$Bu_2{}^iAlCl—Cp_2TiCl_2$ — a new reagent for hydroalumination of disubstituted acetylenes

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A new regio- and stereoselective method for the synthesis of *E*-alkenylchloralanes based on Cp_2TiCl_2-catalyzed hydroalumination of disubstituted acetylenes by diisobutylaluminum chloride was developed. Hydrolysis and deuterolysis of organoaluminum compounds lead to the corresponding *Z*-olefins, and cross-coupling with allyl halides in the presence of $Pd(Ph_3P)_4$ results in the formation of *cis*-4,5-disubstituted 1,4-dienes.

Key words: organoaluminum compounds, metallocomplex catalysts, hydroalumination, carboalumination, disubstituted acetylenes, olefins, 1,2-dienes, titanium complexes.

Hydroalumination of substituted acetylenes by aluminum hydrides ($LiAlH_4$, $NaAlH_4$, $LiAlMe_3H$, $NaAl(OCH_2CH_2OCH_3)_2H_2$, $NaAlMe_3H$, and $(Pr_2{}^iN)_2AlH$) catalyzed by transition metal (Ti, Co, Cr, Ni, Fe) complexes is an accessible and efficient method for the synthesis of alkenylalanes.[1—5] $Bu_3{}^iAl$ [6] and $Bu_2{}^iAlCl$ [7—9] have recently been introduced into synthetic practice as hydrometallation agents for olefins.

To broaden the application of the catalytic hydroalumination of unsaturated compounds by diisobutylaluminum chloride (DIBAC) and to develop a stereoselective method for the synthesis of *E*-alkenylhaloalanes and *Z*-olefins, we have studied the reactions of disubstituted acetylenes with $Bu_2{}^iAlCl$ catalyzed by complex Ti, Zr, and Hf-containing catalysts, which are the most widely used in hydroalumination of olefins. Of the catalysts tested in this reaction, Cp_2TiCl_2 manifested the highest activity and selectivity (Tables 1 and 2).

Because of the results obtained, all subsequent experiments were performed using Cp_2TiCl_2 (5 mol.%) as the catalyst.

It was established that in the presence of Cp_2TiCl_2 DIBAC hydrometallates tolan, octyne-4, and decyne-5 to form the corresponding *E*-alkenylchloralanes **1a—c**. The reactions are accompanied by the formation of equimolar amounts of isobutylene.

Hydrolysis and deuterolysis of compounds **1a—c** result in *Z*-olefins (**2a—c**) or partially deuterated *Z*-olefins (**3a—c**) and conjugated dienes (**4a—c** and **5a—c**). The ratio of olefins and dienes varies from experiment to experiment and on the average is equal to 8 : 2.

These results testify that under the chosen conditions the hydroalumination occurs along with carboalumination of the initial disubstituted acetylenes by the *E*-alkenylchloralanes **1a—c** formed during the reaction.

Depending on the concentration of the catalyst (Cp_2TiCl_2), the ratio of the initial reagents, and the duration of the experiments, the content of the carboalumination products (**6a—c**) and cyclotrimers of the initial acetylenes varies from 15—35%.

The cross-coupling of symmetric dipropyl- and dibutylacetylene with allyl chloride results in the formation of the corresponding 1,4-dienes (**7** and **8**).

Table 1. Effect of the nature and structure of the catalyst (MC) on the yield of compound **1a** in the hydroalumination of tolan by $Bu_2{}^iAlCl$ (tolan : DIBAC : MC = 10 : 20 : 0.5, 22—24 °C, 12 h)

Catalyst	Yield **1a** (%)
Cp_2TiCl_2	92
$Ti(OBu)_4$	37
$TiCl_4$	28
Cp_2ZrCl_2	25
Cp_2HfCl_2	5

Table 2. Effect of the concentration of Cp_2TiCl_2 on the yield of compound **1a** (tolan : DIBAC = 10 : 20, 22—24 °C, 12 h)

Concentration Cp_2TiCl_2 (mol.%)	Yield **1a** (%)
0.1	10
0.5	25
1	40
3	75
5	92
10	95

