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Cycloaluminizing of Acetylenes and 1,4-Enynes in the Presence of Zr-containing Catalysts

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Abstract—Synthetic procedures were developed for preparation of substituted alumacyclopenta-2,4-dienes and 1-ethyl-2(3)-(1-ethyl-3-alumacyclopentylmethyl)-3(2)-alkyl(phenyl)alumacyclopent-2-enes by cycloaluminizing acetylenes and 1,4-enynes using $RAlCl_2$ (R = Et, BuO, Et_2N) and Et_3Al in the presence of Zr-containing catalysts (Cp_2ZrCl_2, $ZrCl_4$).

According to published data [1–3] the catalytic cycloaluminizing of α-olefins, 1,2-dienes, and acetylenes using trialkyl- and alkylhaloalanes afforded alumacyclopropanes, alumacyclopropenes, alumacyclopentanes, and alumacyclopentenes that in the course of a "one-pot" process were converted into practically important 1,3-dienes [4], secondary and tertiary alcohols [5], cyclopropanes [6], cyclobutanes [7], cyclopentanols [8], and five-membered heterocycles [9, 10]. The published data on preparative procedures for substituted alumacyclopenta-2,4-dienes [11, 12] are virtually lacking.

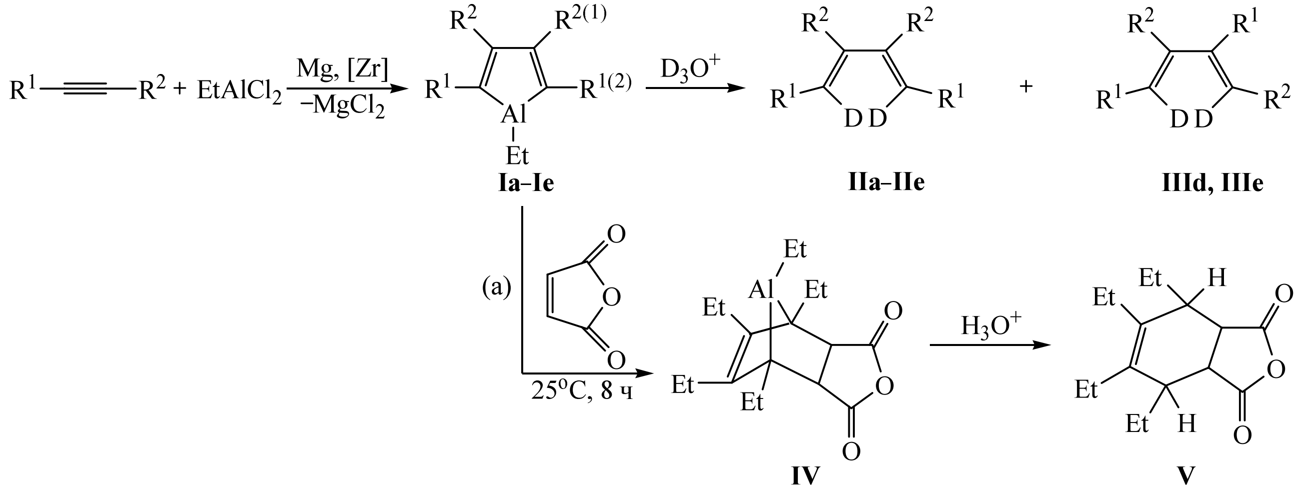
Aiming at extension of applications for cycloaluminizing of unsaturated compounds catalyzed by transition metal complexes and with a goal of developing synthetic procedures for substituted alumacyclopenta-2,4-dienes we studied reactions of mono- and disubstituted acetylenes and 1,4-enynes [4-octyne, 5-decyne, phenylmethylacetylene, phenylallylacetylene, 1-heptyne, butyl-(amyl, phenyl)allylacetylenes] with $RAlCl_2$ (R = Et, BuO, Et_2N) and Et_3Al in the presence of Zr-containing catalysts which were the most active in cycloaluminizing of unsaturated compounds [1, 2]. In experiments with $RAlCl_2$ we used magnesium metal as chlorine ions acceptor [13].

