Cp_2ZrCl_2-Catalyzed cycloalumination of acetylenic alcohols and propargylamines by Et_3Al

I. R. Ramazanov, R. N. Kadikova, and U. M. Dzhemilev*

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347) 284 2750. E-mail: iramazan@inbox.ru

The Cp_2ZrCl_2-catalyzed cycloalumination of acetylenic alcohols and propargylamines by Et_3Al was studied. The process affords 2,3-disubstituted alumacyclopent-2-enes, which were identified by the analysis of the products of their deuterolysis and hydrolysis. The cycloalumination of alkyl- and phenyl-substituted propargylamines proceeds with high regio- and stereoselectivity to give the corresponding allylamine derivatives in high yield. Unlike the phenyl derivatives, the cycloalumination of alkyl-substituted acetylenic alcohols (propargyl, homopropargyl, and bishomopropargyl alcohols) is not regioselective.

Key words: organoaluminum compounds, alumacyclopentenes, cycloalumination, cyclic carboalumination.

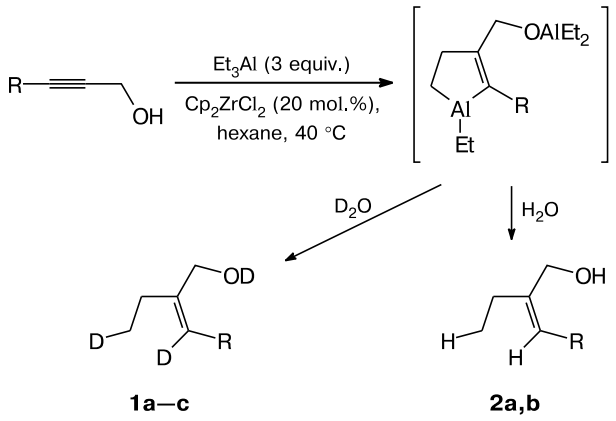
Among numerous methods of synthesis of organoaluminum compounds, the reactions of hydro-, carbo-, and cycloalumination of olefins and acetylenes found the widest use.[1] However, the first two methods are well studied both methodologically and theoretically, while cycloalumination is relatively new promising direction that requires the study of boundaries of application of this reaction and its mechanism. We have earlier[2] reported the synthesis of substituted alumacyclopent-2-enes from alkyl- and phenyl-substituted acetylenes. It was found[3] that the cycloalumination of nonsymmetric alkyl-, phenyl-, and allyl-substituted acetylenes by Et_3Al affords regioisomeric 2,3-disubstituted alumacyclopent-2-enes, whose yield and ratio depend on the nature of substituents in the starting acetylenes.

In order to extend the area of application of the above cycloalumination reaction and taking into account the important role of various functional substituents in the induction of biological activity, in the present work we studied the regularities of the reaction with acetylenic alcohols and amines.

Results and Discussion

Cycloalumination of propargyl alcohols. At room temperature propargyl alcohols are not almost involved in cycloalumination. For instance, in the reaction of hept-2-ynol with Et_3Al (the mole ratio of the reactants is 1 : 3) in hexane in the presence of 10 mol.% Cp_2ZrCl_2 at room temperature, the conversion of the starting propargyl alcohol after 24 h does not exceed 5%. However, the rise of the reaction temperature to 40 °C and an increase in the catalyst concentration to 20 mol.% favor the formation of alumacyclopent-2-enes. In the case of alkyl-substituted propargyl alcohols (hept-2-ynol, non-2-ynol), cycloalumination followed by deuterolysis affords deuterolysis products **1a**,**b** in 37 and 41% yields, respectively (Scheme 1). The reaction occurs stereoselectively to form substituted allyl alcohols of the *Z*-configuration. The cycloalumination of 3-phenylprop-2-ynol requires more rigid conditions and the use of 3 molar equivalents of Et_3Al over propargyl alcohol. However, the reaction product is formed with high regio- and stereoselectivity and in a higher yield (60%) compared to alkyl-substituted propargyl alcohols.

Scheme 1



R = Bu (**1a**), C_6H_{13} (**1b**, **2a**), Ph (**1c**, **2b**)

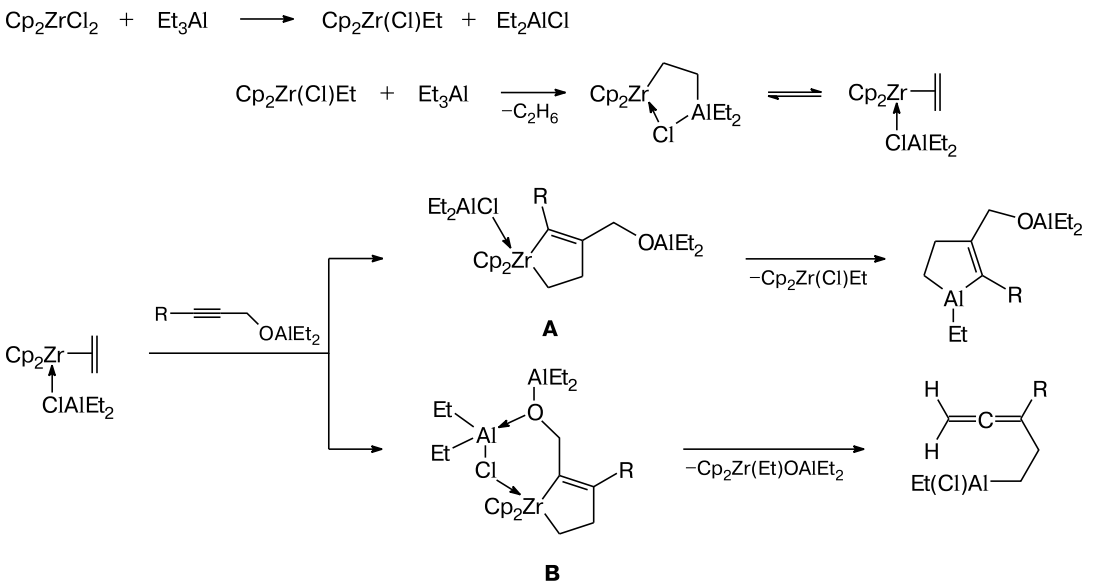
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 96—102, January, 2011.

