Kinetics of Zr-Catalyzed Cycloalumination of Alkenes and Alkynes in the Dzhemilev Reaction

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Abstract—The kinetics and chemoselectivity of cycloalumination of 1-octene and 4-octyne with Et_3Al in the presence of a catalytic amount of Cp_2ZrCl_2 in hexane at various temperatures and ratios between reactants was studied. It was found that chemoselectivity for the formation of aluminacyclopentanes and aluminacyclopentenes was improved and the reaction time was significantly shortened when the cycloalumination reaction was carried out at an elevated temperature (40°C) and an equimolar ratio between an unsaturated compound (4-octyne or 1-octene) and Et_3Al . Quantitative characteristics of the reactivity of a number of alkenes and alkynes, including functionally substituted ones, were obtained.

Keywords: aluminacyclopentanes, aluminacyclopentenes, induction period, temperature effect, cycloalumination, cyclic carboalumination

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INTRODUCTION

The Zr-catalyzed interaction of alkenes and triethylaluminum known as the Dzhemilev reaction of olefin cycloalumination [1, 2] was first discovered in 1989, and it has been widely used to obtain cyclic organoaluminum intermediates from various olefins, acetvlenes, and allenes, including functionally substituted ones. The high reactivity of aluminacyclopentanes and aluminacyclopentenes made it possible to develop efficient single-reactor syntheses of five-membered sulfur-, selenium- [3, 4], and phosphorus-containing [5, 6] heterocycles and spiro compounds [7, 8]. In the course of studying the cycloalumination reaction of functionally substituted acetylenes, we established a significant role of the temperature effect. Thus, the reaction with propargyl alcohols occurred only at 40-50°C [9]. In this context, a question arose on the role of the above effect in the cycloalumination of olefins and acetylenes and its action on the chemoselectivity of the reaction. In this work, we studied the kinetics of conversion of 1-octene and 4-octyne under the Dzhemilev reaction conditions at various temperatures and ratios between reagents (Scheme 1) and reactivity of a number of olefins and acetylenes, including functionally substituted compounds.





EXPERIMENTAL

Starting Substances and Materials

In this work, 98% Et_3Al was used (OAO Redkinskii Opytnyi Zavod). To create an inert atmosphere, pure grade argon (GOST [State Standard] 10157-73) was used. The starting reagents 1-octene and 4-octyne are commercially available.

Methods of Analysis and Physicochemical Characterization

The reaction products were analyzed by gas–liquid chromatography (GLC) on an HRGC 5300 Mega Series chromatograph (Carlo Erba, Italy) with an Ultra-1 glass capillary column ($25 \times 0.2 \text{ mm}$) (Hewlett Packard, the United States) and a flame-ionization detector; the operating temperature was 50–170°C, and helium was a carrier gas.

The ¹H and ¹³C NMR spectra were recorded on an Avance-400 spectrometer (Bruker, Germany) with an

Abbreviations: δ , chemical shifts.



Fig. 1. The time dependence of the concentration of 4-octyne at various temperatures under cycloalumination reaction conditions. Hexane, [4-octyne] = 0.4 M, $[\text{Et}_3\text{Al}] = 1.2 \text{ M}$, and $[\text{Cp}_2\text{ZrCl}_2] = 0.02 \text{ M}$.

operating frequency of 100.62 MHz for ¹³C or 400.13 MHz for ¹H. In the measurement of the ¹H and ¹³C NMR spectra, SiMe₄ and CDCl₃ were used as internal standards, respectively. Chemical shifts (δ) are given in ppm. The elemental composition of the compounds was determined using a Carlo Erba-1106 instrument (Carlo Erba, Italy). The yields of products were found by the GLC of the hydrolysis products of corresponding organoaluminum compounds using an internal standard.