We presumed that the reduction of zirconcocene dichloride (Cp_2ZrCl_2) with Mg in the presence of disubstituted acetylenes afforded zirconacyclopentadienes [14] that would be capable of transmetallation [15] by $EtAlCl_2$ into the corresponding alumacyclopentadienes. We established by our investigations that the reaction of 3-hexyne, 4-octyne, and 5-decycne with $EtAlCl_2$ in the presence of metallic Mg and Cp_2ZrCl_2 catalyst taken in molar ratio 100:75:75:10 under given reaction conditions (20–22°C, THF, 8 h) resulted in 1-ethyl-2,3,4,5-tetraalkylalumacyclopentadienes **Ia–Ic** in 80–90% yields. The reaction products were identified by their ^{13}C NMR spectra and by deuterolysis products **II** (Scheme 1). For instance, in the ^{13}C NMR spectrum of compound **Ia** the characteristic signals of the ethyl group cabon at 2.15 ppm and of sp^2-hybridized C^2 and C^5 atoms at 140.19 ppm are broadened due to the quadrupole interaction with the Al atom (I 5/2). The triplet signal at 123.18 ppm with a characteristic value of the direct coupling constant J_{CD} 24.0 Hz in the spectrum of deuterolysis product **IIa** corresponds to C^3 and C^6 atoms linked to deuterium. In the ^{13}C NMR spectra of compounds **Ib** and **Ic** analogous signals were observed. To obtain a more reliable proof of the structure of alumacyclopentadienes we carried out the reaction of compound **Ia** (Scheme 1) with maleic anhydride along the [4+2]-cyclization pattern to furnish adduct **IV**. The hydrolysis of compound **IV** gave tetrahydro-3,4,5,6-tetraethyl-*o*-phthalic anhydride (**V**) that contained in the ^{13}C NMR spectrum signals at 172.44 ppm characteristic of carbonyl group.

In the reaction mixtures hexaalkylsubstituted benzenes, products of cyclotrimerization of the initial acetylenes, were found in minor amounts (5–10%) [12], and also substituted alumacyclopropenes were present (5–8%). The latter are target products (65–90%) of analogous reaction catalyzed by Cp_2TiCl_2 [12]. At application of $ZrCl_4$ (5 mol%) in this reaction the yield of alumacyclopentadienes **Ia–Ic** was ~70%, however, the content of homotrimerization product of the initial acetylene in the reaction mixture increased.

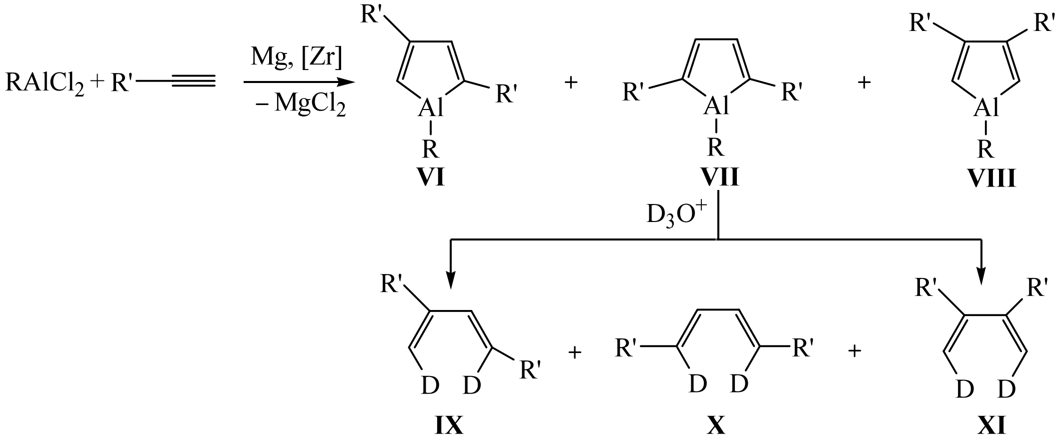
The reaction of $EtAlCl_2$ with phenylmethylacetylene and phenylallylacetylene furnished regioisomeric organo-

Scheme 1.



I–III, $R^1 = R^2 =$ Et (**a**), Pr (**b**), Bu (**c**); $R^1 =$ Ph, $R^2 =$ All (**d**), Me (**e**).

Scheme 2.



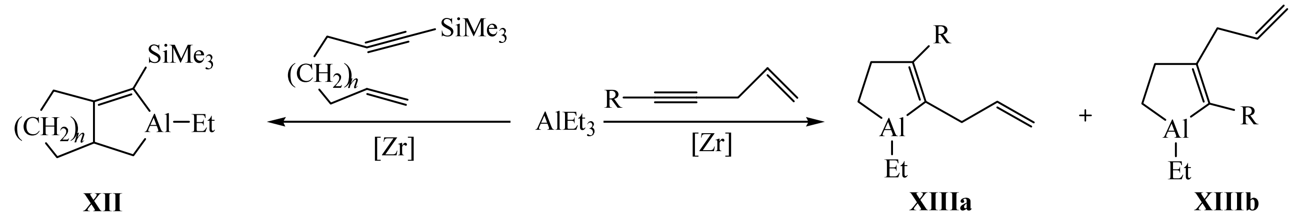
R = Et, BuO, Et_2N; R' = Amyl.

