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An effect of application of chiral aluminium alkoxides and amides as adducts to zirconium catalyzed carbo- and cycloalumination of olefins

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Abstract

This paper is dedicated to a study of properties of the following novel optically active organoaluminium compounds (OACs): (1S,2S)-l,7,7-trimethyl-2-[(dialkylalumina)oxy]-bicyclo[2.2.1]heptanes and (1S)-*N*-(dialkylalumina)-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinolines. The synthesis of the chiral OACs was carried out in the reaction of either natural camphor or salsolidine with both $AlEt_3$ and i-Bu_2AlH. The main goal of the research was to investigate the stereodifferentiating activity of the chiral OACs in the olefin carbo- and cycloalumination reactions, catalyzed by Cp_2ZrCl_2.
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Keywords: Chiral organoaluminium compounds; Cycloalumination; Carboalumination; Camphor; Salsolidine; Optically active shift reagents

1. Introduction

Unlike the application of chiral aluminium alkoxyhydrides and amides in the reactions of asymmetric reduction of carbonyl compounds [1–3], the information regarding utilization of chiral aluminium alkioxides and amides in stereodifferentiating catalytic reactions with olefins is limited. One of the rare examples is presented in [4]. A description of the reaction of hydroalumination of 1,1- disubstituted alkenes in the presence of Ni-contaning complex catalysts activated by chiral ligands is given as follows (see Scheme 1).

Within the reaction, the (−)-*N*-methylsalicylideneamine, (−)-*N*,*N*-dimethylmenthylamine (DMMA), (+)-*N*,*N*-dimethylbornylamine (DMBA), (+)-(R)-*N*,*N*-dimethyl-l-phenylethylamine (DMPEA), (+)-(S,S)-2,3-dimethoxy-l,4-bis-(*N*,*N*-dimethylaminebutane) (DDB) and (−)DIOP [4] were used as chiral ligands. The reaction provides the optical yield of only 2–27% for the chiral high OACs.

It was supposed that introduction of chiral ligands could provide optically active products in the olefin carbo- and cycloalumination reactions which were investigated in [5,6]. These reactions were selected for the research of optical activity of amides and alkoxides due to significant experience gained by the authors during the study of applications and mechanisms of these reactions [11a–11d]. This paper describes an effect of introduction of chiral alkylaluminium alkoxides and amides as catalytic and stoichiometric adducts on the reactions (Scheme 2). The reactions of i-Bu_2AlH with α-methylstyrene and of Et_3Al with either α-methylstyrene or nonene-1 were selected as the model carbo- and cycloalumination reactions. It was assumed that both chiral alkylaluminium alkoxides and amides would be involved in the catalytic Zr-complexes on the both reaction pathways and provide stereochemical results.

The chiral OACs have been obtained, respectively, by the reaction of (1S)-camphor ((1S)-1,7,7-trimethylbicy-

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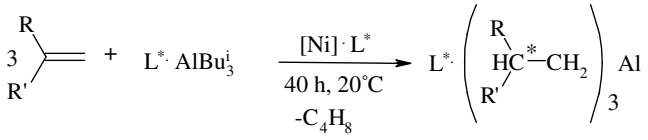


Scheme 1.

clo[2.2.1]heptane-2) and (1S)-salsolidine (hydrochloride (1S)-6,7-dimethoxy-l-methyl-1,2,3,4-tetrahydroisoquinoline) with either i-Bu_2AlH or Et_3Al, and their structures have been investigated. They have been obtained also in situ for the olefin carbo- and cycloalumination reaction. This approach provided results in the investigation of the stereodifferentiating activity of the chiral OACs in the olefin carbo- and cycloalumination reactions, catalyzed by Cp_2ZrCl_2.

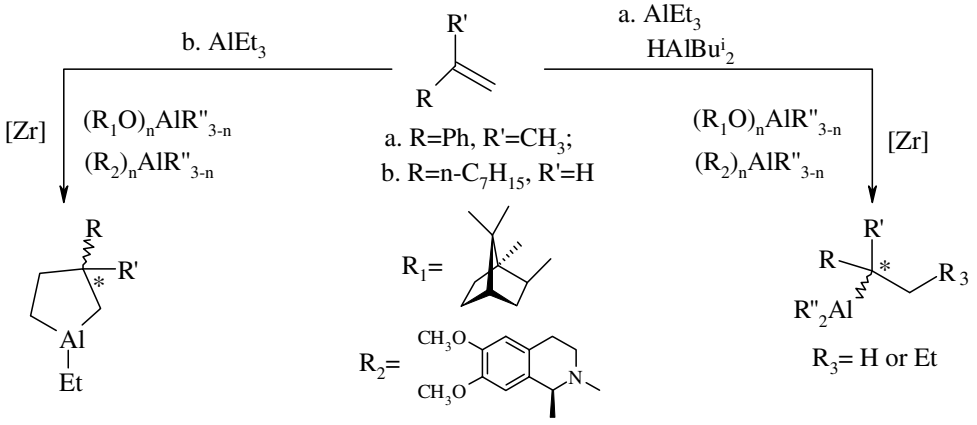
2. Results and discussion

2.1. Structure of chiral alkylaluminium alkoxides and amides obtained in reactions of (1S)-camphor and (1S)-salsolidine with either i-Bu_2AlH or Et_3Al

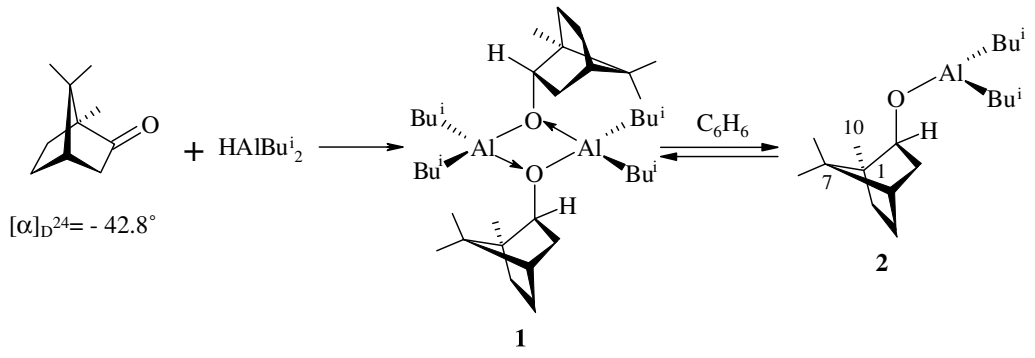
Let us first discuss the reaction of (1S)-camphor with i-Bu_2AlH in benzene. The reaction proceeds via endo-addition of i-Bu_2AlH to (1S)-camphor (Scheme 3). This fact was confirmed by correspondence of chemical shift of C-7 signal in ^{13}C NMR spectra of dimer complex **1** to that shift of the standard exo-camphor alcohol [7a,7b]. This kind of addition is typical for the camphor reduction using metal hydrides [1,8a–8g]. The endo-addition assumes high stereoselectivity of the camphor reduction; therefore, the reaction results in the formation of S-chiral centre at C-2-atom with enantiomeric excess of 98%.