The structure of alumacyclopent-2-enes was established by 1D and 2D NMR spectroscopy of the products of their deuterolysis (**1a—c**) and hydrolysis (**2a,b**). The reaction can afford regio- and stereoisomers with different positions of the substituents at the double bond. In the ^{1}H NMR spectrum of compounds **2a,b**, the singlet character of the methylene group of the hydroxymethyl moiety indicates the geminal arrangement of the ethyl group toward the hydroxymethyl group and makes it possible to unambiguously judge about the position of the hydroxymethyl group, because for another possible regioisomer the methylene group of the hydroxymethyl moiety should appear in the ^{1}H NMR spectrum as a doublet. The NOESY spectrum of compound **1b** distinctly shows the interaction between the methylene group of the hydromethyl moiety and the α-methylene group of the *n*-hexyl substituent, which indicates the *cis*-configuration of the substituted allyl alcohol that formed. The *cis*-configuration of compound **1c**, obtained by the deuterolysis of the cycloalumination product of 3-phenylprop-2-ynol, is indicated by the cross-peak between the signals of the hydrogen atoms of the phenyl group and the methylene group of the hydroxymethyl moiety in the NOESY spectrum.

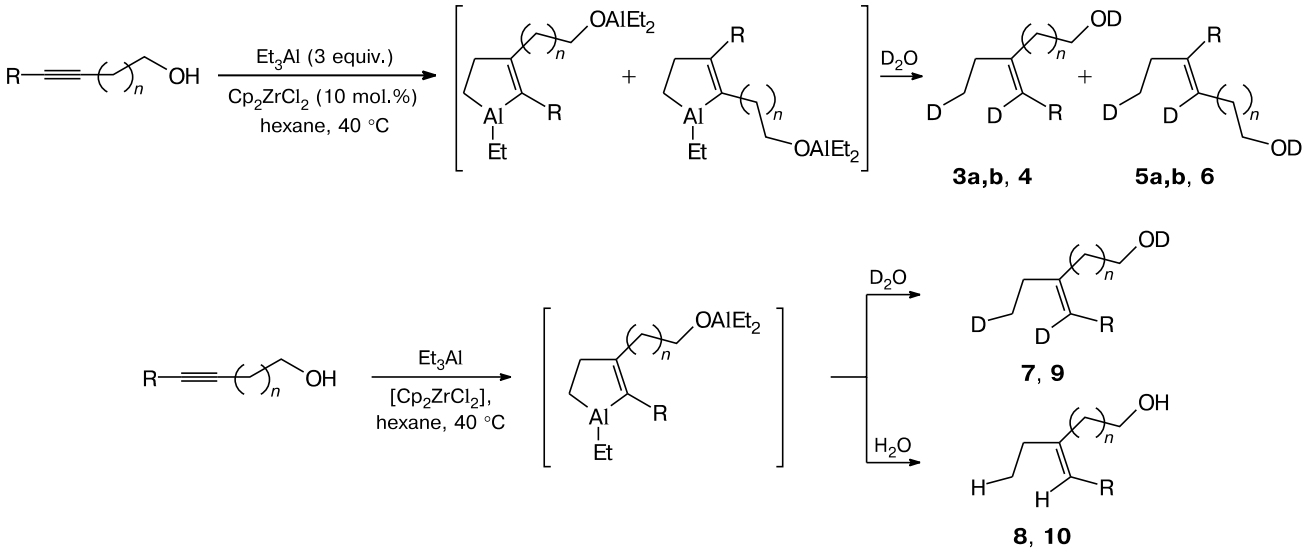
Relatively low yield of the cycloalumination products of alkyl-substituted propargyl alcohols can be explained by the non-regioselective character of the reaction. According to the previously proposed[4] mechanism of cycloalumination, regioisomeric intermediates **A** and **B** are formed at one of the stages of the process (Scheme 2). It is assumed with allowance for the known data[5] that the zirconocene—ethylene complex is formed upon the rearrangement of the five-membered bimetallic intermediate. In the case of alkyl-substituted propargyl alcohols, the reaction is not regioselective and affords, along with alumacyclopentenes, a mixture of compounds, which are, most likely, the dimerization products of allene. The latter could be formed by the β-elimination of the Et_2AlO group in intermediate **B**.

Cycloalumination of but-3-ynol and pent-4-ynol and their derivatives. The results similar to those described above were also obtained in the case of acetylenic alcohols containing two or three methylene groups between the acetylene and hydroxyl functions (but-3-ynol, pent-4-ynol) and also for *n*-butyl-substituted homopropargyl alcohol (Scheme 3). However, unlike the cycloalumination of alkyl-substituted propargyl alcohols, no undesirable rearrangement with the Et_2AlO group elimination occurs and a mixture of regioisomers in a ratio of ~1 : 1 is formed. The reaction is stereoselective and after deuterolysis gives olefins **3—6** in high yield. The phenyl-substituted derivative of homopropargyl alcohol (4-phenylbut-3-ynol) predominantly forms one regioisomer, whose structure was determined by NMR spectroscopy of the products of deuterolysis **7** and hydrolysis **8**. In the NOESY spectrum, the cross-peak between the signals of the hydrogen atoms of the phenyl group and the methylene group $C(2)H_2$ of the hydroxyethyl moiety indicates the *cis*-configuration of compound **7**. The singlet signal of the hydrogen atom at the double bond in the ^{1}H NMR spectrum of hydrolysis product **8** unambiguously indicates the position of the phenyl group in the molecule, since signal splitting should be observed for another regioisomer due to the spin-spin interaction with the methylene group.

Scheme 2



Scheme 3



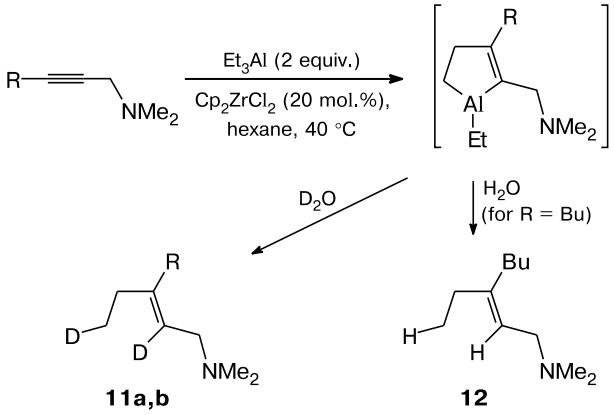
R = H (**3a**, **4**, **5a**, **6**), Bu (**3b**, **5b**); *n* = 1 (**3a,b**, **5a,b**), 2 (**4**, **6**)
R = Ph, *n* = 1 (**7**, **8**); R = $SiMe_3$, *n* = 2 (**9**, **10**)

Interestingly, the cycloalumination of silicon-substituted pent-4-ynol (5-trimethylsilylpent-4-ynol) also occurs with high regioselectivity, unlike the cycloalumination of unsubstitited pent-4-ynol.

