Synthesis and transformations of metallacycles

33.* The first example of cycloalumination of cyclonona-1,2-diene with Et_3Al and $EtAlCl_2$ in the presence of Cp_2ZrCl_2

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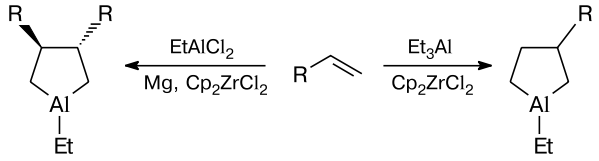
Catalytic cycloalumination of cyclonona-1,2-diene upon treatment with Et_3Al and $EtAlCl_2$ in the presence of Cp_2ZrCl_2, leading to 10-ethyl-10-aluminabicyclo[7.3.0^{1,9}]dodec-8-ene (**1**) and 11-ethyl-11-aluminatricyclo[10.7.0^{1,12}.0^{2,10}]nonadeca-9,12-diene, respectively, was accomplished in high yields. A possibility for the selective transformation of compound **1** to 1-allyl-9-(pent-4-enyl)cyclonon-1-ene and 10-hydroxybicyclo[7.3.0^{1,9}]dodec-8-ene in one preparative step was demonstrated.

Key words: organoaluminum compounds, metal complex catalysis, aluminacyclopentane, cyclic allenes, cycloalumination, zirconocene dichloride.

Reaction of catalytic cycloalumination of olefins (Scheme 1) and acetylenes, discovered in 1989,[2] is widely used in the synthesis of three- and five-membered organoaluminum compounds.[3—8] There is no information on the involvement of conjugated 1,3-dienes into this reaction.

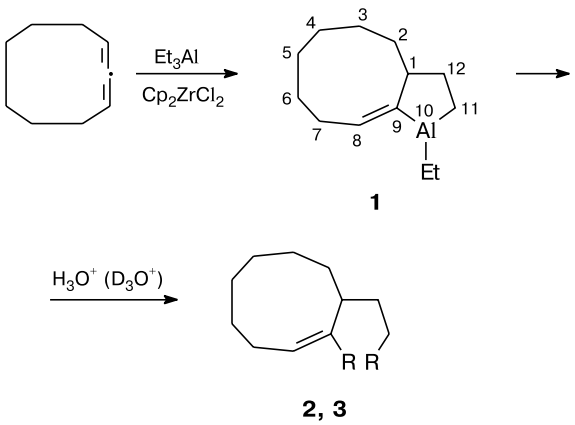
Scheme 1



In order to broaden the scope of application of the reaction indicated above, as well as to elaborate a one-pot method for the synthesis of the earlier poorly available bi- and tricyclic aluminum-containing carbocycles, we studied the reaction of cyclonona-1,2-diene with Et_3Al and $EtAlCl_2$ in the presence of Cp_2ZrCl_2 as the catalyst, which shows the high activity and selectivity in cycloalumination of unsaturated compounds.

We found out that the reaction of cyclonona-1,2-diene with excess of Et_3Al under previously optimized[9,10] conditions (5 mol.% Cp_2ZrCl_2, 4 h, hexane) with high regioselectivity (>95%) leads to 10-ethyl-10-aluminabicyclo[7.3.0^{1,9}]dodec-8-ene (**1**) in >85% yield (Scheme 2).

Scheme 2



R = H (**2**), D (**3**)

Structures of compound **1**, the products of its hydrolysis (**2**) and deuterolysis (**3**) were established by ^{1}H and ^{13}C NMR spectroscopy and chromato-mass spectrometry.

