chemistry proceedings

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Proceeding Paper

Synthesis of Dibenzylbutane and 9,8′-Neo-Lignans via Cyclometalation of Allylbenzene by $EtAlCl_2$ and Mg in the Presence of Zr *ansa*-Complexes †

Pavel V. Kovyazin [1],*, Pavel V. Ivchenko [2], Ilya E. Nifant'ev [2] and Lyudmila V. Parfenova [1]

[1] Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, Prospekt Oktyabrya, 141, 450075 Ufa, Russia; luda_parfenova@ipc-ras.ru
[2] A. V. Topchiev Institute of Petrochemical Synthesis RAS, Leninsky Avenue 29, 119991 Moscow, Russia; phpasha1@yandex.ru (P.V.I.); ilnif@yahoo.com (I.E.N.)
* Correspondence: kpv38@mail.ru

† Presented at the 25th International Electronic Conference on Synthetic Organic Chemistry, 15–30 November 2021; Available online: https://ecsoc-25.sciforum.net/.

Abstract: The aim of the research is the development of a one-pot method for the synthesis of lignans, natural compounds that show a wide spectrum of biological activities. For this purpose, the *ansa*-zirconocenes of various structures were tested as catalysts of allylbenzene cyclometalation with ethylaluminum dichloride ($EtAlCl_2$) and Mg. The effects of the organophosphorus compounds, hexamethylphosphoramide (HMPA) and triphenylphosphine (PPh_3), on the chemo- and regioselectivity of the reaction were studied. The use of η^5-indenyl or fluorenyl *ansa*-complexes with ethanediyl or dimethylsilylene bridges, as well as a biscyclopentadienyl complex with Si-bound ligands as catalysts in the presence of HMPA, yields the formation of cyclometalation products in a total yield of 70%. Cyclometalation product composition is represented by two regioisomers, 3,4-dibenzyl- and 2,4-dibenzyl-substituted alumolanes, with a ratio of (1-2):1, in which hydrolysis provides corresponding dibenzylbutane lignan and 9,8′-neo-lignan.

Keywords: cyclometalation; alkenes; zirconocenes; lignane

Citation: Kovyazin, P.V.; Ivchenko, P.V.; Nifant'ev, I.E.; Parfenova, L.V. Synthesis of Dibenzylbutane and 9,8′-Neo-Lignans via Cyclometalation of Allylbenzene by $EtAlCl_2$ and Mg in the Presence of Zr *ansa*-Complexes. *Chem. Proc.* **2022**, *8*, 60. https://doi.org/10.3390/ecsoc-25-11776

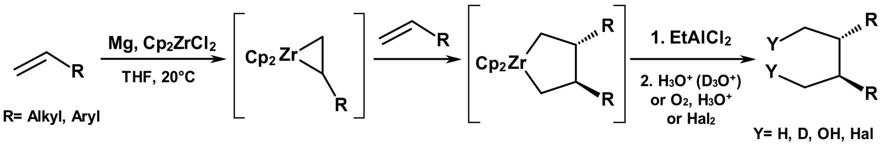
Academic Editor: Julio A. A. Seijas Vázquez

Published: 14 November 2021

1. Introduction

Since 1989, the catalytic cycloalumination of alkenes and acetylenes (Dzhemilev reaction) has been developing as a direction of organoaluminum compound (OAC) chemistry. The reaction provides an effective and stereoselective route for the synthesis of various classes of organic compounds [1,2].

Among the developed methods, the reaction of terminal alkenes or alkynes with OAC and Mg, catalyzed by Cp_2ZrCl_2, which goes through the formation of metallocycles, affords 2,3-disubstituted butanes or 1,4-butanediols with a high diastereoselectivity (Scheme 1) [1–5]. Using this approach, the one-pot diastereoselective method for the synthesis of dibenzylbutane lignans, a group of natural compounds showing a wide range of biological activities [6–12], was developed [13,14].



