Cycloalumination of α,ω-Diolefins with EtAlCl$_2$ Catalyzed by Zirconium Complexes

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Abstract—Cycloalumination of α,ω-diolefins was performed using EtAlCl$_2$ in the presence of metallic magnesium as halide ion acceptor and Cp$_2$ZrCl$_2$ as catalyst. The products were aluminacyclopentanes and carbocycles fused to aluminacyclopentane fragments.

Stereoselective cycloalumination of α-olefins with EtAlCl$_2$ in the presence of metallic magnesium and a catalytic amount of Cp$_2$ZrCl$_2$ leads to *trans*-3,4-dialkylaluminacyclopentanes [1, 2]. The key stage of this reaction is formation of zirconacyclopentane intermediates **I** [3–5] which undergo transmetalation by the action of EtAlCl$_2$ to give the corresponding *trans*-3,4-dialkyl-substituted aluminacyclopentanes (Scheme 1). Our experimental data on the cycloalumination of α-olefins [1, 2] led us to presume that intermolecular cycloalumination of two and more α,ω-diolefin molecules with EtAlCl$_2$ in the presence of Cp$_2$ZrCl$_2$ as catalyst could give rise to carbocycles with fused aluminacyclopentane fragments as shown in Scheme 2.

To check this assumption we examined cycloalumination of hexa-1,5-diene, octa-1,7-diene, deca-1,9-diene, and dodeca-1,11-diene. We found that hexa-1,5-diene reacted with EtAlCl$_2$ at a ratio of 1:2 in the presence of magnesium as halide ion acceptor and Cp$_2$ZrCl$_2$ (10 mol %) as catalyst in THF at ~20°C to give aluminacycloalkanes **V–VII** at a ratio of ~4:3:2 in an overall yield of ~75% (Scheme 3). We failed to isolate cyclic organoaluminum compounds as indivi-

dual substances by vacuum distillation of the reaction mixture since the products decomposed on heating above 120°C; therefore, compounds **V–VII** were identified by analysis of the corresponding deuterolysis products **VIII–X**. As followed from the NMR and mass spectra of **VIII–X**, Cp$_2$ZrCl$_2$-catalyzed cycloalumination of hexa-1,5-diene with EtAlCl$_2$ gave 3,4-bis(but-3-en-1-yl)-1-ethylaluminacyclopentane (**V**), 2,7-diethyltetradecahydrocycloocta[1,2-*c*:5,6-*c'*]-bisaluminacyclopentene (**VI**) having two aluminacyclopentane fragments fused to cyclooctane ring, and 2,7,12-triethylicosahydro-1*H*-cyclododeca[1,2-*c*:5,6-*c'*:9,10-*c''*]trisaluminacyclopentene (**VII**) with three aluminacyclopentane fragments fused to cyclododecane ring.

