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Synthesis and transformations of metallacycles
28.* Reactions of allenes with $EtAlCl_2$ and Et_2AlCl catalyzed by Ti and Zr complexes

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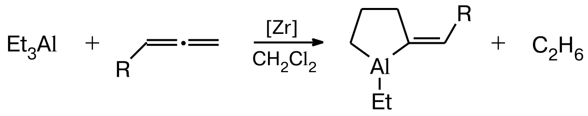
Catalytic cycloalumination of allenes with $EtAlCl_2$ in the presence of Ti or Zr complexes afforded methylidene- and alkyl(benzyl)idenealuminacyclopropanes and the corresponding aluminacyclopentanes, which were identified by analyzing the hydrolysis products. The reactions with the use of Et_2AlCl instead of $EtAlCl_2$ produced 1,2- and 1,4-dialuminum compounds.

Key words: organoaluminum compounds, catalysis, cycloalumination, aluminacyclopropanes, aluminacyclopentanes, allenes.

Cycloalumination of allenes with Et_3Al catalyzed by Cp_2ZrCl_2 afforded 2-alkylidene-1-ethylaluminacyclopentanes (Scheme 1).[2]

Scheme 1



With the aim of extending the scope of this reaction, applying it to other organoaluminum compounds (OAC), and synthesizing new classes of three- and five-membered unsaturated OAC, we studied cycloalumination of alkyl- and phenylallenes with $EtAlCl_2$ in the presence of metallic Mg as the acceptor of chloride ions and Cp_2TiCl_2 as the catalyst, which exhibits[3—6] high activity and selectivity in the formation of three-membered OAC from $EtAlCl_2$ and α-olefins or acetylenes.

Results and Discussion

We studied the reactions of allenes which differ in the nature of the substituent (Ph (**1a**), CH_2Ph (**1b**), Alk) and the length of the alkyl chain (C_6H_{13}, C_8H_{17}, C_9H_{19} (**1c—e**, respectively)) with $EtAlCl_2$. Preliminary experiments demonstrated that the reactions in the presence of Mg and the catalyst Cp_2TiCl_2 (molar ratio $RCH{=}C{=}CH_2 : [Al] : Mg : [Ti] = 20 : 26 : 24 : 1$) afforded in 8—12 h unsaturated cyclic OAC, *viz.*, 3-alkyl(benzyl,phenyl)-1-ethyl-2-methylidenealuminacyclopropanes (**2**), 2-alkyl(benzyl)idene-1-ethylaluminacyclopropanes (**3**), and 2,5-di(alkyl(benzyl)idene)-1-ethylaluminacyclopentanes (**4**), which were identified by analyzing the hydrolysis products.

The effect of the nature of the solvent on the yields and compositions of the reaction products was studied. In THF, cycloalumination of nona-1,2-diene (**1c**) with $EtAlCl_2$ in the presence of 5 mol.% of Cp_2TiCl_2 afforded organoaluminum compounds **2c**, **3c**, and **4c** in the ratio 6 : 1 : 2 in a total yield of ~80% (Scheme 2). In aliphatic (hexane, heptane, cyclohexane) or aromatic (benzene, toluene, xylene) solvents, cycloalumination of allenes did not virtually take place. In diethyl ether, cyclic organoaluminum compounds **2c**, **3c**, and **4c** were generated in the ratio 9 : 1 : 10 in a total yield of ~60%.

The structures of unsaturated cyclic organoaluminum compounds **2—4** were established by analyzing the hydrolysis (**5—7**) or deuterolysis products (**8—10**). According to the ^{13}C NMR spectroscopic data, alkenes **6a,b** (**9a,b**) and **7a—e** (**10a—e**) contain *Z*-disubstituted double bonds, whereas the double bonds in molecules **6c—e** (**9c—e**) have the *Z/E* configurations in a ratio of ~2 : 1. According to the ^1H NMR spectra, hydrolysis products **7a—e** contain the *cis*-double bonds (spin-spin coupling constant of the alkene protons ^3J is 11.7 Hz for **7a**; *cf.* lit. data[7]: $^3J_{trans} = 18$ Hz). The *cis* configuration of the double bond in compounds **7c—e** is confirmed by the fact that their ^{13}C NMR spectra have characteristic[8] high-field signals for the allylic C atoms at δ 26—28. Mass spectrometric analysis of deuterolysis products showed that the mixtures contained dideuterioalkenes **8—10** along with monodeuterated alkenes as the minor products (10—12%),

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* For Part 27, see Ref. 1.

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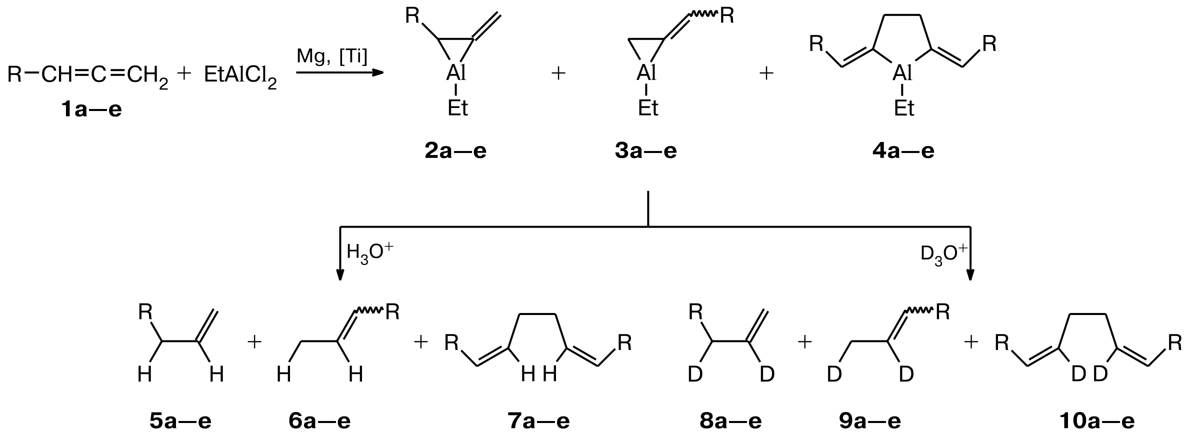
Scheme 2



R = Ph (**a**), CH_2Ph (**b**), $n-C_6H_{13}$ (**c**), $n-C_8H_{17}$ (**d**), $n-C_9H_{19}$ (**e**);
[Ti] = Cp_2TiCl_2

which indicates that cyclometallation was accompanied by competitive hydrometallation of the starting allenes.

