Organometallic Chemistry

Synthesis and transformations of metallacycles
26.* Cp_2ZrCl_2-Catalyzed cycloalumination of substituted allenes with Et_3Al

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Catalytic cycloalumination of 1-alkyl(phenyl)allenes with triethylaluminum (5 mol.% of Cp_2ZrCl_2 as the catalyst, ~20 °C, 4 h, hexane) afforded methylene- and alkyl(benzyl)idene-substituted alumacyclopentanes.

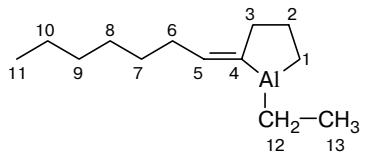
Key words: organoaluminum compounds, catalysis, cyclometallation, alumacyclopentanes, allenes.

Previously, we have demonstrated[2—7] that cycloalumination of aliphatic α-olefins, arylethylenes, norbornenes, and functionally substituted N-, O-, and S-containing α-olefins with Et_3Al or $EtAlCl_2$ in the presence of catalytic amounts of Cp_2ZrCl_2 afforded alumacyclopentanes (ACP).

As part of continuing studies of these reactions and with the aim of extending this procedure, which has been developed for the synthesis of cyclic organoaluminum compounds (OAC), to 1,2-dienes, we examined the reactions of 1-alkyl(aryl)-substituted allenes with Et_3Al catalyzed by zirconium complexes.

We found that the reactions of 1,2-alkadienes with an excess of Et_3Al under the conditions used previously[2,3] (5 mol.% of Cp_2ZrCl_2, 4 h, hexane) afforded regioisomeric alumacyclopentanes **1a—c** and **2a—c** in a ratio of (6—7) : 1 in a total yield of 85—95% depending on the structures of the starting allenes (Scheme 1).

The structures of regioisomeric ACP **1a—c** and **2a—c** and the products of their hydrolysis **3a—c** and **4a—c** and deuterolysis **5a—c** and **6a—c** were established by spectral methods.[8] The numbering of C atoms used for the description of the ^{13}C NMR spectrum of compound **1a** is given below:



Since compounds **2a—c** were obtained as minor products and mixtures of organoaluminum compounds were difficult to separate, we failed to make the reliable assignment of the signals in the ^{13}C NMR spectra. At the same time, the yields of compounds **1a—c** and **2a—c** can be determined by GLC based on the products of their hydrolysis (**3a—c** and **4a—c**, respectively). The subsequent isolation and identification of the deuterolysis products (**5a—c** and **6a—c**, respectively) and the determination of the position of the deuterium atom made it possible to unambiguously judge the structures of the resulting OAC **1a—c** and **2a—c**.

* For Part 25, see Ref. 1.

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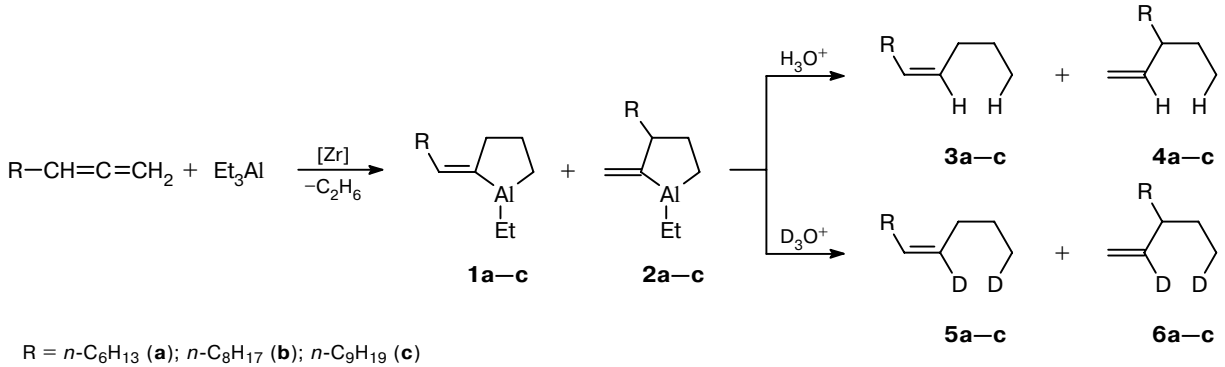
Scheme 1



R = *n*-C_6H_{13} (**a**); *n*-C_8H_{17} (**b**); *n*-C_9H_{19} (**c**)

Thus, the ^{13}C NMR spectrum of olefin **3a** is characterized by the presence of high-field signals for the allylic C(3) and C(6) atoms (δ 29.11 and 27.35, respectively) corresponding to the *Z* configuration of the double bond in the alkane chain of the molecule. In the spectrum of the dideuterated analog of this compound (**5a**), the upfield α-isotopic shifts are observed for the C(1) and C(4) atoms (Δδ = 0.26 and 0.33, respectively). The formation of 1,4-dideuterated hydrocarbons **5a** and **6a** upon deuterolysis of OAC **1a** and **2a** indicates that the Al atoms in the latter compounds are bound simultaneously to two C atoms.