Variation of the reactant ratio, temperature, and reaction time did not affect the yields and ratio of aluminacyclopentanes **V–VII** to an appreciable extent. When AlCl$_3$ was used instead of EtAlCl$_2$, organoaluminum compounds **V** and **VI** were formed at a ratio of ~3:2 in an overall yield of 45%. The cycloalumination of hexa-1,5-diene in the presence of ZrCl$_4$ as catalyst was characterized by reduced selectivity and
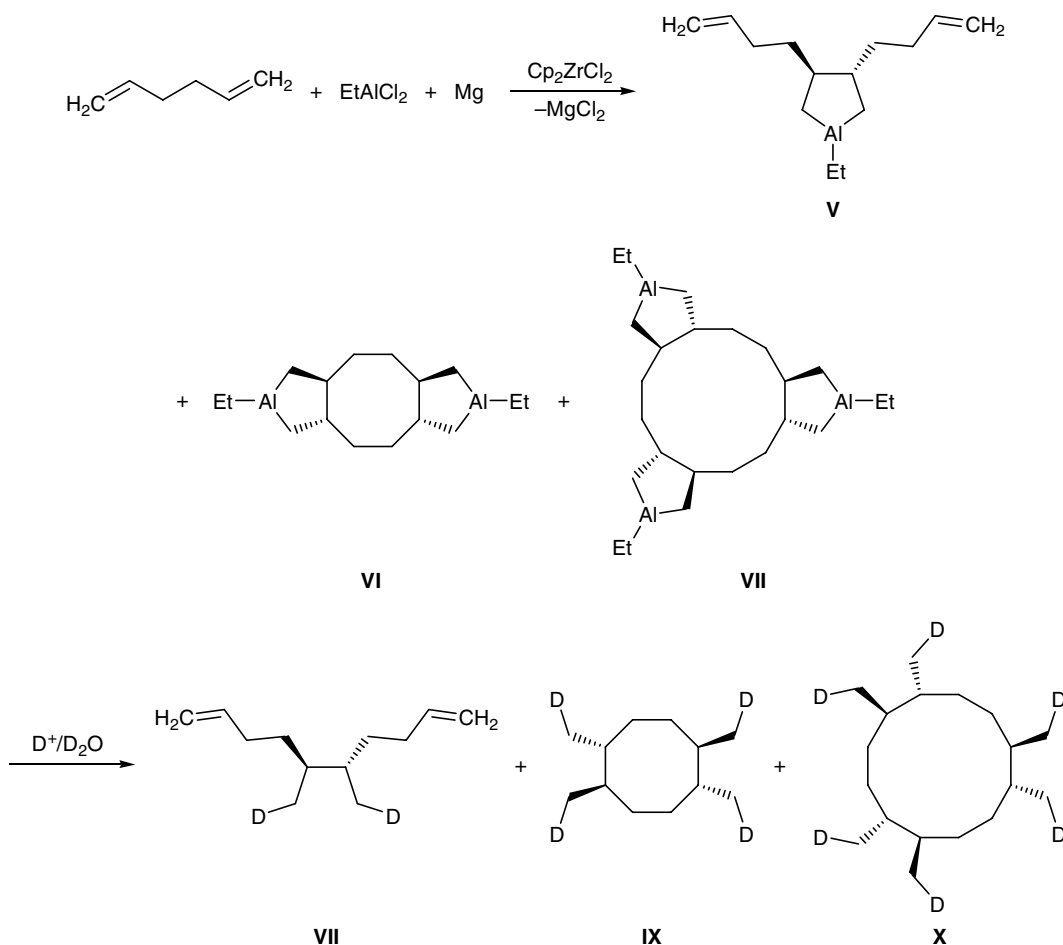
Scheme 1.
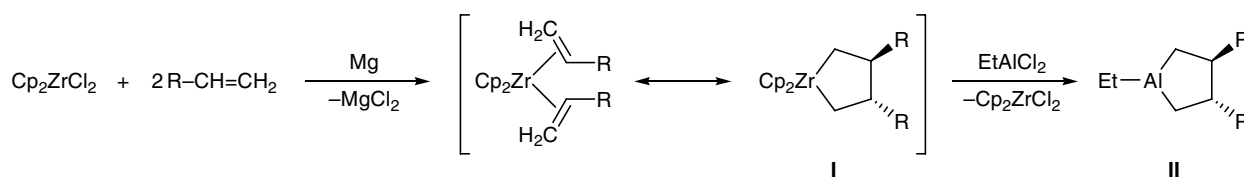
R = Alk.