Cycloalumination of propargylamines. Continuing the study of the catalytic cycloalumination of functionally substituted acetylenes and taking into account availability and wide use of propargylamines in synthetic practice, we examined the regularities of cycloalumination of these compounds. It was found that, unlike alkyl-substituted propargyl alcohols, the cycloalumination of alkyl-substituted propargylamines is regioselective and occurs with high yield. In addition, propargylamines demonstrate a considerably higher reactivity than propargyl alcohols. For example, the interaction of *N*,*N*-dimethylhept-2-yn-1-amine with 2 equiv. Et_3Al in the presence of 20 mol.% Cp_2ZrCl_2 in hexane occurs within 2 h at 40 °C to form (after deuterolysis) (2*Z*)-2-deutero-3-(2-deuteroethyl)-*N*,*N*-dimethylhept-2-en-1-amine (**11a**) in 83% yield (Scheme 4). To determine the structure of 1-ethyl-2-(*N*,*N*-dimethylaminomethyl)-3-*n*-butylalumacyclopent-2-ene, in addition to deuterolysis we carried out hydrolysis to form substituted allylamine **12**, whose triplet signal of the vinylic hydrogen atom in the COSY spectrum has a cross-peak with the doublet of the methylene group of the *N*,*N*-dimethylaminomethyl moiety.

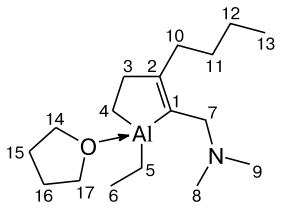
In addition, the NMR spectra for the complex of 1-ethyl-2-(*N*,*N*-dimethylaminomethyl)-3-*n*-butylalumacyclopent-2-ene with THF (**13**) were measured. The HMBC spectrum of complex **13** exhibits cross-peaks between the signals of the quaternary carbon atoms of the double bond

Scheme 4



R = Bu (**a**), C_8H_{17} (**b**)

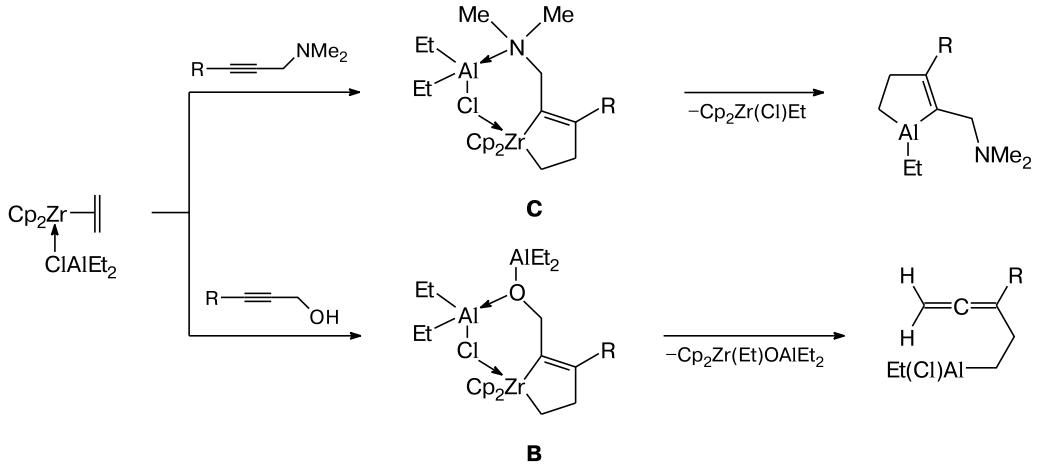
and the signals of the hydrogen atoms of the *N*,*N*-dimethylaminomethyl group.



13

Thus, in the case of alkyl-substituted propargylamines, no undesirable rearrangement with functional group elim-

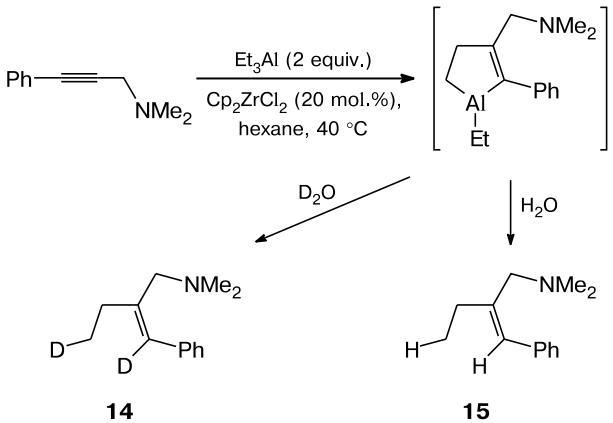
Scheme 5



ination occurs. It is most likely that this is due to a lower electronegativity of the nitrogen atom compared to the oxygen atom and a higher stability of the organozirconium intermediates because of the lower affinity to β-elimination (Scheme 5). Six-membered intermolecular complex **C** with the stronger donor-acceptor bond N→Al due to a higher nucleophilicity of amines compared to alcohols can favor higher (compared to alkyl-substituted propargyl alcohols) regioselectivity of the reaction.

As in the case of acetylenic alcohols, the cycloalumination of phenyl-substituted propargylamine, *viz.*, *N*,*N*-dimethyl-3-phenylprop-2-yn-1-amine, is regioselective, and the regioselectivity is opposite to that observed in the reaction with alkyl-substituted propargylamines (Scheme 6).

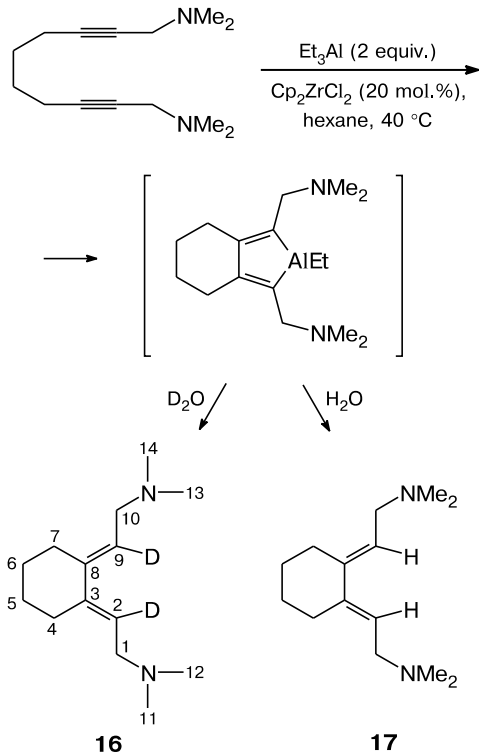
Scheme 6



14 **15**

In the cycloalumination of *N*,*N*,*N*′,*N*′-tetramethyldeca-2,8-diyne-1,10-diamine obtained by the aminomethylation of 1,7-octadiyne by bis(amine),[6] ethylene is displaced from the coordination sphere of the zirconium atom and the reductive coupling of two acetylene moieties of the molecule occurs with the formation of zirconacyclopentadiene, whose subsequent transmetallation in the catalytic cycle and deuterolysis result in the bis(alkylidene) derivative of cyclohexane **16** (Scheme 7). The NOESY spectrum of product **16** shows the interaction of the methylene group of the *N*,*N*-dimethylaminomethyl moiety with the α-methylene group of the cyclohexane ring, indicating the *E*-configuration of the double bonds. In the COSY spectrum of hydrolysis product **17**, the cross-peak between