Kinetic Study of the Cycloalumination Reaction

An olefin or acetylene (2 mmol), Cp_2ZrCl_2 (0.1 mmol, 0.028 g), hexane (5 mL), and Et₃Al (6 mmol) were successively charged in a 50-mL glass reactor placed in a water bath at a temperature of 40°C with a magnetic stirrer in an argon atmosphere, and the contents were stirred at the specified temperature. The GC analysis of hydrolysis products was performed after 5, 10, 15, 30, 60, 90, 120, 180, 240, and 480 min after loading the reagents.

Study of the Reaction Chemoselectivity of 1-Octene and 4-Octyne Cycloalumination

1-Octene or 4-octyne (2 mmol), Cp_2ZrCl_2 (0.1 mmol, 0.028 g), hexane (5 mL), and a specified amount of Et₃Al (2, 4, or 6 mmol) were successively charged in a 50-mL glass reactor placed in a water bath at a temperature of 40°C with a magnetic stirrer in an argon atmosphere, and the contents were stirred at a specified temperature (20, 25, or 40°C). Hexane (5 mL) was added to the reaction mass; 3 mL of D₂O was added dropwise upon cooling the reactor in an ice bath, and the precipitate was filtered off. The aqueous



Fig. 2. The time dependence of the concentration of 1-octene at various temperatures under cycloalumination reaction conditions. Hexane, [1-octene] = 0.4 M, $[\text{Et}_3\text{Al}] = 1.2 \text{ M}$, and $[\text{Cp}_2\text{ZrCl}_2] = 0.02 \text{ M}$.

layer was extracted with diethyl ether; the extract was combined with the organic layer, kept over anhydrous CaCl₂, and concentrated in a vacuum. Individual products were separated on a silica gel column using an ethyl acetate—hexane eluant $(1:10 \rightarrow 1:5)$.

RESULTS AND DISCUSSION

The kinetics of 1-octene and 4-octyne conversion was initially studied under the following cycloalumination reaction conditions: [4-octyne or 1-octene] = 0.4 M, [Et₃Al] = 1.2 M, [Cp₂ZrCl₂] = 0.02 M, hexane, and a temperature of 25° C (Figs. 1 and 2). Under these conditions, the kinetic curve of changes in the concentration of a starting unsaturated compound (1-octene or 4-octyne) has an induction period of 2– 3 h. At least 5 h was required to achieve a 95% conversion of 4-octyne and 1-octene. At a temperature of 0°C, the initial concentration of 4-octyne remained almost unchanged even 24 h after the onset of the reaction. To complete the reaction at 20° C in the case of 4-octyne, at least a day was required.

The duration of an induction period of a catalytic reaction is related to the time taken to establish a steady-state concentration of intermediates involved in a catalytic cycle. An increase in the reaction temperature can accelerate this process and shorten the induction period. Indeed, at a temperature of 40°C and the above ratio between reactants, the reaction was significantly accelerated (Figs. 1 and 2). It should be noted that changes in the shapes of kinetic curves in the reactions with 4-octyne and 1-octene occurred in temperature ranges of 30–40 and 25–30°C, respectively.

The use of a fivefold excess of Et_3Al with respect to 4-octyne at room temperature (22°C) did not lead to a noticeable decrease in the induction period of the



Fig. 3. The time dependence of the concentration of 4-octyne at various molar ratios between octyne-4 and Et₃Al. A reaction temperature of 40°C, [4-octyne] = 0.4 M, [Cp₂ZrCl₂] = 0.04 M, and [Et₃Al] = (1) 0.4, (2) 0.8, and (3) 1.2 M.

reaction. At the same time, at an elevated temperature (40°C) and a rationally justified equimolar ratio between 4-octyne and Et₃Al, the reaction took 1 h to achieve an acetylene conversion of >95% (Fig. 3).