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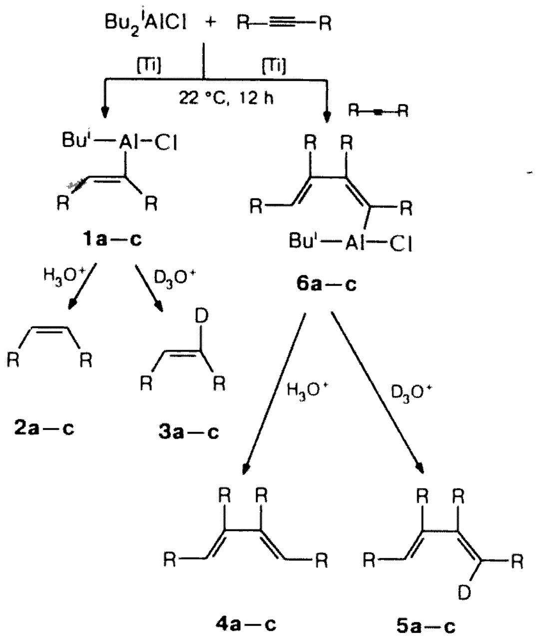
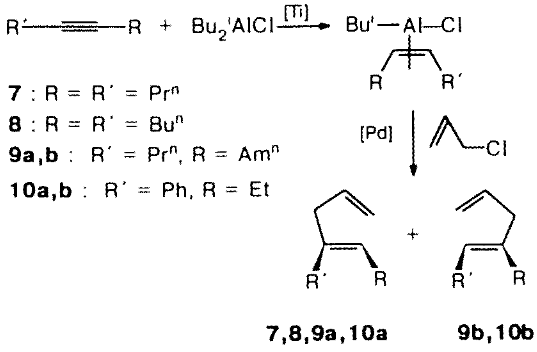


a: R = Ph(92%); **b** = Pr^n(68%); **c**: R = Bu^n(65%)

To elucidate the regioselectivity of the reaction developed and to obtain data on hydroalumination of nonsymmetric acetylenes, we studied the reactions of decyne-4 and phenylethylacetylene with DIBAC under the optimum conditions found. For more reliable identification of the products of the reactions of nonsymmetric acetylenes with Bu$_2^i$AlCl, we cross-coupled the *E*-alkenylchloralanes formed *in situ* with allyl halides. The regioselectivity of hydroalumination was established rather rigorously from the structures of the 1,4-dienes formed.

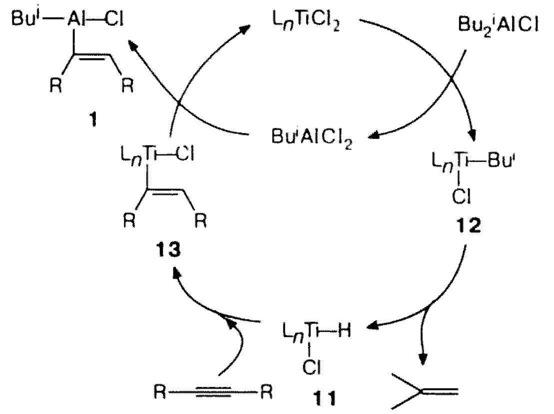
For example, the reaction of decyne-4 with Bu$_2^i$AlCl in the presence of 5 mol.% Cp$_2$TiCl$_2$ results in the formation of a mixture of regioisomeric organoaluminum compounds (OAC), whose cross-coupling[10] without preliminary isolation from the reaction mixture with allyl chloride (3 mol.% Pd(Ph$_3$P)$_4$, THF, OAC : CH$_2$=CH—CHCl = 1 : 3, 0 → 22 °C, 6 h) gives 4,5-dialkylsubstituted 1,4-dienes **9a** and **9b** in a ratio ~1 : 1 in ~60% overall yield. At the same time, hydroalumination of phenylethylacetylene under similar conditions followed by cross-coupling with allyl chloride results in the formation of 4,5-alkyl(phenyl)substituted 1,4-dienes **10a** and **10b** in a ~9 : 1 ratio.



7 : R = R' = Pr^n
8 : R = R' = Bu^n
9a,b : R' = Pr^n, R = Am^n
10a,b : R' = Ph, R = Et

As can be seen, the hydroalumination of 1,2-disubstituted acetylenes by Bu$_2^i$AlCl in the presence of Cp$_2$TiCl$_2$ is fairly stereoselective and makes it possible to obtain *E*-alkenylchloralanes, *Z*-olefins, and 1,4*E*-dienes in one stage.

Based on the published[6] and experimental data, we may propose that the key stage of the reaction is the generation of titanium hydride complexes (**11**) from labile alkyl complexes (**12**) with the formation of isobutylene. The subsequent hydrotitanation of disubstituted acetylenes and transmetallation of titanium alkenyl compounds (**13**) result in the formation of alkenylchloralanes **1**.



