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Organometallic Chemistry

Synthesis and transformation of metallacycles
25.* On a mechanism of the Ni(acac)$_2$-catalyzed conversion of 3-alkyl-1-ethylalumacyclopentanes into 1,1-disubstituted cyclopropanes

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The reactions of 3-alkyl-1-ethylalumacyclopentanes with allyl halides in the presence of Ni(acac)$_2$ as a catalyst were studied by dynamic NMR spectroscopy. Under the action of Ni complexes, alumacyclopentanes initially undergo intramolecular hydride transfer to give but-3-enyl(ethyl)aluminum hydrides and then react with the starting allyl halide, yielding but-3-enyl(ethyl)aluminum halides. Subsequent intramolecular carboalumination affords the corresponding 1,1-disubstituted cyclopropanes.

Key words: organoaluminum compounds, alumacyclopentanes, catalysis, olefins, allyl halides, substituted cyclopropanes.

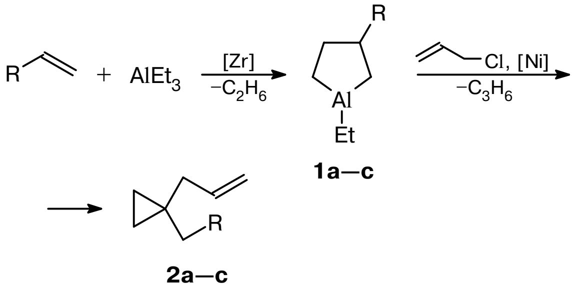
Previously,[2] we showed that 3-alkyl-1-ethylalumacyclopentanes (ACP) **1** obtained by the Cp$_2$ZrCl$_2$-catalyzed reactions of α-olefins with AlEt$_3$[3] react with an excess of allyl chloride in the presence of Ni(acac)$_2$ to give 1,1-disubstituted cyclopropanes. The resulting 1-alkyl-1-allylcyclopropanes **2** were identified by ^{1}H and ^{13}C NMR and IR spectroscopy and mass spectrometry (Scheme 1).

In the present work, this process was studied by dynamic ^{13}C NMR spectroscopy to reveal the mechanism of the reactions of ACP with allyl halides in the presence of Ni(acac)$_2$ and identify intermediate compounds.

Results and Discussion

Alumacyclopentane **1** was mixed with allyl halide and a catalytic amount of Ni(acac)$_2$ in Et$_2$O at −5 °C. The reactions were carried out in a glass reaction vessel in a flow of an inert gas at ~20 °C, with periodically sampling for NMR analysis.

Scheme 1



R = *n*-C$_4$H$_9$ (**a**); *n*-C$_6$H$_{13}$ (**b**); *n*-C$_9$H$_{19}$ (**c**)

The reaction of an ethereal solution of 1-ethyl-3-(*n*-hexyl)alumacyclopentane (**1b**)[3] with a threefold ex-

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* For Part 24 see Ref. 1.

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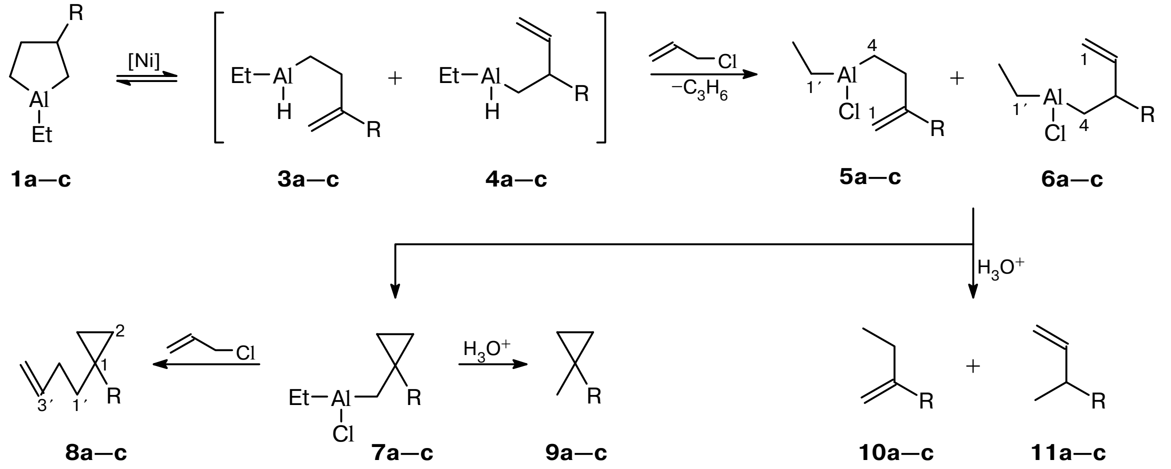
Scheme 2



