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G.A. Tolstikov on occasion of his 75th anniversary

## Cyclomagnesation of Cyclonona-1,2-diene with EtMgR Catalyzed by Cp<sub>2</sub>ZrCl<sub>2</sub>

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**Abstract**—Catalytic cyclomagnesation of cyclonona-1,2-diene with EtMgR (R = Et, Hlg) in the presence of catalyst Cp<sub>2</sub>ZrCl<sub>2</sub> (5 mol%) was performed obtaining according to the reaction conditions either 10-magnesabicyclo[7.3.0<sup>1,9</sup>]dodec-8-ene or 3-ethylcyclonon-1-enyl-2-magnesiummethyl with a high regio- (>96%) and chemoselectivity (>75%).

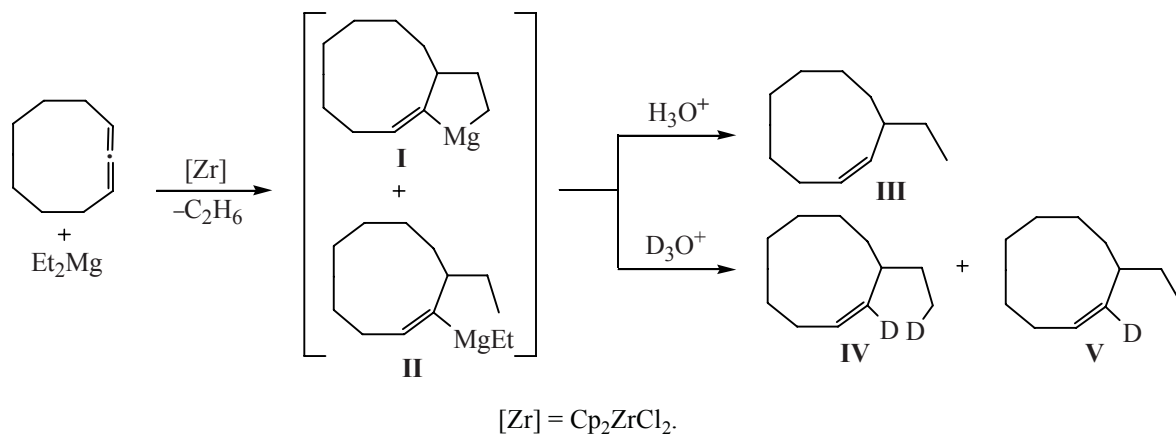
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Cyclomagnesation of terminal allenes with EtMgR (R = Et, Hlg) catalyzed by Cp<sub>2</sub>ZrCl<sub>2</sub> depending on the reaction conditions results in a mixture of regioisomeric magnesacyclopentanes or of carbomagnesation products with a high chemoselectivity [1, 2].