In the ^{13}C NMR spectrum of compound **1**, characteristic of organoaluminum compounds (OAC) upfield signals of α-carbon atoms at δ 0.8 and 18.2, which are broadened due to the quadruple relaxation on the ^{27}Al nuclei ($I_{^{27}Al}$ = 5/2), are observed. In addition, there are resonance lines of carbon atoms of a double bond at δ 142.4 and 166.9 in the spectrum, which are related to C(8) and C(9) atoms of the tri-substituted double bond in vinylic position to the Al atom.[9—11]

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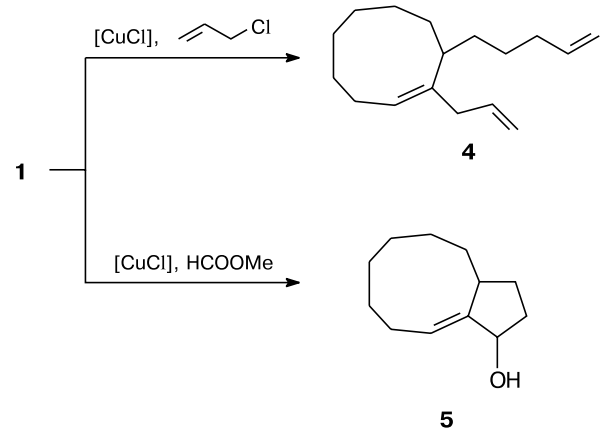
A conclusion about OAC **1** structure was based on the determination of the deuterium atoms positions in the deuterolysis product **3**. Thus, the ^{13}C NMR spectrum of cycloolefin **2** is characterized by the presence of the downfield signals of C(1) and C(2) atoms (δ 129.5 and 135.8) of the double bond in allylic position to the ethyl substituent in cyclononene fragment of the molecule. In the partially deuterated compound **3**, the upfield α-isotopic shifts are observed for C(2) and C(11) atoms ($\Delta\delta = 0.32$ and 0.25, respectively) with a triplet splitting of the C atoms signals on the deuterium atom (C(2), $^1J_{C,D} =$ 23.45 Hz; C(11), $^1J_{C,D} = 19.05$ Hz). Formation of the 1,4-dideuterated compound **3** during the deuterolysis of OAC **1** confirms that Al atoms in the latter are simultaneously connected to C(1) and C(4) atoms.

For the more reliable proof of OAC **1** structure, we carried out the CuCl (10 mol.%) catalyzed cross-coupling reaction[12] of compound **1** with allyl chloride to form 1-allyl-9-(pent-4-enyl)cyclonon-1-ene (**4**) and also conducted the reaction of compound **1** with methyl formate in the presence of CuCl (10 mol.%)[1,13] to obtain 10-hydroxybicyclo[7.3.0^{1,9}]dodec-8-ene (**5**) in 59% yield (Scheme 3). The structures of compounds **4** and **5** were established by ^1H and ^{13}C NMR spectroscopy and chromato-mass spectrometry.

Scheme 3



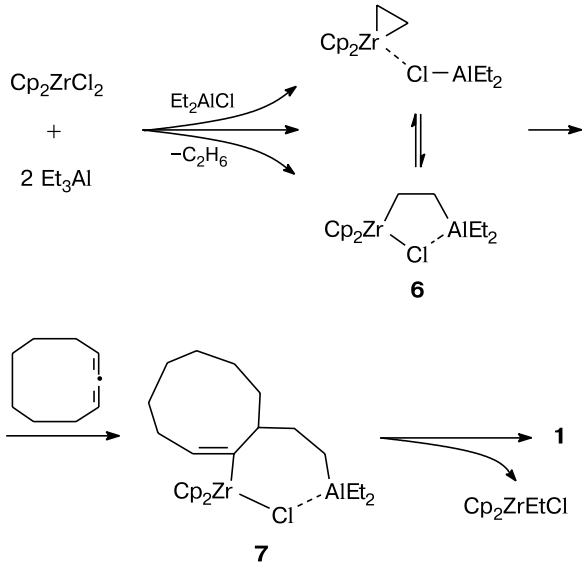
On the basis of the results obtained, the structure of 10-ethyl-10-aluminabicyclo[7.3.0^{1,9}]dodec-8-ene was proposed by us for OAC **1**.

Cycloalumination of cyclonona-1,2-diene takes place in aliphatic (hexane, cyclohexane) and aromatic (benzene, toluene) solvents, as well as in CH_2Cl_2 for 4—5 h. In ether solvents (THF, diethyl ether) or without a solvent, the reaction proceeds in low yield, which is caused by polymerization of the starting allene.