The formation of unsaturated cyclic organoaluminum compounds **2—4** is attributable to transmetallation of the *in situ* generated unsaturated titanacyclopropane and titanacyclopentane intermediates with the starting $EtAlCl_2$ according to a scheme analogous to that proposed in our previous study[9] for cyclometallation of arylethenes. In these processes, the configurations of the *in situ* generated alkylidenetitanacyclopropane and -titanacyclopentane intermediates dictate the stereoconfigurations of the alkylidene-substituted organoaluminum compounds **3** and **4**. Apparently, hydride titanium complexes are responsible for the formation of minor hydrometallation products of allenes. Under the reaction conditions, these complexes are generated through dehydrogenolysis of THF with low-valent titanium complexes,[10] as we have demonstrated previously[11] in the investigation of hydrometallation of α-olefins.

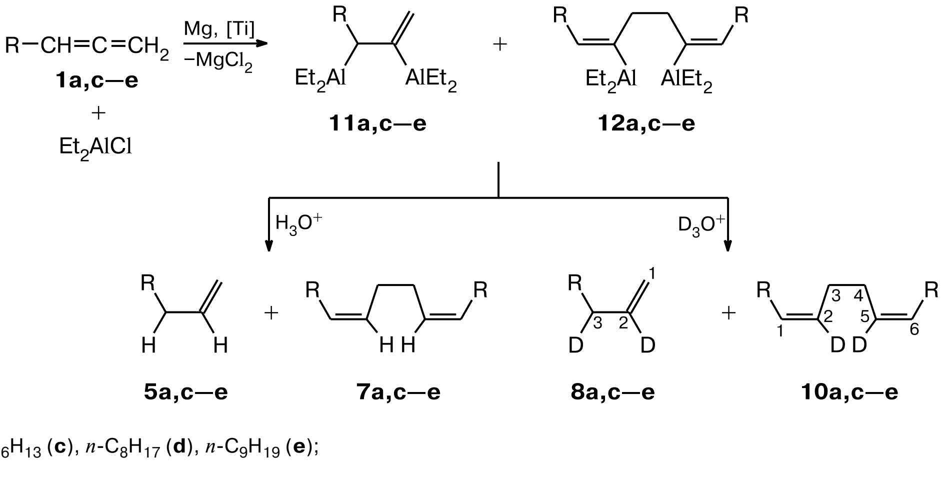
When studying cycloalumination of nona-1,2-diene (**1c**) with $EtAlCl_2$, we found that the reactions with the use of titanium alkoxides or halides ($Ti(OPr^i)_4$ or $TiCl_4$) instead of Cp_2TiCl_2 proceeded less selectively to give 1-ethyl-3-(*n*-hexyl)-2-methylidenealuminacyclopropane **2c** (15—20%), 1-ethyl-2-heptylidenealuminacyclopropane **3c** (8—10%), and a mixture of unidentified unsaturated aluminacyclopentanes and aluminacycloheptanes (55—60%). This is attributable to the insertion of an additional molecule of the starting allene at the Ti—C bond of intermediate titanacyclopentanes followed by transmetallation of *in situ* generated unsaturated titanacycloheptanes with the starting $EtAlCl_2$. Cycloalumination of nona-1,2-diene (**1c**) with $EtAlCl_2$ in the presence of 5 mol.% of Cp_2ZrCl_2 or $ZrCl_4$ afforded organoaluminum compounds **2c** and **3c** in a ratio of ~5 : 1 in ~30% yield and a complex mixture of unsaturated aluminacyclopentanes in ~50% yield.

The reactions with Et_2AlCl instead of $EtAlCl_2$ follow another pathway. Under the optimum conditions, these reactions afford predominantly unsaturated 1,2- and 1,4-dialuminum compounds (Scheme 3). Actually, the reactions of allenes **1a,c—e** with Et_2AlCl in THF in the presence of Cp_2TiCl_2 as the catalyst taken in the [Al] : $RCH=C=CH_2$: Mg : [Ti] ratio of ~44 : 20 : 24 : 1 gave rise to 2-alkyl(phenyl)-1,2-bis(diethylaluminio)-1-methylidenoethanes (**11a,c—e**) and 1,4-dialkyl(benzyl)idene-1,4-bis(diethylaluminio)butanes (**12a,c—e**) in a ratio of ~5 : 4 in a total yield of 75—80%. Mass-spectrometric analysis demonstrated that deuterolysis afforded not only 1,2- and 1,4-dideuterated compounds **8** and **10** but also monodeuterated alkenes in 10—15% yields, which indicates that dialumination was accompanied by competitive hydroalumination of allenes according to a scheme proposed previously.[10]

It should be noted that dialumination of allenes in the presence of Cp_2ZrCl_2 or $ZrCl_4$ (5 mol.%) as the catalyst facilitates the formation of unsaturated acyclic organoaluminum compounds **11** and a complex mixture of unsaturated regioisomeric 1,4-dialuminum compounds (according to the results of GLC and mass spectrometry of deuterolysis products) in a ratio of 1 : 2 in a total yield of ~80%.