Scheme 7



16 **17**

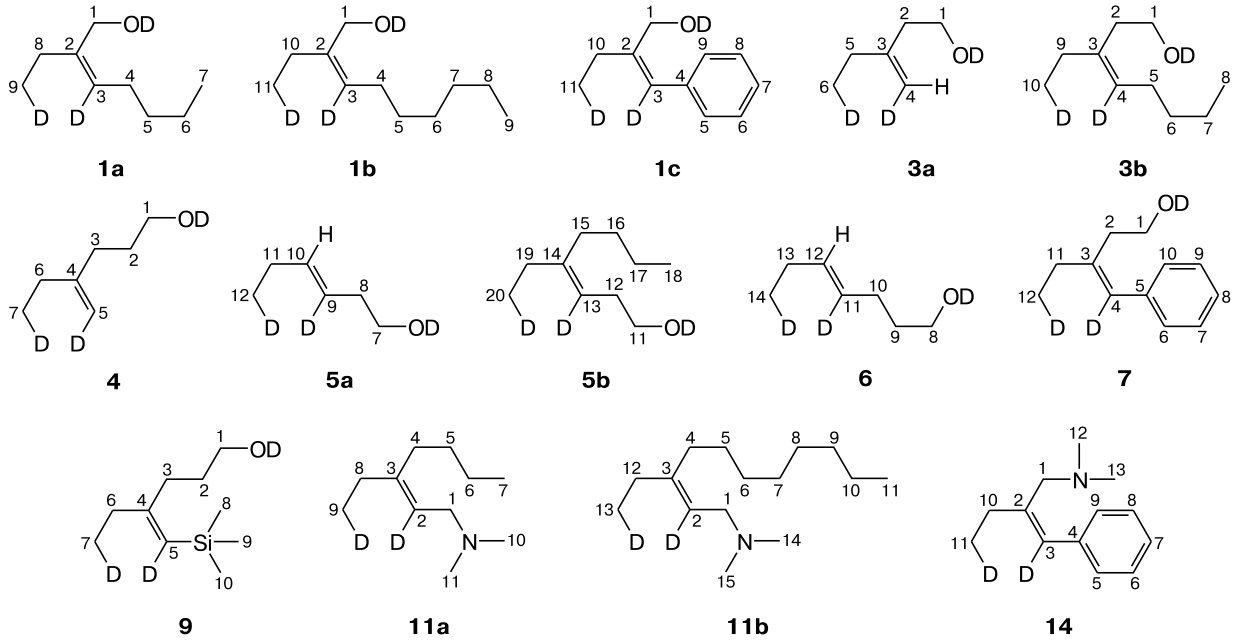


Fig. 1. Numeration of carbon atoms used in the description of the ^{1}H and ^{13}C NMR spectra of the deuterolysis and hydrolysis products.

the triplet signal of the hydrogen atoms at the double bond and the doublet of the methylene group at the nitrogen atom indicates the geminal arrangement of the hydrogen atom and the *N*,*N*-dimethylaminomethyl group at the C atom of the double bond. A similar formation of alkylidene-substituted cyclohexane has earlier[7] been observed for the cycloalumination of trimethyl(oct-7-en-1-yn-1-yl)silane.

Numeration of carbon atoms used in the description of the NMR spectra of the deuterolysis and hydrolysis products is shown in Fig. 1.

Relative reactivity of the acetylenic compounds. Compared to mono- and dialkyl-substituted acetylenes (hex-1-yne, dec-5-yne), the cycloalumination of acetylenic alcohols and amines is more difficult and requires more rigid conditions. We carried out studies aimed at establishing the relative reactivity of functionally substituted acetylenes in the reaction under study. The kinetics of transformations of hex-1-yne, dec-5-yne, hept-2-ynol, oct-3-ynol, and hept-2-ynyl(dimethyl)amine in the reaction with Et_3Al (3 mol. equiv.) in the presence of Cp_2ZrCl_2 (20 mol.% over acetylene) in a hexane solution was studied at constant temperature (40 °C). It was found that the reactivity of the acetylenic compounds decreases in the series: hex-1-yne ($k_{rel} \approx 2.7$) > dec-5-yne ($k_{rel} = 1$) > hept-2-ynyl(dimethyl)amine ($k_{rel} \approx 0.5$) > oct-3-ynol ($k_{rel} \approx 0.2$) > hept-2-ynol ($k_{rel} \approx 0.1$). Thus, alkyl-substituted propargyl alcohol manifests the lowest reactivity in the studied reaction. As mentioned above for the description of the cycloalumination of substituted propargyl alcohols, the phenyl derivative is involved in the reaction more difficultly, which is also characteristic of phenyl-substituted homopropargyl alcohol. The theoretical model explaining the regioselectivity of cycloalumination and relative reactivity of the acetylenic compounds on the basis of the quantum chemical calculations will be developed elsewhere.

Experimental

Commercially available reagents were used. The reactions with the organoaluminum compounds were carried out in dried argon. Hexane was distilled above $Bu^{i}_{3}Al$. Substituted propargyl alcohols were synthesized by the reaction of organomagnesium acetylenes with paraform using the known procedure.[8] Propargylamines were synthesized by the aminomethylation of terminal acetylenes by the described procedure.[6] The reaction products were analyzed on a Carlo Erba chromatograph (glass capillary column Ultra-1 (Hewlett Packard) 25 m × 0.2 mm in size, flame-ionization detector, working temperature 50—170 °C, helium as a carrier gas). Mass spectra were measured on a Finnigan 4021 instrument with an ionizing electron energy of 70 eV, and the temperature of the ionization chamber was 200 °C. Elemental analysis was carried out on a Carlo Erba analyzer, model 1106. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 (^{1}H) and 100.62 MHz (^{13}C)) using $SiMe_4$ and $CDCl_3$, respectively, as internal standards. Yields of the products were determined by GC using an internal standard; TLC was carried out on plates Silufol UV-254 in an AcOEt—hexane (1 : 5) system. Boiling points were determined by Sivolobov´s method.[9]

Cycloalumination of alkyl-substituted propargyl and homopropargyl alcohols and 5-(trimethylsilyl)pent-4-yn-1-ol (general procedure). A glass 50-mL reactor placed in a water bath (40 °C, argon atmosphere) was successively loaded with an acetylenic compound (1 mmol), Cp_2ZrCl_2 (0.2 mmol, 0.058 g), hexane

(5 mL), and Et_3Al (3 mmoL), and the mixture was magnetically stirred for 18 h at 40 °C.