It has been shown that at the room temperature in 1:1 molar ratio at $c = 26$ g 100 ml^{-1}, the formation of alkoxide results in the dimer form (**1**). By applying the cryoscopic method, it was detected that the alkoxide indeed has the dimer structure (Table 1). The dilution of the reaction mixture to $c = 1$ g 100 ml^{-1} reduces the molecular weight of the dimer due to the shift of the equilibrium to the monomer (**2**) with simultaneous decrease of $[\alpha]_D$ (see Table 1). This decrease happens because the number of the chiral centres goes down from 6 for the dimer to 3 for the monomer.

It was supposed that the molecular weight and $[\alpha]_D$ of the aluminium alkoxide would not change in O-containing solvents, for example in 1,4-dioxane. As it is shown in Table 2, a dilution of the solution of aluminium alkoxide **2** in 1,4-dioxane insignificantly varies the molecular weight which is between theoretical



Scheme 2.



Scheme 3.

Table 1
Change in molecular weight and optical rotation angle of molecular complex (1S,2S)-1,7,7-trimethyl-2-[(diisobutylalumina)oxy]bicyclo[2.2.1] heptane (**2**) vs. its concentration in benzene

Concentration (g 100 ml^{-1})	Molecular weight (g mol^{-1})	Dimer concentration (**1**) (%)	$[\alpha]_D^{20}$ [b]
26.4	596 ± 16[a]	100.0	+(26.9 ± 0.7)
15.5	516 ± 10	74.2	+(14.6 ± 0.6)
9.1	452 ± 15	52.6	+(10.2 ± 1.1)
5.3	404 ± 17	36.6	+(6.5 ± 1.1)
3.2	375 ± 15	26.7	+(4.4 ± 0.9)
1.1	322 ± 10	8.6	+(1.4 ± 0.3)

[a] Theoretical molecular weight of dimer (**1**) – 592.9 g mol^{-1}.
[b] $[\alpha]_D^{20}$ [(1S)-camphor] = −42.8° (c = 8 g 100 ml^{-1}, C_2H_5OH).

Table 2
Change in molecular weight and optical rotation angle of molecular complex (1S,2S)-1,7,7-trimethyl-2-[(diisobutylalumina)oxy]bicyclo[2.2.1] heptane (**2**) vs. its concentration in 1,4-dioxane

Concentration (g 100 ml^{-1})	Molecular weight (g mol^{-1})	$[\alpha]_D^{21}$
34.2	517 ± 10[a]	+(14.6 ± 0.4)
20.1	491 ± 9	+(11.7 ± 0.5)
11.8	504 ± 10	+(9.8 ± 0.4)

[a] Theoretical molecular weight of solvate [(**2**) · $C_4H_8O_2$] – 384.6 g mol^{-1} and [(**1**) · $C_4H_8O_2$] – 681.0 g mol^{-1}.

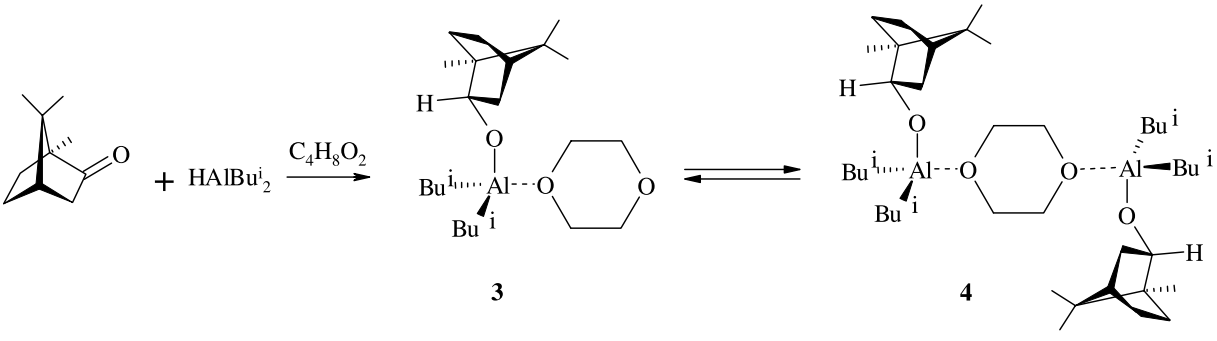
weights of solvates (**2**) · $C_4H_8O_2$ (384 g mol^{-1}) and (**1**) · $C_4H_8O_2$ (593 g mol^{-1}). This fact could be explained by the equilibrium between complexes **3** and **4** as illustrated in Scheme 4. The value of $[\alpha]_D$ decreases insignificantly from +14.6 to +9.8 °C due to the formation of the complex with polar molecules of the solvent.

Let us proceed with the discussion of the reaction of (1S)-camphor with Et_3Al. This reaction provides complex **5**, which was proposed in [9] according to Scheme 5. The structure of the complex **5** has been confirmed by the authors using ^{13}C NMR spectroscopy. The signal that appears at 216.0 ppm and belongs to the carbonyl carbon atom in complex **5** is significantly broadened compared to that signal of initial (1S)-camphor. Moreover, the resonance line of the neighbor quaternary carbon atom at 59.2 ppm is shifted to the low field by 2 ppm and also broadened. The value of $[\alpha]_D$ of (1S)-camphor increases from −42 to −8 °C due to the complex formation. Treatment of the complex with 10% HC1 recovers the (1S)-camphor. Dilution of the complex solution in benzene makes the molecular weight decrease as presented in Table 3. Probably, the decrease occurs because of the complex decomposition into monomeric camphor.

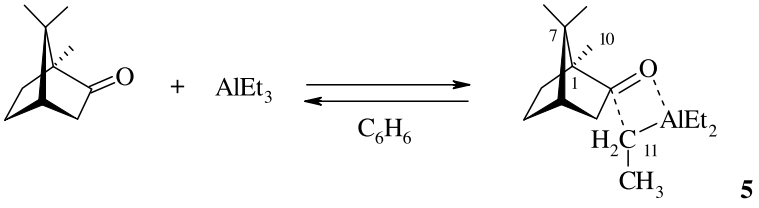
Table 3
Change in molecular weight of complex **5** vs. its concentration in benzene

Concentration of **5** (g 100 ml^{-1})	Molecular weight (g mol^{-1})[a]
14.2	253 ± 5
13.8	238 ± 5
11.5	227 ± 4
9.6	213 ± 4
8.0	204 ± 4
6.0	195 ± 4

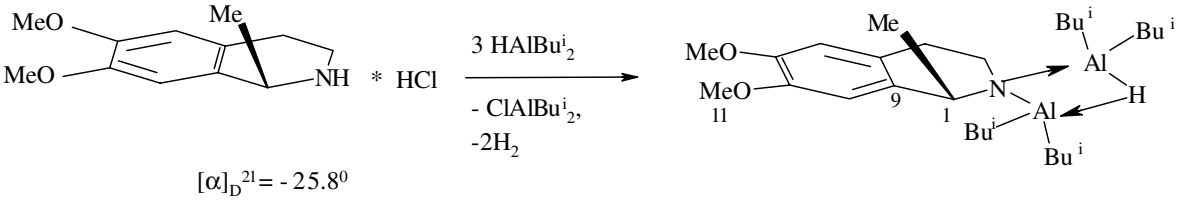
[a] Theoretical molecular weight of complex **5**, 268.4 g mol^{-1}.