The experimental results obtained in the present study and the published data[1—6] on cycloalumination of unsaturated compounds allowed us to suggest the most probable scheme of 1,2- and 1,4-dialumination of allenes in the presence of Cp_2TiCl_2 as the catalyst (Scheme 4). According to this scheme, Mg used in this reaction reduces Cp_2TiCl_2 to "Cp_2Ti". The formally divalent "titanocene" coordinates the allene molecule to form titanacyclo-

Scheme 3



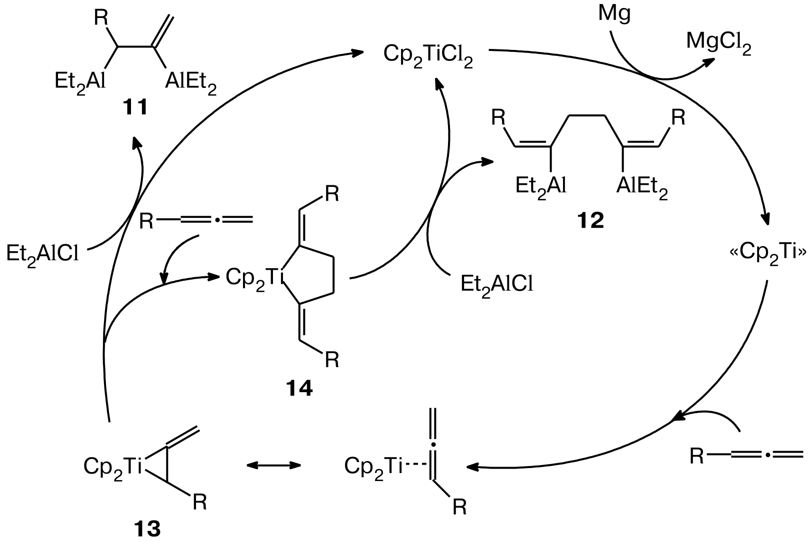
propane intermediate **13** whose transmetallation with Et_2AlCl affords 2-alkyl(phenyl)-1,2-bis(diethylaluminio)-1-methylidenoethane **11**. The insertion of the second allene molecule at the Ti—C bond of titanacyclopropane intermediate **13** facilitates the highly regioselective formation of 2,5-dialkyl(benzyl)idenetitanocyclopentane **14** whose transmetallation with the starting Et_2AlCl affords 1,4-dialkyl(benzyl)idene-1,4-bis(diethylaluminio)butane **12**.

Thus, the reactions of allenes with $EtAlCl_2$ or Et_2AlCl in the presence of Ti- or Zr-containing complex catalysts afford unsaturated aluminacyclopropanes and aluminacyclopentanes or 1,2- and 1,4-dialuminum compounds depending on the structures of the starting OAC.

Experimental

The reactions with organometallic compounds were carried out under dry argon. The starting allenes, Cp_2TiCl_2, and Cp_2ZrCl_2 were prepared according to known procedures.[12—15] Commercially available 86% $EtAlCl_2$ and 86% Et_2AlCl were purchased from the Redkinskii pilot-production plant (Russia). Tetrahydrofuran was distilled from $LiAlH_4$ immediately before use. The GLC analysis of the hydrolysis and deuterolysis products was carried out on a Chrom-5 chromatograph (Ar as the carrier gas, 1200×3-mm column with 5% SE-30 or 15% PEG-6000 on Chromaton N-AW). The IR spectra were measured on a UR-20 spectrometer (films). The mass spectra were recorded on an MKh-1306 mass spectrometer (70 eV, 200 °C). The ^1H NMR spectra were measured on a Tesla BS-567

Scheme 4



spectrometer (100 MHz, Me_4Si as the internal standard) in $CDCl_3$. The ^{13}C NMR spectra were recorded on JEOL FX-90Q (22.5 MHz) and Bruker AM-300 spectrometers (75.46 MHz) with the JMOD mode broad-band and off-resonance proton decoupling. Elemental analysis was performed on a Carlo Erba instrument (model 1106). The yields and ratios of unsaturated OAC were determined by GLC of hydrolysis or deuterolysis products. The spectroscopic parameters of unsaturated OAC **2—4**, **11**, and **12** are not reported because of the complexity of their interpretation (^{13}C NMR spectra of these compounds have high-field signals for the C_α atoms characteristic of OAC, which are broadened due to relaxation on the ^{27}Al nuclei).

Reactions of allenes with $EtAlCl_2$ catalyzed by Cp_2TiCl_2 ($ZrCl_4$). A mixture of Cp_2TiCl_2 ($ZrCl_4$) (0.5 mmol), Mg (powder, 12 mg-at.), THF (10 mL), 1,2-diene (10 mmol), and $EtAlCl_2$ (13 mmol) was placed with stirring in a glass vessel under dry argon at 0 °C. The mixture was warmed to ~20 °C and stirred for 8—12 h. The reaction mixture was treated with 7—10% HCl or DCl in D_2O. The products were extracted with hexane, dried with $MgSO_4$, and isolated by distillation.

The reactions of allenes with Et_2AlCl catalyzed by Cp_2TiCl_2 ($ZrCl_4$) were carried out under the same conditions with the use of 2.2 mol. equiv. of Et_2AlCl (with respect to 1,2-diene).

Allylbenzene (5a). B.p. 74—75 °C (20 Torr). IR, ν/cm^{-1}: 3020, 2950, 2850, 1600, 1490, 1450, 940, 850. ^1H NMR, δ: 3.36 (d, 2 H, $PhC\underline{H}_2$, J = 7 Hz); 4.98—5.64 (m, 3 H, $-CH=CH_2$); 6.94 (m, 5 H, Ph). ^{13}C NMR, δ: 40.16 (t, C(1´)); 115.63 (t, C(3´)); 126.03 (d, C(4)); 128.24 (d, C(3), C(5)); 128.57 (d, C(2), C(6)); 137.45 (d, C(2´)); 143.90 (s, C(1)). MS, m/z: 118 $[M]^+$.

But-3-enylbenzene (5b). B.p. 62—63 °C (10 Torr). ^1H NMR, δ: 2.25—2.42 (m, 2 H, $C\underline{H}_2-C=$); 3.37 (t, 2 H, $PhCH_2$, J = 7 Hz); 4.85—6.08 (m, 3 H, $-CH=CH_2$); 7.00—7.29 (m, 5 H, Ph). ^{13}C NMR, δ: 35.35 (t, C(2´)); 39.00 (t, C(1´)); 114.60 (t, C(4´)); 125.72 (d, C(4)); 128.11 (d, C(3), C(5)); 129.15 (d, C(2), C(6)); 137.61 (d, C(3´)); 138.03 (s, C(1)). MS, m/z: 132 $[M]^+$.

