

Organometallic Chemistry

$(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ -Catalyzed hydroalumination of α -olefins with Et_3Al

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A preparative method for the synthesis of (alkyl)diethylalanes from α -olefins and Et_3Al catalyzed by Cp_2TiCl_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) is proposed.

Key words: organoaluminum compounds, hydroalumination, catalysts, olefins, titanium complexes.

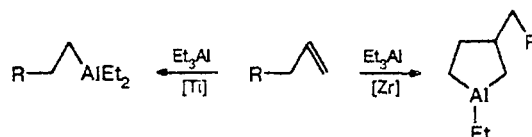
It is known that Bu_3Al ¹ or Bu_2AlCl ²⁻⁴ with catalytic amounts of Cp_2ZrCl_2 are presently used, as a rule, for hydroalumination of olefins by "hydride-free" hydrometallating reagents. Unlike these reagents, Et_3Al hydroaluminates ⁵ α -olefins to give (alkyl)diethylalanes (70 °C, 16 h) in yields not higher than 1%, whereas in the presence of Cp_2ZrCl_2 as the catalyst, the reaction in CH_2Cl_2 results ⁶ in a mixture of organoaluminum compounds (OAC), which are the products of hydro- and carboalumination and β -ethylation of the starting α -olefins in the ~1 : 2 : 1 ratio, respectively.

It has been recently shown ⁷ that Et_3Al hydroaluminates disubstituted acetylenes in the presence of Cp_2TiCl_2 under mild conditions (22–23 °C) to give the corresponding alkenylalanes in sufficiently high yields (75–90%).

In a continuation of these studies and in order to extend the application of Et_3Al as the "hydride-free" hydrometallating reagent and to develop a preparative synthesis of previously difficultly accessible (alkyl)diethylalanes, we studied hydroalumination of mono- and disub-

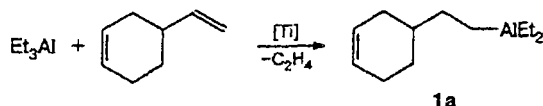
stituted olefins by Et_3Al involving complex catalysts based on Ti and Zr compounds, which exhibit the maximum activity and selectivity in similar reactions. ⁸⁻¹¹

Preliminary experiments have shown that only the Cp_2TiCl_2 catalyst (5 mol.%) gives the highest yields of products of hydroalumination of olefins by triethylaluminum; therefore, subsequent experiments were carried out using this catalyst. Unlike previous results, ⁶ zirconium complexes, for example, Cp_2ZrCl_2 , direct the reaction in hydrocarbon solvents to the formation of alumacyclopentanes. ¹²⁻¹⁴



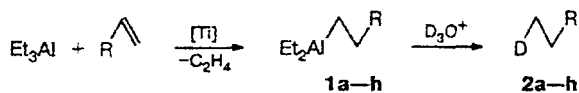
α -Olefins and cyclic and acyclic unsaturated compounds containing the disubstituted double bond were chosen as the starting objects of the study. For example,

the reaction of Et_3Al with 4-vinylcyclohexene (VCH) affords diethyl[(2-(cyclohex-3-enyl)ethyl)alane (**1a**) in ~80% yield. The reaction is accompanied by liberation of an equimolar amount of ethylene.



The study of the effect of the solvent nature on the hydroalumination of VCH established that in halogen-containing (1,2-dichloroethane, CH_2Cl_2 , and CCl_4) and ether-type (THF, Et_2O) solvents, the yield of **1a** does not exceed 10%, whereas in a hydrocarbon medium (hexane, cyclohexane, benzene, and toluene), hydroalumination proceeds with 40–65% yields. When the two-component catalyst $\text{Cp}_2\text{TiCl}_2\text{-Bu}^i\text{AlH}$ (1 : 2, 5 mol.%) is used, the yield of **1a** reaches ~90%. The replacement of Cp_2TiCl_2 by titanium alkoxides ($\text{Ti}(\text{OBu}^n)_4$ or $\text{Ti}(\text{OPr}^i)_4$) results in a decrease in the yield of **1a** to 15–20%. In an excess of Et_3Al (olefin : $\text{Et}_3\text{Al} \approx 1 : 1.2$), the hydroalumination of VCH occurs with higher yields of **1a**.