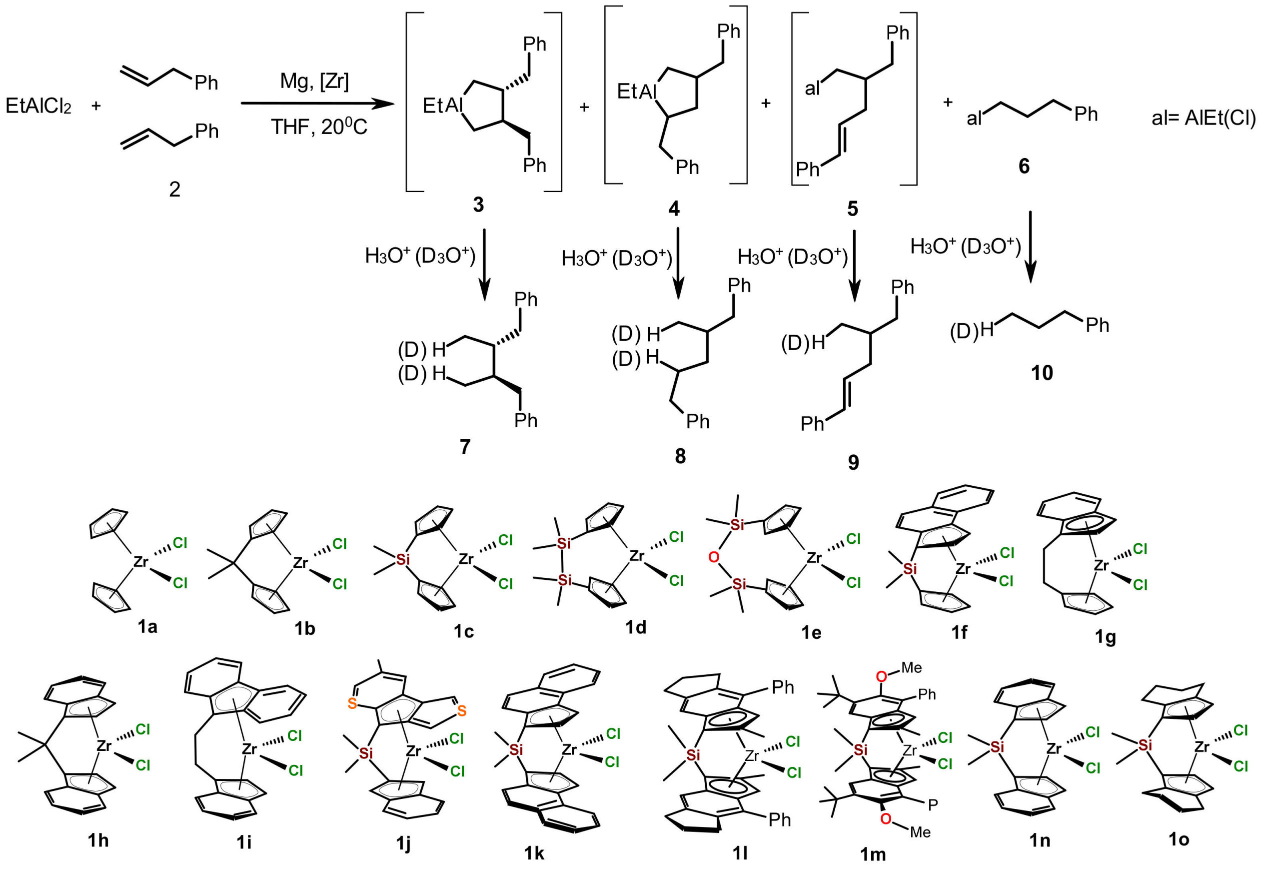
Scheme 1. The reaction of terminal alkenes with OAC and Mg, catalyzed by Cp_2ZrCl_2.

The structure of the catalyst and the composition of the catalytic system significantly influence the reaction rate and the chemo- and stereoselectivity. The *ansa*-effect is well known for zirconocenes [15]. As a rule, it causes an increase in catalyst activity. Moreover, nucleophilic agents can affect the stability of organometallic species. For example, hexamethylphosphoramide (HMPA) possess high solvating ability towards the inorganic ions and organometallic reagents [16–19]. Phosphine ligands can stabilize intermediates, in particular zirconacycles [20,21], which are formed in the course of cyclometalation reactions, and therefore reduce the probability of side processes.