Non-1-ene (5c). B.p. 58—59 °C (30 Torr). IR, ν/cm^{-1}: 2990, 2950, 2850, 1630, 1470, 910. ^1H NMR, δ: 0.81—0.93 (m, 3 H, Me); 1.07—1.46 (m, 10 H, CH_2); 1.81—2.17 (m, 2 H, $C\underline{H}_2-CH=CH_2$); 4.86—5.11 (m, 2 H, $CH_2=$); 5.57—6.04 (m, 1 H, $C\underline{H}=CH_2$). ^{13}C NMR, δ: 14.22 (q, C(9)); 22.87 (t, C(8)); 29.17, 29.37, 29.63 (t, C(4), C(5), C(6)); 32.10 (t, C(7)); 34.05 (t, C(3)); 114.17 (t, C(1)); 139.82 (d, C(2)). MS, m/z: 126 $[M]^+$.

Undec-1-ene (5d). B.p. 77—78 °C (15 Torr). ^1H NMR, δ: 0.77—0.89 (m, 3 H, Me); 1.07—1.46 (m, 14 H, CH_2); 1.80—2.17 (m, 2 H, $C\underline{H}_2-CH=CH_2$); 4.83—5.11 (m, 2 H, $CH_2=$); 5.35—5.58 (m, 1 H, $-C\underline{H}=C-$). ^{13}C NMR, δ: 14.09 (q, C(11)); 22.74 (t, C(10)); 28.98; 29.17; 29.37 (2 C); 29.56 (t, C(4), C(5), C(6), C(7), C(8)); 31.97 (t, C(9)); 33.26 (t, C(3)); 114.04 (t, C(1)); 139.27 (d, C(2)). MS, m/z: 154 $[M]^+$.

Dodec-1-ene (5e). B.p. 90—91 °C (10 Torr). ^1H NMR, δ: 0.83—0.96 (m, 3 H, Me); 1.09—1.46 (m, 16 H, CH_2); 1.81—2.17 (m, 2 H, $C\underline{H}_2-CH=CH_2$); 4.86—5.07 (m, 2 H, $CH_2=$); 5.33—5.58 (m, 1 H, $-C\underline{H}=CH_2$). ^{13}C NMR, δ: 14.22 (q, C(12)); 22.87 (t, C(11)); 29.17; 29.37; 29.56; 29.89 (t, 3 C, C(4), C(5), C(6), C(7), C(8), C(9)); 32.17 (t, C(10)); 34.05 (t, C(3)); 114.17 (t, C(1)); 139.22 (t, C(2)). MS, m/z: 168 $[M]^+$.

((*Z*)-Prop-1-enyl)benzene (6a). B.p. 67—68 °C (15 Torr). ^1H NMR, δ: 1.58 (d, 3 H, Me, J = 7 Hz); 5.33—5.73 (m, 1 H, $MeC\underline{H}=$); 6.40 (d, 1 H, $=C\underline{H}Ph$, $^3J_{H,H}$ = 12.0 Hz); 6.98—7.30 (m, 5 H, Ph). ^{13}C NMR, δ: 14.00 (q, C(3´)); 125.31 (d, C(2´)); 126.03 (d, C(4)); 128.57 (d, C(2), C(6)); 129.37 (d, C(3), C(5)); 131.04 (t, C(1´)); 139.95 (s, C(1)). MS, m/z: 118 $[M]^+$.

((*Z*)-But-2-enyl)benzene (6b). B.p. 64—65 °C (10 Torr). ^1H NMR, δ: 1.58 (d, 3 H, =CMe, J = 7 Hz); 3.36 (d, 2 H, $C\underline{H}_2Ph$, J = 7 Hz); 5.27—5.98 (m, 2 H, $C\underline{H}=C\underline{H}$); 7.02—7.30 (m, 5 H, Ph). ^{13}C NMR, δ: 13.99 (q, C(4´)); 39.20 (t, C(1´)); 122.39 (d, C(3´)); 125.90 (d, C(4)); 128.38 (d, C(3), C(5)); 128.51 (d, C(2), C(6)); 129.74 (t, C(2´)); 141.81 (s, C(1)). MS, m/z: 132 $[M]^+$.

Non-2-ene (*Z*(*E*)) (6c). B.p. 66—67 °C (40 Torr). ^1H NMR, δ: 0.82—0.94 (m, 3 H, Me); 1.20—1.52 (m, 8 H, CH_2); 1.56—1.68 (m, 3 H, =CMe); 1.77—2.13 (m, 2 H, $-CH_2-C=$); 5.21—5.58 (m, 2 H, $-HC=CH-$). ^{13}C NMR, δ: 12.66 (17.86) (q, C(1)); 14.15 (q, C(9)); 22.80 (t, C(8)); 27.03 (32.82) (t, C(4)); 29.17, 29.37 (t, C(5), C(6)); 31.90 (t, C(7)); 123.60 (124.57) (d, C(2)); 130.95 (131.70) (d, C(3)). MS, m/z: 126 $[M]^+$.

Undec-2-ene (*Z*(*E*)) (6d). B.p. 83—84 °C (20 Torr). ^1H NMR, δ: 0.82—0.96 (m, 3 H, Me); 1.04—1.28 (m, 12 H, CH_2); 1.56—1.68 (m, 3 H, =CMe); 1.77—2.13 (m, 2 H, $-C\underline{H}_2-CH=$); 5.27—5.55 (m, 2 H, $-HC=CH-$). ^{13}C NMR, δ: 12.86 (17.96) (q, C(1)); 22.87 (t, C(10)); 27.03 (33.82) (t, C(4)); 28.46, 29.17, 29.56, 29.82 (t, C(5), C(6), C(7), C(8)); 32.17 (t, C(9)); 123.53 (124.51) (d, C(2)); 130.88 (131.73) (d, C(3)). MS, m/z: 154 $[M]^+$.