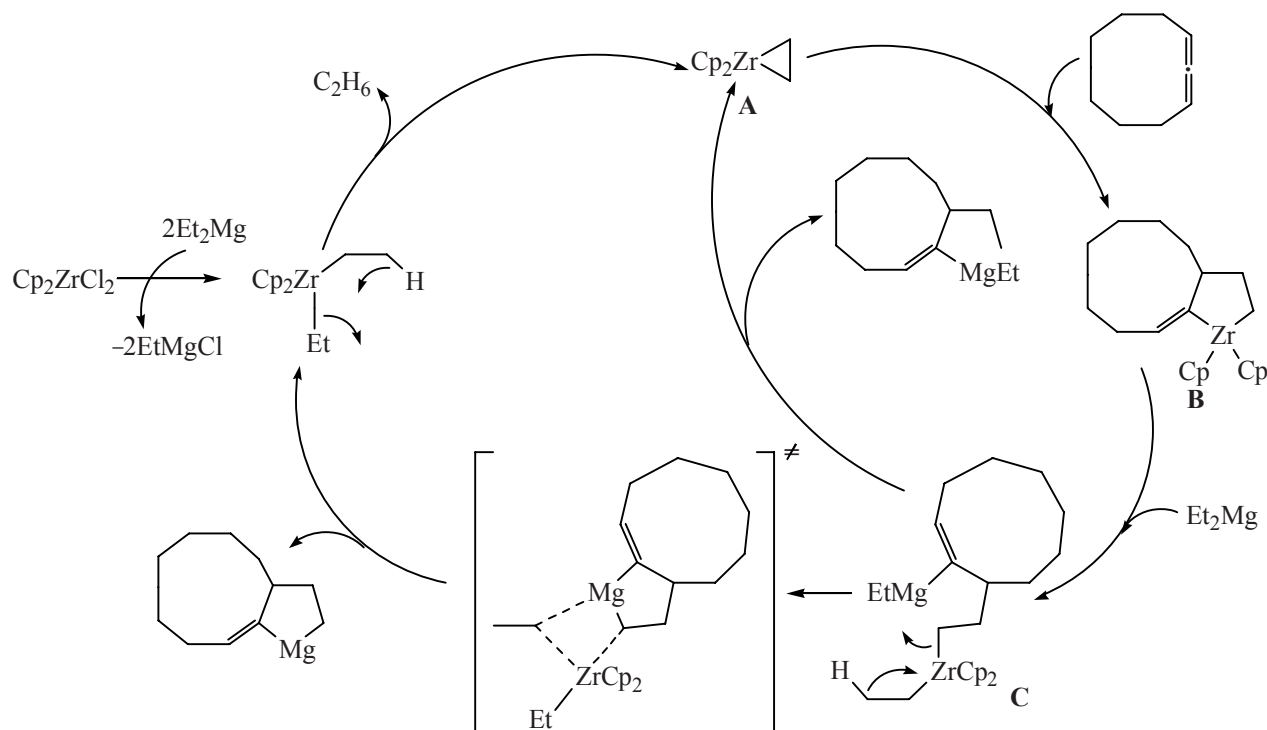
In continuation of the investigation of this reaction, in order to extend it to cyclic allenes, and also aiming at the synthesis of new classes of unsaturated bicyclic organomagnesium compounds we studied a reaction of cyclonona-1,2-diene with EtMgR (R = Et, Hlg) in the presence of the catalyst Cp<sub>2</sub>ZrCl<sub>2</sub> exhibiting a high activity and selectivity in the cyclomagnesation of  $\alpha$ -olefins [3–5], acetylenes [6], terminal 1,2-dienes [1, 2], and compounds of norbornene series [2, 7].

In reaction of cyclonona-1,2-diene with Et<sub>2</sub>Mg (Et<sub>2</sub>O) under the previously found optimal conditions for cyclomagnesation of  $\alpha$ -olefins [3–5] and 1,2-dienes [1, 2] (0°C, 8 h, cyclonona-1,2-diene: Et<sub>2</sub>Mg : Cp<sub>2</sub>ZrCl<sub>2</sub> = 10:20:0.05) organomagnesium compounds **I** and **II** formed in a ratio 91:9 in overall yield 79% (see the scheme). The yield of the reaction products was evaluated by the hydrolysis products **III** and **IV**. The ratio of products of cyclo- **I** and carbomagnesation **II** was estimated from the ratio of dideuterated compounds **IV** and monodeuterated substances **V** by the GC-MS method. The structure of compounds obtained was proved by the