The above-considered results provide evidence that cycloalumination of allenes with Et_3Al gave rise to five-membered OAC **1a** and **2a**. Analogously, we proved the structures of other cyclic OAC, *viz.*, **1b,c** and **2b,c**.

Cyclometallation of 1,2-alkadienes proceeded in aliphatic (hexane or cyclohexane) or aromatic (benzene or toluene) solvents as well as in dichloromethane during 4—5 h (Tables 1 and 2). In ethereal solvents (THF) or in the absence of the solvent, the reactions proceeded in low yields due to polymerization of the starting allene.

At ~0 °C, the reaction in hexane proceeded more slowly and the conversion of the initial 1,2-alkadienes was at most 40% after 8 h. The highest yields of ACP **1b** and **2b** were obtained at 20 °C and at the concentration of the catalyst Cp_2ZrCl_2 equal to 5 mol.%. Under these conditions, the total yield of regioisomeric products **1b** and **2b** was 93%. The total yield of a mixture of ACP **1b** and **2b** falled to 55% as the concentration of the catalyst was decreased to 1 mol.%, the ratio of the regioisomers remaining unchanged.

Table 1. Effect of the nature of the solvent on the yields of ACP **1b** and **2b***

Solvent	Yield of ACP (%)	
	1b	**2b**
Hexane	80	13
Cyclohexane	70	15
Benzene	77	12
Toluene	75	10
CH_2Cl_2	92	3
THF	18	3
—	12	3

* The reaction conditions: ~20 °C, 4 h, *n*-C_8H_{17}—CH=C=CH_2 : Et_3Al : Cp_2ZrCl_2 = 10 : 13 : 0.5.

Table 2. Dependence of the yields of ACP **1b** and **2b** on the reaction time*

Reaction time/h	Yield of ACP (%)	
	1b	**2b**
0.5	36	6
1	47	8
2	62	10
3	75	12
4	80	13
5	82	13

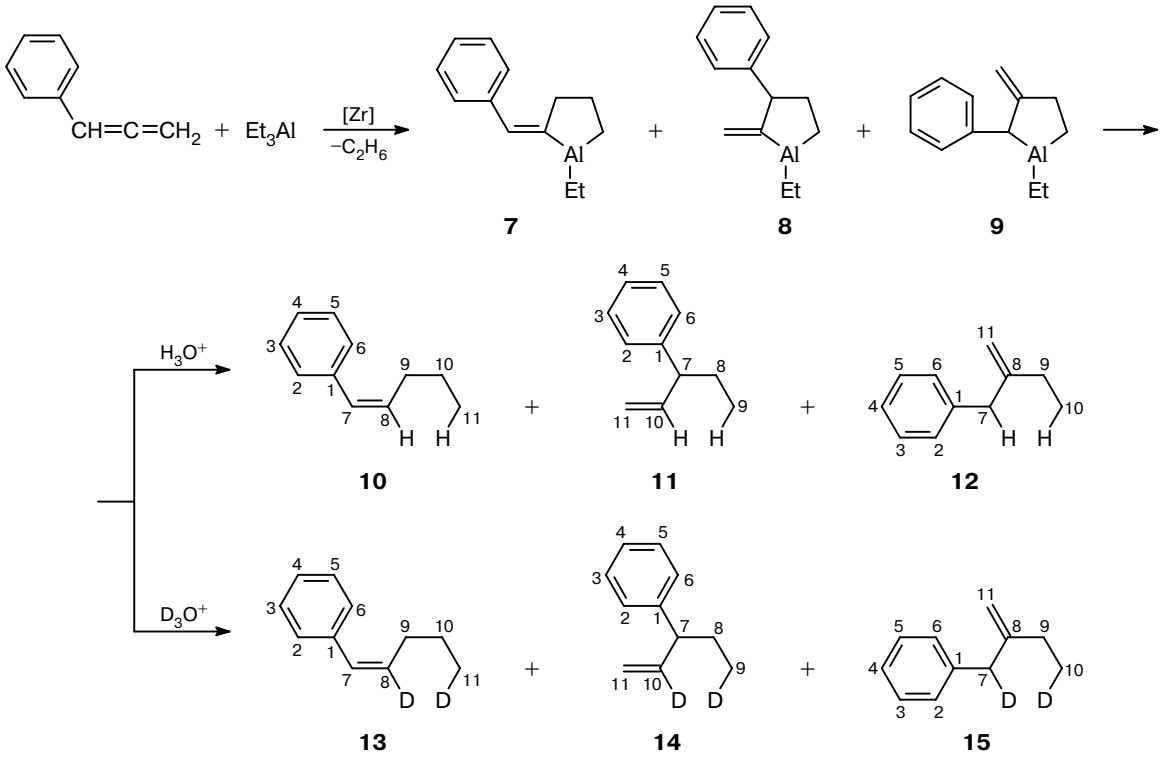
* The reaction conditions: hexane, ~20 °C, *n*-C_8H_{17}—CH=C=CH_2 : Et_3Al : Cp_2ZrCl_2 = 10 : 13 : 0.5.