Deuterolysis and hydrolysis of alumacyclopent-2-enes (general procedure). Hexane (5 mL) was poured to alumacyclopent-2-ene synthesized by the above described procedure, and then 3 mL of D_2O (deuterolysis) or 5 mL of H_2O (hydrolysis) was added dropwise on cooling of the reactor in an ice-cold bath. The precipitate formed was filtered off. The aqueous layer was extracted with diethyl ether, and the extract was joined with the organic layer, stored above anhydrous $CaCl_2$, and concentrated *in vacuo*. Individual products were isolated on a column with silica gel using an AcOEt—hexane (1 : 10 → 1 : 5) mixture as an eluent.

(3*Z*)-1,4-Dideutero-3-(deuteroxymethyl)oct-3-ene (1a). Transparent oily liquid. The yield was 37%, R_f 0.37 (AcOEt—hexane, 1 : 5). Found (%): C, 74.12. $C_9H_{15}D_3O$. Calculated (%): C, 74.42. ^{1}H NMR, δ: 0.91 (t, 3 H, C(7)H_3, J = 6.8 Hz); 1.03 (t, 2 H, C(9)H_2D, J = 7.4 Hz); 1.25—1.40 (m, 6 H, C(4)H_2—C(6)H_2); 2.05—2.20 (m, 4 H, C(4)H_2, C(8)H_2); 4.16 (s, 2 H, C(1)H_2). ^{13}C NMR, δ: 12.59 (t, C(9), $^1J_{C,D}$ = 19.4 Hz); 13.96 (C(7)); 22.31 (C(6)); 27.10, 27.66 (C(4), C(8)); 32.27 (C(5)); 60.37 (C(1)); 139.75 (C(2)). MS, m/z (I_{rel} (%)): 145 [M^+] (1), 126 (18), 110 (29), 97 (33), 83 (31).

(3*Z*)-1,4-Dideutero-3-(deuteroxymethyl)dec-3-ene (1b). Transparent oily liquid. The yield was 41%, R_f 0.44 (AcOEt—hexane, 1 : 5). Found (%): C, 76.01. $C_{11}H_{19}D_3O$. Calculated (%): C, 76.24. ^{1}H NMR, δ: 0.89 (t, 3 H, C(9)H_3, J = 7.2 Hz); 1.05 (t, 2 H, C(11)H_2D, J = 7.6 Hz); 1.20—1.40 (m, 8 H, C(5)H_2—C(8)H_2); 2.07 (t, 2 H, C(4)H_2, J = 7.2 Hz); 2.15 (t, 2 H, C(10)H_2, J = 7.6 Hz); 4.16 (s, 2 H, C(1)H_2). ^{13}C NMR, δ: 12.62 (t, C(11), $^1J_{C,D}$ = 19.5 Hz); 14.12 (C(9)); 22.65 (C(8)); 26.98, 30.13, 31.38 (C(5)—C(7)); 27.54 (C(4)); 27.84 (C(10)); 60.58 (C(1)); 127.19 (C(3)); 140.14 (C(2)).

(2*Z*)-2-Ethylnon-2-en-1-ol (2a). Transparent oily liquid. The yield was 47%, R_f 0.4 (AcOEt—hexane, 1 : 5). Found (%): C, 77.67; H, 13.07. $C_{11}H_{22}O$. Calculated (%): C, 77.58; H, 13.02. ^{1}H NMR, δ: 0.90 (t, 3 H, C(9)H_3, J = 7.4 Hz); 1.05 (t, 3 H, C(11)H_3, J = 7.6 Hz); 1.20—1.40 (m, 8 H, C(5)H_2—C(8)H_2); 1.63 (br.s, 1 H, OH); 2.00—2.10 (m, 2 H, C(4)H_2); 2.10—2.20 (m, 2 H, C(10)H_2); 4.12 (s, 2 H, C(1)H_2); 5.31 (t, 1 H, C(3)H, J = 7.6 Hz). ^{13}C NMR, δ: 12.94 (C(11)); 14.12 (C(9)); 22.66 (C(8)); 26.99, 30.15, 31.38 (C(5)—C(7)); 27.54 (C(4)); 27.85 (C(10)); 60.58 (C(1)); 127.15 (C(3)); 140.11 (C(2)).

Mixture of (1*E*)-1,4-dideutero-2-(2-deuteroxyethyl)but-1-ene (3a) and (3*E*)-1-deuteroxy-3,6-dideuterohex-3-ene (5a). Transparent oily liquid. The yield was 74%, R_f 0.3 (AcOEt—hexane, 1 : 5). Found (%): C, 68.97. $C_6H_9D_3O$. Calculated (%): C, 69.85. ^{1}H NMR, δ: 0.80—1.10 (m, 4 H, C(6)H_2D, C(12)H_2D); 1.90—2.10 (m, 4 H, C(5)H_2, C(11)H_2); 2.26 (t, 2 H, C(8)H_2, J = 6.2 Hz); 2.32 (t, 2 H, C(2)H_2, J = 6.4 Hz); 3.63 (t, 2 H, C(7)H_2, J = 6.2 Hz); 3.72 (t, 2 H, C(1)H_2, J = 6.4 Hz); 4.98 (s, 1 H, C(4)HD); 5.50—5.65 (m, 1 H, C(10)H). ^{13}C NMR, δ: 11.91 (t, C(6), $^1J_{C,D}$ = 20 Hz); 13.45 (t, C(12), $^1J_{C,D}$ = 19 Hz); 25.50 (C(11)); 28.42 (C(5)); 35.79 (C(8)); 39.29 (C(2)); 60.40 (C(1)); 62.03 (C(7)); 109.99 (C(4), $^1J_{C,D}$ = 25 Hz); 124.42 (C(9), $^1J_{C,D}$ = 25 Hz); 135.57 (C(10)); 147.64 (C(3)).

Mixture of (3*Z*)-1,4-dideutero-3-(2-deuteroxyethyl)oct-3-ene (3b) and (3*Z*)-3-deutero-4-(2-deuteroethyl)-1-deuteroxyoct-3-ene (5b). Transparent oily liquid. The yield was 61%, R_f 0.28 (AcOEt—hexane, 1 : 5). Found (%): C, 74.12. $C_{10}H_{17}D_3O$. Calculated (%): C, 75.41. ^{1}H NMR, δ: 0.85—0.95 (m, 6 H, C(8)H_3, C(18)H_3); 0.95—1.05 (m, 4 H, C(10)H_2D, C(20)H_2D); 1.25—1.40 (m, 8 H, C(6)H_2, C(7)H_2, C(16)H_2, C(17)H_2); 1.95—2.10 (m, 4 H, C(5)H_2, C(15)H_2); 2.25—2.40 (m, 4 H, C(2)H_2, C(12)H_2); 3.55—3.65 (m, 4 H, C(1)H_2, C(11)H_2). ^{13}C NMR, δ: 12.65 (t, C(4), C(13), $^1J_{C,D}$ = 19.5 Hz); 14.01 (C(8), C(18)); 22.40, 22.87 (C(7), C(17)); 27.56, 29.48, 29.57, 30.11, 30.83, 31.25, 32.35, 33.51, 61.00, 62.69 (C(1), C(11)); 118.03 (t, C(4), C(13), $^1J_{C,D}$ = 24.5 Hz); 126.79 (t, C(4), C(13), $^1J_{C,D}$ = 25 Hz); 136.34, 145 (C(3), C(14)).