<sup>1</sup>H and <sup>13</sup>C NMR spectra of products formed at the treatment with water and deuterium chloride in D<sub>2</sub>O solution. In the downfield region of the <sup>13</sup>C NMR spectrum of the hydrolysis product **III** two peaks appeared of equal intensity at  $\delta$  129.42 and 135.23 ppm assigned to the carbon atoms of the double bond in the cyclononene fragment. In the upfield region two signals were observed at 12.23 and 24.71 ppm belonging to the ethyl group in the  $\alpha$ -position with respect to the double bond of the cyclononene as showed the signal at 38.64 ppm. The signals were assigned taking into account the additive schemes for the cyclononene [8]. In the <sup>13</sup>C NMR spectrum of the product obtained by treatment with deuterium chloride **IV** upfield  $\alpha$ -isotope shifts were observed for atoms C<sup>2</sup> and C<sup>11</sup> ( $\Delta\delta$  0.22 and 0.29 ppm) with a triplet splitting of the signal by the coupling with the deuterium (C<sup>2</sup> <sup>1</sup>J<sub>C,D</sub> 23.5 Hz and C<sup>11</sup> <sup>1</sup>J<sub>C,D</sub> 19.05 Hz). The splitting of signals belonging to C<sup>2</sup> and C<sup>11</sup> atoms showed that the reaction with the deuterium chloride resulted in 1,4-dideuterated hydrocarbon suggesting the presence of two Mg–C bonds in the initial organomagnesium compound. Therefore based on the performed calculations and on the experimental data the structure of the organomagnesium compound obtained was regarded as 10-magnesabicyclo[7.3.0<sup>1,9</sup>]dodec-8-ene (**I**).



Scheme.



We believe [9, 10] that the formation of cyclic and acyclic organomagnesium compounds involves as the key intermediates zirconacyclopropane (**A**) and zirconacyclopentane complexes (**B**) whose successive transformations under the action of EtMgR (R = Et, Hlg) leads to the formation depending on the reaction conditions either to the products of cyclo- (**I**) or carbomagnesation (**II**) (see the scheme).

It follows from the scheme that the chemoselectivity of the reaction depends on the intramolecular transformations of bimetallic complex **C**. By varying the

reaction temperature, the solvent character (ethyl ether, THF, benzene, diisopropyl ether), and using alternatively Et<sub>2</sub>Mg, EtMgBr, and EtMgCl we found appropriate conditions for selective preparation of products of cyclo- or carbomagnesation of 1,2-cyclononadiene in high yields. For instance, whereas in the reaction of Et<sub>2</sub>Mg with 1,2-cyclononadiene in the presence of 5 mol% of Cp<sub>2</sub>ZrCl<sub>2</sub> in ethyl ether at ~0°C formed prevalingly the product of cyclomagnesation **I**, the reaction of EtMgBr with cyclonona-1,2-diene in THF at 20°C resulted mainly in the carbomagnesation **II**. In this case the

Effect of the organomagnesium compound, solvent, and temperature on the yield and ratio of products of cyclo- and carbomagnesation of cyclonona-1,2-diene

Organomagnesium compound	Solvent	Temperature, °C	Ratio <b>IV</b> : <b>V</b>	Overall yield of compounds <b>IV</b> and <b>V</b> , %
Et <sub>2</sub> Mg	Et <sub>2</sub> O	0	91:9	79
		20	86:14	82
		40	75:25	87
	THF	0	33:67	75
		20	21:79	79
		40	15:85	81
	Et <sub>2</sub> O–benzene, 1:1	0	59:41	84
		20	48:52	91
	Et <sub>2</sub> O–hexane, 1:1	20	47:53	45
EtMgBr		Et <sub>2</sub> O	0	68:32
	20		54:46	53
	THF	0	21:79	49
20		5:95	56	
EtMgCl	Et <sub>2</sub> O	20	55:45	56
	THF	20	8:92	59
Et <sub>2</sub> Mg	<i>i</i> -Pr <sub>2</sub> O	0	61:39	94
EtMgCl	<i>i</i> -Pr <sub>2</sub> O	0	52:48	92
		20	49:51	95
		40	46:54	98

treatment of the reaction mixture with deuterium chloride gave a mixture of di- **IV** and monodeuterated **V** hydrocarbons in a ratio 5:95 in overall yield 56%.

