Dzhemilev Reactions in the Chemistry of Organoaluminium and Organomagnesium Compounds

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Abstract

The history of discovery and application of Dzhemilev reaction which represents catalytic cycloalumination, cyclo- and ethylmagnesiation of olefins, allenes, acetylenes by means of Al and Mg alkyl and halogenoalkyl derivatives with the participation of Ti-, Zr- and Co-containing catalysts is discussed. As the result of this reaction new classes of cyclic organometallic compounds of non-transition metals have been obtained such as aluminacyclopropanes, aluminacyclopropenes, aluminacyclopentanes, aluminacyclopentenes, aluminocyclopenta-2,4-dienes, magnesacyclopentanes, magnesacyclopentenes, magnesacyclopenta-2,4-dienes.

Key words: catalysis, cycloalumination, cyclomagnesiation, ethylmagnesiation, unsaturated compounds, Dzhemilev reaction

The most outstanding achievements in the field of organoaluminium and organomagnesium synthesis for the last 10–15 years are connected with the reactions of catalytic cycloalumination, cyclomagnesiation and ethylmagnesiation of olefins, dienes and acetylenes with the help of Al and Mg alkyl and halogenoalkyl derivatives with the participation Ti-, Zr- and Co-containing catalysts [1–4]. These reactions are known in the world literature as Dzhemilev reactions [5].

The discovery of the reaction of catalytic cycloalumination was preceded by research connected with the studies on linear dimerization and co-dimerization of 1,3-dienes and α-olefins with the participation of Zr-containing catalysts [6–9]. For the dimerization of α-olefins under the action of $Zr(OBu)_4$–Et_2AlCl catalyst it was revealed, that under the conditions of proceeding the reaction alongside with target methylenealkanes **1** approximately 5 % of a product of β-ethylation of initial α-olefin **2** are formed in each experiment.
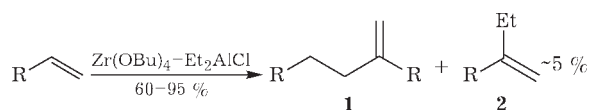
With the increase in the concentration of Et_2AlCl in the catalyst composition the content of compound **2** increased to reach almost 90 % at stoichiometrical amount of Et_2AlCl [10, 11].

With the replacement of $Zr(OBu)_4$ by $Ti(OBu)_4$ or $TiCl_4$ catalysts in the mentioned above reaction one can observe ethylalumination of initial α-olefins [12], whereas 3-substituted aluminacyclopentanes **3** were obtained with high yields using Et_3Al as an initial organoaluminium compound (OAC) and catalyst Cp_2ZrCl_2 [13] in the reaction with α-olefins.
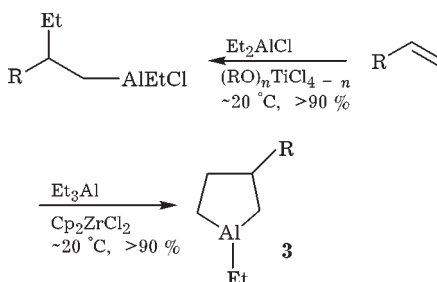
Thus, the minor (~5 %) product **2** identified in the studies on catalytic dimerization of α-olefins has further stimulated the development of novel catalytic reactions ethyl- [12] and cycloalumination of unsaturated compounds [13].

Further we have investigated the margins of application for these reactions in detail. So,

functionally substituted N-, O-, and S-containing α-olefins in the presence of Cp_2ZrCl_2 in catalytic amount enter into the reaction with Et_3Al, to result in the formation of aluminacyclopentanes **4**. Unshared electron pairs at O, N or S atoms in these compounds form intramolecular donor-acceptor complexes [14].

$[Zr] = Cp_2ZrCl_2$; X = OR, SR, NR$_2$.   **4**
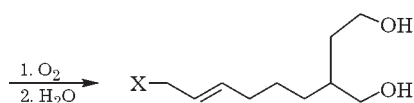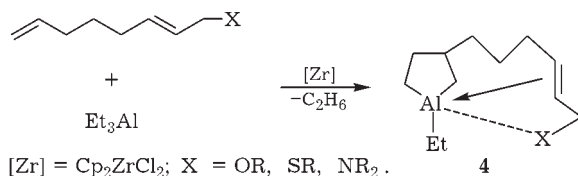
A high stereoselectivity inherent in cycloalumination of olefins was demonstrated by the example of reactions of such cycloolefins as norbornene, norbornadiene and exodicyclopentadiene. In each experiment the cycloalumination of the norbornene double bond occurs in a stereoselective fashion with the formation of corresponding aluminacyclopentanes (ACP) with exoconfiguration [15]. Alongside with Et_3Al one could use higher trialkylalanes R_3Al for the reaction of cycloalumination. For example, the interaction of an equimolar amount of α-olefins with higher trialkylalanes in the presence of 3 mol. % of Cp_2ZrCl_2 during 12 h at room temperature results in a selective formation of 1-alkyl-*trans*-3,4-dialkyl substituted ACP with the yield of 50−75 % [16].