Scheme 4.



Scheme 5.



Scheme 6.

Let us describe the interaction of (1S)-salsolidine with i-Bu_2AlH. Both in benzene and 1.4-dioxane, (1S)-salsolidine completely reacts with i-Bu_2AlH at mole ratio 1:3 and forms (1S)-*N*-(diisobutylalumina)-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (**6**) with 95–98% yield (Scheme 6). At 20 °C, the reaction runs for 0.5–1.5 h.

Unlike for the alkylaluminium alkoxides, dilution of the reaction mixture with benzene makes the molecular weight of the complex **6** increase as shown in Table 4. This increase occurs probably due to formation of dimer (**7**), trimer (**8**) and other oligomeric complexes (Scheme 7). Discussions concerning their structure and formation mechanism are presented in [10a–10l].

The dilution also make the value of $[\alpha]_D$ reduce, which demonstrates low rotating ability of chiral oligomeric complexes (Table 4). For example, the complex **6** contains only one 1S chiral center. Probably, formation of oligomeric complexes neutralizes the stereodifferentiating effect, and, consequently, degrades optical activity of the complexes.

The dilution with 1,4-dioxane similarly affects the molecular weight and value of $[\alpha]_D$ for complexes **7**–**9** (Table 5).

Let us finally discuss the reaction of (1S)-salsolidine with Et_3Al in benzene. The reaction runs at 20 °C for 0.5 h and provides (1S)-*N*-(diethylalumina)-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (**9**) with 95–98% yield. (1S)-Salsolidine completely reacts with fivefold excess of Et_3Al, whereas the reaction with i-Bu_2AlH flows at 1:3 mole ratio. The excessive Et_3Al is supposed to be consumed for coordination with methoxy groups of salsolidine as shown in Scheme 8.

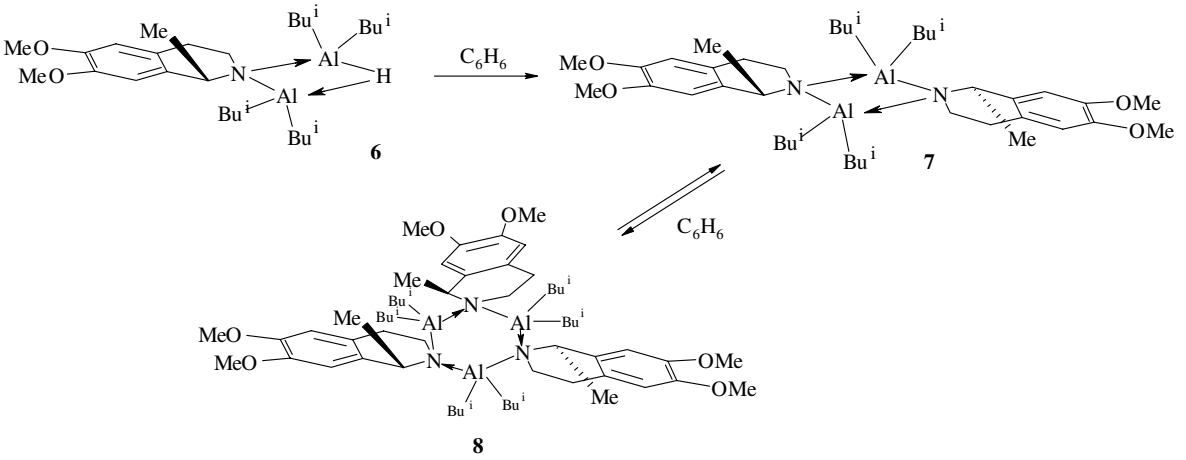
The dilution of the reaction mixture increases themolecular weight of complex **9** (Table 6) due to forma-

Table 4
Change in molecular weight and optical rotation angle of complexes **6**–**8** vs. their concentration in benzene

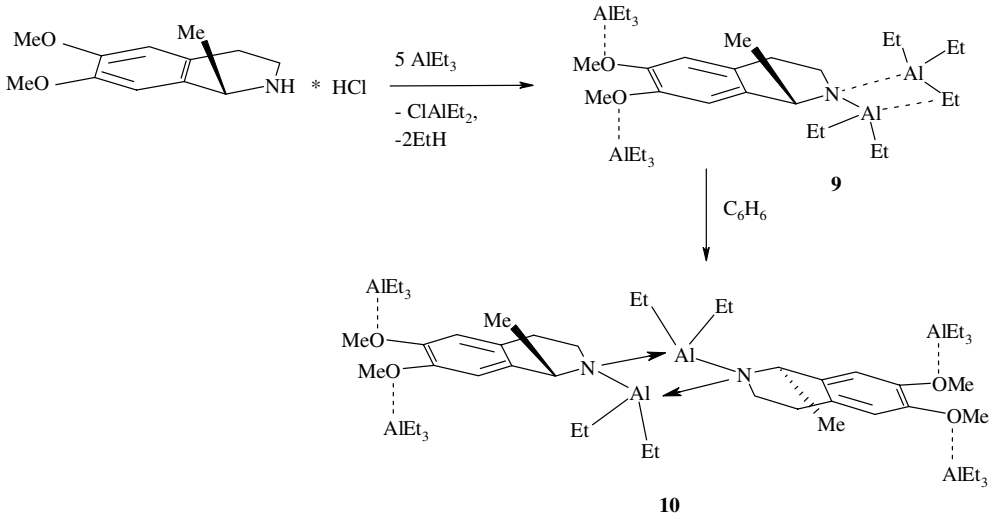
Concentration (g 100 ml^{-1})	Molecular weight (g mol^{-1})	$[\alpha]_D^{20}$
13.4	541 ± 10	+(13.7 ± 0.6)
8.1	664 ± 13	+(10.7 ± 1.0)
4.9	762 ± 15	+(7.6 ± 1.1)
2.9	887 ± 17	+(6.5 ± 1.2)
1.7	1051 ± 21	+(5.3 ± 1.3)

Table 5
Change in molecular weight and optical rotation angle of complexes **6**–**8** vs. their concentration in 1,4-dioxane

Concentration (g 100 ml^{-1})	Molecular weight (g mol^{-1})	$[\alpha]_D^{20}$
14.0	870 ± 19	+(20.1 ± 2.0)
10.5	1119 ± 20	+(19.0 ± 0.4)
7.9	1297 ± 22	+(15.0 ± 0.6)



Scheme 7.