aluminum compounds **Id** and **Ie** that on deuterolysis were converted into 1,4-dideutero-1,3-butadienes **IId** and **IIe, IIId** and **IIIe** in a ratio ~ 3:1. The cycloaluminizing of 1-heptyne with $RAlCl_2$ (R = Et, BuO, Et_2N) in the presence of Mg and 10 mol% of Cp_2ZrCl_2 with respect to the acetylene (THF, 21–22°C, 12 h) furnished a mixture of regioisomeric trisubstituted alumacyclopentadienes in a ratio **VI:VII:VIII** ~ 2:2:1 and an overall yield 55–60%, that were identified by analysis of the deuterolysis products **IX–XI**. Like in the reactions with disubstituted acetylenes here also formed in minor amounts (5–25%) the regioisomeric trialkylbenzenes, the cyclotrimerization products of the initial acetylenes (Scheme 2).

It was shown formerly [16], that the cycloaluminizing of 1,6- and 1,7-enynes with Et_3Al in the presence of Cp_2ZrCl_2 catalyst gave bicycloalumacyclopent-2-enes **XII**, and from 1,4-enynes and Et_3Al under catalysis with Cp_2ZrCl_2 (1,4-enyne:[Al]:[Zr] = 10:25:0.5) under the reaction conditions (~20°C, 8 h, hexane) a mixture of regioisomeric 2,3-disubstituted alumacyclopent-2-enes **XIIIa** and **XIIIb** could be obtained with the retention of the allyl double bond [17].

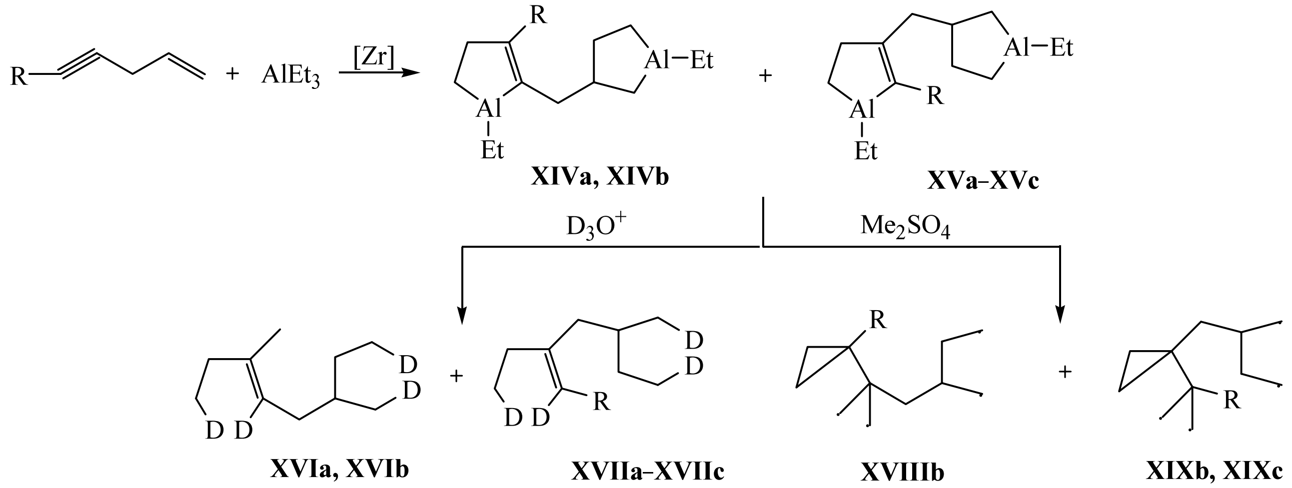
We found that the reaction of 1,4-enynes with fourfold excess of Et_3Al in the presence of 10–15 mol% of Cp_2ZrCl_2 catalyst with respect to the initial 1,4-enyne at 20–21°C in 8–10 h gave rise to regioisomeric (alumacyclopent-3-ylmethyl)alumacyclopent-2-enes **XIVa** and **XIVb**, and **XVa** and **XVb** that were identified by conversion into partly deuterated compounds **XVIa, XVIb**/**XVIIa, XVIIb** ~ 1:1, and also by transformation into 1,1-dialkyl-substituted cyclopropanes **XVIIIb**/**XIXb** ~ 1:1 effected by Me_2SO_4 [18]. The phenylallylacetylene, in

Scheme 3.



R = Bu (**a**), Amyl (**b**), Ph (**c**).

Scheme 4.



contrast to alkylallylacetylenes, in this reaction gave rise predominantly to regioisomer **XVc** (~75%) identified by analysis of the corresponding deuterolysis product **XVIIc** and 1,1-disubstituted cyclopropane **XIXc** (Scheme 4).