Under the optimum conditions (~20 °C, 4 h, hexane, 5 mol.% of Cp_2ZrCl_2), cyclometallation of phenylallene with triethylaluminum afforded mixtures of unsaturated cyclic OAC **7**, **8**, and **9** in a ratio of ~4 : 2 : 1 in a total yield of ~90% (Scheme 2).

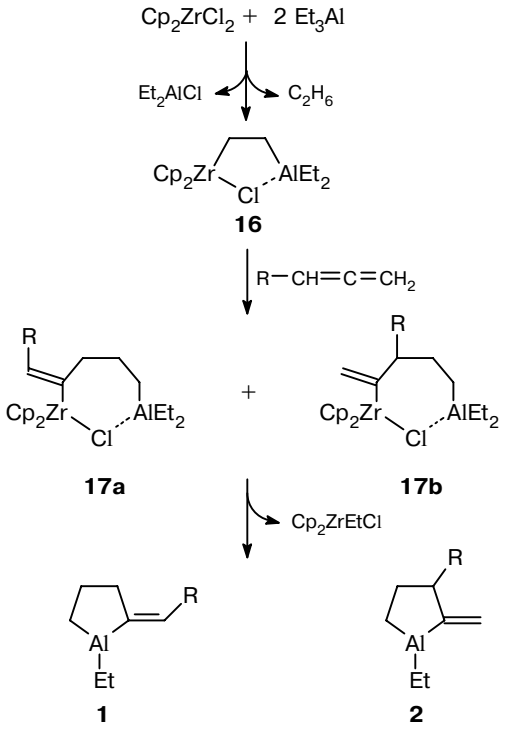
Treatment of unsaturated OAC **7** with an aqueous solution of HCl gave rise to olefin **10** with the *Z* configuration of the double bond, which is characterized by the vicinal spin-spin coupling constant $^3J_{H,H}$ = 11.6 Hz for the *cis*-protons of the double bond (*cf.* lit. data[9]: $^3J_{trans}$ = 18 Hz). Analogously, hydrocarbons **11** and **12** were prepared from compounds **8** and **9**, respectively. Deuterolysis of OAC **7—9** afforded products **13—15**, respectively. Compounds **10—15** were characterized by the physicochemical parameters consistent with their structures (see the Experimental section), which confirmed the structures of the starting OAC **7—9**.

According to the data published in the literature,[10—14] the generation of five-membered OAC in our experiments is attributable to the formation of five- and seven-membered bimetallic Zr—Al complexes **16** and **17a,b** as intermediates whose successive transformations afforded the target regioisomeric unsaturated alumacyclopentanes **1** and **2** according to Scheme 3.

Scheme 2



Scheme 3



The observed regioselectivity of the reaction is, probably, associated with the electron density distribution on the sp^2-hybridized carbon atoms of 1,2-alkadienes or with the π—d interaction between the double bond of the allene and the unoccupied d orbital of the Zr atom. Both alternatives can favor a particular spatial orientation of allenes at the central atom of the catalyst and their insertion at the Zr—C bond to form intermediate bimetallic complexes **17a,b**, which contain the alkylidene or methylene substituents at the C atom bound to the Zr atom. For the same reason, cyclometallation of phenylallene with Et_3Al additionally afforded[3] regioisomeric ACP **9** containing the phenyl substituent at the carbon atom bound to the Al atom.

To summarize, cyclometallation of monosubstituted allenes with triethylaluminum under the action of the catalyst Cp_2ZrCl_2 proceeds both at the terminal and disubstituted double bonds to form regioisomeric unsaturated alumacyclopentanes in high yields.