Scheme 8.

Table 6
Change in molecular weight and optical rotation angle of complexes **9** and **10** vs. their concentration in benzene

Concentration ($g\,100\,ml^{-1}$)	Molecular weight ($g\,mol^{-1}$)[a]	$[\alpha]_D^{20}$
20.6	752 ± 10	$+(12.1 \pm 0.2)$
11.0	790 ± 23	$+(9.5 \pm 0.4)$
8.3	835 ± 16	$+(8.7 \pm 0.7)$
7.2	846 ± 10	$+(5.5 \pm 0.5)$
3.5	945 ± 5	$+(2.6 \pm 0.6)$

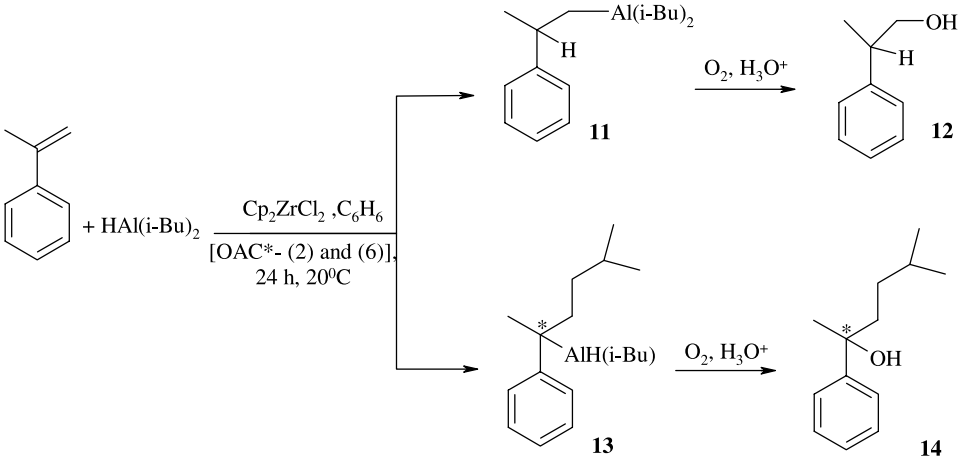
[a] Theoretical molecular weight of complex **9**, 748.1 $g\,mol^{-1}$.

tion of dimeric derivative **10**, which is analogous to the complex **7**; the value of $[\alpha]_D$ decreases with the dilution. Therefore, the formation of dimeric structures also neutralizes the stereodifferentiating effect and degrades optical activity of these complexes.

2.2. An effect of application of synthesized alkylaluminium chiral alkoxides and amides as adducts to carbo- and cycloalumination of olefins

The stereodifferentiating effect of application of synthesized above chiral alkylaluminium alkoxides and amides as catalytic and stoichiometric adducts was studied in reactions of α-methylstyrene carboalumination with either i-Bu_2AlH or Et_3Al, and in reactions of nonene-1 carbo- and cycloalumination with Et_3Al using Cp_2ZrCl_2 catalyst.

It was established that the reactionof α-methylstyrene with i-Bu_2AlH in the presence of Cp_2ZrCl_2 has two pathways and significantly depends on the reaction conditions (Scheme 9). First of all, at room temperature the reaction provides a mixture of hydroalumination (**11**) and carboalumination (**13**) products at 8:9 mole



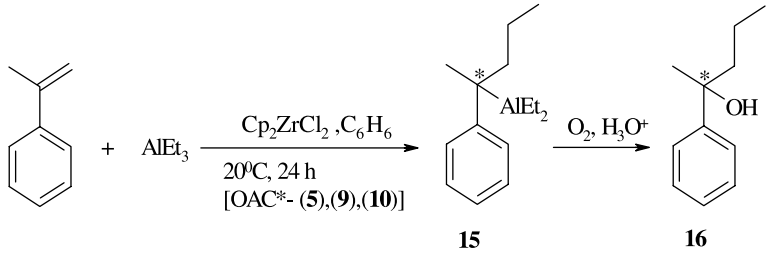
Scheme 9.

Table 7
Influence of chiral OACs **1**, **2** and **6–8** concentration on enantiomeric excess of oxidation and hydrolysis products **12** and **14** in carboalumination reaction of α-methylstyrene by i-Bu_2AlH

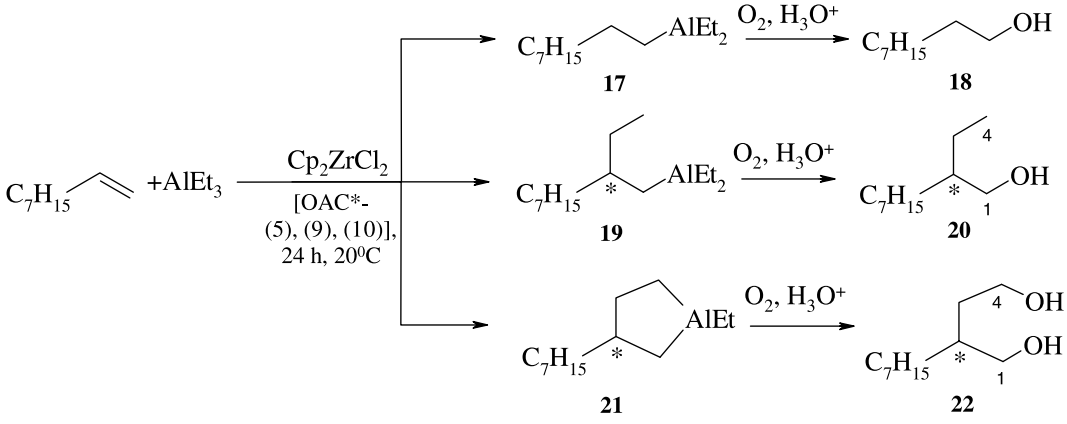
OAC*	Ratio i-Bu_2AlH:camphor (salsolidine):olefin:Cp_2ZrCl_2	Yield of (**12**) (%)	Yield of (**14**) (%)	$[\alpha]_D^{22}$ (**14**) ($CHCl_3$)	ee (**14**) (%)
–	10:0:10:0.5	8	9	0	0
	11:1:10:0.5	2	14	6.8 ± 1.2	14
1–2	15:5:10:0.5	7	10	12.6 ± 2.2	24
	10:10:10:0.5	0	0	–	–
	13:1:10:0.5	30	27	0.9 ± 0.1	2
6–8	25:5:10:0.5	91	1	–	–
	30:10:10:0.5	0	0	–	–

