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Combined cycloalumination of cyclic 1,2-dienes and olefins with $EtAlCl_2$ in the presence of Cp_2ZrCl_2 catalyst

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ABSTRACT

Catalytic intermolecular cycloalumination of cyclo-1,2-dienes and olefins assisted by $EtAlCl_2$ in the presence of Cp_2ZrCl_2 as catalyst gave rise to unsaturated di- and polycyclic aluminacarbocycles.

Recently,[1] we reported the catalytic cycloalumination of cyclo-1,2-dienes assisted by Et_3Al and $EtAlCl_2$–Mg in the presence of Cp_2ZrCl_2 as catalyst to afford bi- and tricyclic organoaluminum compounds (OACs) (Scheme 1).

In order to explore the possibility of combined cycloalumination and also to elaborate procedures for obtaining bi-, tri-, and tetracyclic OACs we have studied the reaction between 1,2-dienes (cyclonona-1,2-diene and cyclotrideca-1,2-diene) and olefins (α-olefins, norbornene) using Cp_2ZrCl_2 as catalyst, which is highly selective and efficient in these reactions.[2] α-Olefins such as hex-1-ene, hept-1-ene, dec-1-ene, styrene, and allyl benzene were selected for investigation.

Based on a model cycloalumination reaction of cyclonona-1,2-diene with hex-1-ene (1:1.2 ratio), it was found that slow dropwise addition of cyclonona-1,2-diene (10 mmol in 15 ml THF) into the reaction mixture containing hex-1-ene (12 mmol), $EtAlCl_2$ (24 mmol), Mg (powder, 36 mmol), and Cp_2ZrCl_2 (1.1 mmol in 15 ml THF) under an argon atmosphere for 3 h led to OAC **1a** in 71% yield (Scheme 2).[3]

Together with OAC **1a**, the total yield of symmetrical products **2a**[4] and **3a**,[1] resulting from homocycloalumination of hex-1-ene or cyclonona-1,2-diene under the chosen conditions, did not exceed 14%.

The structure of OAC **1a** was confirmed by means of ^1H, ^{13}C and Dept 135° NMR, and two-dimensional (HH COSY, HSQC, and HMBC) experiments. In the NMR spectra, strong broadening of signals due to the quadruple relaxation of ^{27}Al nuclei ($I = 5/2$) and due to the presence of stereoisomers in solution was observed. Actually, OAC **1a** corresponds to a complex with a molecule of tetrahydrofuran, in which the cycloalumination reaction was carried out. The aluminum atom is connected to the solvent molecule, and is tetracoordinated. Taking into account the two diastereomeric centers at C9 and C10, it is reasonable to expect an increase in the number of diastereoisomers. Therefore, we have studied in detail the NMR (^1H and ^{13}C) spectra of compounds **4a** and **5a** obtained after acid hydrolysis and deuterolysis of **1a.**

Compounds **4a** and **5a** were analyzed by 1D and 2D NMR experiments. Mass spectra of these compounds were also recorded. Evaluation of the signals in the ^1H and ^{13}C NMR spectra allows unambiguous assignment of the structures. Thus, the position of the alkyl chain substituent in compound **4a** was confirmed by the presence of cross-peaks between the proton H(C1) (δ 5.51) and the quaternary C3 carbon atom in the HMBC spectrum. The double bond *Z*-configuration at the C2 carbon atoms was determined unambiguously by the magnitude of the vicinal spin–spin

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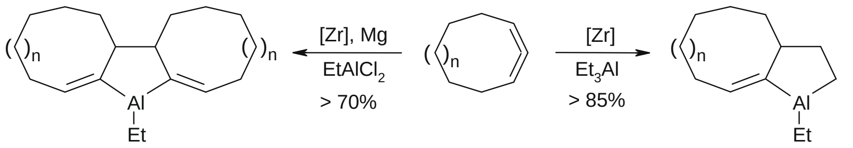
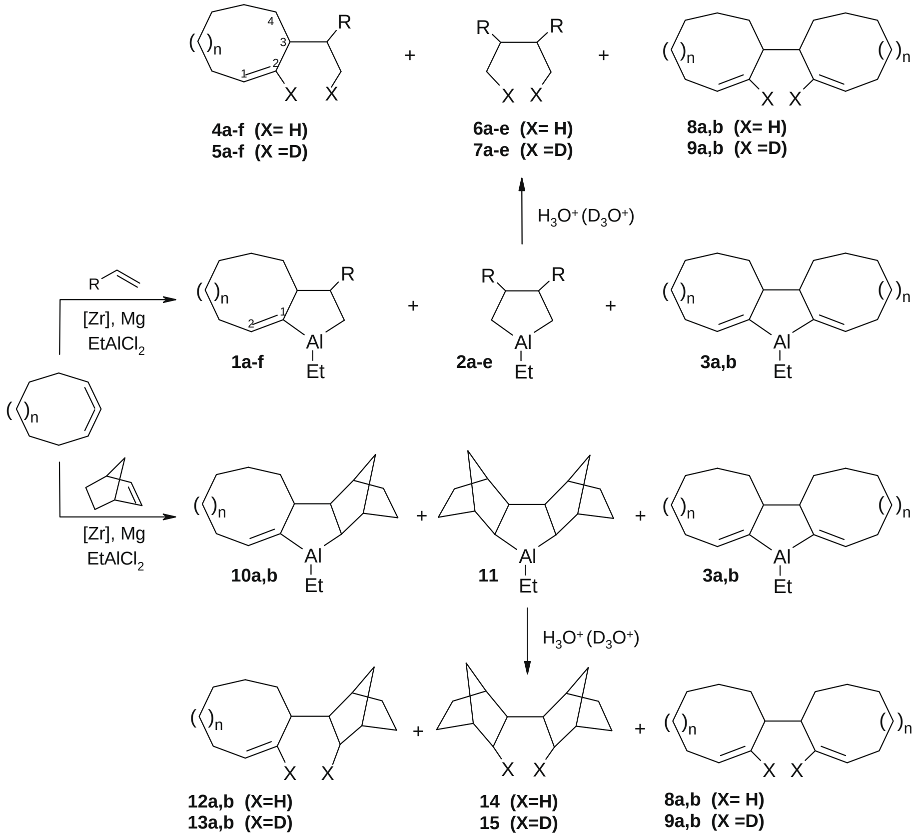