Experimental

The starting allenes and Cp_2ZrCl_2 were prepared according to known procedures.[15,16] The solvents were distilled over $LiAlH_4$ immediately before use; commercial 95% Et_3Al (the Redkinskii pilot-production plant, Russia) was used. The hydrolysis and deuterolysis products were analyzed by GLC on a Chrom-5 chromatograph (a 1200×3-mm column; 5% SE-30 or 15% PEG-6000 on Chromaton N-AW) under a stream of He. The IR spectra were measured on an IR-75 spectrometer (film). The mass spectra were obtained on an MX-1306 spectrometer (70 eV, 200 °C). The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Jeol FX-90 Q (90 and 22.5 MHz) and

Bruker AM-300 (300 and 75 MHz) spectrometers, respectively, with Me_4Si as the internal standard. The ^{13}C NMR spectra of OAC were measured with the use of C_6D_6 as the solvent and the internal standard.

Cp_2ZrCl_2-Catalyzed cyclometallation of allenes with Et_3Al (general procedure). Allene (10 mmol), Cp_2ZrCl_2 (0.5 mol), hexane (10 mL), and Et_3Al (13 mmol) were placed with stirring in a glass reactor under an atmosphere of dry argon at 0 °C. The reaction mixture was heated to 20 °C and stirred for 4 h. Then the mixture was treated with a 7—10% solution of HCl or DCl in D_2O, extracted with hexane, and dried with $MgSO_4$. The reaction products were isolated by vacuum distillation on a Widmer column.

***E*-1-Ethyl-2-hexylidenealumacyclopentane (1a).** ^{13}C NMR, δ: 18.10 (t, C(1)); 32.41 (t, C(2)); 34.88 (t, C(3)); 143.0 (s, C(4)); 170.40 (d, C(5)); 25.45 (t, C(6)); 28.77 (t, C(7)); 29.61 (t, C(8)); 32.15 (t, C(9)); 23.11 (t, C(10)); 14.33 (q, C(11)); 0.81 (t, C(12)); 8.26 (q, C(13)).

***Z*-Undec-4-ene (3a).** B.p. 81 °C (20 Torr). Found (%): C, 85.50; H, 14.10. $C_{11}H_{22}$. Calculated (%): C, 85.71; H, 14.29. IR, ν/cm^{-1}: 3080, 2920, 2850, 2300, 1640, 1460, 910, 720. ^1H NMR, δ: 0.77—0.92 (m, 6 H, Me); 1.06—1.55 (m, 10 H, CH_2); 1.76—1.99 (m, 4 H, CH_2—C=C); 5.26—5.36 (m, 2 H, CH=CH). ^{13}C NMR, δ: 13.89 (q, C(1)); 23.00 (t, C(2)); 29.11 (t, C(3)); 129.71 (d, C(4)); 130.17 (d, C(5)); 27.35 (t, C(6)); 29.89 (t, C(7)); 29.43 (t, C(8)); 31.90 (t, C(9)); 22.74 (t, C(10)); 14.15 (q, C(11)). MS, *m/z*: 154 $[M]^+$.

***Z*-Tridec-4-ene (3b).** B.p. 85 °C (2 Torr). Found (%): C, 85.20; H, 14.20. $C_{13}H_{26}$. Calculated (%): C, 85.71; H, 14.29. IR, ν/cm^{-1}: 3080, 2950, 2900, 2850, 1640, 1450, 1370, 910, 895, 720. ^1H NMR, δ: 0.80—0.96 (m, 6 H, Me); 1.10—1.57 (m, 14 H, CH_2); 1.90—2.11 (m, 4 H, CH_2—C=C); 5.24—5.70 (m, 2 H, CH=CH). ^{13}C NMR, δ: 13.83 (q, C(1)); 23.06 (t, C(2)); 29.30 (t, C(3)); 129.58 (d, C(4)); 130.10 (d, C(5)); 27.42 (t, C(6)); 29.56 (t, C(7)); 29.76 (t, C(8)); 29.76 (t, C(9)); 29.89 (t, C(10)); 32.10 (t, C(11)); 22.87 (t, C(12)); 14.15 (q, C(13)). MS, *m/z*: 182 $[M]^+$.