The replacement of EtMgBr for Et<sub>2</sub>Mg affected the chemoselectivity of the reaction by shifting it to the formation of carbomagnesation products and led to the reduction of the overall yield of the organomagnesium compounds **I** and **II**. The use of EtMgCl instead of EtMgBr did not considerably affect the yield and the ratio of reaction products. The addition of benzene or hexane to the solvent or the use of diisopropyl ether as solvent at any temperature resulted in the formation of a mixture of products of carbo- and cyclomagnesation in a ratio 1:1, but the application of a mixed solvent Et<sub>2</sub>O–benzene, 1:1, or of diisopropyl ether significantly raised the overall yield of the reaction products that in the case of *i*-Pr<sub>2</sub>O reached 98%.

The data on yields and the ratios of the mono- **V** and dideuterated **IV** products are presented in the table.

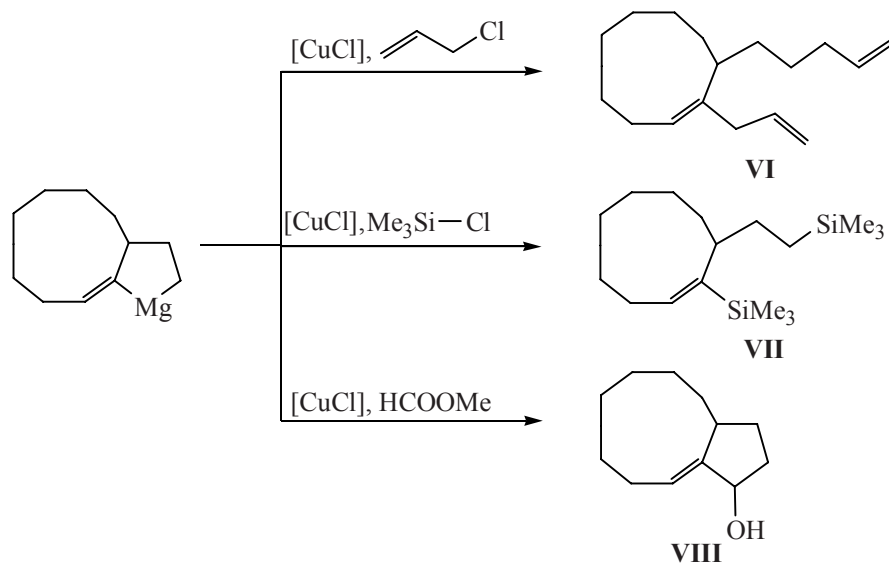
The observed high regioselectivity of the reaction is apparently due to the electron density distribution on the *sp*-hybridized carbon atom of the cyclonona-1,2-diene or to the  $\pi$ -*d*-interaction of the double bond of allene with the vacant *d*-orbital of the Zr atom; the latter can

favor a definite spatial orientation of the cyclonona-1,2-diene on the central atom of the catalyst and its further insertion into the Zr–C bond with the intermediate formation of zirconacyclopentane complex **B** with a double bond in a vinyl position with respect to Zr atom in the cyclononene fragment.

In the course of developing the optimal conditions of the reactions we discovered of cyclo- and carbomagnesation of cyclonona-1,2-diene it was established that increasing the concentration of the zirconium catalyst Cp<sub>2</sub>ZrCl<sub>2</sub> (over 10 mol%) resulted in a lower yield of the target products because of formation of high-molecular substances from the initial cyclonona-1,2-diene. At the use of less than 2 mol% of the catalysts the yield of organomagnesium compounds decreased due to the lower concentration in the reaction mixture of the catalytic active centers.

The change in the ratio of the initial reagents by increasing the content of EtMgR (R = Et, Hlg) with respect to the cyclonona-1,2-diene did not result in the greater overall yield of the target products.

When we established the effect of various factors on the chemoselectivity of the reaction of cyclonona-1,2-diene with EtMgR (R = Et, Hlg) we carried out a number



of transformations of the obtained magnesacyclopentane **II** in order to prove additionally its structure and also to show the promises of applying *one pot* procedures for the syntheses of compounds of complex structures based on the cyclomagnesation of cyclonona-1,2-diene: The cross-coupling of compound **II** with allyl chloride and trimethylchlorosilane in the presence of catalytic quantity of CuCl provided respectively 1-allyl-9-pent-4-en-1-yl-cyclononene (**VI**) and dimethyl{2-[(2-trimethylsilyl)-cyclonon-2-en-1-yl]-ethyl} silane (**VII**), and in the reaction of compound **II** with methyl formate in the presence of CuCl (10 mol%) formed 10-hydroxybicyclo[7.3.0]dodec-8-ene (**VIII**). The structure of compounds obtained was proved by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and by GC-MS method.

