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First Synthesis of Magnesacyclopentadienes from Acetylenes by Treatment with BuMgHlg in the Presence of Zr Complexes

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Abstract—Treatment of internal acetylenes and allenes with BuMgHlg (Hlg = Cl, Br) in the presence of Cp_2ZrCl_2 selectively leads to the formation of substituted magnesacyclopenta-2,4-dienes and alkylidenemagnesacyclopentenes.

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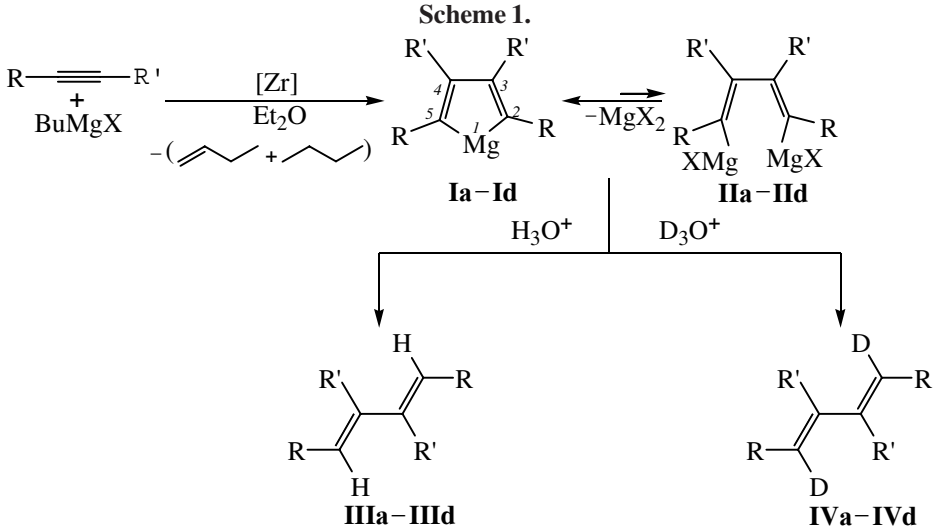
First publication on the direct catalytic preparation of a magnesacyclopentanes from olefins using Grignard reagents or R_2Mg appeared in 1989 [1]. Later this reaction was extended to allenes that in the presence of Ti-containing catalysts gave rise to 2,5-dialkylidenemagnesacyclopentanes in high yields [2]. Until our studies no information was published on the possibility to involve acetylenes into this process.

The target of this study consists in the synthesis of a new class of organomagnesium compounds, magnesacyclopentadienes, by reaction of internal acetylenes with Grignard reagents in the presence of catalysts containing zirconium complexes which are the most active and selective in cyclometallation of unsaturated compounds [3, 4]. As objects of the study were chosen internal acetylenes and available alkylmagnesium halides.

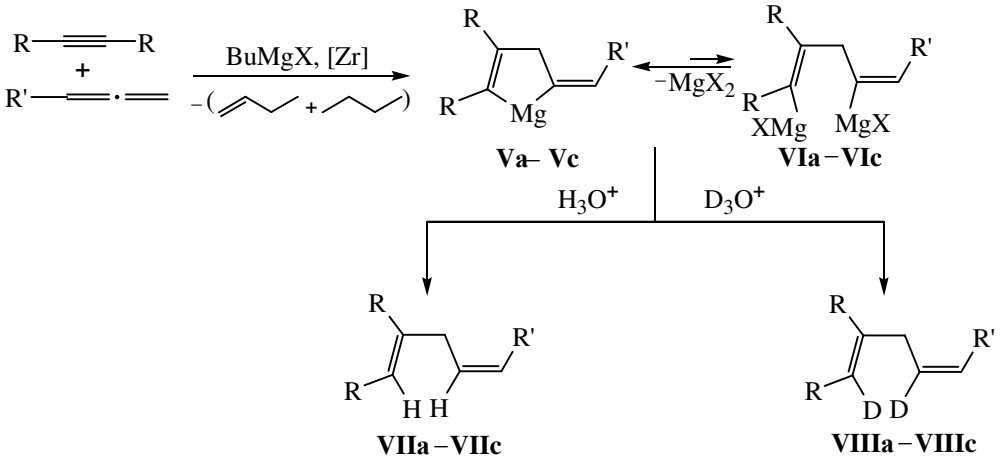
The reaction of 4-octyne with BuMgBr (Et_2O) in molar ratio 1:2 catalyzed by Cp_2ZrCl_2 (10 mol%) gave rise at ~20°C within 2 h to 2,3,4,5-tetrapropylmagnesacyclopentadiene (**Ib**) in ~ 50% yield. The structure and composition of magnesacyclopentadiene **Ib** were established from the ^{13}C NMR spectra and from analysis of products of hydrolysis **IIIb** and of reaction with deuterium oxide **IVb** (Scheme 1).