***Z*-Tetradec-4-ene (3c).** B.p. 97 °C (4 Torr). Found (%): C, 85.60; H, 14.12. $C_{14}H_{28}$. Calculated (%): C, 85.71; H, 14.29. IR, ν/cm^{-1}: 3080, 2950, 2910, 2850, 1450, 910, 895, 720. ^1H NMR, δ: 0.75—0.93 (m, 6 H, Me); 1.17—1.45 (m, 16 H, CH_2); 1.95—2.10 (m, 4 H, CH_2—C=C); 5.10—5.83 (m, 2 H, CH=CH). ^{13}C NMR, δ: 13.50 (q, C(1)); 23.00 (t, C(2)); 29.30 (t, C(3)); 129.97 (d, C(4)); 132.10 (d, C(5)); 27.20 (t, C(6)); 29.50 (t, C(7)); 29.56 (t, C(8)); 29.89 (t, C(9)); 29.76 (t, C(10)); 29.76 (t, C(11)); 32.04 (t, C(12)); 22.87 (t, C(13)); 14.50 (q, C(14)). MS, *m/z*: 196 $[M]^+$.

3-Ethylnon-1-ene (4a). B.p. 77 °C (20 Torr). Found (%): C, 85.52; H, 14.26. $C_{11}H_{22}$. Calculated (%): C, 85.71; H, 14.29. IR, ν/cm^{-1}: 3080, 2900, 2850, 2300, 1640, 1450, 910, 720. ^1H NMR, δ: 0.73—0.98 (m, 6 H, Me); 1.09—1.51 (m, 12 H, CH_2); 1.76—2.07 (m, 1 H, CH—C=C); 4.76—5.69 (m, 3 H, CH_2=CH). ^{13}C NMR, δ: 114.04 (t, C(1)); 143.50 (d, C(2)); 45.95 (d, C(3)); 34.77 (t, C(4)); 27.29 (t, C(5)); 29.56 (t, C(6)); 32.04 (t, C(7)); 22.80 (t, C(8)); 14.22 (q, C(9)); 27.81 (t, C(10)); 11.68 (q, C(11)). MS, *m/z*: 154 $[M]^+$.

3-Ethylundec-1-ene (4b). B.p. 78 °C (2 Torr). Found (%): C, 84.99; H, 14.15. $C_{13}H_{26}$. Calculated (%): C, 85.71; H, 14.29. IR, ν/cm^{-1}: 3080, 2950, 2910, 2840, 1640, 1450, 1370, 910, 895, 720. ^1H NMR, δ: 0.80—0.99 (m, 6 H, Me); 1.10—1.57 (m, 16 H, CH_2); 1.85—2.11 (m, 1 H, CH—C=C); 4.67—5.61 (m, 3 H, CH_2=CH). ^{13}C NMR, δ: 114.10 (t, C(1)); 143.23 (d, C(2)); 46.15 (d, C(3)); 34.96 (t, C(4)); 27.42 (t, C(5)); 29.56 (t, C(6)); 29.76 (t, C(7)); 29.89 (t, C(8)); 32.10 (t, C(9)); 22.87 (t, C(10)); 14.15 (q, C(11)); 27.94 (t, C(12)); 11.68 (q, C(13)). MS, *m/z*: 182 $[M]^+$.

3-Ethyldodec-1-ene (4c). B.p. 95 °C (2 Torr). Found (%): C, 85.52; H, 14.24. $C_{14}H_{28}$. Calculated (%): C, 85.71; H, 14.29. IR, ν/cm^{-1}: 3080, 2940, 2900, 2800, 1450, 910, 895, 720. ^1H NMR, δ: 0.83—0.96 (m, 6 H, Me); 1.20—1.57 (m, 18 H, CH_2); 1.95—2.17 (m, 1 H, CH—C=C); 4.46—5.20 (m, 3 H, CH_2=CH). ^{13}C NMR, δ: 114.20 (t, C(1)); 143.80 (d, C(2)); 45.20 (d, C(3)); 34.80 (t, C(4)); 27.65 (t, C(5)); 29.56 (t, C(6)); 29.76 (t, C(7)); 29.50 (t, C(8)); 29.32 (t, C(9)); 32.10 (t, C(10)); 22.82 (t, C(11)); 14.15 (q, C(12)); 27.74 (t, C(13)); 12.70 (q, C(14)). MS, *m/z*: 196 $[M]^+$.