The reaction rate decreases at ~0 °C in hexane and conversion of the starting 1,2-diene does not exceed 20% for 20 h. The highest yield of OAC **1** was reached at 20 °C with the concentration of Cp_2ZrCl_2 being 5 mol.%. In these conditions, the yield of product **1** was >85%. A decrease in the catalyst concentration to 1 mol.% causes a decrease in the yield of compound **1** to 15%.

The formation of the five-membered OAC can be explained by the formation of five- and seven-membered Zr—Al bimetallic complexes[14] **6** and **7** as the intermediates, the sequential transformation of which finally led to the target unsaturated aluminacyclopentane **1** (Scheme 4).

Scheme 4



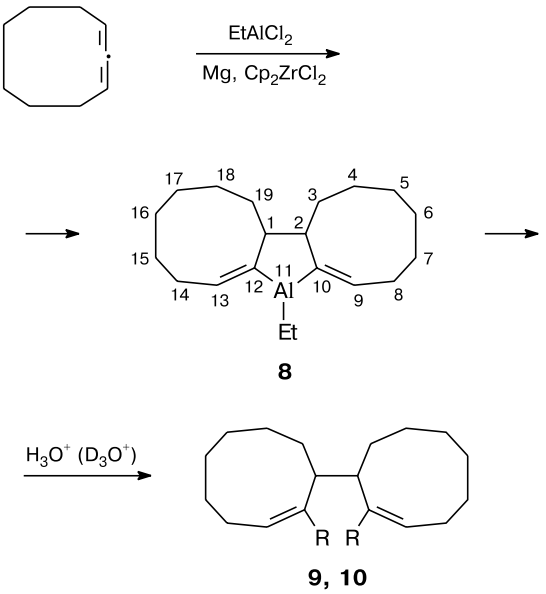
The high regioselectivity of the reaction observed, apparently, is connected with the increased electron density on the sp-hybridized carbon atom of cyclonona-1,2-diene and by the π—d interaction of the allene double bond with the vacant d orbital of Zr atom. This can promote a certain spatial orientation of cyclonona-1,2-diene on the central atom of the catalyst and its subsequent insertion into the Zr—C bond with the intermediate formation of bimetallic complex **7** with the double bond in vinylic position to Zr atom in the cyclononene fragment.

After the positive results on the cycloalumination of cyclonona-1,2-diene upon treatment with Et_3Al were received, we tried to involve this compound into the reaction of intermolecular cyclization[8] by means of $EtAlCl_2$ in the presence of Cp_2ZrCl_2 in order to synthesize 11-ethyl-11-aluminatricyclo[10.7.0^{1,12}.0^{2,10}]nonadeca-9,12-diene (**8**).

In fact, the reaction of cyclonona-1,2-diene with $EtAlCl_2$ in the presence of Mg and Cp_2ZrCl_2 (molar ratio cyclonona-1,2-diene : [Al] : Mg : [Zr] = 20 : 26 : 24 : 1) in THF for 8—10 h leads to product **8** in 71% yield (Scheme 5). Similarly to bicyclic unsaturated OAC **1**, the structure of compound **8** was established by the analysis of the ^1H NMR, ^{13}C NMR, and mass spectra of hydroly-

sis (**9**) and deuterolysis (**10**) products, as well as on the basis of the ^{13}C NMR spectrum of OAC **8**.

Scheme 5



R = H (**9**), D (**10**)

In conclusion, the Cp_2ZrCl_2 catalyzed cycloalumination of cyclonona-1,2-diene **1** with Et_3Al and $EtAlCl_2$ was accomplished for the first time, which leads to the representatives of new classes of OAC, *viz.*, 10-ethyl-10-aluminabicyclo[7.3.0^{1,9}]dodec-8-ene and 11-ethyl-11-aluminatricyclo[10.7.0^{1,12}.0^{2,10}]nonadeca-9,12-diene in high yield and selectivity.