Scheme 2.
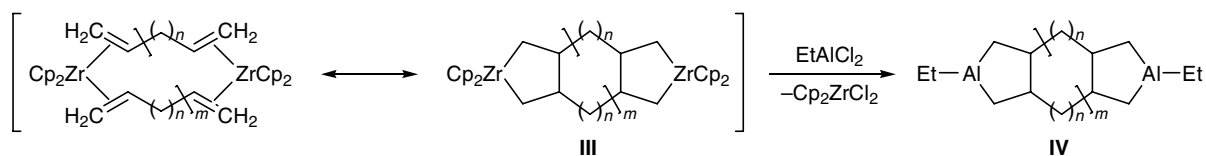
yields of compounds **V**–**VII**; an analogous effect was observed upon replacement of THF as solvent by diethyl ether. All our attempts to increase the selectivity of cycloalumination of hexa-1,5-diene with EtAlCl$_2$ via variation of the reactant concentration, amount of the catalyst, and reaction conditions were unsuccessful. After deuterolysis of mixture **V**–**VII**, hydrocarbons **VIII**–**X** were isolated by fractional distillation under reduced pressure. A fraction boiling at 66–69°C (5 mm) contained a mixture of **VIII** and **IX**.

Compounds **IX** and **X** are shown in Scheme 3 as one possible diastereoisomer, though hydrocarbon **IX** may exist as two stereoisomers, and eight diastereoisomers are possible for compound **X**; unfortunately,

different diastereoisomers of **IX** and **X** are difficult to distinguish by spectral methods.

By cycloalumination of octa-1,7-diene with 2 equiv of EtAlCl$_2$ [THF, Cp$_2$ZrCl$_2$ (10 mol %), 20°C, 8 h] we obtained cyclic organoaluminum compounds **XI**, **XII**, and **XIII** at a ratio of ~6:3:1 (overall yield ~70%). The ratio **XI**:**XII**:**XIII** and the position of the Al–C bonds in the products were determined on the basis of the ^{13}C NMR spectra and GLC data for deuterolysis products **XIV**–**XVI** (Scheme 4). Under the above conditions, the predominant process was intramolecular cycloalumination of initial octa-1,7-diene with formation of aluminabicyclononane **XI**. Intermolecular cycloalumination of two octa-1,7-diene molecules with

Scheme 3.

Scheme 4.
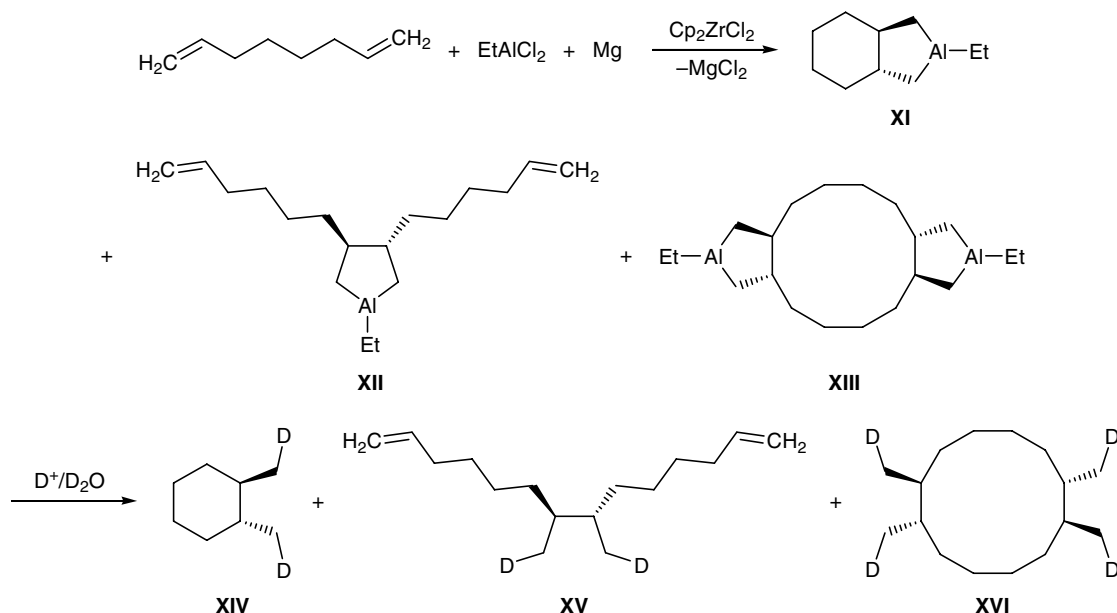
one or two EtAlCl$_2$ molecules leads, respectively, to 1-ethyl-3,4-bis(hex-5-en-1-yl)aluminacyclopentane (**XII**) and cyclododecane **XIII** having two symmetrically fused aluminacyclopentane fragments. The reaction mixture was subjected to deuterolysis, and the deuterolysis products were separated by vacuum distillation. The first fraction contained 1,2-bis(deuteromethyl)cyclohexane (**XIV**), and compounds **XV** and **XVI** were isolated as a fraction boiling at 85–89°C (1 mm).