In continuation of our studies [13,14], the *ansa*-zirconocenes of various structures were tested as the catalysts of the allylbenzene cyclometalation with ethylaluminum dichloride ($EtAlCl_2$) and Mg. The effect of the organophosphorus compounds HMPA and triphenylphosphine (PPh_3) on the chemo- and regioselectivity of the reaction was studied as well.

2. Results and Discussion

The catalytic action of zirconocenes of various structures (**1a–o**) in the reaction of allylbenzene with ethylaluminum dichloride ($EtAlCl_2$) and metallic Mg in tetrahydrofuran (THF) was studied (Scheme 2 and Table 1). HMPA or PPh_3 were used as nucleophilic agents.



Scheme 2. The reaction of allylbenzene with $EtAlCl_2$ and Mg, catalyzed with zirconocenes **1a**–**o** in the presence of HMPA or PPh_3.

It was found that the reaction of allylbenzene with $EtAlCl_2$ and Mg, catalyzed with zirconocenes in the presence of HMPA or PPh_3 affords alumolane regioisomers **3** and **4** (Scheme 2). The acyclic OAC with double bond **5** and hydroalumination product **6** were identified in the product mixture as well. Hydrolysis or deuterolysis of cyclometalation products **3** and **4** provide dibenzylbutane lignan **7** and 9,8′-neo-lignan **8**.

The addition of HMPA to the reaction mixture with catalyst 1a significantly shortens the reaction time (Table 1, entries 2–4). As a result, the reaction proceeds in 48 h with an allylbenzene conversion of 97–99%. The addition of PPh_3 led to a decrease in the substrate conversion to 61–63% (entries 5,6). The alkene conversion reached 70–98% in the reactions catalyzed by *ansa*-zirconocenes. However, among them biscyclopentadienyl and bisindenyl complexes with isopropylidene bridges **1b** and **1h** showed minimal activity (entries 7, 13). The presence of HMPA increased the chemoselectivity of the reaction towards the formation of cyclic OACs (up to 81%). Nevertheless, the regioselectivity of the process decreased.

Table 1. Reaction of allylbenzene with $EtAlCl_2$ and Mg, catalyzed by Zr complexes **1a–o** (22 °C, 72 h, HMPA or PPh_3, THF, mole ratio [Zr]:[Mg]:[$EtAlCl_2$]:[allylbenzene]:[HMPA or PPh_3] = 1:20:25:20:20).

Entry	[Zr]	HMPA/PPh_3	Alkene Conversion, %	Product Yield, %			
				7	8	9	10
1	**1a**	-	98	58	8	23	6
2	**1a**	HMPA (0.6 eq) [a]	97	46	24	14	13
3	**1a**	HMPA [a]	99	44	23	20	12
4	**1a**	HMPA (2 eq) [a]	99	49	23	17	10
5	**1a**	PPh_3	63	29	9	15	10
6	**1a**	PPh_3 (3 eq)	61	23	9	26	5
7	**1b**	HMPA	<1	-	-	-	-
8	**1c**	HMPA	82	24	15	16	25
9	**1d**	HMPA	63	25	15	7	15
10	**1e**	HMPA	48	22	4	7	12
11	**1f**	HMPA	58	22	10	3	6
12	**1g**	HMPA	76	27	25	12	8
13	**1h**	HMPA	<1	-	-	-	-
14	**1i**	HMPA	83	35	23	14	9
15	**1i**	HMPA	70	29	21	2	15
16	**1j**	HMPA	82	36	26	11	7
17	**1k**	HMPA	96	38	41	4	13
18	**1l**	HMPA	98	41	40	5	12
19	**1m**	HMPA	87	46	31	6	4
20	**1n**	-	70	47	13	5	2
21	**1o**	HMPA	6	2	<1	<1	<1

[a] reaction time—48 h.

