Journal of Organometallic Chemistry, 157 (1978) C30—C32

Preliminary communication

APPLICATION OF HYDROALUMINATION REACTIONS IN ORGANIC SYNTHESES. COUPLING REACTIONS OF ORGANOALUMINUM COMPOUNDS WITH ALLYLIC HALIDES CATALYZED BY COPPER COMPOUNDS*

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(Received May 2nd, 1978)

Summary

Hydroalumination of olefins with lithium aluminum hydride followed by treatment with various allylic halides in presence of a catalytic amount of copper(I) chloride resulted in coupling. This new development provides a simple operational method for lengthening the carbon chain of olefins.

The facile addition of the aluminum—hydrogen bond to olefins by catalysis of titanium compounds makes the corresponding organoaluminums as readily available for application in organic syntheses as organoboranes [1—3]. Recently, it was demonstrated that alkenylaluminum compounds which are readily obtainable by the reactions of $i\text{-}Bu_2AlH$ with alkynes are coupled with allyl halides in the absence [4] or in the presence [5] of a stoichiometric amount of copper(I) halide to produce *trans*-1,4-dienes.

We have now found that hydroalumination of olefins with $LiAlH_4$ followed by reaction with various allylic halides in the presence of a catalytic amount of CuCl results in coupling**. The results of the coupling reaction of organoaluminums with 3-halo-1-propene (I), which are shown in Table 1, demonstrate that this procedure is a most convenient and general method for lengthening of the carbon chain of olefins by three atoms***.

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*A part of this work was presented at the 37th Spring Annual Meeting of The Chemical Society of Japan, Kanagawa, April, 1978; Abstr. No. 2L19.

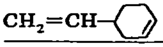
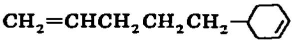
**Recently, Otsuji et al. found independently that $LiAl(C_5H_{11})_2H_2$ and $LiAl(C_6H_{13})_2H_2$, obtained by the hydroalumination with $LiAlH_4$ of 1-pentene or 1-hexene, respectively [2], react with 3-halo-1-propene in the presence of copper(II) acetate to give the corresponding coupling products. By this method, however, a molar excess of 3-halo-1-propene in relation to the olefin was used. Yields (53—64%) were lower than those obtained here, presumably due to the presence of a remaining hydride group in the organoaluminums. The work was presented at a meeting [8].

***$[R_3BCH_3]Cu$ obtained from the reaction of lithium tetraalkylborate with copper(I) halides, reacts with allyl chloride giving coupling products according to the following equation [6].

$$[R_3BCH_3]Cu + CH_2{=}CHCH_2Cl \rightarrow RCH_2CH{=}CH_2$$

TABLE 1

LENGTHENING OF THE CARBON CHAIN OF OLEFINS BY THREE ATOMS VIA THE REACTION OF THE CORRESPONDING $LiAlR_4$ WITH 3-CHLORO-1-PROPENE (I) IN THE PRESENCE OF CuCl

Olefin	Product[a]	Yield[b] (%)
$CH_2{=}CH_2$ [c]	n-$C_3H_7CH{=}CH_2$	70
$CH_3CH{=}CH_2$ [c]	n-$C_4H_9CH{=}CH_2$	65
n-$C_4H_9CH{=}CH_2$ [d]	n-$C_7H_{15}CH{=}CH_2$ [e]	80 (76)[f]
$CH_2{=}CHCH_2CH{=}CHCH_3$ [d]	$CH_3CH{=}CH(CH_2)_4CH{=}CH_2$	68
$CH_2{=}C(CH_3)CH_2CH_2CH{=}CH_2$ [d]	$CH_2{=}C(CH_3)(CH_2)_5CH{=}CH_2$	63
 [d]		77

[a] Identified by GLC and ^1H NMR. [b] Yield by GLC analysis. [c] A 30% excess of $LiAlR_4$ was employed and yield is based on 3-chloro-1-propene. [d] A 20 to 30% excess of 3-chloro-1-propene was employed and yield is based on olefin. [e] 48% and 45% yields of 1-nonene were obtained by using 3-bromo- and 3-iodo-1-propene, respectively. [f] Isolated yield.