Unlike hexa-1,5-diene and octa-1,7-diene, deca-1,9-diene and dodeca-1,11-diene reacted with EtAlCl$_2$ in the presence of Cp$_2$ZrCl$_2$ as catalyst in a selective fashion to give *trans*-3,4-disubstituted aluminacyclopentanes **XVIIa** and **XVIIb** in ~40–45% yield. The ^{13}C NMR spectra of pure compounds **XVIIa** and

XVIIb contained upfield signals at δ_C 11.13 and 11.15 ppm, respectively, due to ring carbon atoms linked to aluminum, while α-carbon atoms in the ethyl groups resonated at δ_C 0.71 and 0.61 ppm. Signals at δ_C 114.29 (114.18) and 139.48 (139.40) ppm were assigned to the double-bonded carbon atoms. The structure of unsaturated organoaluminum compounds **XVIIa** and **XVIIb** was additionally proved by analysis of their deuterolysis and oxidation products **XVIII** and **XIX** (Scheme 5).

In all our experiments on cycloalumination of α,ω-diolefins in the presence of Cp$_2$ZrCl$_2$, the reactions were accompanied by formation of minor products (5–18%) arising from hydroalumination [6] and aluminacyclopropanation [7] of terminal double bonds (in compounds **V**, **XII**, **XVIIa**, and **XVIIb**). These

Scheme 5.
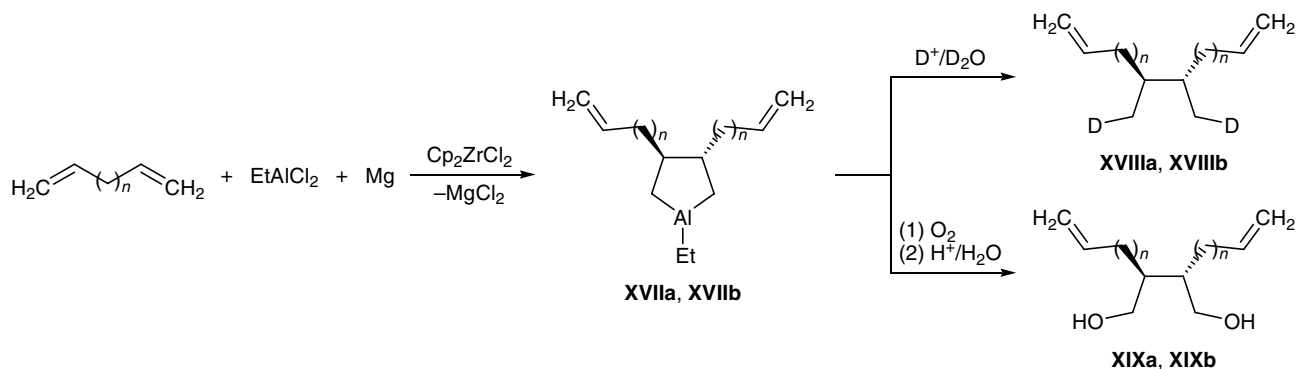
$n = 6$ (**a**), 8 (**b**).

products were also identified on the basis of spectral data. Hydrolysis, deuterolysis, or oxidation of the obtained aluminacyclopentanes gave the corresponding products having *threo* (**VIII**, **XV**, **XVIII**, **XIX**) or *trans* configuration (**IX**, **X**, **XIV**, **XVI**) [8, 9].