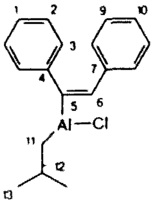
Thus, hydroalumination of disubstituted acetylenes by Bu$_2^i$AlCl under mild conditions in the presence of catalytic amounts of Cp$_2$TiCl$_2$ is a convenient method for the synthesis of *E*-alkenylchloralanes, *Z*-olefins, and 4,5-disubstituted 1,4*E*-dienes with a high degree of stereoselectivity.

Experimental

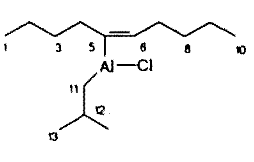
The reactions were carried out in a dry argon atmosphere. GLC analysis was performed on a Chrom-41 instrument in a He flow, column 1200×3 mm, 5% SE-30 or 15% PEG-6000 on Chromaton N-AW IR spectra were recorded on a UR-20 spectrophotometer. Mass spectra were recorded on an MX-1306 instrument with an energy of ionizing electrons of 70 eV and an ionization chamber temperature of 120 °C. ^{13}C NMR spectra of alkenylalanes were recorded on a Jeol-FX-90 Q spectrometer (^{13}C, 22.5 MHz) in the modes with complete and partial proton decoupling. Dilute solutions in absolute Et$_2$O were used with addition of C$_6$D$_6$ for stabilization of the internal field. SiMe$_4$ was used as the internal standard. Solutions of OAC were placed in sealed tubes filled with dry argon. ^{1}H and ^{13}C NMR spectra of compounds **2—5** were recorded on a Bruker AM-300 spectrometer (^{13}C, 75.5 MHz; ^{1}H, 300 MHz). CDCl$_3$ was used as the solvent, and SiMe$_4$ was used as the internal standard.

Synthesis of *E*-alkenylchloralanes. The corresponding acetylene (10 mmol) in a dry argon atmosphere was placed in a

Table 3. ^{13}C NMR spectra of *E*-alkenylchloralanes **1a** and **1c** (Et$_2$O, C$_6$D$_6$, Me$_4$Si)



1a



1c

Com- pound	δ, ppm												
	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
1a	123.64 d	128.72 d	127.42 d	135.58 s	144.20 s	130.75 d	131.60 s	128.21 d	128.21 d	125.79 d	22.91 t	26.37 d	27.94 q
1c	13.71 q	23.63 t	32.70 t	33.55 t	152.55 s	141.65 d	32.51 t	31.66 t	22.78 t	13.71 q	22.13 t	26.70 d	28.53 q

glass 50-mL reactor mounted on a magnetic stirrer, excess (20 mmol) Bu$_2^i$AlCl was added dropwise, then Cp$_2$TiCl$_2$ (0.5 mmol) was added, and the mixture was stirred for 12 h. ^{13}C NMR spectra of α-benzylidenebenzyl(isobutyl)chloralane (**1a**) and dec-5-ene-5-yl(isobutyl)chloralane (**1c**) are presented in Table 3. Analysis of the ^{13}C NMR spectra of OAC **1** indicates that a single stereoisomer is formed in the reaction. For example, in the spectrum of compound **1c**, the broadened singlet signals of the C-5 atom and doublet signals of the C-6 atoms are shifted to the weak-field resonance region of double bond atoms. The considerable weak-field shifts of the α,β-atoms of the double bond of OAC compared to the corresponding signals of the hydrolysis and deuterolysis products are explained by the paramagnetic effect of the Al atom on screening of the C-5 and C-6 nuclei. The configuration of the double bond of alkenylchloroalanes follows from the configurations of the hydrolysis and deuterolysis products.

Products of hydrolysis **2a—c**, **4a—c** or deuterolysis **3a—c**, **5a—c** were obtained by pre-treatment of the reaction mass with 5% HCl or DCl/D$_2$O followed by distillation *in vacuo*. Isolated products **2—5** were identified by comparison with authentic samples.

***Cis*-stilbene (2a)**, n_D^{22} 1.5996, b.p. 105—107 °C (2 Torr) (*cf.* Ref. 11: n_D^{20} 1.6083, b.p. 134 °C (10 Torr)).

Oct-4*Z*-ene (2b), n_D^{22} 1.4136, b.p. 121 °C (*cf.* Ref. 11: n_D^{20} 1.4144, b.p. 122.8 °C).