Hence the reaction of acetylenes with $RAlCl_2$–Mg or 1,4-enynes with Et_3Al catalyzed by Zr compounds permits preparation under mild conditions in sufficient yields of the substituted alumacyclopentadienes and (alumacyclopent-3-ylmethyl)alumacyclopent-2-enes. These findings open the way to the synthesis of new types of five-membered unsaturated cyclic organoaluminum compounds promising for the designed synthesis of heterocycles and the other valuable synthons for the organic synthesis.

EXPERIMENTAL

Products of hydrolysis and deuterolysis were analyzed on a chromatograph Chrom-5, carrier gas He, column 1200×3 mm, stationary phase 5% SE-30 or 15% PEG-6000 on Chromaton N-AW. IR spectra were recorded on spectrometer 75IR (from films), mass spectra were measured on an MKh-1306 instrument at 70 eV and 200°C. ^1H and ^{13}C NMR spectra were registered from solutions in $CDCl_3$ on a spectrometer JEOL FX-90 Q [89.55 (^1H) and 22.5 MHz (^{13}C)]. Yields of compounds were estimated by GLC of the hydrolysis products. The separation of regioisomer mixtures was carried out on a preparative gas chromatograph Carlo Erba Fractovap Mod.GW, carrier gas He, column 4000×6 mm, stationary phase SE-30.

In the study commercial 86% $EtAlCl_2$ and 98% Et_3Al (Public Joint Stock Co "Redkinskii Opytnyi Zavod") were used as received. The initial aluminum amides and alkoxides were prepared by known procedures [19, 20].

The reactions with organometallic compounds were carried out in an atmosphere of dry argon. THF was distilled from $LiAlH_4$ just before use.

Reactions of acetylenes with $EtAlCl_2$ catalyzed by Cp_2ZrCl_2. *General procedure*. Into a glass reactor in an atmosphere of dry argon at ~0°C while stirring was charged 1.0 mmol of Cp_2ZrCl_2, 7.5 gram-atom of powdered Mg, 10 mmol of acetylene, 10 ml of THF, and 7.5 mmol of $EtAlCl_2$. The reaction mixture was warmed to the room temperature (20–22°C), and the stirring was continued for 8 h. To identify the substituted alumacyclopentadienes (for instance, **Ia**) by its ^{13}C NMR spectrum the solvent and unreacted acetylene from the reaction mixture was distilled off in a vacuum, Mg was precipitated from the residue by centrifugation, and under argon the substance thus obtained was transferred into the NMR tube. The identification of the substituted alumacyclopentadienes by the deuterolysis products was performed as follows: The reaction mixture was treated with an 8% DCl solution in D_2O, the products were extracted with ether or hexane, and dried with $MgSO_4$. Compounds **IIa–IIc** and regiisomers mixture **IId, IIe, IIId**, and **IIIe, IX–XI** were isolated by vacuum distillation, regiisomers **IId, IIe, IIId**, and **IIIe** were separated by column chromatography on silica gel L,100/250μ, eluent benzene–ethyl acetate, 5:1, partitioning of **IX–XI** was performed by preparative GLC. Compound **IIb** was identified by comparison with an authentic sample [12].

To obtain adduct **IV** alumacyclopentadiene **Ia** formed *in situ* under the reaction conditions was treated at –5°C with 12 mmol of maleic anhydride, and the reaction mixture was stirred at room temperature for 7 h. Then the reaction mixture at –10°C was treated with 10% HCl. Product **V** was extracted with ether or hexane, dried over $MgSO_4$, and the solvent was removed in a vacuum.

1-Ethyl-2,3,4,5-tetraethylalumacyclopenta-2,4-diene (Ia). ^{13}C NMR spectrum, δ, ppm: 2.15 br.s (Al–$\underline{CH_2}$–CH_3), 9.91 (Al–CH_2–$\underline{CH_3}$), 14.02, 14.28, 22.43, 22.67, 140.19 br.s ($C^{2,5}$), 153.15 ($C^{3,4}$).

1-Ethyl-2,3,4,5-tetrapropylalumacyclopenta-2,4-diene (Ib). ^{13}C NMR spectrum, δ, ppm: 2.71 br.s (Al–$\underline{CH_2}$–CH_3), 10.32 (Al–CH_2–$\underline{CH_3}$), 13.63, 14.02, 22.28, 23.38, 29.43, 31.06, 140.63 br.s ($C^{2,5}$), 153.30 ($C^{3,4}$).

1-Ethyl-2,3,4,5-tetrabutylalumacyclopenta-2,4-diene (Ic). ^{13}C NMR spectrum, δ, ppm: 2.77 br.s (Al–$\underline{CH_2}$–CH_3), 10.51 (Al–CH_2–$\underline{CH_3}$), 13.00, 13.24, 22.02, 23.64, 26.05, 27.29, 28.85, 31.25, 140.70 br.s ($C^{2,5}$), 151.17 ($C^{3,4}$).