Mixture of (1*E*)-1-deutero-2-(2-deuteroethyl)-5-deuteroxypent-1-ene (4) and (3*E*)-1,4-dideutero-7-deuteroxyhept-3-ene (6). Transparent oily liquid. The yield was 78%, R_f 0.34 (AcOEt—hexane, 1 : 5). Found (%): C, 69.25. $C_7H_{11}D_3O$. Calculated (%): C, 71.74. ^{1}H NMR, δ: 0.80—1.10 (m, 4 H, C(6)H_2D, C(12)H_2D); 1.90—2.10 (m, 4 H, C(5)H_2, C(11)H_2); 2.26 (t, 2 H, C(8)H_2, J = 6.2 Hz); 2.32 (t, 2 H, C(2)H_2, J = 6.4 Hz); 3.63 (t, 2 H, C(7)H_2, J = 6.2 Hz); 3.72 (t, 2 H, C(1)H_2, J = 6.4 Hz); 4.98 (s, 1 H, C(4)HD); 5.50—5.65 (m, 1 H, C(10)H). ^{13}C NMR, δ: 11.75 (t, C(7), $^1J_{C,D}$ = 19.1); 13.31 (t, C(14), $^1J_{C,D}$ = 19); 25.20 (C(13)); 28.49 (C(6)); 29.46 (C(10)); 30.60 (C(3)); 32.27 (C(9)); 61.83, 62.06 (C(1), C(8)); 107.38 (C(5), $^1J_{C,D}$ = 23.4); 128.09 (C(11), $^1J_{C,D}$ = 22.7); 138.09 (C(12)); 150.85 (C(4)).

[(1*Z*)-1-Deutero-2-(2-deuteroethyl)-5-deuteroxypent-1-en-1-yl](trimethyl)silane (9). Transparent oily liquid. The yield was 75%, R_f 0.32 (AcOEt—hexane, 1 : 5). Found (%): C, 62.97. $C_{10}H_{19}D_3OSi$. Calculated (%): C, 63.42. ^{1}H NMR, δ: 0.10 (s, 9 H, $SiMe_3$); 0.89 (t, 2 H, C(7)H_2D, J = 6.4 Hz); 1.65—1.80 (m, 2 H, C(2)H_2); 2.10—2.25 (m, 2 H, C(6)H_2); 3.60—3.70 (m, 2 H, C(1)H_2). ^{13}C NMR, δ: 0.27 (3 C, C(8)—C(10)); 12.49 (t, C(7), J = 19 Hz); 28.83 (C(6)); 31.00 (C(2)); 34.36 (C(3)); 63.87 (C(1)); 160.68 (C(4)).

(4*Z*)-4-Ethyl-5-(trimethylsilyl)pent-4-en-1-ol (10). Transparent oily liquid. The yield was 79%, R_f 0.3 (AcOEt—hexane, 1 : 5). Found (%): C, 63.92; H, 11.72. $C_{10}H_{22}OSi$. Calculated (%): C, 64.45; H, 11.90. ^{1}H NMR, δ: 0.10 (s, 9 H, $SiMe_3$); 0.84 (t, 3 H, C(7)H_3, J = 7.4 Hz); 1.50 (br.s, 1 H, OH); 1.60—1.80 (m, 2 H, C(2)H_2); 2.10—2.20 (m, 2 H, C(6)H_2); 3.60—3.70 (m, 2 H, C(1)H_2); 3.66 (s, 1 H, C(5)H). ^{13}C NMR, δ: 0.34 (3 C, C(8)—C(10)); 12.74 (C(7)); 28.95 (C(6)); 31.11 (C(2)); 34.39 (C(3)); 63.94 (C(1)); 160.77 (C(4)).

Cycloalumination of 3-phenylprop-2-yn-1-ol and 4-phenylbut-3-yn-1-ol (general procedure). A 50-mL glass reactor placed in a water bath (40 °C, argon) was successively loaded with an acetylenic compound (1 mmol), Cp_2ZrCl_2 (0.1 mmol, 0.029 g), hexane (3 mL), and Et_3Al (5 mmol). The mixture was magnetically stirred for 24 h at 40 °C. The procedure of further treatment of the reaction mixture and isolation of the product is similar to that described above.

[(1*Z*)-1,4-Dideutero-2-(deuteroxymethyl)but-1-en-1-yl]benzene (1c). Transparent oily liquid. The yield was 60%, R_f 0.35 (AcOEt—hexane, 1 : 5). Found (%): C, 80.32. $C_{11}H_{11}D_3O$. Calculated (%): C, 79.95. ^{1}H NMR, δ: 1.17 (t, 2 H, C(11)H_2D, J = 7.2 Hz); 2.36 (t, 2 H, C(10)H_2, J = 7.2 Hz); 4.31 (s, 2 H, C(1)H_2); 7.20—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 12.46 (t, C(11), $^1J_{C,D}$ = 19.2 Hz); 29.09 (C(10)); 61.03 (C(1)); 126.63 (C(7)); 128.20, 128.72 (4 C, C(5), C(6), C(8), C(9)); 137.28 (C(4)); 142.83 (C(2)).

(2*Z*)-2-Ethyl-3-phenylprop-2-en-1-ol (2b). Transparent oily liquid. The yield was 69%, R_f 0.35 (AcOEt—hexane, 1 : 5). Found (%): C, 81.35; H, 8.74. $C_{11}H_{14}O$. Calculated (%): C, 81.44; H, 8.70. ^{1}H NMR, δ: 1.19 (t, 3 H, C(11)H_3, J = 7.6 Hz);

1.59 (br.s, 1 H, OH); 2.34 (q, 2 H, C(10)H_2, J = 7.6 Hz); 4.32 (s, 2 H, C(1)H_2); 5.32 (s, 1 H, C(3)H); 7.20—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 12.75 (C(11)); 29.07 (C(10)); 61.05 (C(1)); 126.64 (C(7)); 128.20, 128.71 (4 C, C(5), C(6), C(8), C(9)); 137.25 (C(4)); 142.81 (C(2)).