Scheme 1.



[Zr] = Cp_2ZrCl_2; X = Cl, Br; R = R' = Et (**a**), Pr (**b**), Bu (**c**); R = Me_3Si, R' = Bu (**d**).

Scheme 2.



[Zr] = Cp_2ZrCl_2; X = Cl, Br; R = Et, R' = Amyl (**a**); R = Pr, R' = Amyl (**b**); R = Pr, R' = Ph (**c**).

^{13}C NMR spectrum of compound **Ib** contains a downfield signal at 191.10 ppm that we assumed to belong to *sp*²-carbon atom (C^2–Mg) of magnesacyclopentadiene ring. This conclusion was based on previously published data [5] that in the ^{13}C NMR spectrum of a mixture containing 2,5-dihexylidenemagnesacyclopentane and unsaturated acyclic 1,4-dimagnesium compound existing in a Schlenk equilibrium appeared signals at 188.30 and 166.36 ppm belonging respectively to the *sp*²-carbon atoms (C–Mg) in the cyclic and the acyclic compounds respectively. Therefore the presence in the ^{13}C NMR spectrum of compound **Ib** of the signal at 190.16 ppm and no signal in the region ~166 ppm may indicate that for the nixture of compounds **Ib** and **IIb** the Schlenk equilibrium is shifted to magnesacyclopentadiene **Ib**. To prove this assumption we added to a mixture of compounds **Ib** and **IIb** 1,4-dioxane which formed with magnesium dihalide insoluble in ether complex [6] thus shifting the Schlenk equilibrium to the cyclic compound **Ib** [7]. On removing by centrifugation insoluble in ether magnesium dihalide dioxanate ($MgBr_2$·2dio) the ^{13}C NMR spectrum of compound **Ib** contained only the downfield signal of the carbon atom (C^2–Mg) at 190.22 ppm; it also supported the cyclic structure of compound **Ib** obtained in Et_2O. The replacement of the initial BuMgBr by BuMgCl did not significantly influence the yield of the target product, but in reaction carried out in THF the yield of compound **Ib** did not exceed 15%.

Under the developed conditions (~20°C, 2 h, 10 mol% of Cp_2ZrCl_2, Et_2O) reactions of 3-hexyne, 5-decyne, and 1-hexynyltrimethylsilane with excess BuMgHlg (Hlg = Cl, Br) led to the formation of the corresponding magnesacyclopentadienes **Ia, Ic**, and **Id** in 45–50% yields. We believe that the formation of the cyclic structure **I** originates from Zr-containing cyclic intermediates arising under the reaction conditions in keeping with the scheme assumed for the formation of magnesacycles from α-olefins [8] and α,ω -diolefins [9].

We tried further to carry out intermolecular reaction of acetylene and allene in equimolar amounts with BuMgHlg (Hlg = Cl, Br) in the presence of catalyst Cp_2ZrCl_2 in order to obtain alkylidenemagnesacyclopentenes whose stucture contained potentially richer synthetic opportunities than that of magnesacyclopentadienes. Actually, the reaction of a mixture of 3-hexyne and 1,2-octadiene with excess BuMgBr (acetylene–allene–BuMgBr, 1:1:2) in Et_2O in the presence of 10 mol% Cp_2ZrCl_2 within 2 h led to the formation of 2,3-diethyl-5-hexylidenemagnesacyclopent-2-ene (**Va**) in ~45% yield (Scheme 2). In minor quantity (up to 10%) formed 2,3,4,5-tetraethylmagnesacyclopentadiene (**Ia**).