3,6-Dideutero-4,5-diethylocta-3,5-diene (IIa). Yield 90%, bp 80–82°C (1 mm Hg). IR spectrum, cm^{-1}: 2175 (CD). ^1H NMR spectrum, δ, ppm: 0.88–1.00 m (12H, CH_3), 1.97–2.16 m (8H, =C–CH_2). ^{13}C NMR spectrum, δ, ppm: 14.15 ($C^{1,8}$), 14.21, 22.19 ($C^{2,7}$), 22.35, 123.18 t ($C^{3,6}$, J_{CD} 24 Hz), 139.61 ($C^{4,5}$). Found, %: C 85.47; (H+D) 14.16. $[M]^+$ 168. $C_{12}H_{20}D_2$. Calculated, %: C 85.64; H 11.98; D 2.38. *M* 168.

5,7-Dideutero-6,7-dibutyldodeca-5,7-diene (IIc). Yield 80%, bp 143–145°C (2 mm Hg). IR spectrum, cm^{-1}: 2170 (CD). ^1H NMR spectrum, δ, ppm: 0.88–1.00 m (12H, CH_3), 1.13–1.72 m (16H, CH_2), 1.97–2.16 m (8H, =C–CH_2). ^{13}C NMR spectrum, δ, ppm: 13.66, 14.10 ($C^{1,12}$), 22.54, 22.87 ($C^{2,11}$), 27.81 ($C^{3,10}$), 28.00 ($C^{4,9}$), 31.10, 31.25, 125.81 t ($C^{5,8}$, J_{CD} 24 Hz), 141.22 ($C^{6,7}$). Found, % : C 85.45; (H+D) 14.17. $[M]^+$ 142. $C_{20}H_{36}D_2$. Calculated, % : C 85.63; H 12.94; D 1.43. *M* 142.

4,5-Bis[deutero(phenyl)methylidene]octa-1,7-diene (IIg). Yield 56%, R_f 0.52. IR spectrum, cm^{-1}: 3050, 3010, 2950, 2920, 2860, 2175 (CD), 1950, 1600, 1490, 1440, 1380, 1230, 1030, 910, 750, 700. ^1H NMR spectrum, δ, ppm : 2.54–2.77 m (4H, =–CH_2–=), 4.91–5.20 m (4H, CH_2=), 5.85–6.30 m (2H, =CH–), 7.04–7.83 m (10H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 32.82 ($C^{3,6}$), 118.21 ($C^{1,8}$), 115.92 t (J_{CD} 23.5 Hz), 126.86, 128.23 (2C), 128.54 (2C), 131.60 ($C^{2,7}$), 136.75 (C_6H_5), 144.02 ($C^{4,5}$). Found, %: C 91.43; (H+D) 8.17. $[M]^+$ 288. $C_{22}H_{20}D_2$. Calculated, % : C 91.62; H 6.99; D 1.39. *M* 288.

1-(1,4-Dideutero-2,3-dimethyl-4-phenylbuta-1,3-dienyl)benzene (IIe). Yield 54%, R_f 0.48. IR spectrum, cm^{-1}: 3050, 3010, 2960, 2910, 2850, 2180 (CD), 1950, 1710, 1680, 1590, 1530, 1490, 1440, 1250, 1170, 1020, 795, 750, 695. ^1H NMR spectrum, δ, ppm: 2.14 s (6H, CH_3), 7.06–7.40 m (10H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 15.81, 118.26 t (J_{CD} 22.5 Hz), 127.48, 128.23 (2C), 129.52 (2C), 138.75 (C_6H_5), 139.03. Found, %: C 91.31; (H+D) 8.32. $[M]^+$ 236. $C_{18}H_{16}D_2$. Calculated, %: C 91.48; H 6.83; D 1.69. *M* 236.

4-Deutero-6-[deutero(phenyl)methylidene]-5-phenylnona-1,4,8-triene (IIId). Yield 19%, R_f 0.45. IR spectrum, cm^{-1}: 2175 (CD). ^1H NMR spectrum, δ, ppm: 2.55–2.77 m (4H, =–CH_2–=), 4.85–5.22 m (4H, CH_2=), 5.85–6.30 m (2H, =CH–), 7.00–7.83 m (10H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 26.57 (C^7), 33.99 (C^3), 113.13 (C^9), 121.58 (C^1), 126.85, 128.21 (2C), 128.54 (2C), 128.73 t (C^6, J_{CD} 22.0 Hz), 131.62 (C^2), 132.44 (C^8), 137.06 (C_6H_5), 139.46 (C^4), 141.42 (C_6H_5), 144.02 (C^5). The signal of carbon atom linked to deuterium and phenyl at a double bond was not observed. Found, %: C 91.44; (H+D) 8.18. $[M]^+$ 288. $C_{22}H_{20}D_2$. Calculated, % : C 91.62; H 6.99; D 1.39. *M* 288.