Thus the reaction of 1,2-cyclononadiene with EtMgR (R = Et, Hlg) in the presence of the catalyst  $\text{Cp}_2\text{ZrCl}_2$  depending on the reaction conditions led to the formation of products of either carbo- or cyclomagnesation with a high regio- (>96%) and chemoselectivity (>75%).

## EXPERIMENTAL

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were registered on a spectrometer JEOL FX-90 Q [89.55 ( $^1\text{H}$ ) and 22.5 MHz ( $^{13}\text{C}$ )] from solutions in  $\text{CDCl}_3$ . Yields of the organomagnesium compounds were evaluated by GLC of the hydrolysis products on a chromatograph Chrom-5, carrier gas helium, column 1200×3 mm, stationary phase 5% SE-30 or 15% PEG-6000 on Chromaton N-AW. The reactions with organometallic compounds were carried out in an atmosphere of dry argon. The ether solvents were distilled over  $\text{LiAlH}_4$  just before use. The solutions

of EtMgR (R = Et, Hlg) in  $\text{Et}_2\text{O}$  and THF were obtained by procedures from [11].

**Carbo- and cyclomagnesation of 1,2-cyclononadiene with EtMgR (R = Et, Hlg) in the presence of catalyst  $\text{Cp}_2\text{ZrCl}_2$ .** *General procedure.* Into a glass reactor under an atmosphere of dry argon at  $\sim 0^\circ\text{C}$  was charged at stirring 0.5 mmol of  $\text{Cp}_2\text{ZrCl}_2$ , 10 mmol of 1,2-cyclononadiene, and 20 mmol of EtMgR (R = Et, Hlg) in an appropriate ether solvent. The temperature was raised to ambient ( $20\text{--}22^\circ\text{C}$ ), and the stirring was continued for 8 h. For identification of the substituted magnesacyclopentadienes the reaction mixture was treated with 8% solution of DCl in  $\text{D}_2\text{O}$ . The reaction products were extracted into ether or hexane, the extract was dried with  $\text{MgSO}_4$  and subjected to fractionation.

**3-Ethylcyclononene (III).** bp  $81\text{--}83^\circ\text{C}$  (10 mm Hg).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.88 m (3H,  $\text{CH}_3$ ), 1.54 m (12H,  $\text{CH}_2$ ), 2.16 m (3H,  $\text{CH}_2\text{CH}=\text{CHCH}$ ), 5.39 m (2H,  $\text{CH}=\text{CH}$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 12.23 ( $\text{C}^{11}$ ), 24.71 ( $\text{C}^{10}$ ), 26.04 ( $\text{C}^7$ ), 26.21 ( $\text{C}^8$ ), 26.69 ( $\text{C}^5$ ), 26.82 ( $\text{C}^6$ ), 30.24 ( $\text{C}^9$ ), 33.92 ( $\text{C}^4$ ), 38.64 ( $\text{C}^3$ ), 129.42 ( $\text{C}^1$ ), 135.23 ( $\text{C}^2$ ). Found, %: C 86.35; H 12.89.  $[M]^+$  152.  $\text{C}_{11}\text{H}_{20}$ . Calculated, %: C 86.76; H 13.24.  $M$  152.