For VCH : Et_3Al ratios equal to 2 : 1 and 3 : 1, the yields of **1a** calculated per olefin consumed are 64 and 32%, respectively, which indicates that only one ethyl group of the starting Et_3Al participates in the hydroalumination. Hydroalumination of oct-1-ene, dodec-1-ene, hexadec-1-ene, styrene, 1-allylnaphthalene, triethylvinylsilane, and triethoxyvinylsilane under the conditions established gave the corresponding higher OAC **1b–h**. Monodeuterated compounds **2a–h** are the products of their deuterolysis.



a: $\text{R} =$ (~80%); **b**: $\text{R} = \text{C}_6\text{H}_{13}$ (~90%);

c: $\text{R} = \text{C}_{10}\text{H}_{21}$ (~75%); **d**: $\text{R} = \text{C}_{14}\text{H}_{29}$ (~65%);

e: $\text{R} = \text{Ph}$ (~60%); **f**: $\text{R} =$ (~55%);

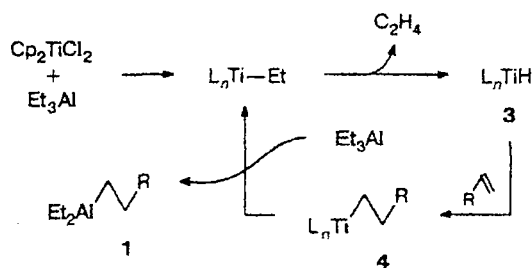
g: $\text{R} = \text{Et}_3\text{Si}$ (~75%); **h**: $\text{R} = (\text{EtO})_3\text{Si}$ (~50%)

The ^{13}C NMR spectra of (alkyl)diethylalanes **1b–d** (Table 1) contain two broadened signals in the upfield region at δ 0.7–0.8 and δ 9–10 corresponding to the C atoms of the ethyl and *n*-alkyl groups directly bound to the Al atom. In the deuterated product **2d**, the region of signals of the Me groups contains a signal at δ -14 (a weak triplet with $^1J_{\text{C-D}} \approx 19$ Hz) belonging to the deuteromethyl group with the isotope effect of chemical shifts of 0.24 ppm.

We failed to involve disubstituted olefins with the nonactivated double bond (cyclohexene, cyclooctene, and hex-2-ene) in hydroalumination. Hydroalumination of functionally substituted O-, N-, and S-containing α -olefins, for example, 1-methoxyocta-(2*E*,7)-diene, 1-phenoxyocta-(2*E*,7)-diene, diethylocta-(2*E*,7)-dienylamine, and *n*-butylocta-(2*E*,7)-dienyl sulfide, occurred with low yields and considerably lower selectivity.

Based on the published data¹ and our experimental results, we can suggest that the catalytic cycle of hydroalumination includes the generation (under the reaction conditions) of active titanium hydride complexes (**3**), which hydrometallate the starting α -olefins to form alkyltitanium complexes (**4**), and their transmetalation under the action of Et_3Al results in the target products **1** according to Scheme 1.

Scheme 1

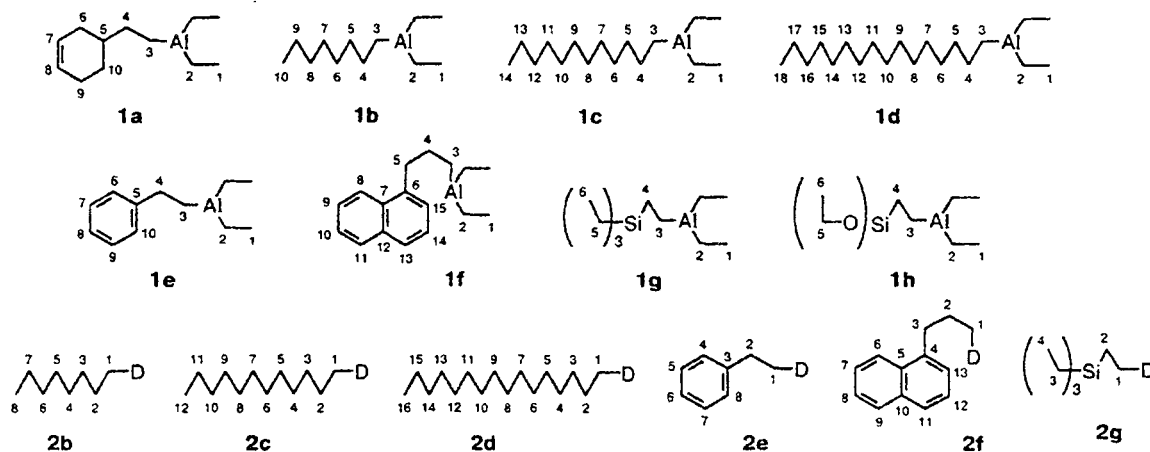


An attempt to hydroaluminate α -olefins by higher trialkylalanes, for example, tris(*n*-octyl)aluminum, was unsuccessful. Perhaps, this is related to the fact that, according to Scheme 1, the formation of a hydride complex **3** requires an olefin molecule to be removed from the coordination sphere of titanium, which is difficult in the case of titanium *n*-octyl complex. Under these conditions, the starting α -olefin that did not enter the reaction isomerizes under the action of low-valence titanium complexes to form less reactive disubstituted olefins.