Dodec-2-ene (*Z*(*E*)) (6e). B.p. 94—95 °C (5 Torr). ^1H NMR, δ: 0.82—0.96 (m, 3 H, Me); 1.09—1.28 (m, 14 H, CH_2); 1.56—1.68 (m, 3 H, =CMe); 1.74—2.13 (m, 2 H, $-C\underline{H}_2-CH=$); 5.27—5.58 (m, 2 H, $-HC=CH-$). ^{13}C NMR, δ: 12.82 (18.02) (q, C(1)); 14.22 (t, C(12)); 22.87 (t, C(11)); 29.17, 29.37, 29.56, 29.89 (2 s, C(5), C(6), C(7), C(8), C(9)); 32.82 (t, C(10)); 123.96 (124.87) (d, C(2)); 130.95 (131.79) (d, C(3)). MS, m/z: 168 $[M]^+$.

(1*Z*,5*Z*)-1,6-Diphenylhexa-1,5-diene (7a). B.p. 180—182 °C (5 Torr). Found (%): C, 92.03; H, 7.20. $C_{18}H_{18}$. Calculated (%): C, 92.30; H, 7.70. IR, ν/cm^{-1}: 3050, 3020, 2920, 2250, 1600, 1500, 1490, 1450, 1080, 1030, 1000, 910, 720, 700. ^1H NMR, δ: 2.20—2.45 (m, 4 H, $CH_2-C=C$); 5.45—5.73 (m, 2 H, $CH_2-C\underline{H}=$); 6.39 (d, 2 H, $=C\underline{H}-Ph$, $^3J_{H,H}$ = 11.7 Hz); 7.04—7.43 (m, 10 H, Ph). ^{13}C NMR, δ: 28.72 (t, C(3), C(4)); 126.59 (d, C_o Ph); 128.15 (d, C_o Ph); 128.73 (d, C_m Ph); 129.45 (d, C(1), C(6)); 131.47 (d, C(2), C(5)); 137.51 (s, C_{ipso} Ph). MS, m/z: 234 $[M]^+$.

(2*Z*,6*Z*)-1,8-Diphenylocta-2,6-diene (7b). B.p. 182—183 °C (2 Torr). Found (%): C, 91.06; H, 8.25. $C_{20}H_{22}$. Calculated (%): C, 91.60; H, 8.40. IR, ν/cm^{-1}: 3050, 3020, 2900, 2800, 1600, 1450, 900, 720, 700. ^1H NMR, δ: 2.20—2.55 (m, 4 H, $CH_2-C=C$); 3.36 (d, 4 H, $Ph-C\underline{H}_2-C=$, J = 7 Hz); 5.45—5.80 (m, 2 H, $CH_2-C\underline{H}=$); 7.00—7.40 (m, 10 H, Ph). ^{13}C NMR, δ: 28.93 (t, C(4), C(5)); 34.49 (t, C(1), C(8)); 126.62 (d, C_p Ph); 128.51 (d, C_o Ph); 129.10 (d, C_m Ph); 129.42 (d, C(2), C(7)); 130.75 (d, C(3), C(6)); 140.33 (s, C_{ipso} Ph). MS, m/z: 262 $[M]^+$.

(7*Z*,11*Z*)-Octadeca-7,11-diene (7c). B.p. 137—139 °C (2 Torr). Found (%): C, 85.90; H, 13.42. $C_{18}H_{34}$. Calculated (%): C, 86.40; H, 13.60. IR, ν/cm^{-1}: 3000, 2950, 2900, 2820, 1640, 1450, 900, 730. ^1H NMR, δ: 0.76—0.90 (m, 6 H, Me); 1.06—1.43 (m, 16 H, CH_2); 1.90—2.33 (m, 8 H, $CH_2-C=C$); 5.28—5.38 (m, 4 H, CH=CH). ^{13}C NMR, δ: 14.22 (q, C(1), C(18)); 22.80 (t, C(2), C(17)); 27.35 (t, C(6), C(13)); 27.55 (t, C(9), C(10)); 29.43, 29.63 (t, C(4), C(5), C(14), C(15)); 32.04 (t, C(3), C(16)); 129.25 (d, C(8), C(11)); 130.49 (d, C(7), C(12)). MS, *m/z*: 250 [M]$^+$.

(9*Z*,13*Z*)-Docosa-9,13-diene (7d). B.p. 189—191 °C (2 Torr). Found (%): C, 86.12; H, 13.50. $C_{22}H_{42}$. Calculated (%): C, 86.27; H, 13.73. IR, ν/cm^{-1}: 3000, 2950, 2850, 1640, 1450, 1380, 970, 810, 790, 720. ^{1}H NMR, δ: 0.76—0.89 (m, 6 H, Me); 1.10—1.45 (m, 24 H, CH_2); 1.95—2.12 (m, 8 H, CH_2—C=C); 5.22—5.35 (m, 4 H, CH=CH). ^{13}C NMR, δ: 14.22 (q, C(1), C(22)); 22.80 (t, C(2), C(21)); 27.35 (t, C(8), C(15)); 27.55 (t, C(11), C(12)); 29.43 (2 C); 29.63, 29.89 (t, C(4), C(5), C(6), C(7), C(16), C(17), C(18), C(19)); 32.04 (t, C(3), C(20)); 129.25 (d, C(10), C(13)); 130.49 (d, C(9), C(14)). MS, *m/z*: 306 [M]$^+$.

(10*Z*,14*Z*)-Tetracosa-10,14-diene (7e). B.p. 217—218 °C (2 Torr). Found (%): C, 85.96; H, 13.60. $C_{24}H_{46}$. Calculated (%): C, 86.23; H, 13.77. IR, ν/cm^{-1}: 3000, 2950, 2920, 2850, 1640, 1480, 1380, 970, 810, 790, 720. ^{1}H NMR, δ: 0.81—0.94 (m, 6 H, Me); 1.19—1.28 (m, 28 H, CH_2); 1.99—2.11 (m, 8 H, CH_2—C=C); 5.32—5.44 (m, 4 H, CH=CH). ^{13}C NMR, δ: 14.22 (q, C(1), C(24)); 22.80 (t, C(2), C(23)); 27.35 (t, C(9), C(16)); 27.55 (t, C(12), C(13)); 29.50 (2 C); 29.70 (3 C) (t, C(4), C(5), C(6), C(7), C(8), C(17), C(18), C(19), C(20), C(21)); 32.04 (t, C(3), C(22)); 129.25 (d, C(11), C(14)); 130.49 (d, C(10), C(15)). MS, *m/z*: 334 [M]$^+$.