ratio and common yield of 17%. The thermal reaction at 60 °C raises the yield of the same products at 1:1 mole ratio to only 27%. The structure of compounds **11** and **13** was established by applying ^{13}C and ^{1}H NMR spectroscopy to the products of their oxidation and hydrolysis – alcohols **12** and **14**, respectively. Second, an addition of chiral alkylaluminium alkoxides **1** and **2** to the reaction mixture does not change the common yield of hydro- and carboalumination products, but also relatively increase the yield of carboalumination product **13** (Table 7). For example, at mole ratio i-Bu_2AlH:(1S)-camphor:olefin:Cp_2ZrCl_2 of 11:1:10:0.5 the ratio of hydro- to carbo- is 1:7. Furthermore, the introduction of alkylaluminium amides **6–8** quickens the reaction and increases the common yield of products on both pathways. However, an increase of chiral complex **7** concentration to a ratio 25:5:10:0.5 of i-Bu_2AlH:(1S)-salsolidine:olefin:Cp_2ZrCl_2 gives a predomination of hydroalumination products to 91%. At mole ratio i-Bu_2AlH:(1S)-camphor of 1:1 or i-Bu_2AlH:(1S)-salsolidin of 3:1, the hydro- and carboalumination reactions appear to be completely blocked. Moreover, an introduction of optically active alkoxide **1** or amide **6** as chiral activators increases the optical yield of organoaluminium compound **13**. These results testify that the chiral alkoxides and amides indeed take part in the generation of a catalytic system.

The reaction of α-methylstyrene with triethylaluminium in the presence of Cp_2ZrCl_2 provides OAC **15** as a carboalumination product with low yield of 7%



Scheme 10.



Scheme 11.

Table 8
Influence of chiral OACs **5**, **9** and **10** concentration on enantiomeric excess of alcohols **20** and **22**

OAC*	Ratio $AlEt_3$:camphor (salsolidine):olefin:Cp_2ZrCl_2	Yield of (**18**) (%)	Yield of (**20**) (%)	Yield of (**22**) (%)	$[\alpha]_D^{22}$ (**22**) ($CHCl_3$)	ee (**22**) (%)
–	10:0:10:0.5	5	0	84	0	0
	11:1:10:0.5	24	29	11	1.2 ± 0.3	5
5	15:5:10:0.5	42	37	19	2.5 ± 0.5	13
	10:10:10:0.5	0	0	0	–	–
	13:1:10:0.5	59	18	3	0.7 ± 0.1	3
9 and **10**	25:5:10:0.5	4	0	0	–	–
	30:10:10:0.5	0	0	0	–	–

(Scheme 10). Oxidation and hydrolysis of the compound **15** gives tertial alcohol **16**. Introduction of complex **5** at mole ratio 15:5:10:0.5 of $AlEt_3$:camphor:olefin:Cp_2ZrCl_2 does not change the yield of compound **16**. On the other hand, application of amides **9** and **10** at mole ratio 25:5:10:0.5 of $AlEt_3$: salsolidine:olefin:Cp_2ZrCl_2 decreases the yield of the carboalumination product to 3%.

The reaction of $AlEt_3$ with nonene-l using Cp_2ZrCl_2 as catalyst gives mainly the cycloalumination product **21**. Presence of complex **5** or amides **9** and **10** in the reaction mixture leads to carbo- and hydroalumination products **17** and **19** (Scheme 11). The structure of compounds **17**, **19** and **21** was confirmed by identifying corresponding products of oxidation and hydrolysis **18**, **20** and **22**. The dependence of product yields upon mole ratios of reagents is presented in Table 8. Addition of camphor increases the yield of hydro- and carboalumination products. However, at mole ratio 1:1 of $AlEt_3$:camphor the reaction becomes inhibited. These facts can have the following explanation. The OACs that contain oxygen or nitrogen coordinate with the central atom of the catalyst and produce relatively stable complexes, which become active in hydro- and carboalumination reactions. Growth of concentration of chiral OACs formed from either (1S)-camphor or (1S)-salsolidine increases the enanthiomeric excess of **20** and **22** only to 13%. Moreover, the chiral OACs obtained from (1S)-camphor provide more effective sterodifferentiating than that obtained from salsolidine (Tables 7 and 8). This effect is probably a result of the structure of the aluminium complexes and the number of active chiral centers in them.

The investigation of optically active alkylaluminium amides and alkoxides allows the authors to formulate the following conclusion. The introduction of oxygen and nitrogen containing chiral OACs into hydro-, carbo- and cycloalumination reactions of α-olefins using Cp_2ZrCl_2 catalyst could indeed provide optically active products. The stereodifferentiating effect of those formation is caused by coordination of chiral alkylaluminium alkoxides and amides with the central atom of the catalyst.

3. Experimental section

3.1. General

All operations were carried out under argon using Schlenk techniques. Solvents were dried by refluxing over $LiAlH_4$ or i-Bu_2AlH and were freshly distilled prior to use. Commercial 91.8% $AlEt_3$ and 74% i-Bu_2AlH were used. The NMR spectra ^1H and ^{13}C were recorded at 25 °C on spectrometers JEOL FX-90Q (90 MHz ^1H, 22.5 MHz ^{13}C) and BRUKER AM-300 (300 MHz ^1H, 75 MHz ^{13}C). The samples were prepared in standard tubes of 5-mm diameter. D_6-benzene and d-chlorophorm were used as internal standard. Chemical shifts of signals of carbon and hydrogen atoms are given in δ-scale (ppm) with respect to TMS. Optical rotation angles $[\alpha]_D$ were determined on polarimeter P-400 (France) with halogen tube with sodium filter as a radiation source with $\lambda = 589.3$ nm. The measurements of $[\alpha]_D$ were performed in a sectional cylindrical glass cell of 53 mm length. The cell was filled with a solution through a glass inlet using syringe under argon. Enantiomeric excess of products was determined using tris[3-(heptafluorbutiryl)-*l*-campharato]europium (III) as a shift-reagent. Addition of the 10 mol% shift-reagent results in a low field shift and a diastereomeric decay of signals that belong to carbon atoms at hydroxy-group of products of OACs oxidation and hydrolysis (**14**, **20** and **22**). The amount of enantiomeric alcohols in the mixture was determined using signal intensity of protons in HCOH-groups. The cryoscopic studies were carried out in a lengthened conic glass cell with three inlets: for argon, for mixer and for Beckman thermometer. The accuracy of melting point detection is 0.005 °C. The hydrolysis products of reaction mixture were analyzed on chromatograph "Chrom-5" (flame-ionizating detector, column 2 m × 3 mm 15% "Peg-6000" or 5% "SE-30" on Chromaton N-AW, 50–190 °C). The yields of the alkylaluminium alkoxides or amides were calculated relative to amount of the initial camphor or salsolidine. The yields of hydro-, carbo- and cycloalumination products were calculated relative to amount of the initial

olefin. Individual optically active alcohols and hydrocarbons were isolated by preparative gas-liquid chromatography (Carlo Erba, column 4 m × 5 mm, 15% "SE-30" on Chromaton N-AW). Purity of the compounds was controlled by ^{1}H and ^{13}C NMR method.