Our results indicate conformational control over the formation of aluminacyclopentanes by catalytic cycloalumination of α,ω-diolefins with EtAlCl₂. Increase in the distance between the terminal double bonds in initial α,ω-diolefins leads to preferential formation of intermolecular monocycloalumination products, *trans*-3,4-disubstituted aluminacyclopentanes. The reason is that longer hydrocarbon chains are characterized by increased number of spatial freedoms [10] of the alkenyl substituents in 3,4-disubstituted aluminacyclopentanes. As a result, the contribution of conformers in which the arrangement of double bonds is favorable for coordination to zirconium (and hence for subsequent intramolecular cycloalumination to give tri- and tetracyclic organoaluminum compounds like **VI**–**XIII**) decreases. Presumably, this factor is responsible for the lack of products arising from intramolecular cyclization of the terminal double bonds in *trans*-3,4-dialkenylaluminacyclopentanes **XVIIa** and **XVIIb** formed in the cycloalumination of deca-1,9-diene and dodeca-1,11-diene.

On the other hand, quantum-chemical calculations of stable conformations of aluminacyclopentane **V** with *trans*-oriented alkenyl groups showed that the formation of dimeric structure **VI** is sterically possible. Constrained scanning of the potential energy surface of compound **V** (B3LYP 6-31G; Gaussian 98) revealed a conformer with spatially close double bonds (~3.0 Å) that are capable of entering the coordination sphere of catalytically active zirconium complex [11, 12] with subsequent formation of compound **VI**.

Thus cycloalumination of unbranched α,ω-diolefins with EtAlCl₂ in the presence of Cp₂ZrCl₂ as catalyst leads to the formation of new di-, tri-, and tetracyclic organoaluminum compounds in which aluminacyclopentane fragments are fused to a carbocycle. The selectivity of the process depends on the number of methylene units separating the terminal double bonds.

EXPERIMENTAL

The hydrolysis and deuterolysis products were analyzed by gas–liquid chromatography on a Chrom-5 instrument (carrier gas helium; 1200×3-mm column packed with 5% SE-30 or 15% PEG-6000 on Chromaton N-AW). The IR spectra were measured from samples prepared as thin films (neat) on a Specord 75IR spectrometer. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1306 spectrometer (ion source temperature 200°C). The ^{1}H and ^{13}C NMR spectra were recorded from solutions in CDCl₃ on a Jeol FX-90 Q instrument at 89.55 and 22.5 MHz, respectively. The yields of organoaluminum compounds were determined by GLC analysis of the corresponding hydrolysis products.

Commercially available 86% EtAlCl₂ and AlCl₃ were used. All reactions with organometallic compounds were carried out in a stream of dry argon. Tetrahydrofuran was distilled over LiAlH₄ just before use. The products were extracted into diethyl ether or hexane, the extracts were dried over MgSO₄, and the products were isolated by vacuum distillation. The oxidation products were isolated by column chromatography on silica gel using hexane–acetone (1:5) as eluent. 1,2-Bis(deuteromethyl)cyclohexane (**XIV**) was identified by comparing with an authentic sample [13].

Density functional quantum-chemical calculations (B3LYP three-parameter exchange-correlation potential, 6-31G basis set) were performed with full geometry optimization using Gaussian 98 software package. Energy parameters and normal vibration frequencies were determined. The calculated vibration frequencies characterized the optimized frequencies as minima (the number of negative Hessian eigenvalues in a given point $N_{imag} = 0$).

Cycloalumination of α,ω-diolefins with EtAlCl₂ in the presence of Cp₂ZrCl₂ (*general procedure*). A glass reactor was charged at ~0°C under dry argon with 1 mmol of Cp₂ZrCl₂, 15 mmol of magnesium powder, 10 mmol of α,ω-diolefin, 10 ml of THF, and 20 mmol of EtAlCl₂ (the reactants were added under stirring). The mixture was stirred for 24 h at 20–22°C and treated with 8% of DCl in D₂O, and partially deuterated hydrocarbons were separated by preparative gas–liquid chromatography.