(1,2-Dideuterioallyl)benzene (8a). B.p. 81—82 °C (30 Torr). Found (%): C, 89.62; H, D, 9.87. $C_9H_8D_2$. Calculated (%): C, 90.00; H, 6.67, D, 3.33. IR, ν/cm^{-1}: 3070, 3050, 3010, 2910, 2170 (C—D), 1600, 1490, 1450, 1020, 920, 700. ^{1}H NMR, δ: 3.35 (s, H, Ph—CHD); 5.04 (s, 2 H, CH_2=CD); 6.38—7.27 (m, 5 H, Ph). ^{13}C NMR, δ: 39.80 (d, C(1´), $J_{C,D}$ = 19.8 Hz); 115.63 (t, C(3´)); 126.03 (d, C(4)); 128.24 (d, C(2), C(6)); 128.37 (d, C(3), C(5)); 137.12 (s, C(2´), $J_{C,D}$ = 23.4 Hz); 143.91 (s, C(1)). MS, *m/z*: 120 [M]$^+$.

(2,3-Dideuteriobut-3-enyl)benzene (8b). B.p. 70—71 °C (15 Torr). Found (%): C, 89.16; H, D, 9.90. $C_{10}H_{10}D_2$. Calculated (%): C, 89.55; H, 7.46; D, 2.99. IR, ν/cm^{-1}: 3075, 3020, 2920, 2840, 2170 (C—D), 1600, 1490, 1450, 1020, 910, 740, 700. ^{1}H NMR, δ: 2.25—2.46 (m, 1 H, CHD—C=C); 3.23—3.44 (m, 2 H, CH_2—Ph); 5.03 (s, 2 H, CH_2=CD); 6.94—7.25 (m, 5 H, Ph). ^{13}C NMR, δ: 35.03 (d, C(2´), $J_{C,D}$ = 19.8 Hz); 38.99 (t, C(1´)); 114.62 (t, C(4´)); C(3´)*; 125.68 (d, C(4)); 128.06 (d, C(3), C(5)); 128.21 (d, C(2), C(6)); 138.03 (s, C(1)). MS, *m/z*: 134 [M]$^+$.

2,3-Dideuterionon-1-ene (8c). B.p. 52—54 °C (20 Torr). Found (%): C, 83.92; H, D, 15.20. $C_9H_{16}D_2$. Calculated (%): C, 84.37; H, 12.50; D, 3.13. IR, ν/cm^{-1}: 3070, 2920, 2830, 2160 (C—D), 1460, 910, 800, 740. ^{1}H NMR, δ: 0.76—0.96 (m, 3 H, Me); 1.29—1.76 (m, 10 H, CH_2); 1.96—2.05 (m, 1 H, CHD—C=C); 4.95 (s, 2 H, CH_2=CD—). ^{13}C NMR, δ: 14.15 (q, C(9)); 22.87 (t, C(8)); 29.34; 29.59; 29.76 (t, C(4), C(5), C(6)); 32.10 (t, C(7)); 34.05 (d, C(3), $J_{C,D}$ = 20.0 Hz); 115.00 (t, C(1)), 139.20 (s, C(2), $J_{C,D}$ = 23.0 Hz). MS, *m/z*: 128 [M]$^+$.

2,3-Dideuterioundec-1-ene (8d). B.p. 72—73 °C (10 Torr). Found (%): C, 84.15; H, D, 15.12. $C_{11}H_{20}D_2$. Calculated (%): C, 84.62; H, 12.82; D, 2.56. IR, ν/cm^{-1}: 3070, 2950, 2910, 2850, 2170 (C—D), 1620, 1450, 900, 810, 750. ^{1}H NMR, δ: 0.76—0.96 (m, 3 H, Me); 1.24—1.59 (m, 14 H, CH_2); 1.94—2.16 (m, 1 H, CHD—C=C); 4.93 (s, 2 H, CH_2=CD—). ^{13}C NMR, δ: 14.11 (q, C(11)); 22.76 (t, C(10)); 28.94; 29.26; 29.46; 29.65 (2 C) (t, C(4), C(5), C(6), C(7), C(8)); 32.06 (t, C(9)); 32.91 (d, C(3), $J_{C,D}$ = 20.5 Hz); 114.00 (t, C(1)); 138.84 (s, C(2), $J_{C,D}$ = 23.4 Hz). MS, *m/z*: 156 [M]$^+$.

2,3-Dideuteriododec-1-ene (8e). B.p. 72—73 °C (2 Torr). Found (%): C, 84.22; H, D, 15.06. $C_{12}H_{22}D_2$. Calculated (%): C, 84.70; H, 12.94; D, 2.36. IR, ν/cm^{-1}: 3065, 2950, 2900, 2800, 2170 (C—D), 1480, 900, 820, 750. ^{1}H NMR, δ: 0.76—0.96 (m, 3 H, Me); 1.20—1.44 (m, 16 H, CH_2); 1.94—2.14 (m, 1 H, CHD—C=C); 4.89 (s, 2 H, CH_2=CD—). ^{13}C NMR, δ: 14.22 (q, C(12)); 22.80 (t, C(11)); 28.98; 29.30; 29.50; 29.69; 29.76 (2 C) (t, C(4), C(5), C(6), C(7), C(8), C(9)); 32.04 (t, C(10)); 33.47 (t, C(3), $J_{C,D}$ = 20.0 Hz); 114.04 (t, C(1)); 138.96 (s, C(2), $J_{C,D}$ = 23.0 Hz). MS, *m/z*: 170 [M]$^+$.