**1-Deutero-9-(2-deuteroethyl)cyclononene (IV).** bp  $81\text{--}83^\circ\text{C}$  (10 mm Hg).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.91 m (2H,  $\text{CH}_2\text{D}$ ), 1.47 m (12H,  $\text{CH}_2$ ), 2.05 m (3H,  $\text{CH}_2\text{CH}=\text{CDCH}$ ), 5.39 t (1H,  $\text{CH}=\text{CD}$ ,  $J$  5.0 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 12.01 ( $\text{C}^{11}$ ,  $J_{\text{C,D}}$  19.05 Hz), 24.67 ( $\text{C}^{10}$ ), 26.04 ( $\text{C}^7$ ), 26.20 ( $\text{C}^8$ ), 26.66 ( $\text{C}^5$ ), 26.79 ( $\text{C}^6$ ), 30.14 ( $\text{C}^9$ ), 33.92 ( $\text{C}^4$ ), 38.61 ( $\text{C}^3$ ), 129.45 ( $\text{C}^1$ ), 135.48 ( $\text{C}^2$ ,  $J_{\text{C,D}}$  23.45 Hz). Found, %: C 85.29; H+D 13.49.  $[M]^+$  154.  $\text{C}_{11}\text{H}_{18}\text{D}_2$ . Calculated, %: C 85.63; H 11.76; D 2.61.  $M$  154.

**1-Deutero-9-ethylcyclononene (V).** bp 81–83°C (10 mm Hg). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.90 m (3H, CH<sub>3</sub>), 1.45 m (12H, CH<sub>2</sub>), 2.01 m (3H, CH<sub>2</sub>CH=CDCH), 5.41 t (1H, CH=CD, *J* 5.0 Hz). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 12.11 (C<sup>11</sup>), 24.69 (C<sup>10</sup>), 26.12 (C<sup>7</sup>), 26.18 (C<sup>8</sup>), 26.67 (C<sup>5</sup>), 26.75 (C<sup>6</sup>), 30.21 (C<sup>9</sup>), 33.87 (C<sup>4</sup>), 38.63 (C<sup>3</sup>), 129.34 (C<sup>1</sup>), 135.38 (C<sup>2</sup>, *J*<sub>C,D</sub> 23.5 Hz). Found, %: C 85.32; H+D 13.21. [*M*]<sup>+</sup> 153. C<sub>11</sub>H<sub>19</sub>D. Calculated, %: C 86.19; H 12.49; D 1.32. *M* 153.

**Reaction of 10-magnesabicyclo[7.3.0<sup>1,9</sup>]dodec-8-ene with allyl chloride and trimethylchlorosilane catalyzed by CuCl. General procedure.** Into a glass reactor under an atmosphere of dry argon at 0°C was charged at stirring 10 mmol of allene, 0.5 mmol of Cp<sub>2</sub>ZrCl<sub>2</sub>, and 20 mmol of EtMgR (R = Et, Hlg) in Et<sub>2</sub>O. The temperature was raised to ambient (20–21°C), and the stirring was continued for 4 h, then at –20°C 1 mmol of CuCl was added, and slowly dropwise 25 mmol of allyl chloride (trimethylchlorosilane), the reaction mixture was warmed to room temperature and stirred for 6 h, then it was treated with 7–10% aqueous HCl, the reaction products were extracted into hexane, the extract was dried with MgSO<sub>4</sub>, and the products were isolated by vacuum distillation.

**1-Allyl-9-pent-4-en-1-ylcyclononene (VI).** Yield 71%, bp 122–123°C (1 mm Hg). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.48 m (14H, CH<sub>2</sub>), 2.07 m (5H, CH<sub>2</sub>CH=CHCH), 2.71 d (2H, CH=CHCH<sub>2</sub>CH=CH), 4.81 m (4H, CH=CH<sub>2</sub>), 5.42 m (3H, CH=CH<sub>2</sub>). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 27.11 (C<sup>5</sup>), 27.24 (C<sup>11</sup>), 27.34 (C<sup>4</sup>), 27.79 (C<sup>6</sup>), 29.91 (C<sup>7</sup>), 31.97 (C<sup>12</sup>), 32.88 (C<sup>8</sup>), 33.43 (C<sup>10</sup>), 34.05 (C<sup>3</sup>), 35.48 (C<sup>15</sup>), 38.93 (C<sup>9</sup>), 114.31 (C<sup>14</sup>), 115.58 (C<sup>17</sup>), 127.43 (C<sup>2</sup>), 137.73 (C<sup>16</sup>), 138.99 (C<sup>13</sup>), 140.17 (C<sup>1</sup>). Found, %: C 87.12; H 11.95. [*M*]<sup>+</sup> 232. C<sub>17</sub>H<sub>28</sub>. Calculated, %: C 87.86; H 12.14.