Note that the mechanism of cycloalumination of olefins and acetylenes was previously considered in

detail in the publications of Dzhemilev and Negishi with coauthors [11, 12]. However, the effect of temperature on the rate of reaction has not yet been studied and discussed. According to a recent theoretical study of the cycloalumination reaction of 1-propene [12], the stages of Cp_2ZrEt_2 and zirconacyclopropane formation are the rate-limiting stages of the overall process. An earlier experimental work by Balaev et al. [13] also confirmed the conclusion that the rate of formation of a zirconacyclopropane intermediate controls the rate of a cyclometalation reaction. Thus, when Cp_2ZrCl_2 and Et_3Al were mixed in a molar ratio of 1:2 in an NMR ampoule, the maximum concentration of a zirconacyclopropane intermediate was detected approximately 20 min after the onset of the reaction at a temperature of 20–25°C. Under the catalytic conditions described above, the rate of generation of zirconocene intermediates should be lower. Thus, it is reasonable to relate the duration of an induction period in the test catalytic reaction with the rate of formation of the zirconacyclopropane intermediate and the duration of the establishment of its steady-state concentration in the reaction system.

Because the cycloalumination reaction is accompanied by the formation of by-products, the effects of temperature and a ratio between the reagents on the chemoselectivity of the conversion was studied. It is well known that the products of carboalumination, hydroalumination, and cyclic dimerization were also obtained along with aluminacylopent-2-enes in the course of the catalytic cycloalumination of disubstituted acetylenes (Scheme 2) [10, 11].



With the use of equimolar amounts of 5-decyne and Et_3Al at 40°C, the reaction selectivity for aluminacyclopent-2-ene noticeably increased and the fraction of by-products decreased (Table 1). An increase in the 5-decyne hydroalumination product content with the use of 3 equiv of Et_3Al can be related to the presence of an impurity of aluminum hydride Et_2AlH in Et_3Al in an amount of ~5% (evaluated from the ¹H NMR spectrum of a commercial Et_3Al sample). In all cases, the amount of carboalumination products estimated from the ¹³C NMR spectra did not exceed 5%. A similar study was conducted for 1-octene. According to Tyumkina et al. [12], the interaction of α -olefins with Et₃Al catalyzed by Cp₂ZrCl₂ proceeds with the predominant formation of aluminacyclopentanes; however, carboalumination and hydroalumination products and methylene alkanes were also detected in the reaction mass (Scheme 3) [13].

Temperature, °C	Time, h	[4-octyne] : [Et ₃ Al] ratio	Yield of 1 , %	Yield of 3 , %	Yield of 4 , %
20	18	1:3	65	26	9
40	2	1:1	74	12	14
40	2	1:2	59	19	22
40	2	1:3	54	21	25

Table 1. Effects of the reaction temperature and the [4-octyne]: $[Et_3Al]$ molar ratio on the composition of the deuterolysis products of the reaction mixture

Table 2. Effects of the reaction temperature and the [1-octene]: $[\text{Et}_3\text{Al}]$ molar ratio on the composition of the reaction mixture

Temperature,°C	Time, h	[1-octene] : [Et ₃ Al] ratio	Yield of 5 , %	Yield of 8 , %
20	8	1:3	73	27
40	2	1:1	78	22
40	2	1:2	72	28
40	2	1:3	71	29



It was found that, in the reaction performed at 40°C and an equimolar ratio between 1-octene and Et_3Al , the chemoselectivity of aluminacyclopentane conversion slightly increased, as compared with that under standard reaction conditions ([1-octene] : $[Et_3Al] = 1 : 3, 23^{\circ}C$). In addition, the reaction time significantly shortened (Table 2). The fraction of carboalumination products and methylene alkanes, which was estimated from ¹³C NMR spectra, did not exceed 5% in all cases. Thus, in the cycloalumination reaction performed at an elevated temperature $(40^{\circ}C)$ and an equimolar ratio between the unsaturated compound (4-octyne or 1-octene) and Et₃Al, the chemoselectivity of the formation of aluminacyclopentanes and aluminacyclopentenes was improved and the reaction time was significantly shortened.