3.2. Synthesis of dimer complex (1S,2S)-1,7,7-trimethyl-2-[(diisobutylalumina)oxy]-bicyclo[2.2.1]heptane (1)

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon, filled with 12 ml benzene and 2.5 ml 74% i-Bu_2AlH (13 mmol). (1S)-1,7,7-trimethyl-bicyclo[2.2.1]heptane-2-on ((1S)-camphor) (0.705 g, 13 mmol, $[\alpha]_D^{24} = -42.8°$ ($c = 8$ g 100 ml^{-1}, C_2H_5OH)) was added by a small portions to the mixture. The mixture was stirred for 1 h at r.t. Dimer (1S, 2S)-1,7,7-trimethyl-2-[(diisobutylalumina)oxy]bicyclo[2.2.1]heptane (**1**) was obtained with 95–98% yield. ^{1}H NMR (C_6D_6) 0.79 (s, 6H, CH_3), 0.97 (s, 3H, Me), 1.11 (m, 1H, CH), 2.12 (m, 4H, CH_2), 4.29 (m, 1H, CHO), 0.45 (d, 4H, $AlCH_2$, $^3J_{HH} = 6.8$ Hz), 1.24 (d, 12H, $AlCH_2CHCH_3$, $^3J_{HH} = 5.6$ Hz), 1.98–2.25 (m, 1H, $AlCH_2CH$). ^{13}C NMR (C_6D_6) δ 13.64 (q, C_{10}), 20.63 (q, C_8), 21.19 (q, C_9), 24.10 (br. t, C_{11}), 26.28 (d, C_{12}), 27.37 (t, C_5), 28.88 (q, C_{13}), 35.43 (t, C_6), 42.55 (t, C_3), 45.62 (d, C_4), 47.03 (s, C_7), 50.12 (s, C_1), 83.95 (d, C_2).

Further, the reaction mixture was treated with 10% solution of HCl. The solvent was removed and the dry residue was extracted by ethyl alcohol. The extract was filtered and evaporated. (1S, 2S)-1,7,7-Trimethyl-bicyclo[2.2.1]heptan-2-ol (isoborneol) ($[\alpha]_D^{21} = -33.5°$ ($c = 4$ g 100 ml^{-1}, C_2H_5OH)) was obtained. ^{1}H and ^{13}C NMR spectra were identical with those of authentic sample [7a,7b].

3.3. Reaction of (1S)-Camphor with $AlEt_3$

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon, filled with 12 ml benzene and 1.6 ml 91.8% $AlEt_3$ (13 mmol). Small portions of (1S)-camphor (0.705 g, 13 mmol) were added to the reaction mixture, which was stirred for 1 h at r.t. Complex **5** was obtained. ^{13}C NMR ($CDCl_3$) δ 0.48 (t, C_{11}), 9.25 (q, C_{10}), 10.36 (q, C_{12}), 18.88 (q, C_8), 19.60 (q, C_9), 26.88 (t, C_5), 30.20 (t, C_6), 43.33 (d, C_4), 43.53 (t, C_3), 47.23 (s, C_7), 59.20 (br. s, C_1).

The reaction mixture was treated with 10% HCl and the product was extracted by benzene. The extract was filtered and evaporated. (1S)-Camphor was observed. ^{1}H and ^{13}C NMR spectra were identical with those of authentic sample [7a,7c,7d].

3.4. Synthesis of (1S)-2-(diisobutylalumina)-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (6)

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon, filled with 12 ml benzene and 2.9 ml 74% i-Bu_2AlH (15 mmol). (1S)-6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride ((1S)-salsolidine) (1.219 g, 5 mmol, $[\alpha]_D^{21} = -25.8°$ ($c = 2$ g 100 ml^{-1}, C_2H_5OH)) was added by small portions, and reaction mixture was stirred for 1 h at r.t. Complex **6** was obtained with 96% yield. ^{13}C NMR (C_6D_6) δ 19.51 (q, C_{10}), 23.22 (br. t, C_{13}), 26.21 (d C_{14}), 28.62 (q C_{15}), 37.98 (t, C_3), 51.38 (t, C_2), 55.67 (q, C_{11},C_{12}), 71.01 (d, C_1), 113.11 (d, C_5, C_8), 125.90 (s, C_4), 130.91 (s, C_9), 149.11 (s, C_6, C_7).

The reaction mixture was treated with 10% HCl. The solvent was evaporated, and the dry residue was extracted by ethyl alcohol. The extract was filtered and evaporated. (1S)-6,7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline ($[\alpha]_D^{19} = -22.4 \pm 2.$ 6° ($c = 2.8$ g 100 ml^{-1}, C_2H_5OH)) was formed. ^{1}H and ^{13}C NMR spectra were identical with those of authentic sample [7a].

3.5. Synthesis of (1S)-2-(diethylalumina)-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (9)

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon, filled with 12 ml benzene and 1.8 ml 91.8% $AlEt_3$ (15 mmol). (1S)-Salsolidine hydrochloride (0.731 g, 3 mmol) was added by small portions to the reaction mixture, which was stirred for 1 h at r.t. Complex **9** was formed with 95% yield. ^{13}C NMR (C_6D_6) δ 19.51 (q, C_{10}), 23.22 (br. t, C_{13}), 26.21 (d, C_{14}), 28.62 (q, C_{15}), 37.98 (t, C_3), 51.38 (t, C_2), 55.67 (q, C_{11},C_{12}), 71.01 (d, C_1), 113.11 (d, C_5, C_8), 125.90 (s, C_4), 130.91 (s, C_9), 149.11 (s, C_6, C_7).

The reaction mixture was treated with 10% HCl. The solvent was removed and the dry residue was extracted by ethyl alcohol. The extract was filtered and evaporated. (1S)-6,7-Dimethoxy-1-methyl-1,2,3,4-terahydroisoquinoline was obtained [7a].

3.6. Reaction of α-methylstyrene with (i-Bu)$_2$AlH in the presence of (1S,2S)-1,7,7-trimethyl-2-[(diisobutylalumina)oxy]bicyclo[2.2.1]heptane (2)

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon, filled with 12 ml benzene, 2.1 ml 74% i-Bu_2AlH (11 mmol) and 0.054 g (1S)-camphor (1 mmol). The mixture was stirred for 30 min. Then Cp_2ZrCl_2 (0.146 g, 0.5 mmol) and α-methylstyrene (1.182 g, 10 mmol) were added. The mixture was stirred for 24 h, blown by dry oxygen and treated with 10% HCl at 0 °C. The products were extracted by hexane; the upper layer was dried over $CaCl_2$. Yields of alcohols **12** and **14** were determined by GLC. ^{1}H and ^{13}C NMR spectra of 2-phenylpropan-1-ol (**12**) were identical with those of authentic sample [7a].