**Trimethyl{2-[(2-trimethylsilyl)-2-cyclononenyl]-ethyl}silane (VII).** Yield 69%, bp 118–119°C (1 mm Hg). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: –0.06 s (9H, CH<sub>3</sub>SiCH<sub>2</sub>), 0.09 s (9H, CH<sub>3</sub>SiC=), 0.29 m [2H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>], 1.48 m (12H, CH<sub>2</sub>), 2.08 m (3H, CH<sub>2</sub>CH=CCH), 5.52 m (1H, CH=C). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: –1.79 (C<sup>12</sup>, C<sup>13</sup>, C<sup>14</sup>), –0.9 (C<sup>15</sup>, C<sup>16</sup>, C<sup>17</sup>), 18.52 (C<sup>11</sup>), 26.23 (C<sup>5</sup>), 27.21 (C<sup>10</sup>), 27.67 (C<sup>6</sup>), 29.75 (C<sup>4</sup>), 30.17 (C<sup>3</sup>), 33.92 (C<sup>7</sup>), 38.74 (C<sup>2</sup>), 41.44 (C<sup>1</sup>), 136.04 (C<sup>8</sup>), 142.17 (C<sup>9</sup>). Found, %: C 68.53; H 11.98. [*M*]<sup>+</sup> 296. C<sub>17</sub>H<sub>36</sub>Si<sub>2</sub>. Calculated, %: C 68.83; H 12.23. *M* 296.

**10-Hydroxybicyclo[7.3.0<sup>1,9</sup>]dodec-8-ene (VIII).** Into a glass reactor under an atmosphere of dry argon at 0°C was charged at stirring 10 mmol of allene, 0.5 mmol of Cp<sub>2</sub>ZrCl<sub>2</sub>, and 20 mmol of EtMgR (R = Et, Hlg) in

Et<sub>2</sub>O. The reaction mixture was warmed to room temperature (20–21°C) and stirred for 4 h. Then at –15°C was added 1 mmol (10 mol%) of CuCl, and slowly dropwise 15 mmol of methyl formate. The reaction mixture was warmed to room temperature and stirred for 6–8 h, then it was treated with 7–10% aqueous HCl, the reaction products were extracted into hexane, and the extract was dried with MgSO<sub>4</sub>. The reaction product was isolated by column chromatography on silica gel L, 180/250  $\mu$ , eluent hexane–ethyl acetate, 10:1. Yield 67%, *R<sub>f</sub>* 0.45, bp 129–130°C (1 mm Hg). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.18–1.84 m (14H, CH<sub>2</sub>), 2.08 m (2H, CH<sub>2</sub>CH=CH), 2.62 m (1H, =CHCH), 4.91 m (1H, CHOH), 5.55 m (1H, CH=C). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 24.12 (C<sup>5</sup>), 25.81 (C<sup>6</sup>), 25.91 (C<sup>4</sup>), 26.79 (C<sup>3</sup>), 27.05 (C<sup>12</sup>), 32.55 (C<sup>11</sup>), 33.98 (C<sup>2</sup>), 35.81 (C<sup>7</sup>), 53.49 (C<sup>1</sup>), 74.77 (C<sup>10</sup>), 131.02 (C<sup>8</sup>), 133.82 (C<sup>9</sup>). Found, %: C 79.36; H 10.78. [*M*–18]<sup>+</sup> 162. C<sub>12</sub>H<sub>20</sub>O. Calculated, %: C 79.94; H 11.18. *M* 180.

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