R = n-C_4H_9 (**a**); n-C_6H_{13} (**b**); n-C_9H_{19} (**c**)

cess of allyl chloride in the presence of freshly sublimed 5 mol. % $Ni(acac)_2$ begins with the formation of unsaturated regioisomeric organoaluminum compounds (OAC) **5b** and **6b** (Scheme 2).

The ^{13}C NMR spectra of these compounds show characteristic highfield signals from the α-carbon atoms of OAC at δ 0.2—16.2, which are broadened owing to ^{27}Al quadrupole relaxation ($I_{^{27}Al} = 5/2$). In addition, their ^{13}C NMR spectra contain signals at δ 155.1 and 107.1 from the doubly bonded C atoms in **5b** and signals at δ 148.2 and 111.5 from the vinyl group in **6b**. Apparently, low-valence Ni complexes initiate the β-hydride transfer[4] causing *in situ* reversible opening of ACP **1b**. The resulting regioisomeric aluminum hydrides **3b** and **4b** reduce the starting allyl chloride to propylene[5], irreversibly giving OACs **5b** and **6b**. Indeed, the evolution of gaseous propylene was observed in these experiments.

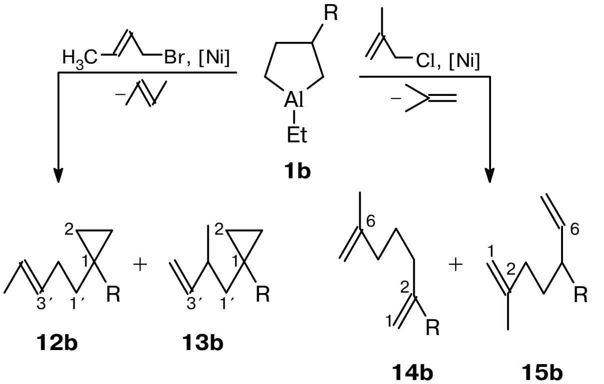
In the NMR spectrum recorded an hour after the starting reagents (ACP, allyl chloride and $Ni(acac)_2$) were mixed, the intensities of signals at δ 155.1 and 107.1 characteristic of the sp^2-hybridized carbon atoms in OAC **5b** noticeably decreased. After 24 h, the NMR spectrum of this mixture does not virtually contain resonance lines from the doubly bonded C atoms in **5b**. Hydrolysis of the mixture yields 1-(but-3-enyl)-1-(n-hexyl)cyclopropane (**8b**), probably, through intramolecular cyclization of **5b** into OAC **7b**, which then undergoes cross-linking with the starting allyl chloride to give **8b** in ~65% yield (see Scheme 2). A minor reaction product (~20%) was identified as olefin **11b**.

The study of the process dynamics showed that, unlike OAC **5b**, compound **6b** is not involved in the aforesaid transformation, being virtually unchanged throughout the reaction time. Hydrolysis of the reaction mixture (~1 h after the reaction started) gives 1-(n-hexyl)-1-methylcyclopropane (**9b**), 2-ethyloct-1-ene (**10b**), and 3-methylnon-1-ene (**11b**) in the ratio 4 : 1 : 7, respectively (GLC data). This indicates the *in situ* formation of intermediate regioisomeric OACs **5b**, **6b**, and **7b**.

ACPs **1a** and **1c** react in a similar manner with allyl chloride to give the corresponding unsaturated acyclic OACs, which are transformed *in situ* (~20 °C, 8 h, Et_2O) into 1,1-substituted cyclopropanes **8a,c**. The hydrolysis products contain, along with 1,1-disubstituted cyclopropanes **8a,c**, olefins **10a,c** and **11a,c** in the ratio 12 : 1 : 3, respectively (the total yield was ~80%).

To find out how the structure of the starting allyl halide influences the direction of cross-linking, the catalytic transformations of ACP **1b** in the presence of crotyl bromide and methallyl chloride were studied (Scheme 3). The reaction of OAC **1b** with crotyl bromide ($Ni(acac)_2$ (5 mol. %), ether, 21—22 °C, 8-9 h) gives regioisomeric cyclopropanes **12b** and **13b** (1 : 1) in 60% yield, suggesting the formation of the target products according to Scheme 2.