Dec-4*Z*-ene (2c), n_D^{22} 1.4243, b.p. 52—53 °C (10 Torr) (*cf.* Ref. 11: n_D^{20} 1.4252, b.p. 170.6 °C).

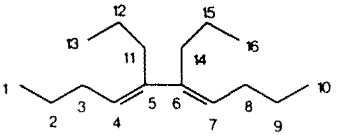
1-Deutero-*cis*-1,2-diphenylethylene (3a), n_D^{20} 1.6012, b.p. 97—98 °C (1 Torr). IR, ν/cm^{-1}: 2240 (C—D), 1600, 720 (Ar). ^{1}H NMR, δ: 6.56 (s, 1 H, CH), 7.20 (s, 10 H, Ph). ^{13}C NMR, δ: 127.01 (d, C-1), 128.32 (d, C-2), 128.20 (d, C-3), 137.31 (s, C-4), 129.95 (t, C-5, $^1J_{(C-D)}$ = 24.0 Hz), 130.16 (d, C-6), 137.23 (s, C-7), 128.20 (d, C-8), 128.32 (d, C-9), 127.01 (d, C-10). Mass spectrum, *m/z*: 181 [M$^+$].

4-Deuterooct-4*Z*-ene (3b), n_D^{20} 1.4249, b.p. 122—123 °C. IR, ν/cm^{-1}: 2292 (C—D). Mass spectrum, *m/z*: 113 [M$^+$].

5-Deuterodec-5*Z*-ene (3c), n_D^{20} 1.4249, b.p. 62—63 °C (15 Torr). IR, ν/cm^{-1}: 2225 (C—D). ^{1}H NMR, δ: 0.90 (t, 6 H, CH$_3$), 1.08—1.48 (m, 8 H, CH$_2$), 1.80—2.08 (m, 4 H, CH$_2$), 5.65 (m, 1 H, CH). ^{13}C NMR, δ: 13.52 (q, C-1), 22.02 (t, C-2), 31.48 (t, C-3), 26.93 (t, C-4), 129.60 (t, C-5, $^1J_{(C-D)}$ = 23.0 Hz), 129.72 (d, C-6), 26.93 (t, C-7), 31.48 (t, C-8), 22.02 (t, C-9), 13.52 (t, C-10). Mass spectrum, *m/z*: 141 [M$^+$].

1,2,3,4-Tetraphenylbuta-1,3-diene (4a), m.p. 185 °C (*cf.* Ref. 12, m.p. 183.5—184.5 °C).

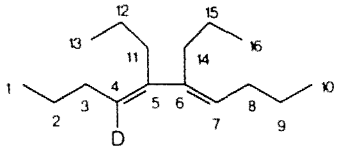
5,6-Di-*n*-propyldeca-4,6-diene (4b). ^{13}C NMR, δ: 13.95 (q, C-1, C-10), 23.02 (t, C-2, C-9), 30.38 (t, C-3, C-8), 126.08 (d, C-4, C-7), 141.42 (s, C-5, C-6), 31.31 (t, C-11, C-14), 22.12 (t, C-12, C-15), 14.13 (q, C-13, C-16). Mass spectrum, *m/z*: 222 [M$^+$].



6,7-Di-*n*-butyldodeca-5,7-diene (4c). Mass spectrum, *m/z*: 278 [M$^+$].

1-Deutero-1,2,3,4-tetraphenylbuta-1,3-diene (5a), m.p. 184—185 °C. IR, ν/cm^{-1}: 2243 (C—D).

4-Deutero-5,6-di-*n*-propyldeca-4,6-diene (5b). ^{13}C NMR, δ: 13.95 (q, C-1, C-10), 23.02 (t, C-2, C-9), 30.12 (t, C-3), 125.70 (t, C-4, $^1J_{(C-D)}$ = 24.0 Hz), 141.22 (s, C-5), 141.41 (s, C-6), 126.08 (d, C-7), 30.38 (t, C-8), 31.31 (t, C-11, C-14), 22.12 (t, C-12, C-15), 14.13 (q, C-13, C-16). Mass spectrum, *m/z*: 223 [M$^+$].



5-Deutero-6,7-di-*n*-butyldeca-5,7-diene (5c). Mass spectrum, *m/z*: 279 [M$^+$].

Cross-coupling products **7—10** were identified by comparison with authentic samples.[13]

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