***Z*-1,4-Dideuteroundec-1-ene (5a).** B.p. 75 °C (14 Torr). Found (%): C, 84.42; H, D, 15.25. $C_{11}H_{20}D_2$. Calculated (%): C, 84.62; H, 12.82; D, 2.56. IR, ν/cm^{-1}: 3080, 2920, 2850, 2160 (CD), 1450, 910, 790, 720. ^1H NMR, δ: 0.77—0.91 (m, 5 H, Me); 1.22—1.53 (m, 10 H, CH_2); 1.90—2.07 (m, 4 H, CH_2—C=C); 5.37 (t, 1 H, CD=CH, ^3J = 7 Hz). ^{13}C NMR, δ: 13.63 (t, C(1), $^1J_{C,D}$ = 19.5 Hz); 22.80 (t, C(2)); 29.11 (t, C(3)); 129.38 (s, C(4), $^1J_{C,D}$ = 23.4 Hz); 130.04 (d, C(5)); 27.29 (t, C(6)); 29.89 (t, C(7)); 29.30 (t, C(8)); 31.90 (t, C(9)); 22.80 (t, C(10)); 14.22 (q, C(11)). MS, *m/z*: 156 $[M]^+$.

***Z*-1,4-Dideuterotridec-4-ene (5b).** B.p. 90 °C (4 Torr). Found (%): C, 84.62; H, D, 15.10. $C_{13}H_{24}D_2$. Calculated (%): C, 84.78; H, 13.04; D, 2.18. IR, ν/cm^{-1}: 3080, 2950, 2900, 2850, 2170 (CD), 1640, 1450, 1370, 910, 895, 720. ^1H NMR, δ: 0.83—0.96 (m, 5 H, Me); 1.10—1.48 (m, 14 H, CH_2); 1.92—2.10 (m, 4 H, CH_2—C=C); 5.34 (t, 1 H, CD=CH, ^3J = 7 Hz). ^{13}C NMR, δ: 12.75 (t, C(1), $^1J_{C,D}$ = 19.1 Hz); 23.06 (t, C(2)); 29.56 (t, C(3)); 129.58 (s, C(4), $^1J_{C,D}$ = 23.0 Hz); 132.40 (d, C(5)); 27.42 (t, C(6)); 29.76 (t, C(7)); 29.76 (t, C(8)); 29.80 (t, C(9)); 29.89 (t, C(10)); 32.10 (t, C(11)); 22.87 (t, C(12)); 14.15 (q, C(13)). MS, *m/z*: 184 $[M]^+$.

***Z*-1,4-Dideuterotetradec-4-ene (5c).** B.p. 95 °C (4 Torr). Found (%): C, 84.46; H, D, 15.05. $C_{14}H_{26}D_2$. Calculated (%): C, 84.55; H, 13.13; D, 2.02. IR, ν/cm^{-1}: 3080, 2950, 2850, 2170 (CD), 1450, 910, 895, 720. ^1H NMR, δ: 082—0.95 (m, 5 H, Me); 1.21—1.45 (m, 16 H, CH_2); 1.95—2.10 (m, 4 H, CH_2—C=C); 5.32 (t, 1 H, CD=CH, ^3J = 7 Hz). ^{13}C NMR, δ: 13.50 (t, C(1), $^1J_{C,D}$ = 19.1 Hz); 22.80 (t, C(2)); 29.30 (t, C(3)); 129.25 (s, C(4), $^1J_{C,D}$ = 22.0 Hz); 129.97 (d, C(5)); 27.35 (t, C(6)); 29.50 (t, C(7)); 29.76 (t, C(8)); 29.76 (t, C(9)); 29.76 (t, C(10)); 29.50 (t, C(11)); 32.04 (t, C(12)); 22.80 (t, C(13)); 14.15 (q, C(14)). MS, *m/z*: 198 $[M]^+$.

2-Deutero-3-(2-deuteroethyl)non-1-ene (6a). B.p. 74 °C (20 Torr). Found (%): C, 84.30; H, D, 15.13. $C_{11}H_{20}D_2$. Calculated (%): C, 84.62 H, 12.82; D, 2.56. IR, ν/cm^{-1}: 3080, 2920, 2850, 2160 (CD), 1450, 910, 790, 720. ^1H NMR, δ: 0.83—0.94 (m, 5 H, Me); 1.28—1.53 (m, 12 H, CH_2); 1.93—2.07 (m, 1 H, CH—C=C); 4.69—5.55 (m, 2 H, $CD=CH_2$). ^{13}C NMR, δ: 113.91 (t, C(1)); 45.82 (d, C(3)); 34.77 (t, C(4)); 27.29 (t, C(5)); 29.56 (t, C(6)); 31.90 (t, C(7)); 22.80 (t, C(8)); 14.22 (q, C(9)); 27.74 (t, C(10)); 13.89 (t, C(11), $^1J_{C,D}$ = 20.5 Hz). MS, *m/z*: 156 $[M]^+$.