Scheme 1.



Scheme 2.

interaction constant (SSIC), ${}^3J$ (H(C1), H(C2)) = 10 Hz.[5] The location of the deuteriums at C2 and C15 in partially deuterized compound **5a** was confirmed by the absence of a proton signal at 5.23 ppm in the ^{1}H NMR spectrum, and also by the triplet splitting for the C2 and C15 carbon signals at δ 132.9 (${}^1J_{CD}$ = 23 Hz) and δ 16.3 (${}^1J_{CD}$ = 19 Hz), respectively.

A comparison between the ^{13}C NMR spectra of the OAC **1a** and the hydrocarbon **4a** shows that the chemical shifts of the carbon atoms in the cyclononene unit C3–C8 and the C13–C16 alkyl chain have insignificant variations. The signals of the double bond carbon atoms are shifted down field. This is particularly manifested by the C1 carbon atom, the resonance of which is observed at δ 177.5 (176.5). The C11, C15, and C17 carbon atoms also exhibit two signals per carbon atom (1:2 line intensity ratio), possibly due to diastereomers. The ^{13}C NMR spectrum of OAC **1a** also demonstrates the expected bands at δ 10.1 and δ 1.6 (1.2), which are attributable to the ethyl group bound to the aluminum atom. The cyclopentane ring C11 carbon atom adjacent to Al resonated at δ 9.5 and δ 10.0.

In spite of the proximity of the chemical shifts belonging to the adjacent C11 and C17 carbon atoms, it was possible to identify them unambiguously from the HSQC and HMBC experiments, since the chemical shifts of the corresponding protons differed from each other. Cross-peaks in the HMBC spectrum between C11 and H17 (C17 and H11) indicated formation of a cyclic aluminum-containing moiety. The ^{27}Al NMR spectrum exhibited a signal at δ 135, which corresponds to the area of tetracoordinated aluminum atoms.

Thus, we have identified compounds **1a**, **4a**, and **5a** as 12-ethyl-10-*n*-butyl-12-aluminabicyclo[7.3.0^{1,9}]dodec-1(2)-ene, 3-(1-methylpentyl)cyclonon-1-ene, and 2-deutero-3-(1-deuteromethylpentyl)cyclonon-1-ene, respectively.

Together with hex-1-ene, unsaturated compounds such as hept-1-ene, dec-1-ene, styrene, allyl benzene, and norbornene have been used in the combined cycloalumination reaction with cyclonona-1,2-diene. These reactions were shown to proceed analogously to those described above. In each experiment, together with the target aluminacyclopentanes **1b**–**e** and **3a**, the products of homocycloalumination of α-olefins **2b**–**e** or norbornene **11** and cyclonona-1,2-diene **3a** were observed, the total amount of which varied in the range of 10–15%, and were identified from the products of hydrolysis **6b**–**e**, **8a**, and **14** and deuterolysis **7b**–**e**, **9a**, and **15**. The structure of all the OACs was proved by spectral methods, and also by comparison with known samples.[4,6]

Similar to cyclonona-1,2-diene, cyclotrideca-1,2-diene was found to participate in the combined cycloalumination reaction with α-olefins or norbornene in the presence of $EtAlCl_2$ and Cp_2ZrCl_2 to afford the corresponding OACs **1f** and **10b** in yields of