Experimental

Chromatographic analysis was carried out on a Chrom-5 instrument (column: 1200×3 mm; stationary phase: silicon SE-30 (5%) on Chromaton N-AW-HMDS (0.125—0.160 mm); carrier gas: helium (47 mL min^{-1})) under the temperature programming from 50 to 250 °C at the speed of 8 °C min^{-1}. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90 Q spectrometer (89.55 (^1H) and 22.5 MHz (^{13}C)) in $CDCl_3$ relatively to Me_4Si. For the ^{13}C NMR spectra, C_6D_6 was used as the solvent and internal standard. Chromato-mass spectral analysis was performed on a Finigan 4021 (glass capillary column: 50000×0.25 mm; stationary phase: HP-5, carrier gas: helium; under the temperature programming from 50 to 300 °C at the speed of 5 °C min^{-1}; the evaporator temperature: 280 °C; the source of ions temperature: 250 °C; 70 eV). Elemental analysis was performed on a Karlo Erba 1106 analyzer. The yields of the products were determined by GLC. The purity of the reaction products was controlled on Silufol UV-254 plates with visualization in iodine vapors. Reactions with organometallic compounds were carried out in the flow of dry argon. Solvents were dried and distilled before use. Catalyst Cp_2ZrCl_2 was synthesized from $ZrCl_4$ according to the procedure described earlier.[15] Commercially available Et_3Al (95%) and $EtAlCl_2$ (86%) (OAO "Redkinskii Experimental Factory") were used.

Cycloalumination of cyclonona-1,2-diene 1 with Et_3Al, catalyzed by Cp_2ZrCl_2. Allene (10 mmol), Cp_2ZrCl_2 (0.5 mmol), hexane (15 mL), and Et_3Al (12 mmol) were placed with stirring into a glass reactor under atmosphere of dry argon at 0 °C. The temperature was let to reach 20—21 °C and this was stirred for 4 h. The reaction mixture was treated with 7—10% aqueous HCl or DCl in D_2O, the reaction products were extracted with hexane, dried with $MgSO_4$, and isolated by distillation *in vacuo*.

10-Ethyl-10-aluminabicyclo[7.3.0^{1,9}]dodec-8-ene (1). ^{13}C NMR, δ: 0.8 (t, C(13)); 8.7 (q, C(14)); 18.2 (t, C(11)); 25.0 (t, C(5)); 25.8 (t, C(6)); 26.2 (t, C(3)); 26.5 (t, C(4)); 30.2 (t, C(7)); 30.9 (t, C(12)); 34.9 (t, C(2)); 46.7 (d, C(1)); 137.5 (s, C(9)); 166.9 (d, C(8)).

3-Ethylcyclonon-1-ene (2). B.p. 81—83 °C (10 Torr). Found (%): C, 86.35; H, 12.89. $C_{11}H_{20}$. Calculated (%): C, 86.76; H, 13.24. ^1H NMR, δ: 0.89 (m, 3 H, Me); 1.50 (m, 12 H, CH_2); 2.10 (m, 3 H, —C<u>H</u>$_2$—CH=CH—C<u>H</u><); 5.36 (m, 2 H, —CH=CH—). ^{13}C NMR, δ: 12.3 (q, C(11)); 24.6 (t, C(10)); 26.0 (t, C(7)); 26.2 (t, C(8)); 26.7 (t, C(5)); 26.8 (t, C(6)); 30.2 (t, C(9)); 33.9 (t, C(4)); 38.7 (d, C(3)); 129.6 (d, C(1)); 135.8 (d, C(2)). MS, *m/z*: 152 [M]$^+$.

2-Deutero-3-(2-deuteroethyl)cyclonon-1-ene (3). B.p. 81—83 °C (10 Torr). Found (%): C, 85.29; H, 13.49. $C_{11}H_{18}D_2$. Calculated (%): C, 85.63; H, 11.76; D, 2.61. ^1H NMR, δ: 0.91 (m, 2 H, CH_2D); 1.47 (m, 12 H, CH_2); 2.05 (m, 3 H, —C<u>H</u>$_2$—CD=CH—C<u>H</u><); 5.39 (t, 1 H, —CH=CD—, J = 5.0 Hz). ^{13}C NMR, δ: 12.0 (t, C(11), $^1J_{C,D}$ = 19.05 Hz); 24.7 (t, C(10)); 26.0 (t, C(7)); 26.2 (t, C(8)); 26.7 (t, C(5)); 26.8 (t, C(6)); 30.1 (t, C(9)); 33.9 (t, C(4)); 38.6 (d, C(3)); 129.5 (d, C(10)); 135.5 (s, C(2), $^1J_{C,D}$ = 23.45 Hz). MS, *m/z*: 154 [M]$^+$.