[(1*Z*)-1,4-Dideutero-2-(2-deuteroxyethyl)but-1-en-1-yl]benzene (7). Transparent oily liquid. The yield was 67%, R_f 0.26 (AcOEt—hexane, 1 : 5). Found (%): C, 80.55. $C_{12}H_{13}D_3O$. Calculated (%): C, 80.40. ^{1}H NMR, δ: 1.15 (t, 2 H, C(12)H_2D, J = 7.2 Hz); 2.25 (t, 2 H, C(11)H_2, J = 7.2 Hz); 2.65—2.75 (m, 2 H, C(2)H_2); 3.75—3.95 (m, 2 H, C(1)H_2); 7.20—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 12.55 (t, C(12), J = 19.2 Hz); 29.80 (C(11)); 33.95 (C(2)); 61.03 (C(1)); 126.23 (C(8)); 128.21, 128.69 (C(6), C(7), C(9), C(10)); 138.03 (C(5)); 140.48 (C(3)).

(3*Z*)-3-Ethyl-4-phenylbut-3-en-1-ol (8). Transparent oily liquid. The yield was 75%, R_f 0.3 (AcOEt—hexane, 1 : 5). Found (%): C, 81.69; H, 9.11. $C_{12}H_{16}O$. Calculated (%): C, 81.77; H, 9.15. ^{1}H NMR, δ: 1.16 (t, 3 H, C(12)H_3, J = 7.2 Hz); 2.25 (q, 2 H, C(11)H_2, J = 7.2 Hz); 2.70—2.80 (m, 2 H, C(2)H_2); 3.60—3.80 (m, 2 H, C(1)H_2); 6.46 (s, 1 H, C(4)H); 7.20—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 12.86 (C(12)); 29.93 (C(11)); 33.98 (C(2)); 61.07 (C(1)); 126.23 (C(8)); 128.21, 128.71 (C(6), C(7), C(9), C(10)); 138.10 (C(5)); 140.56 (C(3)).

Cycloalumination of substituted propargylamines (general procedure). A 50-mL glass reactor placed in a water bath (40 °C, argon) was successively loaded with an acetylenic compound (1 mmol), Cp_2ZrCl_2 (0.2 mmol, 0.058 g), hexane (5 mL), and Et_3Al (2 mmol). The mixture was magnetically stirred for 3 h at 40 °C. The procedure of further treatment of the reaction mixture is similar to that described above. Individual compounds were isolated by distillation under reduced pressure.

(2*Z*)-2-Deutero-3-(2-deuteroethyl)-*N*,*N*-dimethylhept-2-en-1-amine (11a). Transparent oily liquid. The yield was 83%, b.p. 91—93 °C (15 Torr). Found (%): C, 76.91; N, 7.03. $C_{11}H_{21}D_2N$. Calculated (%): C, 77.12; N, 8.18. ^{1}H NMR, δ: 0.90 (t, 3 H, C(7)H_3, J = 6.8 Hz); 0.98 (t, 2 H, C(9)H_2D, J = 7.2 Hz); 1.20—1.40 (m, 4 H, C(5)H_2, C(6)H_2); 1.95—2.10 (m, 4 H, C(4)H_2, C(8)H_2); 2.21 (s, 6 H, C(10)H_3, C(11)H_3); 2.88 (s, 2 H, C(1)H_2). ^{13}C NMR, δ: 12.40 (t, C(9), $^1J_{C,D}$ = 19.3 Hz); 14.00 (C(7)); 22.82 (C(6)); 29.40 (C(8)); 30.28 (C(5)); 30.69 (C(4)); 45.23 (2 C, C(10), C(11)); 56.74 (C(1)); 120.34 (t, C(2), $^1J_{C,D}$ = = 23.5 Hz); 141.24 (C(3)). MS, m/z: 171 [M^+].

(2*Z*)-2-Deutero-3-(2-deuteroethyl)-*N*,*N*-dimethylundec-2-en-1-amine (11b). Transparent oily liquid. The yield was 88%, b.p. 105—108 °C (1 Torr). Found (%): C, 79.11; N, 6.68. $C_{15}H_{29}D_2N$. Calculated (%): C, 79.22; N, 6.16. ^{1}H NMR, δ: 0.89 (t, 2 H, C(13)H_2D, J = 6.4 Hz); 1.01 (t, 3 H, C(11)H_3, J = 7.2 Hz); 1.25—1.45 (m, 12 H, C(5)H_2—C(10)H_2); 2.04 (t, 2 H, C(4)H_2, J = 6.0 Hz); 2.15—2.30 (m, 2 H, C(12)H_2); 2.22 (s, 6 H, C(14)H_3, C(15)H_3); 2.90 (s, 2 H, C(1)H_2). ^{13}C NMR, δ: 12.74 (t, C(13), $^1J_{C,D}$ = 19 Hz); 14.09 (C(11)); 22.66 (C(10)); 28.49, 29.28, 29.52, 29.56, 29.78 (5 C, C(4)—C(8)); 30.58 (C(12)); 31.89 (C(9)); 45.27 (2 C, C(14), C(15)); 56.87 (C(1)); 120.52 (t, C(2), $^1J_{C,D}$ = 24 Hz); 144.36 (C(3)).

(2*Z*)-3-Ethyl-*N*,*N*-dimethylhept-2-en-1-amine (12). Transparent oily liquid. The yield was 85%, b.p. 85—87 °C (10 Torr). Found (%): C, 77.72; H, 13.80; N, 8.41. $C_{11}H_{23}N$. Calculated (%): C, 78.03; H, 13.69; N, 8.27. ^{1}H NMR, δ: 0.92 (t, 3 H, C(7)H_3, J = 6.8 Hz); 1.02 (t, 2 H, C(9)H_2D, J = 7.2 Hz); 1.25—1.40 (m, 4 H, C(5)H_2, C(6)H_2); 2.00—2.10 (m, 4 H, C(4)H_2, C(8)H_2); 2.24 (s, 6 H, C(10)H_3, C(11)H_3); 2.93 (d, 2 H, C(1)H_2, J = 6.8 Hz); 5.22 (t, 1 H, C(2)H, J = 6.8 Hz). ^{13}C NMR, δ: 12.73 (C(9)); 14.03 (C(7)); 22.84 (C(6)); 29.58 (C(8)); 30.31 (C(5)); 30.71 (C(4)); 45.15 (2 C, C(10), C(11)); 56.77 (C(1)); 120.24 (C(2)); 141.26 (C(3)).