Scheme 3



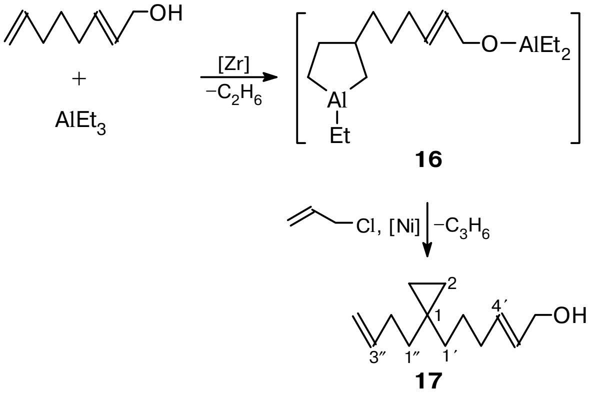
R = n-C_6H_{13}

The reaction of ACP **1b** with a threefold excess of methallyl chloride in the presence of 5 mol. % $Ni(acac)_2$

initially yields regioisomers **5b** and **6b**, which are involved *in situ* in cross-linking with an excess of methallyl chloride. The latter process occurs faster than intramolecular carboalumination with the formation of cyclopropane-containing OACs of the type **7b**. As the result, a mixture of regioisomeric heptadienes **14b** and **15b** (1 : 1) is formed in ~65% total yield.

The proposed method opens the route to the synthesis of various 1,1-disubstituted cyclopropanes whose structures are dependent on those of the starting α-olefins and allyl halides. In particular, the cycloalumination of 2*E*,7-octadienol under the action of $AlEt_3$ in the presence of 5 mol. % Cp_2ZrCl_2 followed by the $Ni(acac)_2$-catalyzed reaction of OAC **16** [6] with allyl chloride in Et_2O gives 1,1-disubstituted cyclopropane **17** in ~50% yield (Scheme 4).

Scheme 4



Thus, the study of catalytic transformations of 3-alkyl-1-ethylalumacyclopentanes with allyl halides and the identification of the reaction intermediates made it possible to propose the most plausible mechanism for the formation of 1,1-disubstituted cyclopropanes (through intermediate acyclic unsaturated organoaluminum compounds) and develop a preparative method for the synthesis of cyclopropanes from 1-ethyl-3-alkylalumacyclopentanes and allyl halides in the presence of Ni complexes as catalysts.

Experimental

Reactions with OAC were carried out in an atmosphere of dry argon. Solvents were distilled over $LiAlH_4$ immediately before use. Commercially available 98% $AlEt_3$ (Joint-Stock Company "Nizhnekamskneftekhim") was used. The reaction products were analyzed on a Chrom-5 chromatograph (flame ionization detector, column 200 × 0.3 cm with 15% PEG-6000 or 5% SE-30 on Chromaton N-AW, 50—190 °C). ^1H and ^{13}C NMR spectra were recorded on JEOL FX-90Q (90 and 22.5 MHz, respectively; with complete or partial proton decoupling for ^{13}C) and Bruker AM-300 spectrometers (300 and 75.46 MHz, respectively) with $CDCl_3$ as the internal standard, except for OAC (C_6D_{12}). IR spectra were obtained with an IR-75 spectrometer (thin film). Mass spectra were recorded on a Finnigan 4021 spectrometer (EI, 70 eV, ionization chamber temperature 200 °C).

Synthesis of 1-alkyl-1-(but-3-enyl)cyclopropanes. Cp_2ZrCl_2 (0.5 mmol) obtained according to the known procedure,[7] α-olefin (10 mmol), and $AlEt_3$ (12 mmol) were placed in a glass reaction vessel in an atmosphere of dry Ar at 0 °C. The reaction mixture was stirred at 21—23 °C for 8 h. To 3-alkyl-1-ethylalumacyclopentane that formed[3] Et_2O (8 mL), freshly sublimed $Ni(acac)_2$ (0.5 mmol), and allyl chloride (methallyl chloride or crotyl bromide) (36 mmol) were added at −5 °C, and the resulting mixture was stirred at ~20 °C for 8—10 h. The course of the process was monitored by dynamic ^1H and ^{13}C NMR spectroscopy; samples (0.5 mL) were withdrawn at regular intervals. After 8—10 h, the reaction mixture was hydrolyzed with 10% HCl to give 1-alkyl-1-(but-3-enyl)cyclopropanes **8**, **12**, and **13**. ACP **16** was obtained according to the known procedure[6] from 2*E*,7-octadienol with a 2.5-fold excess of $AlEt_3$ and a threefold excess of allyl chloride with respect to AlEt.