2-Deutero-3-(2-deuteroethyl)undec-1-ene (6b). B.p. 75 °C (2 Torr). Found (%): C, 84.50; H, D, 15.07. $C_{13}H_{24}D_2$. Calculated (%): C, 84.78; H, 13.04; D, 2.18. IR, ν/cm^{-1}: 3080, 2950, 2840, 2170 (CD), 1640, 1450, 1370, 910, 895, 720. ^1H NMR, δ: 0.83—0.95 (m, 5 H, Me); 1.12—1.57 (m, 16 H, CH_2); 1.90—2.27 (m, 1 H, CH—C=C); 4.60—5.69 (m, 2 H, $CD=CH_2$). ^{13}C NMR, δ: 115.04 (t, C(1)); 45.96 (d, C(3)); 34.90 (t, C(4)); 27.94 (t, C(5)); 29.52 (t, C(6)); 29.80 (t, C(7)); 29.89 (t, C(8)); 32.10 (t, C(9)); 22.80 (t, C(10)); 14.15 (q, C(11)); 27.74 (t, C(12)); 12.74 (t, C(13), $^1J_{C,D}$ = 20.4 Hz). MS, *m/z*: 184 $[M]^+$.

2-Deutero-3-(2-deuteroethyl)dodec-1-ene (6c). B.p. 93 °C (2 Torr). Found (%): C, 84.55; H, D, 15.12. $C_{14}H_{26}D_2$. Calculated (%): C, 84.85; H, 13.13; D, 2.02. IR, ν/cm^{-1}:

3080, 2940, 2900, 2800, 2170 (CD), 1450, 910, 895, 720. ^{1}H NMR, δ: 0.82—0.95 (m, 5 H, Me); 1.21—1.45 (m, 18 H, CH_2); 1.95—2.18 (m, 1 H, CH—C=C); 4.68—5.23 (m, 2 H, CD=CH_2). ^{13}C NMR, δ: 113.91 (t, C(1)); 45.82 (d, C(3)); 34.83 (t, C(4)); 27.68 (t, C(5)); 29.76 (t, C(6)); 29.76 (t, C(7)); 29.50 (t, C(8)); 29.30 (t, C(9)); 32.10 (t, C(10)); 22.80 (t, C(11)); 14.15 (q, C(12)); 27.35 (t, C(13)); 11.36 (t, C(14), $^1J_{C,D}$ = 19.1 Hz). MS, *m/z*: 198 $[M]^+$.

***Z*-1-Pentenylbenzene (10).** B.p. 78 °C (6 Torr). Found (%): C, 90.10; H, 9.28. $C_{11}H_{14}$. Calculated (%): C, 90.41; H, 9.59. IR, ν/cm^{-1}: 3080, 2900, 1450, 910, 750, 700. ^{1}H NMR, δ: 0.93 (t, 3 H, Me, ^3J = 7 Hz); 1.27—1.68 (m, 2 H, CH_2); 2.18—2.44 (m, 2 H, CH_2—C=C); 5.51—5.80 (m, 1 H, CH=C); 6.33—6.50 (m, 1 H, CH=C); 7.16—7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 133.09 (s, C(1)); 128.86 (d, C(2), C(6)); 128.15 (d, C(3), C(5)); 126.52 (d, C(4)); 128.94 (d, C(7)); 128.54 (d, C(8)); 30.80 (t, C(9)); 23.26 (t, C(10)); 13.96 (q, C(11)). MS, *m/z*: 146 $[M]^+$.

1-[(1-Ethyl)-2-propenyl]benzene (11). B.p. 71 °C (10 Torr). Found (%): C, 90.25; H, 9.40. $C_{11}H_{14}$. Calculated (%): C, 90.41; H, 9.59. IR, ν/cm^{-1}: 3080, 2950, 2920, 2860, 1640, 1600, 1490, 1450, 1375, 910, 730, 700. ^{1}H NMR, δ: 0.86 (t, 3 H, Me, ^3J = 7 Hz); 1.57—1.81 (m, 2 H, CH_2); 3.18 (q, 1 H, CH—Ph, ^3J = 7 Hz); 4.90—5.13 (m, 2 H, CH_2=C); 5.77—6.15 (m, 1 H, CH=C); 7.07—7.38 (m, 5 H, Ph). ^{13}C NMR, δ: 144.54 (s, C(1)); 127.69 (d, C(2), C(6)); 128.41 (d, C(3), C(5)); 126.13 (d, C(4)); 51.80 (d, C(7)); 28.39 (t, C(8)); 12.20 (q, C(9)); 142.33 (d, C(10)); 114.10 (t, C(11)). MS, *m/z*: 146 $[M]^+$.