The most active catalysts in the reaction of allylbenzene with Et_2AlCl and Mg was found to be *ansa*-complexes with ethanediyl (**1g**,**i**) (entries 12,14) or dimethylsilylene (**1i–m**) bridges (entries 15–20), containing η^5-indenyl or fluorenyl fragments, as well as a biscyclopentadienyl complex with Si-bound ligands (**1c**) (entry 8). In the presence of these complexes, the conversion of allylbenzene was 70–98% and the reaction proceeded with the predominant formation of cyclometallation products 3,4 with a total yield of up to 70% and a regioisomer ratio 3:4 = (1–3.6):1. However, despite the increase in the activity and chemoselectivity of catalytic systems based on Zr *ansa*-complexes due to the introduction of HMPA, the regioselectivity of the reaction decreased (see, for example, complex **1m**,**n**, entries 19, 20). The use of a Si-bound bistetrahydroindenyl (**1o**) instead of a bisindenyl ligand (**1m**) in the catalyst structure leads to an almost complete loss of activity.

3. Materials and Methods

General Procedures

All operations for organometallic compounds were performed under argon according to Schlenk technique. THF and diethyl ether were dried and distilled from sdium/benzophenone before use. Commercially available allylbenzene (98%, Acros) and $EtAlCl_2$ (97%, Merck). CAUTION: the pyrophoric nature of aluminum alkyl compounds requires special safety precautions in their handling. Zirconocenes **1a–1o** were synthesized according to known procedures: **1a** [22], **1b** [23], **1c** [24], **1d** [25], **1e** [26], **1f**, **1g**, **1i** [27,28], **1h** [29], **1j** [30,31], **1k** [32,33], **1l** [34], **1m** [35], **1n** [**36**], **1o** [37] from $ZrCl_4$ (98%, Acros).

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (400.13 MHz (^1H), 100.62 MHz (^{13}C)) (Bruker, Rheinstetten, Germany). As solvents and the internal standards, CD_2Cl_2 and $CDCl_3$ were employed. The 1D and 2D NMR spectra (COSY HH, HSQC, HMBC, NOESY) were recorded using standard Bruker pulse sequences. The yields of OAC products were determined by analyzing the mixture of deuterolysis or hydrolysis products **7–10** using a gas chromatograph-mass spectrometer GCMS-QP2010 Ultra (Shimadzu, Tokyo, Japan) equipped with the GC-2010 Plus chromatograph (Shimadzu, Tokyo, Japan), TD-20 thermal desorber (Shimadzu, Tokyo, Japan), and an ultrafast quadrupole mass-selective detector (Shimadzu, Tokyo, Japan).

The obtained NMR and the mass spectral characteristics of compounds **7–10** correspond to the literature data [13,14].

4. Conclusions

It was shown that the structure of the η^5-ligand at the Zr atom significantly affects the activity of the system, and the presence of HMPA increases the yield of cyclometalation products up to 77%. The reaction proceeds with the formation of regioisomers of 3,4-dibenzyl- and 2,4-dibenzyl-substituted alumolanes with a ratio (1-2):1, which hydrolysis provides corresponding dibenzylbutane and 9,8$'$-neo-lignans.

Author Contributions: Conceptualization, L.V.P.; methodology, P.V.K. and L.V.P.; validation, L.V.P. and P.V.K.; formal analysis, P.V.K., P.V.I. and I.E.N.; investigation, P.V.K.; resources, P.V.K. and L.V.P.; data curation, P.V.K. and L.V.P.; writing—original draft preparation, P.V.K. and L.V.P.; writing—review and editing, L.V.P.; visualization, P.V.K. and L.V.P.; supervision, L.V.P.; project administration, P.V.K.; funding acquisition, L.V.P. All authors have read and agreed to the published version of the manuscript.

Funding: The studies were carried out in accordance with the Federal Program No. AAAA-A19-119022290004-8. The work was also supported by the TIPS RAS State Plan (in part of the synthesis of zirconocene dichloride complexes).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors acknowledge the use of equipment in the Agidel Collective Use Centre at the Institute of Petrochemistry and Catalysis of RAS.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds are not available from the authors.

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