Under the above conditions 4-octyne and 1,2-octadiene or 4-octyne and 1-(1,2-propadienyl)benzene reacted with excess BuMgHlg (Hlg = Cl, Br) giving the corresponding alkyl(benzyl)idenemagnesacyclopentanes **Vb** and **Vc** in 45–50% yield. Alongside the latter minor amounts of the corresponding 2,3,4,5-substituted magnesacyclopentadienes **Ia** and **Ib** were isolated from the reaction mixture in an yield not exceeding 15%.

Thus we first succeded to involve into the Cp_2ZrCl_2-catalyzed reaction with BuMgHlg (Hlg = Cl, Br) acetylenes and their equimolar mixture with allenes and to obtain a new class of organomagnesium compounds: magnesacyclopentadienes and 2-alkylidenemagnesacyclopentenes possessing a wide synthetic potential, and also interesting as new cocatalysts in the Ziegler–Natta systems and

promising organomagnesium reagents in organic and organometallic syntheses.

EXPERIMENTAL

Products of hydrolysis and of reaction with deuterium oxide were analyzed on a chromatograph Chrom-5 in a helium flow, column 1200× 3 mm, stationary phase 5% SE-30 or 15% PEG-6000 on Chromaton N-AW. IR spectra were recorded on a spectrophotometer 75IR from films, mass spectra were obtained on MKh-1306 instrument at 200°C, ionizing electrons energy 70 eV. ^{1}H and ^{13}C NMR spectra were registered from solutions in $CDCl_3$ on a spectrometer JEOL FX-90 Q [89.55 (^{1}H) and 22.5 MHz (^{13}C)]. The yields of organo-magnesium compounds were determined based on GLC analysis of their hydrolysis products. The reactions with organomagnesium compounds were carried out in a dry argon flow. Ethyl ether was distilled over $LiAlH_4$ just before use. A solution of BuMgHlg (Hlg = Cl, Br) in Et_2O was prepared by procedure from [10].

Acetylene reaction with BuMgHlg (Hlg = Cl, Br) catalyzed by Cp_2ZrCl_2. Into a glass reactor under atmosphere of dry argon at ~ 0°C was charged while stirring 1.0 mmol of Cp_2ZrCl_2, 10 mmol of acetylene, and 20 mmol of BuMgHlg (Hlg = Cl, Br) (2 M solution in Et_2O). The temperature was raised to ambient (20–22°C), and the mixture was stirred for 2 h. In order to identify the substituted magnesacyclopentadienes by the products of reaction with deuterium oxide the reaction mixture was treated with 8% DCl in D_2O. The reaction products were extracted with ether or hexane, the extracts were dried over $MgSO_4$, the target products were isolated by fractional distillation. Compounds **IVa–IVc** were identified by comparison with authentic samples [11, 12].

2,3,4,5-Tetraethylmagnesacyclopenta-2,4-diene (Ia). *a*. Reaction in ether solution. ^{13}C NMR spectrum, δ, ppm: 13.38 ($C^{14,17}$), 14.16 ($C^{8,11}$), 20.87 ($C^{13,16}$), 22.76 ($C^{7,10}$), 31.29 ($C^{12,15}$), 32.04 ($C^{6,9}$), 132.75 ($C^{3,4}$), 190.16 ($C^{2,5}$).

b. Reaction in 1,4-dioxane–ether mixture. ^{13}C NMR spectrum, δ, ppm: 13.41 ($C^{14,17}$), 14.55 ($C^{8,11}$), 21.00 ($C^{13,16}$), 22.82 ($C^{7,10}$), 30.89 ($C^{12,15}$), 31.68 ($C^{6,9}$), 132.75 ($C^{3,4}$), 190.22 ($C^{2,5}$).

2,3,4,5-Tetrapropylmagnesacyclopenta-2,4-diene. *a*. Reaction in ether solution. ^{13}C NMR spectrum, δ, ppm: 14.13 ($C^{11,13}$), 14.26 ($C^{7,9}$), 31.29 ($C^{10,12}$), 32.07 ($C^{6,8}$), 133.92 ($C^{3,4}$), 191.10 ($C^{2,5}$).

b. Reaction in 1,4-dioxane–ether mixture. ^{13}C NMR spectrum, δ, ppm: 14.23 ($C^{11,13}$), 14.88 ($C^{7,9}$), 31.84 ($C^{10,12}$), 32.33 ($C^{6,8}$), 133.79 ($C^{3,4}$), 191.07 ($C^{2,5}$).