1-[2-Deutero-1-(2-deutero-1-methyl-2-phenyl-ethenyl)-1-propenyl]benzene (IIIe). Yield 18%, R_f 0.42. IR spectrum, cm^{-1}: 2180 (CD). ^1H NMR spectrum, δ, ppm: 1.55 d (3H, CH_3, *J* 7.0 Hz), 1.72 s (3H, CH_3), 6.78–7.29 m (10H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 18.57, 22.28, 123.27 t (C–Ph, J_{CD} 23.5 Hz), 126.13, 126.59, 128.08 (4C), 129.25 (4C), 133.03 t (=$\underline{C}$HD–CH_3, J_{CD} 23.5 Hz), 137.77 (C_6H_5), 138.55 (=$\underline{C}$–CH_3), 139.79 (C_6H_5), 145.51 (=$\underline{C}$–Ph). Found, %: C 91.29; (H+D) 8.30. $[M]^+$ 236. $C_{18}H_{16}D_2$. Calculated, %: C 91.48; H 6.83; D 1.69. *M* 236.

1,7,8,9,10-Pentaethyl-4-oxo-10-alumatricyclo-[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (IV). ^{13}C NMR spectrum, δ, ppm (C_6D_6): 7.15 (Al–<u>CH</u>$_2$–CH$_3$), 9.60 (Al–CH$_2$–<u>CH</u>$_3$), 12.50, 14.13, 20.18, 25.70, 40.86, 42.79, 135.91, 172.77.

4,5,6,7-Tetraethyl-3a,4,7,7a-tetrahydro-1,3-isobenzofurandione (V). Yield 85%. IR spectrum, cm^{-1}: 1670 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.80 t (6H, CH$_3$, *J* 7.0 Hz), 1.22 t (6H, CH$_3$, *J* 7.0 Hz), 1.78–1.89 m (2H, CH), 1.98–2.18 m (8H, CH$_2$), 3.30–3.88 m (2H, CH). ^{13}C NMR spectrum, δ, ppm: 12.23, 14.65, 19.82, 20.40, 40.32 ($C^{4,7}$), 42.56 ($C^{3,8}$), 138.08 ($C^{5,6}$), 172.24 ($C^{2,9}$). Found, %: C 72.48; H 8.96. $[M]^+$ 264. $C_{16}H_{24}O_3$. Calculated, % : C 72.69; H 9.15. *M* 264.

1,4-Dideutero-2(pentyl)nona-1,3-diene (IX). Yield 24%, n_D^{20} 1.4568. IR spectrum, cm^{-1}: 3080, 2970, 2920, 2180 (CD), 1640, 1380, 1480, 970, 890, 790, 720. ^{1}H NMR spectrum, δ, ppm: 0.89 t (6H, CH$_3$, *J* 6.8 Hz), 1.13–1.72 m (12H, CH$_2$), 1.97–2.16 m (4H, =C–CH$_2$), 4.85 s (1H, CHD=C), 6.04 s (1H, CH=). ^{13}C NMR spectrum, δ, ppm: 14.22, 22.67, 22.80, 27.09, 29.50, 31.58, 31.90, 32.17, 33.73, 136.45 (C^3), 149.68 (C^2). The signals of carbon atoms linked to deuterium at a double bond were not observed. Found, %: C 84.59; (H+D) 15.02. $[M]^+$ 198. $C_{14}H_{26}D_2$. Calculated, % : C 84.77; H 13.21; D 2.02. *M* 198.

6,9-Dideuterotetradeca-6,8-diene (X). Yield 24%, n_D^{20} 1.4436. IR spectrum, cm^{-1}: 3030, 2950, 2920, 2850, 2180 (CD), 1640, 1480, 1380, 990, 950, 790, 720. ^{1}H NMR spectrum, δ, ppm: 0.88 t (6H, CH$_3$, *J* 7.0 Hz), 1.10–1.72 m (12H, CH$_2$), 1.97–2.30 m (4H, –CH$_2$–C=), 5.99 s (2H, –HC=CD–). ^{13}C NMR spectrum, δ, ppm: 14.09, 22.61, 25.01, 31.90, 32.75, 133.35 ($C^{7,8}$). The signals of carbon atoms linked to deuterium at a double bond were not observed. Found, %: C 84.43; (H+D)15.00. $[M]^+$ 196. $C_{14}H_{26}D_2$. Calculated, %: C 84.59; H 13.21; D 2.02.