Thus, the $\text{Et}_3\text{Al-Cp}_2\text{TiCl}_2$ reagent hydroaluminates successfully α -olefins and allows preparation of earlier difficultly accessible diethylalkylalanes with a sufficiently high selectivity.

Experimental

The reactions were carried out in an atmosphere of dry argon. GLC analysis was performed on a Chrom-41 chromatograph using He as the carrier gas, column 1200×3 mm, 5% SE-30 or 15% PEG-6000 on Chromaton N-AW, and flame-ionization detector. GLC analysis of organosilicon compounds was performed under similar conditions, but with a katharometer as the detector. The ^{13}C NMR spectra of (alkyl)diethylalanes **1** and deuterolysis products **2** were recorded on a JEOL FX-90 Q spectrometer (22.5 MHz) in regimes with complete and partial

Table 1. ^{13}C NMR spectra of (alkyl)diethylalanes **1** and products of deuterolysis of **2** (δ)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16
1a	8.86 q	0.68 br.t	8.90 br.t	28.83 t	38.59 d	32.47 t	127.35 d	129.10 t	25.84 t	31.95 t						
1b	8.86 q	0.68 br.t	9.38 br.t	25.71 t	36.50 t	30.00 t	29.81 t	32.54 t	23.24 t	14.33 q						
1c	8.86 q	0.68 br.t	9.84 br.t	25.71 t	36.11 t	30.26 t	29.94 t	29.94 t	30.26 t	29.94 t	29.94 t	33.19 t	23.17 t	14.33 q		
1d*	8.80 q	0.74 br.t	9.90 br.t	25.71 t	36.11 t					30.26 (t, C-6—C-14)					29.94 t	32.47 t
1e	8.93 q	0.74 br.t	11.32 t	32.02 t	147.18 s	128.65 d	128.00 d	125.72 d	128.00 d	128.65 d						
1f	9.51 q	1.39 t	12.18 t	28.25 t	38.78 t	140.42 s	134.24 s	127.54 d	124.23 d	125.92 d	128.72 d	131.71 s	128.00 d	123.77 d	128.72 d	
1g	8.80 q	0.87 br.t	8.28 br.t	5.10 t	3.67 t	7.50 q										
1h	8.66 q	1.00 br.t	9.30 br.t	5.23 t	59.27 t	18.36 q										
2b	14.00** td	23.04 t	31.89 t	29.81 t	29.81 t	31.89 t	23.04 t	14.29 q								
2c	13.89** td	22.87 td	32.17 t	29.89 t	29.63 (t, C-5—C-8)				29.89 t	32.17 t	22.87 t	14.15 q				
2d	13.96** td	22.76 td	32.06 t	29.46 t				29.87 (t, C-5—C-12)					29.46 t	32.06 t	22.76 t	14.18 q
2e	15.32** td	28.91 t	144.28 s	127.89 d	128.34 d	125.68 d	128.34 d	127.89 d								
2f	13.96** td	23.84 t	35.09 t	138.68 s	133.74 s	127.24 t	123.99 t	125.68 t	128.80 d	132.12 s	128.34 d	123.53 d	128.47 d			
2g	7.44*** td	3.28 t	3.67 t	7.63 q												

* The ^{13}C NMR spectrum also contains the following signals (δ): 23.17 (t, C-17) and 14.33 (q, C-18). ** $J_{\text{C-D}} = 19$ Hz. *** $J_{\text{C-D}} = 19.1$ Hz.

proton decoupling. Dilute solutions in anhydrous Et_2O with addition of C_6D_6 for internal field stabilization were used. SiMe_4 was used as the internal standard. Solutions of OAC were sealed under argon.

Synthesis of (alkyl)diethylalanes 1a–h. An olefin (10 mmol) and Cp_2TiCl_2 (0.5 mmol) were placed in a 50-mL reactor in an atmosphere of dry argon at -5 – 0 °C. Et_3Al (12 mmol) was added dropwise to the mixture, the temperature was increased to 30 – 35 °C, and the mixture was stirred for 8 h. The reaction with (triethoxy)vinylnsilane was carried out with a fourfold

excess of Et_3Al . Deuterolysis of OAC **1** was performed by treatment with 20% DCl in D_2O at -5 °C followed by stirring of the reaction mixture at -20 °C for ~ 2 h. Yields of **1** were determined by GLC of the hydrolysis or deuterolysis products.

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