(2*Z*)-3-Deutero-2-(2-deuteroethyl)-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine (14). Transparent oily liquid. The yield was 60%, b.p. 111—115 °C (5 Torr). Found (%): C, 79.11; N, 6.68. $C_{13}H_{17}D_2N$. Calculated (%): C, 81.62; N, 7.32. ^{1}H NMR, δ: 1.16 (t, 2 H, C(11)H_2D, J = 7.2 Hz); 2.15 (s, 6 H, C(12)H_3, C(13)H_3); 2.15—2.20 (m, 2 H, C(10)H_2); 2.38 (s, 2 H, C(1)H_2); 7.15—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 12.59 (t, C(11), $^1J_{C,D}$ = = 19 Hz); 28.55 (C(10)); 45.43 (2 C, C(12), C(13)); 58.52 (C(1)); 126.91 (C(7)); 127.92, 129.13 (C(5), C(6), C(8), C(9)); 131.69 (C(4)).

(2*Z*)-*N*,*N*-Dimethyl-3-phenylpent-2-en-1-amine (15). Transparent oily liquid. The yield was 75%, b.p. 83—88 °C (1 Torr). Found (%): C, 82.31; H, 10.06; N, 7.52. $C_{13}H_{19}N$. Calculated (%): C, 82.48; H, 10.12; N, 7.40. ^{1}H NMR, δ: 1.22 (t, 3 H, C(11)H_3, J = 7.4 Hz); 2.19 (s, 6 H, C(12)H_3, C(13)H_3); 2.10—2.20 (m, 2 H, C(10)H_2); 2.43 (s, 2 H, C(1)H_2); 6.48 (s, 1 H, C(3)H); 7.10—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 12.81 (C(11)); 28.59 (C(10)); 45.51 (2 C, C(12), C(13)); 58.58 (C(1)); 126.06 (C(3)); 127.04 (C(7)); 127.95, 129.19 (C(5), C(6), C(8), C(9)); 131.70 (C(4)).

(1*E*,2*E*)-1,2-Bis[1-deutero-2-(dimethylamino)ethylidene]cyclohexane (16). Transparent oily liquid. The yield was 81%, b.p. 114—117 °C (1 Torr). Found (%): C, 75.31; N, 11.21. $C_{14}H_{24}D_2N_2$. Calculated (%): C, 74.94; N, 12.49. ^{1}H NMR, δ: 1.55—1.70 (m, 4 H, C(5)H_2, C(6)H_2); 2.15—2.30 (m, 16 H, C(4)H_2, C(7)H_2, C(11)H_3—C(14)H_3); 3.19 (s, 4 H, C(1)H_2, C(10)H_2). ^{13}C NMR, δ: 26.51 (2 C, C(5), C(6)); 29.00 (2 C, C(4), C(7)); 45.20 (4 C, C(11)—C(14)); 56.29 (2 C, C(1), C(10)); 119.47 (t, 2 C, C(2), C(9), J = 23.5 Hz); 144.47 (2 C, C(3), C(8)).

(2*E*,2′*E*)-2,2′-Cyclohexane-1,2-diylidenebis(*N*,*N*-dimethylethanamine) (17). Transparent oily liquid. The yield was 70%, b.p. 110—115 °C (1 Torr). Found (%): C, 75.51; H, 11.66; N, 12.72. $C_{14}H_{26}N_2$. Calculated (%): C, 75.62; H, 11.79; N, 12.60. ^{1}H NMR, δ: 1.55—1.70 (m, 4 H, C(5)H_2, C(6)H_2); 2.15—2.35 (m, 16 H, C(4)H_2, C(7)H_2, C(11)H_3—C(14)H_3); 2.93 (d, 4 H, C(1)H_2, C(10)H_2, J = 7.2 Hz); 5.48 (t, 2 H, C(2)H, C(9)H, J = 7.2 Hz). ^{13}C NMR, δ: 26.52 (2 C, C(5), C(6)); 29.05 (2 C, C(4), C(7)); 45.19 (4 C, C(11)—C(14)); 56.39 (2 C, C(1), C(10)); 119.84 (2 C, C(2), C(9)); 144.57 (2 C, C(3), C(8)).

Complex of 1-ethyl-2-(*N*,*N*-dimethylaminomethyl)-3-*n*-butylalumacyclopent-2-ene with THF (13). The cycloalumination of *N*,*N*-dimethylhept-2-yn-1-amine was carried out according to the procedure described above. After the end of the reaction, hexane was distilled off from the reaction mixture under reduced pressure. The mixture was placed in an ampule of the NMR spectrometer under an argon flow, and 1 equiv. of THF (over Et_3Al) was added. To record NMR spectra, HSQC, COSY, HMBC, and NOESY procedures and toluene-d_8 as an internal standard were used. ^{13}C NMR, δ: 13.78 (C(13)); 22.77 (C(12)); 45.25 (2 C, C(8), C(9)); 67.18 (C(7)); 137.04 (C(1)); 160.43 (C(2)).

Kinetic study of the cycloalumination reaction. The above described procedure of cycloalumination of alkyl-substituted propargyl and homopropargyl alcohols was used. The temperature of the bath was 40 °C. The hydrolysis products were analyzed by GC 5, 10, 15, 30, 60, 90, 120, 180, 240, and 480 min after the reactants were loaded. The relative rate constant of transforma-

tion (k_{rel}) was determined by the ratio of the half-reaction time of dec-5-yne to the half-reaction time of the acetylenic compound in the reaction under study.

This work was financially supported by the Ministry of Science and Education of the Russian Federation (Grant NSh-4105.2010.3).

References

1. G. A. Tolstikov, U. M. Dzhemilev, A. G. Tolstikov, *Alyuminii-organicheskie soedineniya v organicheskom sinteze* [*Organoaluminum Compounds in Organic Synthesis*], Geo, Novosibirsk, 2009, 645 pp. (in Russian).
2. U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, *Mendeleev Commun.*, 1992, 135.
3. U. M. Dzhemilev, A. G. Ibragimov, I. R. Ramazanov, M. P. Luk´yanova, A. Z. Sharipova, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, 465 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 484].
4. U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov, G. A. Tolstikov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1989, 207 [*Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1989, **38**, 194].
5. E.-I. Negishi, D. Y. Kondakov, D. Choueiry, K. Kasai, T. Takahashi, *J. Am. Chem. Soc.*, 1996, **118**, 9577.
6. M. G. Shaibakova, I. G. Titova, A. G. Ibragimov, U. M. Dzhemilev, *Zh. Org. Khim.*, 2008, 1141 [*Russ. J. Org. Chem. (Engl. Transl.)*, 2008, **44**, 1126].
7. E.-I. Negishi, J.-L. Montchamp, L. Anastasia, A. Elizarov, D. Choueiry, *Tetrahedron Lett.*, 1998, **39**, 2503.
8. S. Nowotny, C. E. Tucker, C. Jubert, P. Knochel, *J. Org. Chem.*, 1995, **60**, 2762.
9. H. G. O. Becker, W. Berger, G. Domschke, *Organikum. Organisch-chemisches Grundpraktikum*, Wiley—VCH, Berlin, 1998.

Received June 8, 2010;
in revised form November 3, 2010