3-Butylbut-3-enyl(ethyl)aluminum chloride (5a). ^{13}C NMR, δ: 1.1 (br.t, C(1′)); 8.7 (q, C(2′)); 14.1 (q, C(4″)); 16.7 (br.t, C(4)); 22.9 (t, C(3″)); 30.5 (t, C(2″)); 35.7 (t, C(1″)); 39.6 (t, C(3)); 106.6 (t, C(1)); 154.5 (s, C(2)).

Ethyl(3-hexylbut-3-enyl)aluminum chloride (5b). ^{13}C NMR, δ: 1.2 (br.t, C(1′)); 9.0 (q, C(2′)); 14.5 (q, C(6″)); 16.2 (br.t, C(4)); 23.4 (t, C(5″)); 28.7 (t, C(2″)); 30.0 (t, C(3″)); 32.6 (t, C(4″)); 36.5 (t, C(1″)); 40.5 (t, C(3)); 107.1 (t, C(1)); 155.1 (s, C(2)).

Ethyl(3-nonylbut-3-enyl)aluminum chloride (5c). ^{13}C NMR, δ: 1.5 (br.t, C(1′)); 8.8 (q, C(2′)); 14.3 (q, C(9″)); 16.8 (br.t, C(4)); 23.1 (t, C(8″)); 28.3 (t, C(2″)); 28.4 (t, C(6″)); 29.8 (t, C(3″)); 29.9 (t, C(5″)); 30.1 (t, C(7″)); 32.4 (t, C(4″)); 36.1 (t, C(1″)); 40.1 (t, C(3)); 106.7 (t, C(1)); 154.6 (s, C(2)).

2-Butylbut-3-enyl(ethyl)aluminum chloride (6a). ^{13}C NMR, δ: 1.1 (br.t, C(1′)); 8.7 (q, C(2′)); 14.1 (q, C(4″)); 16.7 (br.t, C(4)); 23.1 (t, C(3″)); 29.0 (t, C(2″)); 31.7 (t, C(1″)); 41.4 (d, C(3)); 111.1 (t, C(1)); 147.7 (d, C(2)).

Ethyl(2-hexylbut-3-enyl)aluminum chloride (6b). ^{13}C NMR, δ: 1.2 (br.t, C(1′)); 9.0 (q, C(2′)); 14.5 (q, C(6″)); 16.2 (br.t, C(4)); 23.4 (t, C(5″)); 28.4 (t, C(2″)); 30.3 (t, C(3″)); 32.1 (t, C(4″)); 32.7 (t, C(1″)); 41.8 (t, C(3)); 111.5 (t, C(1)); 148.2 (s, C(2)).

Ethyl(2-nonylbut-3-enyl)aluminum chloride (6c). ^{13}C NMR, δ: 1.5 (br.t, C(1′)); 8.8 (q, C(2′)); 14.3 (q, C(9″)); 16.8 (br.t, C(4)); 23.1 (t, C(8″)); 28.1 (t, C(2″)); 29.9 (t, C(3″)); 29.9 (t, C(6″)); 30.1 (t, C(5″)); 31.8 (t, C(7″)); 32.4 (both t, C(1″), C(4″)); 41.5 (t, C(3)); 111.2 (t, C(1)); 147.8 (s, C(2)).

1-(But-3-enyl)-1-butylcyclopropane (8a). B.p. 63—64 °C (10 Torr), n_D^{22} 1.4390. IR, ν/cm^{-1}: 3085, 2970, 2935, 2870, 1645, 1470, 1390, 1025, 1010, 925. ^1H NMR, δ: 0.22 (s, 4 H, H(2), H(3), both ring); 0.89 (m, 3 H, Me); 1.20—1.39 (m, 4 H, H(2″), H(3″)); 1.39—1.68 (m, 4 H, H(1′), H(1″)); 1.81—2.11 (m, 2 H, H(2′)); 4.68—5.70 (m, 3 H, H(3′), H(4′)). ^{13}C NMR, δ: 12.1 (t, C(2)); 14.2 (q, C(4″)); 19.2 (s, C(1)); 23.1 (t, C(3″)); 28.9 (t, C(2″)); 31.1 (t, C(2′)); 35.7 (both t, C(1′), C(1″)); 113.8 (t, C(4′)); 139.4 (d, C(3′)). Found (%): C, 86.61; H, 13.04. $C_{11}H_{20}$. Calculated (%): C, 86.76; H, 13.24.