1,4-Dideutero-2,3-di(pentyl)buta-1,3-diene (XI). Yield 12%. IR spectrum, cm^{-1}: 2175 (CD). ^{1}H NMR spectrum, δ, ppm: 0.89 t (6H, CH$_3$, *J* 7.0 Hz), 1.13–1.72 m (12H, CH$_2$), 1.97–2.16 m (4H, =C–CH$_2$), 4.69 s (2H, –C=CHD). ^{13}C NMR spectrum, δ, ppm: 14.15, 22.67, 28.19, 29.23, 31.96, 146.68 ($C^{2,3}$). The signals of carbon atoms linked to deuterium at a double bond were not observed. Found, %: C 84.40; (H+D) 14.98. $[M]^+$ 196. $C_{14}H_{26}D_2$. Calculated, %: C 84.59; H 13.21; D 2.02.

Reactions of 1,4-enynes with Et_3Al catalyzed by Cp_2ZrCl_2. Into a glass reactor in an atmosphere of dry argon at ~0°C while stirring was charged 1.5 mmol of Cp_2ZrCl_2, 10 mmol of an appropriate 1,4-enyne, 10 ml of hexane, and 40 mmol of Et_3Al. The reaction mixture was warmed to the room temperature (20–22°C), and the stirring was continued for 8–10 h. The reaction mixture was treated with 8% DCl in D_2O. The reaction products were extracted with ether or hexane, the extracts were dried with $MgSO_4$, passed through a small bed of aluminum oxide, the solvent was distilled off, and the residue was subjected to a fractional distillation in a vacuum.

The 1,1-disubstituted cyclopropanes were obtained by adding dropwise at 0°C 42 mmol of dimethyl sulfate to the stirred solutions of bicyclic organoaluminum compounds **XIVb** and **XVb** obtained *in situ* under reaction conditions. The reaction mixture was stirred for 12 h at 20°C. Then the reaction mixture was subjected to hydrolysis with 10% HCl. The organic substances were extracted into ether or hexane, the extract was washed with Na_2CO_3 till neutral reaction, and dried with $CaCl_2$. The reaction products were isolated by vacuum distillation.

(*Z*)-1,5-Dideutero-6-(2-deuteroethyl)-3-(deuteromethyl)dec-5-ene (XVIa)/(*Z*)-1,6-dideutero-5-(2-deuteroethyl)-3-(deutero-methyl)dec-5-ene (XVIIa) ~(1:1). Yield 78%, bp 65–69°C (2 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.78–0.98 m (9H, CH$_3$, CH$_2$D), 1.04–1.48 m (7H, CH, CH$_2$), 1.88–2.14 m (6H, CH$_2$–=). ^{13}C NMR spectrum (**XVIa**), δ, ppm: 11.47 t (*J* 19.1 Hz), 12.86 (C^1, *J* 19.1 Hz), 14.20 (C^{10}), 18.90 t (*J* 19.1 Hz), 22.96 (C^9), 28.09, 29.80 (C^8), 30.17 (C^2), 31.26 (C^7), 34.71 (C^4), 37.43 (C^3), 121.87 (C^5, *J* 22.0 Hz), 139.50 (C^6). ^{13}C NMR spectrum (**XVIIa**), δ, ppm: 11.47 t (*J* 19.1 Hz), 12.88 t (C^1, *J* 19.1 Hz), 14.20 (C^{10}), 18.97 t (*J* 19.1 Hz), 22.96 (C^9), 28.46, 29.80 (C^8), 30.40 (C^2), 32.31 (C^7), 33.45 (C^4), 35.72 (C^3), 123.85 t (C^6, *J* 22 Hz), 141.67 (C^5). Found, %: C 84.42; (H+D) 12.58. $[M]^+$186. $C_{13}H_{22}D_4$. Calculated, %: C 83.80; H 11.90; D 4.30. *M* 186.