4,5-Diethylocta-3,5-diene (IIIa), bp 89–91°C (15 mm Hg.). IR spectrum, ν, cm^{-1}: 3080, 2950, 2900, 2850, 1640, 1450, 1370, 910, 895, 720. ^{1}H NMR spectrum, δ, ppm: 0.82–1.05 m (12H, CH_3), 2.06–2.25 m (8H, =C–CH_2), 5.25–5.75 (2H, –HC=C–). ^{13}C NMR spectrum, δ, ppm: 13.77, 14.55 ($C^{1,8}$), 20.93, 21.23 ($C^{2,7}$), 126.50 ($C^{3,6}$), 141.23 ($C^{4,5}$). Found, %: C 86.27; H 13.06. $[M]^+$ 166. $C_{12}H_{22}$. Calculated, %: C 86.67; H 13.33.

5,6-Dipropyldeca-4,6-diene (IIIb). bp 95–97°C (1 mm Hg). IR spectrum, ν, cm^{-1}: 3000, 2950, 2850, 1640, 1420, 1380, 970, 810, 790, 720. ^{1}H NMR spectrum, δ, ppm: 0.85–1.23 m (12H, CH_3), 1.33–1.75 m (8H, CH_2), 1.96–2.35 m (8H, =C–CH_2), 5.25-5.65 (2H, HC=C). ^{13}C NMR spectrum, δ, ppm: 13.89, 14.61 ($C^{1,10}$), 22.03, 23.27 ($C^{2,9}$), 30.04, 30.30 ($C^{3,8}$), 126.10 ($C^{4,7}$), 141.41 ($C^{5,6}$). Found, %: C 86.07; H 13.16. $[M]^+$ 222. $C_{16}H_{30}$. Calculated, %: C 86.40; H 13.60.

6,7-Dibutyldodeca-5,7-diene (IIIc). bp 137–139°C (1 mm Hg). IR spectrum, ν, cm^{-1}: 3000, 2950, 2900, 2820, 1640, 1450, 900, 730. ^{1}H NMR spectrum, δ, ppm: 0.86–1.12 m (12H, CH_3), 1.23–1.79 m (16H, CH_2), 1.98–2.26 m (8H, =C–CH_2), 5.25–5.85 (2H, HC=C). ^{13}C NMR spectrum, δ, ppm: 13.76, 14.13 ($C^{1,12}$), 22.56, 22.97 ($C^{2,11}$), 27.83 ($C^{3,10}$), 28.05 ($C^{4,9}$), 31.13, 31.29, 125.86 ($C^{5,8}$), 141.27 ($C^{6,7}$). Found, %: C 85.95; H 13.17. $[M]^+$ 278. $C_{20}H_{38}$. Calculated, %: C 86.25; H 13.75.

2,3-Dibutyl-1,3-butadiene-1,4-diylbistrimethylenesilane (IIId). bp 108–110°C (1 mm Hg). IR spectrum, ν, cm^{-1}: 3080, 2920, 2850, 2300, 1640, 1460, 910, 720. ^{1}H NMR spectrum, δ, ppm: 0.30–0.42 [18H, $CSi(CH_3)_3$], 0.85–0.95 m (6H, CH_3), 1.1–1.5 m (8H, CH_2), 1.95–2.10 m (4H, =C–CH_2), 5.52–5.83 m (2H, C=CH). ^{13}C NMR spectrum, δ, ppm: 0.28 ($C^{13,14,15,16,17,18}$), 14.15 ($C^{7,11}$), 23.21 ($C^{6,10}$), 31.82 ($C^{5,9}$), 33.93 ($C^{4,8}$), 125.32 ($C^{2,3}$), 161.08 ($C^{1,12}$). Found, %: C 68.85; H 12.02. $[M]^+$ 310. $C_{18}H_{38}Si_2$. Calculated, %: C 69.14; H 11.61.