(2,3-Dideuterio-(*Z*)-prop-1-enyl)benzene (9a). B.p. 73—74 °C (20 Torr). Found (%): C, 89.32; H, D, 9.66. $C_9H_8D_2$. Calculated (%): C, 90.00; H, 6.67; D, 3.33. IR, ν/cm^{-1}: 3020, 2950, 2850, 2160 (C—D), 1650, 1450, 940, 850. ^{1}H NMR, δ: 1.58 (br.s, 2 H, CH_2D); 6.39 (br.s, 1 H, —CH=CD); 7.00—7.27 (m, 5 H, Ph). ^{13}C NMR, δ: 13.89 (t, C(3´), $J_{C,D}$ = 19.0 Hz); C(2´)*; 126.00 (d, C(4)); 128.40 (d, C(2), C(6)); 129.76 (d, C(3), C(5)); 130.20 (d, C(1´)); 139.95 (s, C(1)). MS, *m/z*: 120 [M]$^+$.

(3,4-Dideuterio-(*Z*)-but-2-enyl)benzene (9b). B.p. 72—73 °C (15 Torr). Found (%): C, 89.14; H, D, 10.27. $C_{10}H_{10}D_2$. Calculated (%): C, 89.55; H, 7.46; D, 2.99. IR, ν/cm^{-1}: 3080, 2920, 2160 (C—D), 1650, 1460, 900, 740, 700. ^{1}H NMR, δ: 1.60 (br.s, 2 H, CH_2D); 3.36 (d, 2 H, —CH_2—Ph, *J* = 7 Hz); 5.42 (t, 1 H, CH=CD, *J* = 7 Hz); 7.00—7.25 (m, 5 H, Ph). ^{13}C NMR, δ: 13.89 (t, C(4´), $J_{C,D}$ = 20.4 Hz); C(3´)*; 39.25 (t, C(1´)); 125.90 (d, C(4)); 128.35 (d, C(3), C(5)); 128.52 (d, C(2), C(6)); 130.00 (d, C(2´)); 141.81 (s, C(1)). MS, *m/z*: 134 [M]$^+$.

1,2-Dideuterionon-2-ene (*Z*(*E*)-9c)). B.p. 67—68 °C (40 Torr). Found (%): C, 83.88; H, D, 15.36. $C_9H_{16}D_2$. Calculated (%): C, 84.37; H, 12.50; D, 3.13. IR, ν/cm^{-1}: 3030, 2950, 2850, 2170 (C—D), 1640, 1450, 900, 850, 720. ^{1}H NMR, δ: 0.82—0.94 (m, 3 H, Me); 1.04—1.38 (m, 8 H, CH_2); 1.56 and 1.68 (both s, 2 H, CH_2D—C=C); 1.86—2.34 (m, 2 H, CH_2—C=C); 5.21—5.52 (m, 1 H, CH=CD—). ^{13}C NMR, δ: 12.48 (17.99) (t, C(1), $J_{C,D}$ = 19.5 Hz); 14.15 (q, C(9)); 23.06 (t, C(8)); 26.96 (33.99) (t, C(4)); 29.63, 29.80 (t, C(5), C(6)); 32.40 (t, C(7)); 123.53 (124.51) (s, C(2), $J_{C,D}$ = 22.4 Hz); 130.88 (131.73) (t, C(3)). MS, *m/z*: 128 [M]$^+$.

1,2-Dideuterioundec-2-ene (*Z*(*E*)-9d)). B.p. 83—84 °C (20 Torr). Found (%): C, 84.17; H, D, 15.14. $C_{11}H_{20}D_2$. Calculated (%): C, 84.62; H, 12.82; D, 2.56. IR, ν/cm^{-1}: 3020, 2900, 2850, 2170 (C—D), 1620, 1450, 900, 720. ^{1}H NMR, δ: 0.82 (m, 3 H, Me); 1.04—1.36 (m, 12 H, CH_2); 1.56 and 1.61 (both s, 2 H, CH_2D—C=C); 1.92—2.12 (m, 2 H, CH_2—C=C); 5.25—5.56 (m, 1 H, CH=CD). ^{13}C NMR, δ: 12.76 (17.87) (t, C(1), $J_{C,D}$ = 19.0 Hz); 14.22 (q, C(11)); 22.80 (t, C(10)); 26.96 (33.83) (t, C(4)); 29.17, 29.55, 29.75, 29.86 (t, C(5), C(6), C(7), C(8)); 32.04 (t, C(9)); 123.66 (124.57) (s, C(2), $J_{C,D}$ = 22.4 Hz); 131.01 (131.79) (d, C(3)). MS, *m/z*: 156 [M]$^+$.

1,2-Dideuteriododec-2-ene (*Z*(*E*)-9e). B.p. 94—95 °C (5 Torr). Found (%): C, 84.37; H, D, 15.06. $C_{12}H_{22}D_2$. Calculated (%): C, 84.70; H, 12.94; D, 2.36. IR, ν/cm^{-1}: 3025, 2950, 2900, 2850, 2170 (C—D), 1620, 1450, 920, 710. ^{1}H NMR, δ: 0.82—0.94 (m, 3 H, Me); 1.05—1.41 (m, 14 H, CH_2); 1.56 and 1.61 (both s, 2 H, CH_2D—C=C); 1.92—2.16 (m, 2 H, CH_2—C=C); 5.32—5.65 (m, 1 H, CD=CH). ^{13}C NMR, δ: 12.75 (17.99) (t, C(1), $J_{C,D}$ = 20.5 Hz); 14.15 (q, C(12)); 22.80

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* The signal is not observed.

* The signal is not observed.

(t, C(11)); 27.45 (t, C(9)); 27.03 (34.05) (t, C(4)); 29.40, 29.68, 29.76, 29.80 (2 C) (t, C(5), C(6), C(7), C(8)); 32.04 (t, C(10)); 123.66 (124.57) (s, C(2), $J_{\text{C,D}}$ = 22.4 Hz); 130.95 (131.79) (d, C(3)). MS, *m/z*: 170 $[M]^+$.