***threo*-5,6-Bis(deuteromethyl)deca-1,9-diene (VIII).** Yield 33%. IR spectrum, ν, cm⁻¹: 3095, 2985, 2940, 2870, 1640, 1470, 1010, 930. ^{1}H NMR spectrum, δ, ppm: 0.85 t (4H, CH₂D, *J* = 7.0 Hz), 1.15–1.50 m (6H, CH, CH₂), 1.90–2.33 m (4H, =CHC**H₂**), 4.45 d (4H, =CH₂, *J* = 7.0 Hz), 5.51–5.98 m (2H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 14.15 t (*J* = 19.5 Hz), 31.86, 34.89, 35.99, 113.95, 139.23. Found: *m/z* 168 [*M*]⁺. C₁₂H₂₀D₂. Calculated: *M* 168.

1,2,5,6-Tetrakis(deuteromethyl)cyclooctane (IX). Yield 25%. ^{1}H NMR spectrum, δ, ppm: 0.98 d (8H, CH₂D, *J* = 7.0 Hz), 1.27–1.51 m (12H, CH, CH₂). ^{13}C NMR spectrum, δ_C, ppm: 18.84 (*J* = 19.5 Hz),

31.17, 38.08. Found: *m/z* 172 $[M]^+$. $C_{12}H_{20}D_4$. Calculated: *M* 172.

1,2,5,6,9,10-Hexakis(deuteromethyl)cyclododecane (X). Yield 17%, bp 131–133°C (2 mm). ^{1}H NMR spectrum, δ, ppm: 0.98 d (12H, CH$_2$D, *J* = 7.0 Hz), 1.28–1.53 m (18H, CH, CH$_2$). ^{13}C NMR spectrum, δ, ppm: 20.14 t (*J* = 19.0 Hz), 31.25, 38.22. Found, %: C 83.27; H+D 16.12; *m/z* 258 $[M]^+$. $C_{18}H_{30}D_6$. Calculated, %: C 83.65; H 11.70; D 4.65. *M* 258.

***threo*-7,8-Bis(deuteromethyl)tetradeca-1,13-diene (XV).** Yield 21%. ^{1}H NMR spectrum, δ, ppm: 0.85 d (4H, CH$_2$D, *J* = 7.0 Hz), 1.12–1.48 m (14H, CH, CH$_2$), 1.88–2.31 m (4H, =CHCH$_2$), 4.48 d (4H, =CH$_2$, *J* = 7.0 Hz), 5.49–5.88 m (2H, CH=). ^{13}C NMR spectrum, δ$_C$, ppm: 14.12 t (*J* = 19.5 Hz), 26.15, 29.27, 33.86, 34.73, 36.53, 114.19, 139.13. Found: *m/z* 224 $[M]^+$. $C_{16}H_{28}D_2$. Calculated: *M* 224.

1,2,7,8-Tetrakis(deuteromethyl)cyclododecane (XVI). Yield 7%. ^{1}H NMR spectrum, δ, ppm: 0.98 d (8H, CH$_2$D, *J* = 7.0 Hz), 1.87–2.51 m (20H, CH, CH$_2$). ^{13}C NMR spectrum, δ$_C$, ppm: 19.15 t (*J* = 19.0 Hz), 31.95, 38.86. Found: *m/z* 228 $[M]^+$. $C_{16}H_{28}D_4$. Calculated: *M* 228.

1-Ethyl-3,4-bis(oct-7-en-1-yl)aluminacyclopentane (XVIIa). ^{13}C NMR spectrum, δ$_C$, ppm: 0.71, 8.05, 11.13, 28.18, 29.10, 29.31, 29.85, 33.96, 37.95, 44.15, 114.29, 139.48.

1-Ethyl-3,4-bis(dec-9-en-1-yl)aluminacyclopentane (XVIIb). ^{13}C NMR spectrum, δ$_C$, ppm: 0.61, 7.38, 11.15, 28.18, 28.65, 28.93, 29.18, 29.31, 29.72, 33.71, 38.11, 44.10, 114.18, 139.40.