Reaction of 10-ethyl-10-aluminabicyclo[7.3.0^{1,9}]dodec-8-ene with allyl chloride, catalyzed by CuCl. Allene (10 mmol), Cp_2ZrCl_2 (0.5 mmol), hexane (15 mL), and Et_3Al (12 mmol) were placed with stirring into a glass reactor under atmosphere of dry argon at 0 °C. The temperature was let to reach 20—21 °C and this was stirred for 4 h, then, at −20 °C, CuCl (1 mmol) was added and allyl chloride (36 mmol) was slowly and dropwise added, the temperature was raised to ~20 °C, and this was stirred for 6 h. The reaction mixture was treated with 7—10% aq. HCl, the reaction products were extracted with hexane, dried with $MgSO_4$, and isolated by distillation *in vacuo*.

1-Allyl-9-(pent-4-enyl)cyclonon-1-ene (4). B.p. 122—123 °C (1 Torr). Found (%): C, 87.12; H, 11.95. $C_{17}H_{28}$. Calculated (%): C, 87.86; H, 12.14. ^1H NMR, δ: 1.48 (m, 14 H, CH_2); 2.07 (m, 5 H, —C<u>H</u>$_2$—CH=CH—C<u>H</u><); 2.71 (d, 2 H, —CH=CH—C<u>H</u>$_2$—CH=CH—); 4.81 (m, 5 H, —CH=C<u>H</u>$_2$); 5.42 (m, 2 H, —C<u>H</u>=CH$_2$). ^{13}C NMR, δ: 27.1 (t, C(5)); 27.2 (t, C(11)); 27.3 (t, C(4)); 27.8 (t, C(6)); 29.9 (t, C(7)); 32.0 (t, C(12)); 32.9 (t, C(8)); 33.4 (t, C(10)); 34.1 (t, C(3)); 35.5 (t, C(15)); 38.9 (d, C(9)); 114.3 (t, C(14)); 115.6 (t, C(17)); 127.4 (d, C(2)); 137.7 (d, C(16)); 139.0 (d, C(13)); 140.2 (s, C(1)). MS, *m/z*: 232 [M]$^+$.

Reaction of 10-ethyl-10-aluminabicyclo[7.3.0^{1,9}]dodec-8-ene with methyl formate, catalyzed by CuCl. Allene (10 mmol), Cp_2ZrCl_2 (0.5 mmol), hexane (15 mL), and Et_3Al (12 mmol) were placed with stirring into a glass reactor under atmosphere of dry argon at 0 °C. The temperature was let to reach 20—21 °C

and this was stirred for 4 h. Then, at −15 °C, CuCl (1 mmol, 10 mol.%) was added and methyl formate (15 mmol) was slowly and dropwise added. The temperature was raised to ~20 °C, and this was stirred for 6—8 h. The reaction mixture was treated with 7—10% aq. HCl, the reaction products were extracted with hexane, and dried with $MgSO_4$. The product was isolated by column chromatography (silica gel L, 180/250 μ; eluent: hexane—ethyl acetate, 10 : 1).