2,3-Dibutyl-1,4-dideutero-1,3-butadiene-1,4-diylbistrimethylenesilane (IVd). bp 108–110°C (1 mm Hg). IR spectrum, ν, cm^{-1}: 2170 (CD). ^{1}H NMR spectrum, δ, ppm: 0.32–0.41 [18H, $CSi(CH_3)_3$], 0.83–0.96 m (6H, CH_3), 1.11–1.53 m (8H, CH_2), 1.96–2.15 m (4H, =C–CH_2). ^{13}C NMR spectrum, δ, ppm: 0.24($C^{13,14,15,16,17,18}$), 14.06 ($C^{7,11}$), 23.11 ($C^{6,10}$), 31.72 ($C^{5,9}$), 33.86 ($C^{4,8}$), 125.60 ($C^{2,3}$), 160.72 t ($C^{1,12}$, $J_{C,D}$ 24.0 Hz). Found, %: C 68.85; (H+D) 12.02. $[M]^+$ 312. $C_{18}H_{36}Si_2D_2$. Calculated, %: C 69.14; H 11.61; D 1.29.

Reaction of a mixture of acetylenes and allenes with BuMgHlg (Hlg = Cl, Br) catalyzed by Cp_2ZrCl_2. Into a glass reactor under atmosphere of dry argon at ~ 0°C was charged while stirring 1.0 mmol of Cp_2ZrCl_2, 10 mmol of acetylene, 10 mmol of allene, and 20 mmol of BuMgHlg (Hlg = Cl, Br) (2 M solution in Et_2O). The temperature was raised to ambient (20–22°C), and the mixture was stirred for 2 h. In order to identify the substituted alkylidenemagnesacyclopentenes by the products of reaction with deuterium oxide the reaction mixture was treated with 8% DCl in D_2O. The reaction products were extracted with ether or hexane, the extracts were dried over $MgSO_4$, the target products were isolated by fractional distillation.

4-Ethyl-3,6-dodecadiene (VIIa). bp 102–104°C (5 mm Hg). IR spectrum, ν, cm^{-1}: 3030, 2900, 2800, 1650, 1490, 1450, 1000, 910, 890, 720, 700. ^1H NMR spectrum, δ, ppm: 0.87–0.93 m (9H, CH_3), 1.1–1.58 m (6H, CH_2), 1.95–2.69 m (8H, =C–C$\underline{H}_2$), 5.45–5.82 m (3H, C=C$\underline{H}$). ^{13}C NMR spectrum, δ, ppm: 13.38, 14.02 (C^{12}), 14.65 (C^1), 20.19 (C^2), 22.85 (C^{11}), 23.78, 27.21 (C^8), 29.69 (C^9), 30.29 (C^{10}), 36.34 (C^5), 125.68 (C^3), 128.15 (C^6), 130.89 (C^7), 131.77 (C^4). $[M]^+$ 194. Found, %: C 86.03; H 12.99. $C_{14}H_{26}$. Bû ×θCλε-νO, %: C 86.52; H 13.48.

5-Propyl-4,7-tridecadiene (VIIb). bp 98–100°C (1 mm Hg). IR spectrum, ν, cm^{-1}: 3035, 2950, 2860, 1640, 1470, 1450, 1390, 1000, 910, 890, 730. ^1H NMR spectrum, δ, ppm: 0.90–1.15 m (9H, CH_3), 1.21–1.59 m (10H, CH_2), 1.95–2.70 m (8H, =C–C$\underline{H}_2$), 5.55–5.85 m (3H, C=C$\underline{H}$). ^{13}C NMR spectrum, δ, ppm: 13.86, 14.05 (C^{13}), 14.59 (C^1), 22.08, 22.89 (C^{12}), 23.31 (C^2), 27.35 (C^9), 29.76 (C^{10}), 30.15, 30.28 (C^{11}), 30.46 (C^3), 37.15 (C^6), 126.18 (C^4), 129.15 (C^7), 130.65 (C^8), 131.18 (C^5). $[M]^+$ 222. Found, % : C 85.92; H 13.12. $C_{16}H_{30}$. Calculated, % : C 86.40; H 13.60.