Cyclic organoaluminium compounds obtained from available olefins could be transformed without preliminary isolation into substituted cyclopropanes [17], cyclobutanes [18], thiophanes, selenophanes [19], phospholanes [20], cyclopentanols and their ethers [21], 1,4-butandiols, 1,3-diene hydrocarbons [22] including those of isoprenoid structure.

Methylcyclobutanes, as against acyclic hydrocarbons with a low-reactive 1,1-disubstituted double bond, can be involved in the reaction of cycloalumination. Using the cycloalumination reaction of methylenecyclobutanes by means of the excess of Et_3Al in the presence of 5 mol. % of Cp_2ZrCl_2 (4 h, pentane) corresponding spiroalanes were obtained [23] (Scheme 1).

In 1997 we have for the first time succeeded in performing the cycloalumination of arylolefins (styrene, *ortho*- and *para*-methylstyrenes), as well as of 1,4-diphenyl-1,3-butadiene by means of $EtAlCl_2$ in the presence of Mg (as an acceptor of halide ions) and Cp_2TiCl_2 catalyst with the obtaining of corresponding aluminacyclopropanes with the yield of 65−85 % [24]. In the minor amounts (up to 10 %) aryl substituted aluminacyclopentanes are formed.

Alongside with the use of 1,3-dienes, the reactions of catalytic cycloalumination can be carried out with the participation of 1,2-dienes, which results in the formation of corresponding 2-alkylidenealuminacyclopentanes. Cycloalumination of 1,2-alkadienes by means of Et_3Al under the action of Cp_2ZrCl_2 catalyst (5 mol. %, ~20 °C, 4 h) proceeds in aliphatic (70−80 %) and
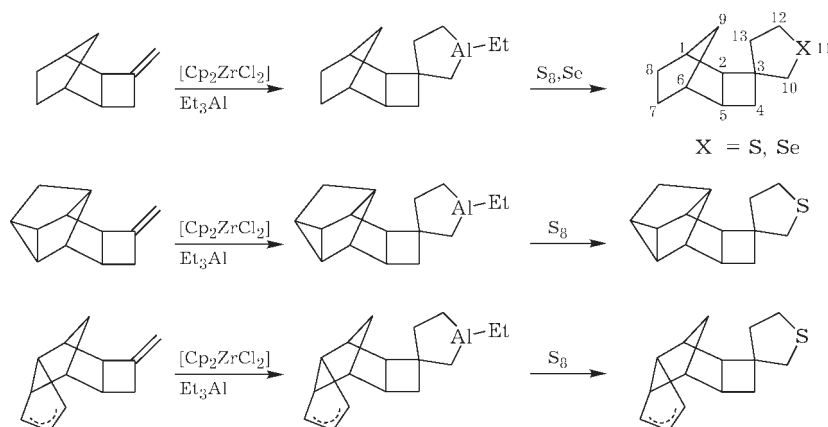

Scheme 1.
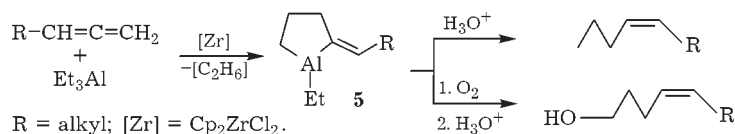
Scheme 2.

aromatic (75−77 %) solvents, as well as in methylenedichloride (92 %) with the formation of 1-ethyl-2-alkylidenealuminacyclopentanes **5** [25] (Scheme 2).

The further mastering the reaction of catalytic olefins cycloalumination with the help of Et₃Al under the action of Zr-containing catalysts developed in 1989 resulted in the synthesis of novel classes of unsaturated cyclic organoaluminium compounds such as aluminacyclopentenes and aluminacyclopentdienes *via* catalytic cycloalumination of acetylenes. It was demonstrated in [26] that the reaction of disubstituted acetylenes with Et₃Al in the presence of Cp_2ZrCl_2 catalyst at ~20 °C results in the formation of 1-ethyl-2,3-dialkyl(aryl)aluminacyclopent-2-enes **6** with the yield of 75−90 %:
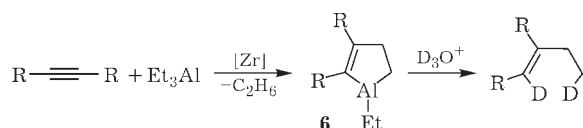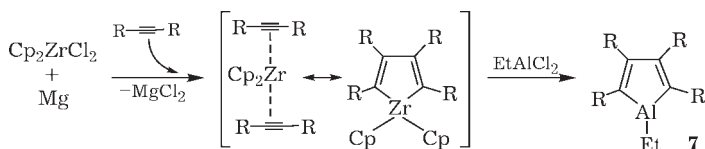

In 1992 a novel method was proposed for the synthesis of aluminacyclopenta-2,4-dienes **7** based on the cycloalumination of disubstituted acetylenes with the help of RAlCl₂ (R = Et, BuO, Et₂N, Cl) under the action of Cp_2ZrCl_2

catalyst which is widely used in the reaction of cycloalumination of acetylenes by means of Et₃Al (Scheme 3).