2,5-Dideuterio-(1*Z*,5*Z*)-1,6-diphenylhexa-1,5-diene (10a). B.p. 180—182 °C (5 Torr). Found (%): C, 91.16; H, D, 8.26. $C_{18}H_{16}D_2$. Calculated (%): C, 91.53; H, 6.77; D, 1.70. IR, ν/cm^{-1}: 3030, 2900, 2800, 2165 (C—D), 1600, 1500, 1450, 1080, 900, 720, 700. ^{1}H NMR, δ: 2.42 (br.s, 4 H, CH_2—C=C); 6.40 (br.s, 2 H, C=C<u>H</u>—Ph); 7.04—7.55 (m, 10 H, Ph). ^{13}C NMR, δ: 28.72 (t, C(3), C(4)); 126.59 (d, C_p Ph); 128.15 (d, C_o Ph); 128.73 (d, C_m Ph); 129.45 (d, C(1), C(6)); 131.47 (s, C(2), C(5), *J* = 23.4 Hz); 137.51 (s, C_{ipso} Ph). MS, *m/z*: 236 $[M]^+$.

3,6-Dideuterio-(2*Z*,6*Z*)-1,8-diphenylocta-2,6-diene (10b). B.p. 182—183 °C (2 Torr). Found (%): C, 90.56; H, D, 8.94. $C_{20}H_{20}D_2$. Calculated (%): C, 90.90; H, 7.58; D, 1.52. IR, ν/cm^{-1}: 3050, 3020, 2900, 2800, 2160 (C—D), 1600, 1500, 1450, 900, 720, 700. ^{1}H NMR, δ: 2.45 (br.s, 4 H, CH_2—C=C); 3.36 (d, 4 H, Ph—C<u>H</u>$_2$—, *J* = 7 Hz); 5.43 (t, 2 H, CD=CH, *J* = 7 Hz); 7.00—7.35 (m, 10 H, Ph). ^{13}C NMR, δ: 28.90 (t, C(4), C(5)); 34.42 (t, C(1), C(8)); 126.60 (d, C_p Ph); 128.52 (d, C_o Ph); 129.06 (d, C_m Ph); 129.40 (d, C(2), C(8)); 130.40 (s, C(3), C(6), $J_{\text{C,D}}$ = 22.5 Hz); 140.38 (s, C_{ipso} Ph). MS, *m/z*: 264 $[M]^+$.

8,11-Dideuterio-(7*Z*,11*Z*)-octadeca-7,11-diene (10c). B.p. 137—138 °C (2 Torr). Found (%): C, 85.33; H, D, 14.08. $C_{18}H_{32}D_2$. Calculated (%): C, 85.71; H, 12.70; D, 1.59. IR, ν/cm^{-1}: 3040, 3020, 2900, 2850, 2170 (C—D), 1640, 1450, 900, 720, 700. ^{1}H NMR, δ: 0.82—0.95 (m, 6 H, Me); 1.07—1.46 (m, 16 H, CH_2); 1.81—2.07 (m, 8 H, CH_2—C=C); 5.38 (t, 2 H, CD=CH, *J* = 7 Hz). ^{13}C NMR, δ: 14.22 (q, C(1), C(18)); 22.80 (t, C(2), C(17)); 27.42 (t, C(6), C(9), C(10), C(13)); 29.43, 29.63 (t, C(4), C(5), C(14), C(15)); 31.90 (t, C(3), C(16)); C(8)*; C(11)*; 130.30 (d, C(7), C(12)). MS, *m/z*: 252 $[M]^+$.

10,13-Dideuterio-(9*Z*,13*Z*)-docosa-9,13-diene (10d). B.p. 190—192 °C (2 Torr). Found (%): C, 85.41; H, D, 13.96. $C_{22}H_{40}D_2$. Calculated (%): C, 85.71; H, 12.99; D, 1.30. IR, ν/cm^{-1}: 3040, 3025, 2900, 2850, 2170 (C—D), 1640, 1450, 900, 720, 700. ^{1}H NMR, δ: 0.82—0.95 (m, 6 H, Me); 1.08—1.51 (m, 24 H, CH_2); 1.89—2.07 (m, 8 H, CH_2—C=C); 5.36 (t, 2 H, CD=CH, *J* = 7 Hz). ^{13}C NMR, δ: 14.15 (q, C(1), C(22)); 22.87 (t, C(2), C(21)); 27.41 (t, C(8), C(11), C(12), C(15)); 29.56 (4 C); 29.76 (4 C) (t, C(4), C(5), C(6), C(7), C(16), C(17), C(18), C(19)); 32.17 (t, C(3), C(20)); C(10)*; C(13)*; 130.17 (d, C(9), C(14)). MS, *m/z*: 308 $[M]^+$.

11,14-Dideuterio-(10*Z*,14*Z*)-tetracosa-10,14-diene (10e). B.p. 218—219 °C (2 Torr). Found (%): C, 85.29; H, D, 14.06. $C_{24}H_{44}D_2$. Calculated (%): C, 85.71; H, 13.09; D, 1.20. IR, ν/cm^{-1}: 3035, 2900, 2850, 2170 (C—D), 1620, 1450, 970, 720, 700. ^{1}H NMR, δ: 0.82—0.94 (m, 6 H, Me); 1.08—1.52 (m, 28 H, CH_2); 1.90—2.07 (m, 8 H, CH_2—C=C); 5.36 (t, 2 H, CD=CH, *J* = 7 Hz). ^{13}C NMR, δ: 14.15 (q, C(1), C(24)); 22.80 (t, C(2), C(23)); 27.42 (t, C(9), C(12), C(13), C(16)); 29.56 (2 C), 29.76 (3 C) (t, C(4), C(5), C(6), C(7), C(8), C(17), C(18), C(19), C(20), C(21)); 32.04 (t, C(3), C(22)); 130.40 (d, C(10), C(15)); C(11)*; C(14)*. MS, *m/z*: 236 $[M]^+$.

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* The signal is not observed.