1-(But-3-enyl)-1-hexylcyclopropane (8b). B.p. 72—74 °C (5 Torr), n_D^{22} 1.4445. IR, ν/cm^{-1}: 3085, 2970, 2940, 2870, 1650, 1470, 1385, 1025, 1015, 925. ^1H NMR, δ: 0.18 (s, 4 H, H(2), H(3), both ring); 0.88 (m, 3 H, Me); 1.18—1.29 (m, 8 H, H(2″), H(3″), H(4″), H(5″)); 1.40—1.65 (m, 4 H, H(1′), H(1″)); 1.70—2.03 (m, 2 H, H(2′)); 4.52—5.55 (m, 3 H, H(3′), H(4′)). ^{13}C NMR, δ: 12.1 (t, C(2)); 14.1 (q, C(6″)); 19.2 (s, C(1)); 22.5 (t, C(5″)); 26.6 (t, C(2″)); 29.7 (t, C(3″)); 31.1 (t, C(2′)); 32.0 (t, C(4″)); 35.6 (t, C(1′)); 36.0 (t, C(1″));

113.8 (t, C(4′)); 139.4 (d, C(3′)). Found (%): C, 86.48; H, 13.24. $C_{13}H_{24}$. Calculated (%): C, 86.59; H, 13.41.

1-(But-3-enyl)-1-nonylcyclopropane (8c). B.p. 88—90 °C (2 Torr), n_D^{22} 1.4499. IR, ν/cm^{-1}: 3085, 2970, 2940, 2870, 1650, 1470, 1385, 1025, 1010, 925. ^{1}H NMR, δ: 0.21 (s, 4 H, H(2), H(3), both ring); 0.88 (m, 3 H, Me); 1.15—1.30 (m, 14 H, H(2″), H(3″), H(4″), H(5″), H(6″), H(7″), H(8″)); 1.38—1.66 (m, 4 H, H(1′), H(1″)); 2.08—2.20 (m, 2 H, H(2′)); 4.70—5.80 (m, 3 H, H(3′), H(4′)). ^{13}C NMR, δ: 12.1 (t, C(2)); 14.1 (q, C(9″)); 19.2 (s, C(1)); 22.8 (t, C(8″)); 26.6 (t, C(2″)); 29.4 (t, C(6″)); 29.6 (t, C(3″)); 29.7 (both t, C(4″), C(5″)); 31.1 (t, C(2′)); 32.0 (t, C(7″)); 35.5 (t, C(1′)); 36.1 (t, C(1″)); 113.9 (t, C(4′)); 139.4 (d, C(3′)). Found (%): C, 86.15; H, 13.43. $C_{16}H_{30}$. Calculated (%): C, 86.41; H, 13.59.

1-Hexyl-1-methylcyclopropane (9b). B.p. 80—83 °C (50 Torr), n_D^{22} 1.4413. IR, ν/cm^{-1}: 2905, 2970, 2872, 1460, 1380, 1010, 925. ^{1}H NMR, δ: 0.18 (s, 4 H, H(2), H(3), both ring); 0.86 (t, 3 H, C(5″)Me, J = 6.1 Hz); 0.92 (s, 3 H, C(1)Me); 1.20—1.53 (m, 8 H, H(2″), H(3″), H(4″), H(5″)); 2.28 (t, 2 H, H(1″), J = 6.6 Hz). ^{13}C NMR, δ: 13.1 (t, C(2)); 14.2 (q, C(6″)); 15.5 (s, C(1)); 22.8 (t, C(5″)); 27.0 (q, C(1′)); 29.6 (t, C(3″)); 29.8 (t, C(2″)); 32.0 (t, C(4″)); 39.6 (t, C(1″)). Found (%): C, 85.35; H, 14.28. $C_{10}H_{20}$. Calculated (%): C, 85.63; H, 14.37.