Table 1
Combined cycloalumination of cyclic 1,2-dienes and olefins

Entry	Cyclic 1,2-diene	Olefin	Yields of aluminacyclopentanes **1**–**3**, **10** and **11**[a] (%)			Total yield (%)
1	Cyclonona-1,2-diene	Hex-1-ene	71 (**1a**)	11 (**2a**)	3 (**3a**)	85
2	Cyclonona-1,2-diene	Hept-1-ene	68 (**1b**)	9 (**2b**)	4 (**3a**)	81
3	Cyclonona-1,2-diene	Dec-1-ene	63 (**1c**)	7 (**2c**)	6 (**3a**)	76
4	Cyclonona-1,2-diene	Styrene	65 (**1d**)	11 (**2d**)	4 (**3a**)	80
5	Cyclonona-1,2-diene	Allyl benzene	62 (**1e**)	8 (**2e**)	5 (**3a**)	75
6	Cyclonona-1,2-diene	Norbornene	67 (**3a**)	10 (**11**)	4 (**3a**)	81
7	Cyclotrideca-1,2-diene	Hex-1-ene	58 (**1f**)	13 (**2a**)	1 (**3b**)	72
8	Cyclotrideca-1,2-diene	Norbornene	60 (**3b**)	12 (**11**)	1 (**3b**)	73

[a] Determined by GLC of the acid hydrolysis products.

58% and 60%, together with homocycloalumination products **2a**, **11**, and cyclotrideca-1,2-diene **3b** (Table 1). The mixtures of hydrolysis products were extracted with hexane and purified by distillation in vacuo. All the products were isolated in 95–98% purity.

In conclusion, we have described for the first time the Cp_2ZrCl_2 catalyzed combined cycloalumination of cyclic allenes with olefins (or norbornene) assisted by $EtAlCl_2$. As a result, unsaturated bi- and polycyclic OACs were obtained in high yields with high selectivity. We envisage that these OACs can be used for the synthesis of carbocyclic,[2c,7] heterocyclic,[8] and bifunctional[1,2b,9] compounds.

Acknowledgments

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Supplementary data

Supplementary data (Spectral data for compounds **4b**–**f**, **5b**–**f**, **12a**,**b**, and **13a**,**b**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.12.115.

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3. *Reaction between cyclic 1,2-dienes and olefins in the presence of* $EtAlCl_2$ *and* Cp_2ZrCl_2: A glass reactor under a dry argon atmosphere at ambient temperature was charged under stirring with 10 ml of THF, Mg (36 mmol), Cp_2ZrCl_2 (1.1 mmol), olefin (12 mmol), and $EtAlCl_2$ (24 mmol). A solution of cyclic 1,2-diene (10 mmol) in 10 ml of THF was then added dropwise over 3 h. The mixture was stirred for an additional 2 h. The reaction mixture (crude **1a–f** or **10a,b**) was quenched with an 8–10% aqueous solution of HCl (or DCl, 10–12% solution in D_2O). The organic layer was diluted with hexane, separated, and dried over $MgSO_4$. Evaporation and vacuum distillation furnished the target products **4a**–**f**, **12a**,**b** or **5a**–**f**, **13a**,**b**. 12-Ethyl-10-*n*-butyl-12-aluminabicyclo[7.3.0^{1,9}]dodec-1(2)-ene (**1a**): ^{1}H NMR (400 MHz, C_7D_8): δ 5.13 (br s, 1H), 1.0–1.92 (br m, 22H), 0.8–1.0 (br m, 3H), 0.4–0.75 (br m, 3H), −0.4–0.2 (m, 4H); ^{13}C NMR (100 MHz, C_7D_8): δ 177.5 (176.5), 130.8, 44.5, 42.0, 36.1, 32.6, 30.7, 27.5, 26.8, 26.1, 26.0, 24.5, 23.6, 14.9, 10.1, 10.0 (9.5), 1.6 (1.2). ^{27}Al NMR (104.28 MHz, C_7D_8): 135 ppm. 3-(1-Methylpentyl)cyclonon-1-ene (**4a**): bp 133–135 °C (10 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (m, 1H), 5.23 (m, 1H), 2.37 (m, 1H), 2.19 (m, 1H), 2.08 (m, 1H), 1.15–1.65 (m, 17H), 0.89 (t, J = 7 Hz, 3H), 0.81 (d, J = 7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.3, 129.3, 41.1, 38.4, 34.9, 31.8, 29.7, 26.8, 26.5, 26.3, 26.0, 25.3, 23.3, 16.6, 14.4. MS, *m/z*: 208 (M^+). Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 86.31; H, 13.55%. 2-Deutero-3-(1-deuteromethylpentyl)cyclonon-1-ene (**5a**): bp 133–135 °C (10 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (t, J = 8 Hz, 1H), 2.36 (m, 1H), 2.18 (m, 1H), 2.07 (m, 1H), 1.14–1.66 (m, 17H), 0.86 (t, J = 7 Hz, 3H), 0.79 (d, J = 7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.9 (t, J_{CD} = 23 Hz), 129.2, 40.9, 38.3, 35.1, 32.5, 31.7, 27.1, 26.4, 26.3, 26.0, 25.3, 22.9, 16.3 (t, J_{CD} = 19 Hz), 14.3. MS, *m/z*: 210 (M^+). Anal. Calcd for $C_{15}H_{26}D_2$: C, 85.63; H, 12.46; D, 1.91. Found: C, 85.49; H + D, 14.36.
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