To quantify the effect of the nature of a substituent at the multiple bond on the reactivity of an olefin or

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acetylene under the conditions of a cycloalumination reaction, we studied the kinetics of conversion of a number of unsaturated compounds under analogous conditions at a constant temperature $(40^{\circ}C)$ (Table 3). The GC analysis of the hydrolysis products was carried out 10, 20, 30, 60, 90, 120, and 180 min after loading the reagents. The relative reactivity was determined based on a ratio between the half-times of 1-octene or 1-octyne and an olefin or acetylene substrate. An analysis of the kinetic curves of conversion of a number of unsaturated compounds showed that the reactivity of olefins under the conditions of a cycloalumination reaction decreased in the order 1-octene > α -allylnaphthalene > styrene > allylbenzene > norbornene > trimethylvinylsilane, and the reactivity of acetylenes decreased in the order 1-octyne > phenylacetylene > 4-octyne > butyl(trimethylsilyl)acetylene > octyl(trimethylsilyl)acetylene. The relative reaction activity of functionally substituted acet-

Olefin	$k_{ m rel}$	Acetylene	K _{rel}
1-Octene	1	1-Octyne	1
α -Allylnaphthalene	0.22	Phenylacetylene	0.53
Styrene	0.18	4-Octyne	0.17
Allylbenzene	0.15	Butyl(trimethylsilyl)acetylene	0.09
Norbornene	0.05	Octyl(trimethylsilyl)acetylene	0.06
Trimethylvinylsilane	0.01		

Table 3. Relative reactivity of a number of olefins and acetylenes under cycloalumination reaction conditions *

* Reaction conditions: 40°C, hexane, [alkene or alkyne] = 0.4 M, $[Et_3AI] = 1.2 \text{ M}$, and $[Cp_2ZrCl_2] = 0.02 \text{ M}$.

ylenes in the test reaction was evaluated in the same way. At a constant temperature $(40^{\circ}C)$, we studied the kinetics of conversion of 1-hexyne, 5-decyne, 2-heptynol, 3-octynol, and 2-heptinyl(dimethyl)amine in a reaction with $Et_{3}Al$ (3 molar equivalents) in the presence of $Cp_{2}ZrCl_{2}$ (20 mol % on an acetylene basis) in a solution of hexane ([acetylene] = 0.2 M, [Et₃Al] = 0.6 M, and $[Cp_2ZrCl_2] = 0.04$ M). We found that the reactivity of acetylene compounds decreased in the order 1-hexyne (2.7) > 5-decyne (1.0) > heptinyl(dimethyl)amine (0.5) > 3-octynol (0.2) > 2-heptynol (0.1). An alkylsubstituted propargyl alcohol exhibited the lowest activity in the test reaction. Note that the above assessment of the reactivity of functionally substituted acetylenes should not be taken as a characteristic of triple bond activity in the above compounds with respect to a cycloalumination reaction because a portion of Et₃Al was consumed in a reaction with hydroxyl groups and complexation with a nitrogen or oxygen atom. Moreover, side reactions of the hydroalumination and isomerization of intermediate zirconacyclopentenes (in the case of alkyl-substituted propargyl alcohols) occurred along with the process of cycloalumination. A similar study conducted with respect to functionally substituted olefins under identical conditions (40°C. $[olefin] = 0.2 \text{ M}, [Et_3Al] = 0.2 \text{ M}, \text{ and } [Cp_2ZrCl_2] =$ 0.02 M) showed that, in general, the introduction of a nitrogen, sulfur, or oxygen atom into an unsaturated compound decreased its relative reactivity in the order 1-octene (1.0) > 3-(heptylsulfanyl)-1-propene (0.21) > *tert*-octylallylamine $(0.18) \approx 1$ -decen-4-ol (0.17).

CONCLUSIONS

Thus, we first discovered an induction period in the cycloalumination of alkyl-substituted olefins and acetylenes. We found that the induction period was significantly shortened as the reaction temperature of the cycloalumination of alkyl- and phenyl-substituted and organosilicon olefins and acetylenes was increased to 40° C. We obtained quantitative characteristics of the reactivity of a number of olefins and acetylenes, including functionally substituted compounds.

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