2-Ethyloct-1-ene (10b). B.p. 82—84 °C (50 Torr), n_D^{22} 1.4221. IR, ν/cm^{-1}: 3080, 2960, 2950, 2930, 2880, 2855, 1645, 1465, 1375, 890, 725. ^{1}H NMR, δ: 0.89 (6 H, Me); 1.20—1.64 (m, 8 H, H(4), H(5), H(6), H(7)); 1.90—2.28 (m, 4 H, H(3), H(1′)); 4.69—4.82 (m, 2 H, H(1)). ^{13}C NMR, δ: 12.5 (q, C(2′)); 14.2 (q, C(8)); 22.8 (t, C(7)); 27.9 (t, C(4)); 28.9 (t, C(5)); 29.2 (t, C(6)); 31.9 (t, C(1′)); 36.4 (t, C(3)); 107.3 (t, C(1)); 152.0 (s, C(2)). MS, m/z: 140 [M]$^+$. Found (%): C, 85.32; H, 14.28. $C_{10}H_{20}$. Calculated (%): C, 85.63; H, 14.37.

3-Methylnon-1-ene (11b). B.p. 78—81 °C (50 Torr), n_D^{22} 1.4223. IR, ν/cm^{-1}: 3090, 2970, 2925, 2865, 1650, 1475, 1385, 1010, 930, 740, 700. ^{1}H NMR, δ: 0.86 (t, 3 H, C(8)Me, J = 6.1 Hz); 0.98 (d, 3 H, C(3)Me, J = 4.2 Hz); 1.08—1.35 (m, 10 H, H(4), H(5), H(6), H(7), H(8)); 1.58—1.69 (m, 1 H, H(3)); 4.92—5.01 (m, 2 H, H(1)); 5.44—5.88 (m, 1 H, H(2)). ^{13}C NMR, δ: 14.2 (q, C(9)); 20.3 (q, C(1′)); 22.8 (t, C(8)); 27.4 (t, C(5)); 29.6 (t, C(6)); 32.0 (t, C(7)); 36.8 (t, C(4)); 37.9 (d, C(3)); 112.3 (t, C(1)); 145.1 (d, C(2)). MS, m/z: 140 [M]$^+$. Found (%): C, 85.33; H, 14.29. $C_{10}H_{20}$. Calculated (%): C, 85.63; H, 14.37.

1-Hexyl-1-(*trans*-pent-3-enyl)cyclopropane (12b). B.p. 78—81 °C (2 Torr), n_D^{22} 1.4621. ^{1}H NMR, δ: 0.04 (s, 4 H, H(2), H(3), both ring); 0.84 (t, 3 H, C(5″)Me, J = 6.4 Hz); 1.11—1.35 (m, 12 H, H(1′), H(1″), H(2″), H(3″), H(4″), H(5″)); 1.74—2.02 (m, 2 H, H(2′)); 1.45—1.69 (m, 3 H, C(4′)Me); 4.66—5.59 (m, 2 H, H(3″), H(4″)). ^{13}C NMR, δ: 10.3 (t, C(2)); 14.2 (q, C(6″)); 17.9 (q, C(5′)); 18.6 (s, C(1)); 22.8 (t, C(5″)); 25.8 (t, C(2′)); 28.0 (t, C(2″)); 29.6 (t, C(3″)); 32.1 (t, C(4″)); 37.2 (t, C(1″)); 38.2 (t, C(1′)); 124.6 (d, C(4′)); 131.5 (d, C(3′)). Found (%): C, 86.21; H, 13.39. $C_{14}H_{26}$. Calculated (%): C, 86.52; H, 13.48.

1-Hexyl-1-(2-methylbut-3-enyl)cyclopropane (13b). B.p. 73—75 °C (2 Torr), n_D^{22} 1.4541. ^{1}H NMR, δ: 0.15 (s, 4 H, H(2), H(3), both ring); 0.88—1.04 (m, 6 H, Me); 1.04—1.36 (m, 12 H, H(1′), H(1″), H(2″), H(3″), H(4″), H(5″)); 1.80—2.10 (m, 1 H, H(2′)); 4.66—5.59 (m, 3 H, H(3′), H(4′)). ^{13}C NMR, δ: 11.4 (t, C(2)); 14.2 (q, C(6″)); 19.3 (q, MeC(4′)); 19.7 (s, C(1)); 22.8 (t, C(5″)); 28.5 (t, C(2″)); 29.2 (t, C(3″)); 32.1 (t, C(4″)); 35.0 (t, C(2′)); 43.7 (t, C(1″)); 45.2 (t, C(1′)); 114.2 (d, C(4′)); 143.3 (d, C(3′)). Found (%): C, 86.22; H, 13.40. $C_{14}H_{26}$. Calculated (%): C, 86.52; H, 13.48.

