butyllithium were added.

After warming the solution to room temperature, a mole of the carbonyl compound was added. After a few hours the reaction mixture was worked up and the olefins separated chromatographically. Work is in progress in our laboratory in order to study the stereochemical course of this novel reaction. The first interesting results in this field, made on benzaldehyde are indicative for a strong dependence of the trans-cis ratio of the olefins obtained from the reaction conditions like temperature (cfr. Table I) and solvent (6).

We are attempting to improve the yields wich are not very satisfactory especially if the carbonyl compound carries hydrogen atoms in α position. This is very probably due to enolat formation competing with the normal addition of the reagent to the carbonyl double bond.

Acknowledgement- We wish to thank Prof.A.Quilico for the helpful discussion and for his interest in this work.

REFERENCES

1) H.C.Brown,G.Zweifel - *J.Am.Chem.Soc.* **83** 3834 (1961)
2) G.Cainelli,G.Dal Bello,G.Zubiani - *Tetrahedron letters* 3429 (1965)
3) Both species are probably present in equilibrium. Supporting evidence to this point is to be published in the next future.
4) G.Zweifel,H.Arzoumanian - *Tetrahedron letters* 2535 (1966)
5) It is not completly clear if the authors attribute to our intermediate only the structure of a 1-lithio-1-boro-alkane or if they think that a part of it may be present as the corresponding ate-complex with the organo-lithium reagent.
6) At least in the few cases we studied it seems possible to obtain trans or cis olefins in almost pure condition. More details on this interesting point is to be published in the next future.