5-Methyl-2-phenylhexane-2-ol (14). ^{1}H NMR ($CDCl_3$) δ 0.91 (d, 6H, CH_3, $^3J_{H-H} = 6.35$ Hz); 0.80–1.35 (m, 2H, CH_2); 1.59 (s, 3H, CH_3); 1.67–2.09 (m, 3H, CH, $CH_2C_6H_5$); 2.44 (s, 1H, OH); 7.10–7.34 (m, 5H, C_6H_5).

^{13}C NMR ($CDCl_3$) δ 22.61 (d, C_6, C_7), 28.33 (s, C_5), 30.15 (s, C_1), 32.88 (s, C_3), 41.98 (s, C_4), 74.69 (s, C_2), 124.83 (d, C_9), 126.46 (d, C_{11}), 128.08 (d, C_{10}). 147.9 (s, C_8).

The experiment was repeated with the addition of 5 mmol of (1S)-camphor (0.771 g); 15 mmol of $(i\text{-}Bu)_2AlH$ (2.9 ml) are required for this amount.

3.7. Reaction of α-methylstyrene with $(i\text{-}Bu)_2AlH$ in the presence of (1S)-2-(diisobutylalumina)-6,7-dimethoxy-1-methyl-1,2,3,4- tetrahydroisoquinoline (**6**)

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon, filled with 9 ml of benzene, 0.244 g of (1S)-salsolidine (1 mmol) and 2.5 ml of $(i\text{-}Bu)_2AlH$ (13 mmoles) and mixed for 30 min. Then, Cp_2ZrCl_2 (0.146 g, 0.5 mmol) and α-methylstyrene (1.182 g, 10 mmol) were added to the reaction mixture. The reaction mixture was stirred for 24 h, blown by dry oxygen and decomposed by 10% solution of HCl at 0 °C. The products were extracted by hexane; the upper layer was dried over $CaCl_2$. Yields of alcohols **12** and **14** were determined by GLC.

The experiment was repeated with the addition of 5 mmol of (1S)-salsolidine (1.210 g); 26 mmol of $(i\text{-}Bu)_2AlH$ (5 ml) are required for this amount. Yields are listed in Table 7.

3.8. Reaction of α-methylstyrene with $AlEt_3$ in the presence of adducts of Complex (**5**)

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon, filled with 6 ml of benzene, 0.542 g of camphor (1 mmol) and 1.4 ml of $AlEt_3$ (91.8%) (11 mmol), and the reaction mixture was stirred for 30 min. Then Cp_2ZrCl_2 (0.146 g, 0.5 mmol) and α-methylstyrene (1.182 g, 10 mmol) were added to the reaction mixture. The reaction mixture was stirred for 24 h, blown by dry oxygen and decomposed by 10% solution of HCl at 0 °C in order to obtain alcohol **16**. The products were extracted by hexane; the upper layer was dried over $CaCl_2$. Yields of carboalumination products were determined by GLC.

The experiment was repeated with the addition of 5 mmol of the camphor (0.771 g); 15 mmol of $AlEt_3$ (1.9 ml) are required for this amount.

*2-Phenylpentan-2-ol (**16**).* ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3, CH_3, $^3J_{H\text{-}H} = 6.3$ Hz,); 1.20-1.35 (m, 2H, CH_2); 1.50 (s, 3H, CH_3); 1.75 (t, 2H, CH_2C $^3J_{H\text{-}H} = 6.3$ Hz); 2.55 (s, 1H, OH); 7.18-7.40 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ 14.48 (q, C_5), 17.34 (q, C_1), 30.15 (t, C_4), 46.60 (t, C_3), 74.82 (s, C_2), 124.83 (d, C_7), 126.52 (d, C_9), 128.15 (d, C_8), 148.11 (s, C_6).

3.9. Reaction of α-methylstyrene with $AlEt_3$ in the presence of adducts of chiral OACs (**9**), (**10**)

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon and filled with 6 ml of benzene, 0.243 g of (1S)-salsolidine hydrochloride (1 mmol) and 1.9 ml of $AlEt_3$ (91.8%) (15 mmol), and the reaction mixture was stirred for 30 min. Then 0.146 g of Cp_2ZrCl_2 (0.5 mmol), 1.182 g of α-methylstyrene (10 mmol) were added. The reaction mixture was stirred for 24 h, blown by dry oxygen and decomposed by 10% solution of HCl at 0 °C in order to obtain alcohol **16**. The products were extracted by hexane, the upper layer was dried over $CaCl_2$. Yields of carboalumination products were determined by GLC.

The experiment was repeated with the addition of 5 mmol of hydrochloride (1S)-salsolidine (1.219 g); 25 mmol of $AlEt_3$ (3.14 ml) are required for this amount.

3.10. Reaction of nonene-1 with $AlEt_3$ in the presence of adducts of complex **5**

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon, filled with 6 ml of benzene, 0.154 g of camphor (1 mmol) and 1.4 ml of $AlEt_3$ (91.8%) (11 mmol), and the reaction mixture was stirred for 30 min. Then, 0.146 g of Cp_2ZrCl_2 (0.5 mmol) and 1.262 g of nonene-1 (10 mmol) were added. The reaction mixture was stirred for 24 h, blown by dry oxygen and decomposed by 10% solution of HCl at 0 °C. The products were extracted by hexane; the upper layer was dried over $CaCl_2$. Yields of the products of carboalumination were determined by GLC. Nonan-1-ol (**18**) [7a], 2-ethylnonan-l-ol (**20**) and 7-heptylbutan-l,4-diol (**22**) were formed.

*2-Ethylnonan-1-ol (**20**).* ^{1}H NMR ($CDCl_3$) δ 0.82–0.96 (m, 6H, CH_3); 1.10-1.65 (m, 14H, CH_2); 1.93–2.18 (m, 1H, CH); 3.51-3.99 (m, 2H, $C\underline{H}_2OH$); 4.66 (m, 1H, OH). ^{13}C NMR ($CDCl_3$) δ 11.10 (t, C_4), 14.09 (q, C_{11}), 22.67 (t, C_{10}), 23.32 (t, C_3), 26.90 (t, C_6), 28.52 (t, C_8), 29.43 (t, C_7), 31.84 (t, C_9), 32.49 (t, C_5), 39.38 (d, C_2), 65.98 (t, C_1).