2-Hexyl-6-methylhepta-1,6-diene (14b). B.p. 99—101 °C (5 Torr), n_D^{22} 1.4421. ^{1}H NMR, δ: 0.81 (t, 3 H, C(5′)Me, J = 6.1 Hz); 1.04—1.34 (m, 10 H, H(1′), H(2′), H(3′), H(4′), H(5′)); 1.01 (s, 3 H, C(2)Me); 1.86—2.01 (m, 6 H, H(3), H(4), H(5)); 4.40—5.67 (m, 4 H, H(1), H(7)). ^{13}C NMR, δ: 14.2 (q, C(6′)); 21.1 (q, C(6)Me); 22.7 (t, C(5′)); 27.2 (t, C(4)); 29.2 (t, C(3′)); 29.5 (t, C(2′)); 32.0 (t, C(4′)); 35.7 (t, C(1′)); 36.2 (t, C(3)); 37.6 (t, C(5)); 108.7 (t, C(7)); 109.9 (t, C(1)); 146.0 (s, C(6)); 150.1 (s, C(2)). MS, m/z: 194 [M]$^+$. Found (%): C, 86.21; H, 13.39. $C_{14}H_{26}$. Calculated (%): C, 86.52; H, 13.48.

5-Hexyl-2-methylhepta-1,6-diene (15b). B.p. 79—81 °C (2 Torr), n_D^{22} 1.4422. ^{1}H NMR, δ: 0.81 (t, 3 H, C(5′)Me, J = 6.1 Hz); 1.04—1.34 (m, 12 H, H(4), H(1′), H(2′), H(3′), H(4′), H(5′)); 1.86—1.93 (m, 2 H, C(3)); 1.93—2.10 (m, 1 H, C(5)); 4.40—5.67 (m, 5 H, H(1), H(6), H(7)). ^{13}C NMR, δ: 14.2 (q, C(6′)); 22.5 (q, C(6)Me); 22.7 (t, C(5′)); 29.6 (t, C(3′)); 29.8 (t, C(2′)); 32.0 (t, C(4)); 33.0 (t, C(4′)); 35.2 (t, C(3)); 35.5 (t, C(1′)); 43.9 (t, C(5)); 109.6 (t, C(1)); 114.4 (t, C(7)); 143.4 (d, C(6)); 146.4 (s, C(2)). MS, m/z: 194 [M]$^+$. Found (%): C, 86.32; H, 13.38. $C_{14}H_{26}$. Calculated (%): C, 86.52; H, 13.48.

1-(But-3-enyl)-1-(6-hydroxyhex-4-enyl)cyclopropane (17). B.p. 120—123 °C (1 Torr), n_D^{22} 1.4902. IR, ν/cm^{-1}: 3360, 3080, 3010, 2935, 2865, 1645, 1470, 1105, 1030, 985, 925. ^{1}H NMR, δ: 0.24 (s, 4 H, H(2), H(3), both ring); 1.10—1.62 (m, 6 H, H(1′), H(2′), H(1″)); 1.84—2.20 (m, 4 H, H(3′), H(2″)); 3.83 (s, 1 H, OH); 4.15 (d, 2 H, H(6′), J = 4.0 Hz); 4.82—5.90 (m, 5 H, H(4′), H(5′), H(3″), H(4″)). ^{13}C NMR, δ: 12.0 (t, C(2)); 19.0 (s, C(1)); 26.1 (t, C(2′)); 31.0 (t, C(2″)); 32.4 (t, C(3′)); 35.5 (t, C(1′)); 35.5 (t, C(1″)); 63.8 (q, C(6)); 113.9 (t, C(4″)); 129.0 (d, C(4′)); 133.6 (d, C(5′)); 139.3 (d, C(3″)). Found (%): C, 80.41; H, 11.53; O, 7.61. $C_{14}H_{24}O$. Calculated (%): C, 80.36; H, 11.41; O, 8.23.

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