4-Propyl-1-phenyl-1,4-octadiene (VIIc). bp 128–130°C (1 mm Hg). IR spectrum, ν, cm^{-1}: 3030, 2940, 2860, 1650, 1490, 1450, 1395, 1050, 920, 870, 720. ^1H NMR spectrum, δ, ppm: 0.89–1.13 m (6H, CH_3), 1.25–1.68 m (4H, CH_2), 1.95–2.29 m (4H, =C–C$\underline{H}_2$), 2.55–3.15 (2H, =C–C$\underline{H}_2$–C=), 5.45–6.82 m (3H, C$\underline{H}$=CCH$_2\underline{H}$C=C$\underline{H}$Ph), 7.23–7.65 (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 13.83, 14.03 (C^8), 23.11, 25.55 (C^7), 32.84 (C^6), 35.68, 38.80 (C^3), 125.84 (C^5), 126.59, 127.47, 129.52, 129.98 (C^2), 130.92 (C^1), 136.84, 137.96 (C^4). $[M]^+$ 228. Found, %: C 89.11; H 10.02. $C_{17}H_{24}$. Calculated, %: C 89.41; H 10.59.

3,6-Dideutero-4-ethyl-3,6-dodecadiene (VIIIa). bp 102–104°C (5 mm Hg). IR spectrum, ν, cm^{-1}: 2160 (CD). ^1H NMR spectrum, δ, ppm: 0.88–0.91 m (9H, CH_3), 1.12–1.68 m (6H, CH_2), 1.89–2.47 m (8H, =C–C$\underline{H}_2$), 5.38–5.79 m (1H, C=C$\underline{H}$). ^{13}C NMR spectrum, δ, ppm: 13.35, 14.05 (C^{12}), 14.72 (C^1), 20.26 (C^2), 22.78 (C^{11}), 23.56, 27.32 (C^8), 29.74 (C^9), 30.41 (C^{10}), 36.54 (C^5), *(C^3), *(C^6), 130.73 (C^7), 132.87 (C^4). $[M]^+$ 196. Found, %: C 85.31; (H+D) 14.02. $C_{14}H_{24}D_2$. Calculated, %: C 85.63; H 12.32; D 2.05.

4,7-Dideutero-5-propyl-4,7-tridecadiene (VIIIb). bp 98–100°C (1 mm Hg). IR spectrum, cm^{-1}: 2175 (CD). ^1H NMR spectrum, δ, ppm: 0.91–1.17 m (9H, CH_3), 1.23–1.61 m (10H, CH_2), 1.95–2.72 m (8H, =C–C$\underline{H}_2$), 5.49–5.78 t (1H, C=C$\underline{H}$). ^{13}C NMR spectrum, δ, ppm: 13.79, 14.01 (C^{13}), 14.46 (C^1), 22.12, 22.84 (C^{12}), 23.29 (C^2), 27.31 (C^9), 29.64 (C^{10}), 30.09, 30.31 (C^{11}), 30.52 (C^3), 37.23 (C^6), *(C^4), *(C^7), 130.38 (C^8), 131.28 (C^5). Found, %: C 85.07; (H+D) 13.96. $[M]^+$ 224. $C_{16}H_{28}D_2$. Calculated, %: C 85.63; H 12.58; D 1.79.

2,5-Dideutero-4-propyl-1-phenyl-1,4-octadiene (VIIIc). bp 128–130°C (1 mm Hg).IR spectrum, ν,cm^{-1}: 2170 (CD). ^1H NMR spectrum, δ, ppm: 0.90–1.15 m (6H, CH_3), 1.25–1.65 m (4H, CH_2), 1.95–2.30 m (4H, =C–C$\underline{H}_2$), 2.55–3.25 (2H, =CC$\underline{H}_2$C=), 6.80 s (1H, DC=C$\underline{H}$Ph), 7.25–7.85 (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 13.85, 14.08 (C^8), 23.12, 25.65 (C^7), 32.83 (C^6), 35.72, 38.85 (C^3), *(C^5), 126.61, 127.32, 129.49, *(C^2), 130.95 (C^1), 136.86, 138.56 (C^4). $[M]^+$ 230. Found, %: C 88.25; (H+D) 11.02. $C_{17}H_{22}D_2$. Calculated, %: C 88.63; H 9.63; D 1.74.

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