By analogy with the reaction of catalytic cycloalumination, in 1989 we have performed the process of cyclomagnesiation of olefins with the use of R₂Mg in the presence of Cp_2ZrCl_2 catalyst. It has been established that the interaction of styrene with R₂Mg (R = Pr^n, Bu^n, Hex^n) in THF/Et₂O solution under the action of catalytic amounts of Cp_2ZrCl_2 results in the formation of a mixture of 2,4-disubstituted magnesacyclopentanes with a ratio **8** : **9** approximately equal to 1 : 3, the overall yield amounting to ~80 % [27] (Scheme 4).

The derivatives of styrene [*ortho-*, *meta-*, *para-*methyl, *meta-*(*tert-*butyl)styrene] enter into the reaction with R₂Mg catalyzed by Cp_2ZrCl_2 with the formation of magnesacyclopentanes with the yield >70 % [28].

The cyclomagnesiation of norbornenes with by means of Pr$_2^n$Mg or Bu$_2^n$Mg and Cp_2ZrCl_2 catalyst (3 mol. %) in THF/Et₂O solution (22 °C, 8 h) results in the formation of polycyclic OMC with the yield of 80−95 % [29] (Scheme 5).

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Scheme 7.

By the contrast with R_2Mg (R = Pr^n, Hex^n, Oct^n), the reagents such as EtMgX or Et_2Mg can react with α-olefins in the presence of catalytic amounts of Cp_2ZrCl_2 with the formation of the products resulted from ethylmagnesiation **10** or cyclomagnesiation **11** depending on the conditions of performing the reaction (Scheme 6).

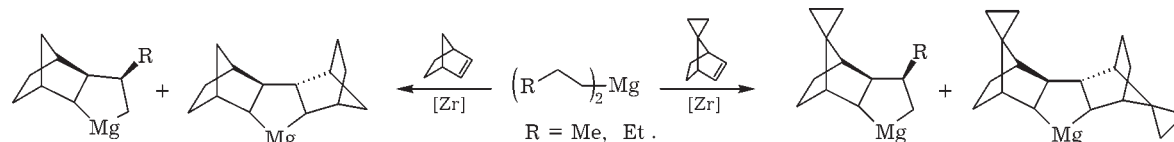The direction of the reaction depends on the nature of a solvent, temperature and the ratio of initial reagents. For example, in THF (2 eq. of EtMgX, ~20 °C, 16 h) the products of ethylmagnesiation are formed with a high selectivity (**10** : **11** = 95 : 5), whereas mainly 1,4-dimagnesium compounds (**10** : **11** = 15 : 85).are obtained when this reaction is carried out in Et_2O with 4 eq. of Et_2Mg (0 °C, 16 h).

Allenes enter into the reaction with Et_2Mg in the presence of Cp_2ZrCl_2 with the formation of the products of carbo- (20 °C, THF) or cyclomagnesiation (0 °C, Et_2O) [30]. 2,5-Dialkylidenemagnesacyclopentanes **12** and/or 1,4-dimagnesium compounds were obtained via cyclomagnesiation of 1,2-dienes with the help of EtMgX (X = Cl, Br) in the presence of activated Mg and Cp_2TiCl_2 catalyst. The most probable intermediate stages determining the formation of unsaturated OMC **12**, represent Cp_2TiCl_2 reduction up to Cp_2Ti, selective formation of intermediate 2,5-dialkylidenetitanacyclopentanes and remetallation them to yield EtMgX (Scheme 7).

In order to develop these prospective studies we carried out cyclo- and ethylmagnesiation of 1,2-cyclononadiene with the use of EtMgR (R = Et, Hlg) in the presence of Cp_2ZrCl_2 catalyst (5 mol. %) in THF or Et_2O solution with the obtaining of 10-magnesabicyclo-[7.3.0^{1,9}]dodec-8-ene **13** or 3-ethylcyclonone-1-enyl-2-ethylmagnesium **14** depending on the conditions of performing the reaction [31]. The interaction between Et_2Mg and 1,2-cyclononadiene in the presence of 5 mol. % of Cp_2ZrCl_2 in diethyl ether at the temperature of ~0 °C results in the formation of organomagnesium compounds **13** and **14** with a ratio of 91 : 9 and

Scheme 8.

Схема 9.

the total yield of 79 %. A product of carbo-magnesiation **14** (Scheme 8) is formed in THF at the temperature of ~20 °C.

It has been demonstrated in the publications for 2006−2007 [32] that the interaction between disubstituted acetylenes with BuMgBr in Et$_2$O solution in the presence of Cp$_2$ZrCl$_2$ catalyst (10 mol. %) under soft conditions (~20 °C, 2 h) results in the formation of tetrasubstituted magnesacyclopentadienes **15** with the yield of ~50 %. The replacement of source BuMgBr by BuMgCl does not exert any considerable effect on the yield of target magnesacyclopentadiene, however with carrying out the reaction in THF medium the yield of **15** does not exceed 15 % (Scheme 9).

The reactions discovered by Dzhemilev *et al.* in the field of organic and organometallic chemistry are widely used in the world practice for obtaining the major monomers, materials, pharmaceutical preparations and other valuable products.

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