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ALKYL-ALKYL COUPLING OF LITHIUM ALKYLALUMINATES AND ALKYL-ALLYL CROSS-COUPLING OF THE ALUMINATES WITH ALLYLIC HALIDES BY THE USE OF COPPER (II) ACETATE: AN APPLICATION OF THE CATALYTIC HYDROALUMINATION OF OLEFINS TO ORGANIC SYNTHESIS

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Lithium alkyl-1-trihydroaluminates, which are prepared by the catalytic hydroalumination of α-olefins with $LiAlH_4$ in the presence of a catalytic amount of a titanium-aluminium complex, undergo the alkyl-alkyl coupling reaction upon treatment with copper (II) acetate. The reaction of lithium alkylaluminates with allylic halides in the presence of copper (II) acetate affords the alkyl-allyl cross-coupling products.

Coupling reactions between two different alkyl groups via organometallic complexes have received considerable attention as a useful and attractive tool of the formation of carbon-carbon bonds.1) Recently, Negishi and his coworkers2) have reported the alkenyl-alkenyl and alkenyl-alkyl cross-couplings by the reaction of alkenylaluminiums or alkenylaluminates with organic halides using nickel (II) or palladium complexes as a catalyst. Recent investigations have also proved that organoaluminium compounds act as unique nucleophiles and can be employed as useful reagents in organic synthesis.3)

We have developed a convenient method for the preparation of lithium alkyl-1-trihydroaluminates by the hydroalumination of α-olefins with $LiAlH_4$ under the influence of a catalytic amount of a titanium-aluminium complex which is formulated as $Cp_2Ti(AlH_3)_2$.4,5) Subsequently we have studied the application of these alkylaluminates in organic synthesis. We now wish to report the coupling reaction of alkylaluminates and the cross-coupling reactions of alkylaluminates with allylic halides in the presence of copper (II) acetate [$Cu(OAc)_2$].

Hydroalumination of α-olefins with $LiAlH_4$ in the presence of a titanium-aluminium complex in THF gave lithium alkyl-1-trihydroaluminates [1] in high yields, and treatment of a THF solution of [1] with $Cu(OAc)_2$ at room temperature afforded the alkyl-alkyl coupling products.

A typical procedure of the coupling reactions is shown in an example of the conversion of 1-octene to hexadecane: Hydroalumination of 1-octene was carried out in a similar manner as described previously,6) using Cp_2TiCl_2 (1.28 mmol), $LiAlH_4$ (25.6 mmol), and 1-octene (25.6 mmol) in THF (30 ml). The resulting mixture was stirred for 3 h at 60°C and filtered under argon. The filtrate, which contained lithium octyl-1-trihydroaluminate, was added to anhydrous $Cu(OAc)_2$ (61.4 mmol)

Table 1. Homo-coupling of Lithium Alkyl-1-trihydroaluminates

R^1	$Li[R^1AlH_3]$ (mmol)a)	Product	Yield (%)b)
C_6H_{13}	16.5	$n\text{-}C_{12}H_{26}$	62
C_8H_{17}	22.7	$n\text{-}C_{16}H_{34}$	52
$PhCH_2CH_2$	5.4	Diphenyl-c) butanes	74
$\underset{CH_3}{PhCH}$	trace		

a) The quantities of lithium alkyl-1-trihydroaluminates were determined by GLC analysis of the alkyl bromides obtained by the bromination of the aluminates with Br_2. b) The yields were determined by GLC. c) Diphenylbutanes obtained were found to contain 1,4-(39%), 1,3-(21%), d,l-1,2-(20%), and meso-1,2-diphenylbutanes (20%).

Table 2. Coupling of Two Different Lithium Alkyl-1-trihydroaluminates

$Li[R^1AlH_3]$ and $Li[R^2AlH_3]$ R^1 or R^2	(mmol)a)	Products distribution (%)	
$R^1=C_6H_{13}$	16.5	$n\text{-}C_{12}H_{26}$	20b)
$R^2=C_8H_{17}$	23.1	$n\text{-}C_{14}H_{30}$	52b)
		$n\text{-}C_{16}H_{34}$	28b)
$R^1=C_6H_{13}$	16.8	$n\text{-}C_{12}H_{26}$	43
$R^2=PhCH_2CH_2$	10.9	$1\text{-}PhC_8H_{17}$	43
		$2\text{-}PhC_8H_{17}$	14
		Diphenyl-butanes	trace

a) The quantities of lithium alkyl-1-trihydroaluminates were determined by GLC analysis of the alkyl bromides obtained by the bromination of the aluminates with Br_2. b) Theoretical distribution of the products calculated for the mixture of aluminates used was 17% of $n\text{-}C_{12}H_{26}$, 49% of $n\text{-}C_{14}H_{30}$, and 34% of $n\text{-}C_{16}H_{34}$. These values are in accordance with the experimental values cited in this table.

under argon at 0°C. The mixture was stirred for 0.5 h at room temperature, acidified with 100 ml of 2M HCl, and then extracted with ether. The ethereal extract was dried (Na_2SO_4) and evaporated. Distillation of the residue gave hexadecane as a major product. The GLC analysis of the above residue indicated that the reaction mixture contained hexadecane (5.87 mmol), 1-octene (4.01 mmol), and octane (0.92 mmol).