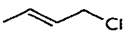
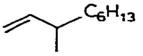
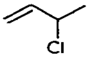
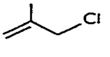
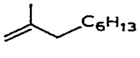
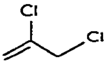
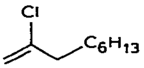
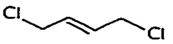
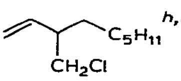
$$4\ RCH{=}CH_2 \xrightarrow[TiCl_4]{LiAlH_4} LiAl(CH_2CH_2R)_4 \xrightarrow[(X\,=\,Cl,\ Br\ or\ I)]{4\ CH_2{=}CHCH_2X/CuCl} 4\ RCH_2CH_2CH_2CH{=}CH_2$$

It is worthy of note that all of the four alkyl groups on aluminum can participate in the reaction. In addition to CuCl, various other copper compounds such as CuBr, CuI, CuCN, $CuCl_2$ and $Cu(OAc)_2$ also are effective catalysts.

We utilized $LiAl(C_6H_{13})_4$ in a brief exploration of the applicability of this reaction to other allylic halides. Our results are summarized in Table 2. Various al-

TABLE 2

COUPLING PRODUCTS OF THE REACTIONS OF $LiAl(C_6H_{13})_4$ WITH ALLYLIC CHLORIDES

Allylic chlororide[a]		Product[b]	Yield[c] %
	(II)	 (65),  (35)	47
	(III)	 [e] (>99)	66 (54)[d]
	(IV)	 [f]	57
	(V)	 [g,i]	68
	(VI)	 [h,i]	66 (61)[d]

[a] A 20% excess of the allylic chlorides was used. [b] Identified by GLC and ^1H NMR. Characteristic NMR signals are shown in notes e—h. [c] Yield by GLC analysis and based on olefin. [d] Isolated yield. [e] (CCl_4) δ 5.36 (m, 2H, olefinic), 1.60 (d, 3H, CH_3—C=). [f] (C_6D_6) δ 4.67 (br, 2H, olefinic), 1.65 (s, 3H, CH_3—C=). [g] (C_6D_6) δ 4.82 (s, 1H, olefinic), 4.99 (s, 1H, olefinic), 2.17 (t, 2H, —CH_2—C(Cl)=). [h] (C_6D_6), δ 4.75—5.10 (m, 2H, CH_2=), 5.26—5.70 (m, 1H, —CH=), 3.17 (d, 2H, —CH_2Cl). [i] Mass spectral data support the structures.

lylic chlorides (II—VI) reacted satisfactorily to give the coupling products. Especially noteworthy is the variety of structural modifications of the allylic unit which can be accomodated, including the presence of a heteroatom.

These reactions are not restricted to organoaluminates, since $Al(C_2H_5)_3$ couples with allylic halides in a similar manner. In this case, however, excellent yields were realized only by using equimolar amounts of $Al(C_2H_5)_3$ and allylic halide. Thus the reactions of $Al(C_2H_5)_3$ with I, III and VI gave 1-pentene, 2-hexene (*trans*/*cis* = 22) and 3-chloromethyl-1-pentene in 70, 78 and 92% yields, respectively, based on allylic chloride.

The following procedure for the preparation of 1-nonene is representative. Lithium aluminum hydride, 360 mg (9.5 mmol), was added to a mixture of 80 mg (0.45 mmol) of $TiCl_4$ and 3.0 g (35.8 mmol) of 1-hexene in 30 ml of THF. After 3 h under nitrogen at 25°C, the temperature was lowered to 0°C and 3.5 g (46.0 mmol) of 3-chloro-1-propene and 0.5 g (5 mmol) of CuCl were added. The mixture was stirred for 10 minutes at 0°C and then for 12 h at room temperature. After hydrolysis, GLC analysis indicated the presence of 1-nonene in 80% yield based on 1-hexene; it contained only traces of the homocoupling products. 1-Nonene was isolated as follows. 10 ml of 2 *N* hydrochloric acid was added to the reaction mixture, then the THF layer was separated and the aqueous layer was extracted with 10 ml of ether. The combined THF and ether layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was distilled to give 3.42 g (76% yield based on 1-hexene) of 1-nonene. Although the function of the catalyst is not clear at present, an organocopper compound, formed by the reaction of copper(I) chloride and the organoaluminum, seems to play an important role, as was noted in the case of copper-catalyzed reactions of Grignard reagents and organic halides [7].

This coupling reaction could provide a new route to many complex molecules difficult to prepare by other methods, and a study to find the scope and limitations of this method is now in progress.

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