*7-Heptylbutan-1 4-diol (**22**).* ^{1}H NMR ($CDCl_3$) δ 0.74 (t, 3H, CH_3, $^3J_{H\text{-}H} = 5.61$ Hz); 1.10–1.25 (m, 10H, CH_2); 1.35–2.00 (m, 5H, CH, CH_2); 3.49–3.65 (m, 4H, $C\underline{H}_2OH$); 4.15 (m, 2H, OH). ^{13}C NMR ($CDCl_3$) δ 14.09 (q, C_{11}), 22.67 (t, C_{10}), 27.01 (t, C_6), 29.30 (t, C_8), 29.89 (t, C_7), 31.84 (t, C_3, C_9), 35.74 (t, C_5), 39.38 (d, C_2), 60.71 (t, C_4), 65.98 (t, C_1).

The experiment was repeated with the addition of 5 mmol of camphor (0.771 g); 15 mmol of $AlEt_3$ (1.9 ml) are required for this amount.

3.11. Reaction of nonene-1 with $AlEt_3$ in the presence of adducts of chiral OACs (**9**) and (**10**)

A glass reactor of 50 ml was fixed on a magnetic stirrer under argon, filled with 6 ml of benzene, 0.244 g of hydrochloride (1S)-salsolidine (1 mmol) and 1.9 ml of $AlEt_3$ (91.8%) (15 mmol), and the reaction mixture was stirred for 30 min. Then, 0.146 g of Cp_2ZrCl_2 (0.5 mmol)

and 1.262 g of nonene-1 (10 mmol) were added. The reaction mixture was stirred for 24 h, blown by dry oxygen and decomposed by 10% of HCl solution at 0 °C. The products were extracted by hexane; the upper layer was dried over $CaCl_2$. Ratio of products was determined by GLC. Nonan-1-ol (**18**) [7a], 2-ethylnonan-1-ol (**20**) and 7-heptylbutan-1,4-diol (**22**) were formed.

The experiment was repeated with the addition of 5 mmol of hydrochloride salsolidine (1.21 g); 25 mmol of $AlEt_3$ (3.14 ml) is required for this amount.

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References

[1] A. Xajos, Komplexe Hydride und inke Anwendung inder Organischen Chemie, Veb Deutscher Verlag der Wissenschaften, Berlin, 1966, 624 p.
[2] V.A. Pavlov, T.V. Simonova, E.P. Klabunovskii, Bull. Acad. Sci. USSR, Div. Chem. Sci. 36 (1987) 770.
[3] K. Maruoka, H. Yamamoto, Angew. Chem. 97 (1988) 3967.
[4] G. Giacomelli, L. Bertero, L. Lardicci, Tetrahedron Lett. 22 (1981) 883.
[5] U.M. Dzhemilev, A.G. Ibragimov, O.S. Vostrikova, G.A. Tolstikov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 34 (1985) 43.
[6] U.M. Dzhemilev, A.G. Ibragimov, A.P. Zolotarev, R.R. Muslukhov, G.A. Tolstikov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 38 (1989) 194.
[7] (a) Integrated Spectral Data Base System for Organic Compounds, National Institute of Materials and Chemical Research Tsukuba, Ibaraki 305-8565, Japan. Available from www.aist.-go.jp/RIODB/SDBS
(b) M.L. Sierra, J.P. Oliver, J.V. Srini, R. Kumar, Organometallics 11 (1992) 206;
(c) D.G. Morris, M. Murray, J. Chem. Soc. Perkin Trans. (1976) 1579;
(d) Shinichi Ueji, Tetrahedron Lett. 21 (1980) 475.
[8] (a) E.C. Ashby, J.R. Boone, J. Org. Chem. 41 (1976) 2890;
(b) E.C. Ashby, S.A. Noding, A.B. Goel, J. Org. Chem. 45 (1980) 1028;
(c) H.C. Brown, V. Varma, J. Org. Chem. 39 (1974) 1631;
(d) S. Krishnamurthy, H. Brown, J. Am. Chem. Soc. 98 (1976) 3383;
(e) H.C. Brown, S. Krishnamurthy, Nung Min Yoon, J. Org. Chem. 41 (1976) 1778;
(f) H. John, S. Akiyama, F.J. Cedar, M.J. Bennet, R.M. Tuggu, J. Am. Chem. Soc. 96 (1974) 274;
(g) W. Hans, F. Ben, Tetrahedron 32 (1976) 2831.
[9] G.A. Tolstikov, V.P. Ur'ev, Organoaluminium synthesis, Nauka, 1979.
[10] (a) T.R.R. McDonald, W.S. McDonald, Proc. Chem. Soc. (1963) 382;
(b) O.T. Beachley, G.E. Coates, G. Kohnstam, J. Chem. Soc. (1965) 3248;
(c) J.L. Atwood, G.D. Stuky, J. Am. Chem. Soc. 92 (1970) 285;
(d) K. Gosling, G.M. McLaughlin, G.A. Sim, J.D. Smith, Chem. Commun. (1970) 1617;
(e) M. Cesari, G. Perego, G. Del Piero, S. Cucinella, E. Cernia, J. Organomet. Chem. 78 (1974) 203;
(f) G. Perego, G. Del Piero, M. Cesari, A. Zazatta, G. Dozzi, J. Organomet. Chem. 87 (1975) 53;
(g) G. Del Piero, M. Cesari, G. Dozzi, A. Mazzei, J. Organomet. Chem. 129 (1977) 281;
(h) K.M. Waggoner, P.P. Power, J. Am. Chem. Soc. 113 (1991) 3385;
(i) D.M. Choquette, M.J. Timm, J.L. Hobbs, T.M. Nicholson, M.M. Olmstead, R.P. Planalp, Inorg. Chem. 32 (1993) 2600;
(j) C. Schnitter, S.D. Waezsada, H.W. Roesky, M. Teichert, I. Uson, E. Parisini, Organometallics 16 (1997) 1197;
(k) C.J. Harlah, S.G. Bott, A.R. Barron, J. Chem. Soc., Dalton Trans. (1997) 637;
(l) J.E. Park, B.-J. Bae, Y. Kim, J.T. Park, I.-H. Suh, Organometallics 18 (1999) 1059.
[11] (a) U.M. Dzhemilev, A.G. Ibragimov, Russ. Chem. Rev. 69 (2) (2000) 121;
(b) L.M. Khalilov, L.V. Parfenova, S.V. Rusakov, A.G. Ibragimov, U.M. Dzhemilev, Russ. Chem. Bull., Int. Ed. 49 (2000) 2051;
(c) S.V. Rusakov, L.M. Khalilov, L.V. Parfenova, A.G. Ibragimov, O.A. Ponomarev, U.M. Dzhemilev, Russ. Chem. Bull., Int. Ed. 50 (2001) 2336;
(d) A.V. Balaev, L.V. Parfenova, I.M. Gubaidullin, S.V. Rusakov, S.I. Spivak, L.M. Khalilov, U.M. Dzhemilev, Dokl. Phys. Chem. 381 (2001) 279.