(*Z*)-6-Deuteroethyl-3-deuteromethyl-1,5-dideuteroundec-5-eneεν (XVIb)/(*Z*)-1,6-dideutero-5-(2-deuteroethyl)-3-(deuteromethyl)undec-5-ene (XVIIb) ~(1:1). Yield 80%, bp 65–68°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.78–0.98 m (9H, CH$_3$, CH$_2$D), 1.05–1.50 m (9H, CH, CH$_2$), 1.82–2.18 m (6H, CH$_2$–=). ^{13}C NMR spectrum (**XVIb**), δ, ppm: 11.49 t (C^1, *J* 19.1 Hz), 12.85 t (*J* 19.1 Hz), 14.22 (C^{11}), 18.96 t (*J* 19.1 Hz), 22.93 (C^{10}), 28.07, 29.50 (C^8), 29.76 (C^9), 30.15 (C^2), 32.04 (C^7), 34.77 (C^4), 37.43 (C^3), 121.97 t (C^5, *J* 22.00 Hz), 139.59 (C^6). ^{13}C NMR spectrum (**XVIIb**), δ, ppm: 11.49 t (*J* 19.1 Hz), 12.85 t (C^1, *J* 19.1 Hz), 14.22 (C^{11}), 18.96 t (*J* 19.1 Hz), 22.93 (C^{10}), 28.46, 29.50 (C^{8}), 29.76 (C^{9}), 30.41 (C^{2}), 32.36 (C^{7}), 33.47 (C^{4}), 35.74 (C^{3}), 124.64 t (C^{6}, *J* 22.0 Hz), 141.61 (C^{5}). Found, % : C 85.43; (H+D) 12.58. $[M]^+$ 200. $C_{14}H_{24}D_4$. Calculated, % : C 85.64; H 12.32; D 2.04. *M* 200.

1-[(*Z*)-1,6-Dideutero-2-(2-deuteroethyl)-4-(deuteromethyl)-1-hex-1-enyl]benzene (XVIIc). Yield 75%, bp 102–103°C (2 mm Hg). IR spectrum, cm^{-1}: 3400, 2950, 2910, 2855, 2170 (CD), 1700, 1600, 1450, 750, 700. ^{1}H NMR spectrum, δ, ppm: 0.72–0.99 m (6H, CH_2D), 1.06–1.73 m (3H, CH, CH_2), 2.08–2.23 m (4H, CH_2–=), 7.02–7.56 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 11.56 t (*J* 19.1 Hz), 12.79 t (C^{6}, *J* 19.1 Hz), 19.02 t (*J* 19.1 Hz), 29.66, 29.99 (C^{5}), 32.84 (C^{3}), 37.45 (C^{4}), 125.63, 127.90 (2C), 128.94 (2C), 139.01 (C_6H_5), 143.99 (C^{2}). The signal of carbon atom linked to deuterium at a double bond was not observed. Found, %: C 87.12; (H+D) 12.49. $[M]^+$ 206. $C_{15}H_{18}D_4$. Calculated, %: C 87.33; H 8.79; D 3.88. *M* 206.

2,4-Dimethyl-2-(1-pentylcyclopropyl)hexane (XVIIIb)/2-methyl-2-[1-(2-methylbutyl)cyclopropyl]heptane (XIXb) ~(1:1). Yield 76%, bp 121–124°C (2 mm Hg). IR spectrum, cm^{-1}: 3080, 2950, 2900, 2850, 2170 (CD), 1450, 1380, 1140, 800, 760. ^{1}H NMR spectrum, δ, ppm: 0.10–0.22 m (2H, CH_2, *c*-Pr), 0.36–0.48 m (2H, CH_2, *c*-Pr), 0.74–0.98 m (5H, CH_3), 1.17–1.58 m (3H, CH_2, CH). ^{13}C NMR spectrum (**XVIIIb**), δ, ppm: 7.27, 7.36 (*c*-Pr), 11.68 (C^{6}), 14.22, 20.98, 22.87, 24.10 (*c*-Pr), 25.08 (2C), 26.51, 30.93 (C^{5}), 32.75 (C^{4}), 32.88, 33.08, 35.22 (C^{2}), 40.42 (C^{3}). ^{13}C NMR spectrum (**XIXb**), δ, ppm: 6.92, 6.78 (*c*-Pr), 11.68, 14.22 (C^{7}), 20.98, 22.87 (C^{6}), 24.82 (*c*-Pr), 25.08 (2C), 26.51(C^{4}), 30.93, 31.45, 32.75(C^{5}), 33.08(C^{3}), 35.03 (C^{2}), 39.77. Found, % : C 85.44; H 14.22. $[M - C_2H_4]^+$ 196. $C_{16}H_{32}$. Calculated, % : C 85.63; H 14.37.

1-{1-Methyl-1-[1-(2-methylbutyl)cyclo-propyl]-ethyl}benzene (XIXc). Yield 67%. ^{1}H NMR spectrum, δ, ppm: 0.10–0.36 m (2H, CH_2, *c*-Pr), 0.58–0.95 m (14H, CH_2, *c*-Pr, CH_3), 1.17–1.58 m (5H, CH_2, CH), 6.98–7.40 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 8.24 (2C, *c*-Pr), 11.62, 20.72, 26.57 (2C), 29.56 (*c*-Pr), 30.47, 31.12, 39.45, 40.49, 125.48, 126.85 (2C), 127.76 (2C), 141.85 (C_6H_5). Found, % : C 88.46; H 11.20. $[M - C_2H_4]^+$ 202. $C_{17}H_{26}$. Calculated, %: C 88.62; H 11.38.

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