***threo*-9,10-Bis(deuteromethyl)octadeca-1,17-diene (XVIIIa).** Yield 45%, bp 149–151°C (2 mm). ^{1}H NMR spectrum, δ, ppm: 0.85 d (4H, CH$_2$D, *J* = 7.0 Hz), 1.15–1.50 m (22H, CH, CH$_2$), 1.90–2.33 m (4H, =CHCH$_2$), 4.45 d (4H, =CH$_2$, *J* = 7.0 Hz), 5.51–5.98 m (2H, CH=). ^{13}C NMR spectrum, δ$_C$, ppm: 14.13 t (*J* = 19.5 Hz), 27.70, 29.03, 29.26, 29.72, 33.89, 34.96, 36.63, 114.22, 139.39. Found, %: C 85.62; H+D 14.18; *m/z* 280 $[M]^+$. $C_{20}H_{36}D_2$. Calculated, %: C 85.56; H 12.94; D 1.50. *M* 280.

***threo*-11,12-Bis(deuteromethyl)docosa-1,21-diene (XVIIIb).** Yield 42%, bp 178–181°C (1 mm). ^{1}H NMR spectrum, δ, ppm: 0.85 d (4H, CH$_2$D, *J* = 7.0 Hz), 1.15–1.50 m (30H, CH, CH$_2$), 1.90–2.33 m (4H, =CHCH$_2$), 4.45 d (4H, =CH$_2$, *J* = 7.0 Hz), 5.51–5.98 m (2H, CH=). ^{13}C NMR spectrum, δ$_C$, ppm: 14.09 t (*J* = 19.5 Hz), 27.79, 28.65, 28.90, 29.15, 29.27, 29.61, 33.86, 34.89, 36.65, 114.23, 139.41. Found, %: C 84.45; H+D 14.22. $C_{24}H_{44}D_2$. Calculated, %: C 85.63; H 13.18; D 1.19.

2,3-Bis(oct-7-en-1-yl)butane-1,4-diol (XIXa). Yield 33%, R_f 0.60 (hexane–acetone, 10:3). IR spectrum, ν, cm^{-1}: 3340, 2955, 2875, 1480, 1395, 1065, 730. ^{1}H NMR spectrum, δ, ppm: 1.08–1.75 m (22H, CH, CH$_2$), 1.86–2.28 m (4H, =CHCH$_2$), 3.25–3.75 m (4H, C**H$_2$**OH), 4.47 d (4H, =CH$_2$, *J* = 7.0 Hz), 5.54–5.87 m (2H, CH=). ^{13}C NMR spectrum, δ$_C$, ppm: 27.75, 29.08, 29.28, 29.76, 33.94, 34.82, 36.74, 61.88, 114.02, 139.15. Found, %: C 77.48, H 12.38. $C_{20}H_{38}O_2$. Calculated, %: C 77.36; H 12.34.

2,3-Bis(dec-9-en-1-yl)butane-1,4-diol (XIXb). Yield 25%, R_f 0.58 (hexane–acetone, 10:3). IR spectrum, ν, cm^{-1}: 3340, 2950, 2870, 1480, 1390, 1060, 730. ^{1}H NMR spectrum, δ, ppm: 1.10–1.83 m (30H, CH, CH$_2$), 1.82–2.58 m (4H, =CHCH$_2$), 3.25–3.75 m (4H, C**H$_2$**OH), 4.47 d (4H, =CH$_2$, *J* = 7.0 Hz), 5.48–5.76 m (2H, CH=). ^{13}C NMR spectrum, δ$_C$, ppm: 27.79, 28.65, 28.90, 29.15, 29.27, 29.61, 33.86, 34.89, 36.65, 62.15, 114.02, 139.51. Found, %: C 78.75; H 12.70. $C_{24}H_{46}O_2$. Calculated, %: C 78.62; H 12.65.

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