10-Hydroxybicyclo[7.3.0^{1,9}]dodec-8-ene (5). R_f 0.45, b.p. 129—130 °C (1 Torr). Found (%): C, 79.16; H, 10.78; O, 8.49. $C_{12}H_{20}O$. Calculated (%): C, 79.94; H, 11.19; O, 8.87. ^{1}H NMR, δ: 1.18—1.84 (m, 14 H, CH_2); 2.08 (m, 2 H, —C<u>H</u>$_2$—CH=CH—); 2.62 (m, 1 H, =CH—C<u>H</u><); 4.91 (m, 1 H, >C<u>H</u>—OH); 5.55 (m, 1 H, —CH=C<). ^{13}C NMR, δ: 24.1 (t, C(5)); 25.8 (t, C(6)); 25.9 (t, C(4)); 26.8 (t, C(3)); 27.1 (t, C(12)); 32.6 (t, C(11)); 34.0 (t, C(2)); 35.8 (t, C(7)); 53.5 (d, C(1)); 74.8 (d, C(10)); 131.0 (d, C(8)); 133.8 (s, C(9)). MS, *m/z*: 180 $[M]^+$.

Reaction of cyclonona-1,2-diene with $EtAlCl_2$, catalyzed by Cp_2ZrCl_2. Catalyst Cp_2ZrCl_2 (0.5 mmol), Mg powder (12 mg-at.), THF (10 mL), cyclonona-1,2-diene (10 mmol), and $EtAlCl_2$ (13 mmol) were placed with stirring into a glass reactor under atmosphere of dry argon at 0 °C. The temperature was let to reach ~20 °C and this was stirred for 8—10 h. The reaction mixture was treated with 7—10% aq. HCl or DCl in D_2O, the reaction products were extracted with hexane, dried with $MgSO_4$, and isolated by distillation *in vacuo*.

11-Ethyl-11-aluminatricyclo[10.7.0^{1,12}.0^{2,10}]nonadeca-9,12-diene (8). ^{13}C NMR, δ: 0.7 (t, C(20)); 6.2 (q, C(21)); 24.9 (t, C(7), C(15)); 25.1 (t, C(6), C(16)); 26.9 (t, C(5), C(17)); 28.4 (t, C(4), C(18)); 32.0 (t, C(8), C(14)); 32.8 (t, C(3), C(19)); 45.2 (d, C(1), C(2)); 144.5 (s, C(10), C(12)); 173.5 (d, C(9), C(13)).

3-(Cyclonon-2-enyl)cyclonon-1-ene (9). B.p. 144—145 °C (1 Torr). Found (%): C, 87.14; H, 11.85. $C_{18}H_{30}$. Calculated (%): C, 87.73; H, 12.27. ^{1}H NMR, δ: 1.21 (m, 16 H, CH_2); 1.63 (m, 8 H, —C<u>H</u>$_2$—CH=CH—C<u>H</u><); 2.45 (m, 2 H, >C—CH—); 5.21 (m, 4 H, —CH=CH—). ^{13}C NMR, δ: 24.96 (t, C(8), C(14)); 25.0 (t, C(7), C(15)); 26.0 (t, C(6), C(16)); 28.7 (t, C(5), C(17)); 32.5 (t, C(9), C(13)); 33.8 (t, C(4), C(18)); 42.5 (d, C(3), C(10)); 128.8 (d, C(1), C(12)); 133.9 (s, C(2), C(11)). MS, *m/z*: 246 $[M]^+$.

2-Deutero-3-(2-deuterocyclonon-2-enyl)cyclonon-1-ene (10). B.p. 144—145 °C (1 Torr). Found (%): C, 86.74; H, 12.06. $C_{18}H_{28}D_2$. Calculated (%): C, 87.02; H, 11.36; D, 1.62. ^{1}H NMR, δ: 1.18 (m, 16 H, CH_2); 1.58 (m, 8 H, —C<u>H</u>$_2$—CH=CH—C<u>H</u><); 2.48 (m, 2 H, >C—CH—); 5.13 (m, 2 H, —CH=CD—). ^{13}C NMR, δ: 25.0 (t, C(8), C(14)); 25.1 (t, C(7), C(15)); 26.2 (t, C(6), C(16)); 28.9 (t, C(5), C(17)); 31.9 (t, C(9), C(13)); 33.3 (t, C(4), C(18)); 42.3 (d, C(3), C(10)); 129.2 (d, C(1), C(12)).* MS, *m/z*: 248 $[M]^+$.

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* Signals of C(2) and C(11) atoms are not observed.