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gem-DIMETALLIC COMPOUNDS:REACTION OF gem-DIALUMINUM COMPOUNDS WITH ALDEHYDES AND KETONES

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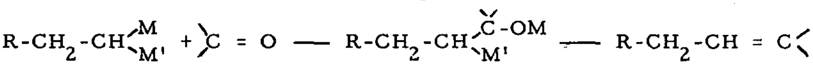
We recently reported (1) that the reaction between geminal organometallic compounds of general formula $R\text{-}CH_2\text{-}CH\langle^{M}_{M'}$

($M = Li, M' = -B(C_6H_{11})_2$ or $-B(C_6H_{11})_2(C_4H_9)]^{\ominus}\ Li^{\oplus}$) and benzaldehyde or ketones results in the formation of olefins following the scheme:



$$R\text{-}CH_2\text{-}CH\langle^{M}_{M'} + \rangle C = O \longrightarrow R\text{-}CH_2\text{-}CH\langle^{\rangle C\text{-}OM}_{M'} \longrightarrow R\text{-}CH_2\text{-}CH = C\langle$$

This "Wittig like" olefin synthesis from carbonyl compounds should be extendable to all gem-dimetallic compounds containing at least one organometallic bond capable of addition to a carbonyl group.

It is known (2) that the aluminum-carbon bond can add in certain cases to the carbonyl group of aldehydes and ketones like a Grignard reagent, forming the corresponding carbinols. On the other hand β-substituted aluminum compounds of the general formula $-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Al\langle$ are shown (3) to eliminate easily the heteroatoms yielding the corresponding olefins.

On these grounds it was to be expected that gem-dialuminum compounds were able to give the above illustrated olefination reaction. To verify this hypothesis we studied the behavior towards aldehydes and ketones of the bis-1,1-diisobutyl-alanylalkanes which are readily obtainable via hydroalumination of 1-alkynes (4).

Treatment of bis-1,1-diisobutylalanylhexane (obtained by heating at 90° under nitrogen for 5 hours one mole of hexyne with two moles of diisobutylaluminum hydride) in heptane or tetrahydrofuran at 0° for 30 minutes with an equimolecular amount of an aldehyde or ketone results in the formation of the expected olefines in yields ranging from 15 to 30% (Table 1).

TABLE 1.

Olefins obtained starting from bis-1,1-diisobutylalanylhexane.

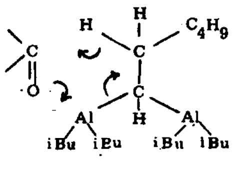
Starting carbonyl compounds	Olefins obtained	Temp. C°	Yield %	trans-cis ratio
1. Benzaldehyde [a]	1-phenyl-hept-1-ene	0	25-30	63,1/36,9
2. "	"	25	-	71,9/28,1
3. Benzaldehyde [b]	"	0	18-20	58,6/41,4
4. "	"	25	-	60,7/39,3
5. Cinnamaldehyde [a]	1-phenyl-nona-1,3-diene	0	25-30	not det.
6. Lauraldehyd [a]	Octadecan-6-ene	0	15-20	" "
7. Undecan-6-one [a]	6-nPentyl-dodec-6-ene	0	15-20	-
8. Cyclohexanone [a]	n-hexylidencyclohexane	0	15-20	-
9. Acetophenone [a]	2-phenyl-oct-2-ene	0	15-20	not det.

a = solvent : heptane

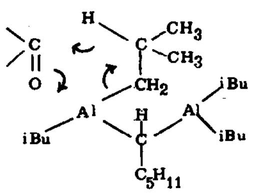
b = solvent : tetrahydrofuran.

In all cases studied, extensive reduction of the carbonyl compounds to the corresponding alcools were observed as major side reaction. This fact, which of course decreases the synthetic value of this new approach to olefins (5), is not unexpected. It is indeed known that trialkylalanes, expecially those containing isobutyl groups, behave in many cases as reducing agents toward carbonyl compounds (6).

In analogy with the mechanism proposed by Wittig (7) for the trialkylaluminums, the following two reaction patterns could be considered for the reduction in our case:



A



B

If B takes an important part in the over all reaction the use of dimethylaluminum hydride in the preparation of the gem-dialuminum compounds should increase the yield of olefins. Work is in progress in our laboratory to improve the yields and to study the stereochemistry of this reaction.

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5. It has been reported that the transmetalation product between bis-1,1-(diisobutylalanyl) hexane and lithium-alkyls reacts with formaldeyde yielding 70% of 1-heptene.
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