When a mixture of two different alkylaluminates, [1] and [1'], which had been prepared separately from two different olefins, was treated with $Cu(OAc)_2$,

$$RCH{=}CH_2 + LiAlH_4 \xrightarrow[THF]{Cp_2TiCl_2\text{-}LiAlH_4} \underset{[1]}{Li[R^1AlH_3]} \xrightarrow[THF]{Cu(OAc)_2} 1/2\ \underset{[2]}{R^1\text{-}R^1} \qquad (1)$$

$$[1] + \underset{[1']}{Li[R^2AlH_3]} \xrightarrow[THF]{Cu(OAc)_2} 1/2\ [2] + 1/2\ \underset{[2']}{R^2\text{-}R^2} + \underset{[3]}{R^1\text{-}R^2} \qquad (2)$$

$$[1] + Cu^{II}(OAc)_2 \longrightarrow \underset{[4]}{Cu^{I}[R^1Al(OAc)H_2]} + LiOAc + 1/2\ H_2 \qquad (3)$$

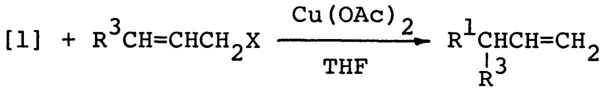
$$[4] + Cu^{II}(OAc)_2 \longrightarrow \underset{[5]}{Cu\text{-}R^1} + Cu^{I}[Al(OAc)_3H] + 1/2\ H_2 \qquad (4)$$

$$[5] \longrightarrow 1/2\ [2] + Cu(0) \qquad (5)$$

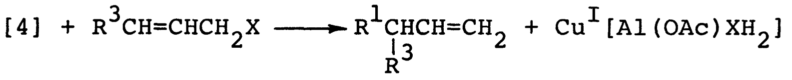
$$[5] + \underset{[5']}{Cu\text{-}R^2} \longrightarrow 1/2\ [2] + 1/2\ [2'] + [3] + 2Cu(0) \qquad (6)$$

the alkyl-alkyl homo- and cross-coupling products were obtained in a statistical ratio. These coupling reactions are illustrated in Eqs. 1 and 2. The results are summarized in Tables 1 and 2. The feature of the reactions can be explained in terms of the pathways represented in Eqs. 3 - 6. The first step of the reactions is the reduction of Cu(II) to Cu(I), accompanied by the formation of a copper(I) aluminate [4] and evolution of H_2. In the second step, [4] is converted into an alkylcopper [5] with an additional evolution of H_2. Finally, the thermolysis of [5] gives [2]. Treatment of a mixture of alkylaluminates [1] and [1'] with $Cu(OAc)_2$ gives homo- and cross-coupling products [2], [2'] and [3] via the thermolysis of a mixture of two different alkylcoppers [5] and [5'] (Eq. 6). The stepwise evolution of H_2 and its stoichiometry as represented in Eqs. 3 and 4 was confirmed by quantitative measurements of H_2 evolved.[7)]

Alkylaluminate [1] reacted effectively also with allylic halides in the presence of $Cu(OAc)_2$, giving the alkyl-allyl cross-coupling products (see Eq. 7). The results are summarized in Table 3. This cross-coupling reaction was able to conduct in an one-pot manner by adding allyl halides to [1] before treating the reaction mixture with $Cu(OAc)_2$. Plausible pathways of the cross-coupling



$$[1] + R^3CH{=}CHCH_2X \xrightarrow[\text{THF}]{Cu(OAc)_2} R^1\underset{R^3}{C}HCH{=}CH_2 \qquad (7)$$



$$[4] + R^3CH{=}CHCH_2X \longrightarrow R^1\underset{R^3}{C}HCH{=}CH_2 + Cu^{I}[Al(OAc)XH_2] \qquad (8)$$

Table 3. Cross-coupling of Lithium Alkyl-1-trihydroaluminates with Allylic Halides

$Li[R^1AlH_3]$ R^1	$R^3CH{=}CHCH_2X$ R^3	X	Product	Yield (%)[a)]
C_5H_{11}	H	Br	$C_6H_{13}CH{=}CH_2$	53
C_8H_{17}	H	Br	$C_9H_{19}CH{=}CH_2$	62
C_8H_{17}	H	Cl	$C_9H_{19}CH{=}CH_2$	64
C_8H_{17}	Ph	Br	$C_8H_{17}\underset{Ph}{C}HCH{=}CH_2$	45

a) The yields were determined by GLC.

reaction are shown in Eqs. 3 and 8. The reaction appears to be an S_N2' substitution on allyl halides with a carbanion derived from an alkylaluminate [4]. This is in contrast with the alkyl-alkyl coupling reactions of alkylaluminates, in that an alkyl-radical intermediate genarated from [5] is involved: The intermediary of alkyl radicals in the alkyl-alkyl coupling reactions is supported by the facts that (1) the reaction of lithium phenyl-1-trihydroaluminate with $Cu(OAc)_2$ gave a mixture of four diphenylbutane isomers (see footnote of Table 1) and (2) the coupling reactions using two different alkylaluminates afforded [2], [2'], and [3] in a statistical ratio of 1:1:2.

The following results were also obtained for the coupling reactions reported. (1) The alkyl-alkyl coupling of [1] occurred by the use of $AgNO_3$ as an oxidizing agent, although the yields of [2] were low as compared with those obtained by the use of $Cu(OAc)_2$. (2) No coupling products were isolated upon treatment of [1] with CuX, CuX_2 (X=Cl, Br, or I) or $Mn(OAc)_3$. (3) Alkylaluminiums, which can readily be prepared by the reaction of the corresponding alkylaluminates with $AlCl_3$, gave no coupling products upon treatment with $Cu(OAc)_2$. (4) The coupling reactions did not occur when diethyl ether and hexane were employed as solvents.

The scope and detailed mechanisms of the coupling reactions will be discussed in a full paper.

References and Notes

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7) The reaction of [1] with an equimolar amount of $Cu(OAc)_2$ resulted in the evolution of a half molar amount of H_2, and the subsequent addition of an equimolar amount of $Cu(OAc)_2$ to the reaction mixture caused a further evolution of a half molar amount of H_2. The amount of H_2 evolved was determined by its volumetric analysis.

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