1-[(2-Ethyl)-2-propenyl]benzene (12). B.p. 73 °C (6 Torr). Found (%): C, 90.34; H, 9.28. $C_{11}H_{14}$. Calculated (%): C, 90.41; H, 9.59. IR, ν/cm^{-1}: 3080, 2950, 1500, 1450, 910, 720, 700. ^{1}H NMR, δ: 1.02 (t, 3 H, Me, ^3J = 7 Hz); 1.95 (q, 2 H, CH_2, ^3J = 7 Hz); 3.35 (s, 2 H, CH_2—Ph); 4.74—4.82 (m, 2 H, CH_2=); 5.77—6.15 (m, 1 H, CH=); 7.02—7.23 (m, 5 H, Ph). ^{13}C NMR, δ: 139.56 (s, C(1)); 126.06 (d, C(2), C(6)); 130.88 (d, C(3), C(5)); 126.13 (d, C(4)); 43.35 (d, C(7)); 145.90 (C(8)); 28.33 (t, C(9)); 12.27 (q, C(10)); 109.94 (t, C(11)). MS, *m/z*: 146 $[M]^+$.

1-[(2,5-Dideutero)-1-pentenyl]benzene (13). B.p. 75 °C (6 Torr). Found (%): C, 89.07; H, D, 10.50. $C_{11}H_{12}D_2$. Calculated (%): C, 89.19; H, 8.11; D 2.70. IR, ν/cm^{-1}: 3080, 2950, 2160 (CD), 1500, 1450, 910, 750, 700. ^{1}H NMR, δ: 0.85 (tt, 2 H, CH_2D, $^2J_{H,D}$ = 2 Hz, $^3J_{H,H}$ = 2 Hz); 1.24—1.59 (m, 2 H, CH_2); 2.24 (t, 2 H, CH_2—C=C, ^3J = 7 Hz); 6.32 (t, 1 H, CH=C, ^4J = 2 Hz); 7.16—7.30 (m, 5 H, Ph). ^{13}C NMR, δ: 137.90 (s, C(1)); 128.80 (d, C(2), C(6), C(7)); 128.15 (d, C(3), C(5)); 126.46 (d, C(4)); 30.70 (t, C(9)); 23.13 (t, C(10)); 13.63 (t, C(11), $^1J_{C,D}$ = 19.1 Hz). MS, *m/z*: 148 $[M]^+$.

1-[2-Deutero-1-(2-deuteroethyl)-2-propenyl]benzene (14). B.p. 70 °C (10 Torr). Found (%): C, 89.02; H, D, 10.20. $C_{11}H_{12}D_2$. Calculated (%): C, 89.19; H, 8.11; D 2.70. IR, ν/cm^{-1}: 3080, 2950, 2170 (CD), 1500, 1450, 910, 750, 700. ^{1}H NMR, δ: 0.74—0.90 (m, 2 H, CH_2D); 1.57—1.77 (m, 2 H, CH_2); 3.13 (t, 1 H, CH—Ph, ^3J = 7 Hz); 4.73—5.05 (m, 2 H, CH_2=C); 7.08—7.38 (m, 5 H, Ph). ^{13}C NMR, δ: 144.77 (s, C(1)); 127.69 (d, C(2), C(6)); 128.41 (d, C(3), C(5)); 126.13 (d, C(4)); 51.67 (d, C(7)); 28.26 (t, C(8)); 11.94 (t, C(9), $^1J_{C,D}$ = 19.0 Hz); 142.54 (d, C(10)); 113.91 (t, C(11)). MS, *m/z*: 148 $[M]^+$.

1-[1-Deutero-2-(2-deuteroethyl)-2-propenyl]benzene (15). B.p. 70 °C (6 Torr). Found (%): C, 89.10; H, D, 10.50. $C_{11}H_{12}D_2$. Calculated (%): C, 89.19; H, 8.11; D 2.70. IR, ν/cm^{-1}: 3080, 2950, 2170 (CD), 1500, 1450, 910, 720, 700. ^{1}H NMR, δ: 0.77—0.93 (m, 2 H, CH_2D); 1.19—1.81 (m, 2 H, CH_2); 3.62—3.65 (m, 1 H, CH—Ph); 4.46—5.12 (m, 2 H, CH_2=C); 7.16—7.27 (m, 5 H, Ph). ^{13}C NMR, δ: 145.19 (s, C(1)); 128.54 (d, C(2), C(6)); 128.86 (d, C(3), C(5)); 128.15 (d, C(4)); 43.29 (d, C(7)); 23.19 (t, C(9)); 13.70 (t, C(10), $^1J_{C,D}$ = 19.1 Hz); 109.23 (t, C(11)). MS, *m/z*: 148 $[M]^+$.

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