ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 12, pp. 1804–1808. © Pleiades Publishing, Ltd., 2007.
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Synthesis of 1,2,3,4-Tetrasubstituted Aluminacyclopent-2-enes Using Cp_2ZrCl_2 as Catalyst

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Received April 19, 2007

Abstract—Efficient procedures have been developed for the synthesis of 1,2,3,4-tetrasubstituted aluminacyclopent-2-enes via intermolecular cycloalumination of terminal olefins and acetylenes with $EtAlCl_2$ or cycloalumination of acetylenes with higher trialkylalanes in the presence of Cp_2ZrCl_2 as catalyst.

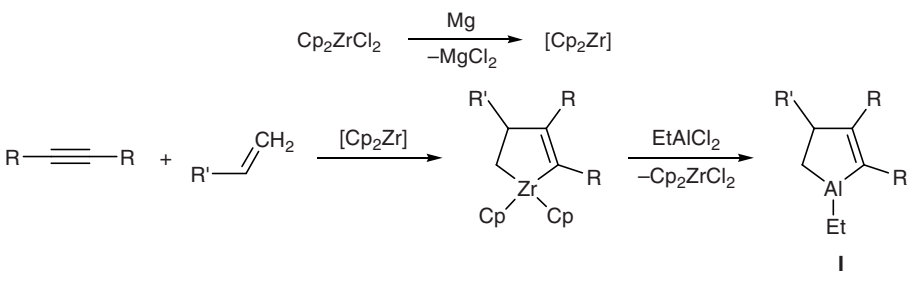
DOI: 10.1134/S107042800712010X

Cyclic organoaluminum and organomagnesium compounds are promising reagents for selective one-step preparation of carbo- and heterocycles from olefins, dienes, and acetylenes [1–3]. We previously showed [4] that cycloalumination of acetylenes with $EtAlCl_2$ in the presence of zirconium catalyst Cp_2ZrCl_2 gives substituted aluminacyclopentadienes. These data led us to presume that tetrasubstituted aluminacyclopent-2-enes could be obtained by joint cycloalumination of acetylenes and olefins under analogous conditions [4]. This assumption was based on the fact that zirconocene generated *in situ* from Cp_2ZrCl_2 is capable of coordinating acetylene and olefin molecules with formation of zirconacyclopent-2-enes [5–8]. Transmetalation of the latter with dihaloalanes was expected to produce aluminacyclopent-2-enes according to Scheme 1.

With the above in mind, we examined the reaction of a 1:1 hex-3-yne–oct-1-ene mixture with $EtAlCl_2$ in the presence of Cp_2ZrCl_2 and metallic magnesium (as halide ion acceptor) at an [Al]–substrate–[Mg]–[Zr] molar ratio of 12:10:12:1 (THF, 8 h, 20–22°C). As a result, we obtained the expected products, 1,2,3-triethyl-4-hexylaluminacyclopent-2-ene (**IIa**), 1,2,3,4,5-pentaethylaluminacyclopenta-2,4-diene (**IIIa**), and 1-ethyl-*trans*-3,4-dihexylaluminacyclopentane (**IVa**), at a ratio of ~3:6:2 with an overall yield of ~85% (Scheme 2). Cyclic organoaluminum compounds **IIa**–**IVa** were identified by analysis of the corresponding deuterolysis products **Va**–**VIIa**, as well as by comparing compounds **VIa** and **VIIa** with samples obtained previously [4, 9].

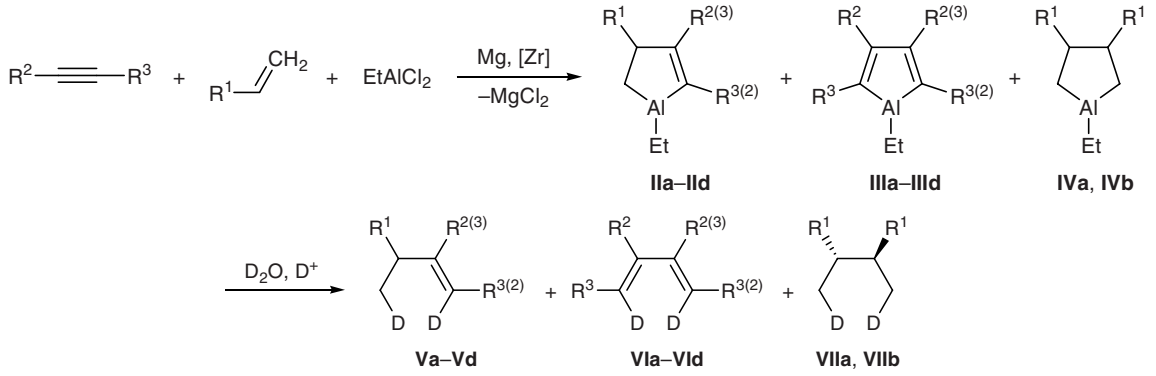
We succeeded in changing the reaction direction toward preferential formation of aluminacyclopent-2-ene **IIa** by slowly adding (over a period of ~6 h) a mixture of oct-1-ene and $EtAlCl_2$ in THF to a solution of Cp_2ZrCl_2 in toluene containing hex-3-yne and metallic magnesium. The mixture was then stirred for 4 h at 20–22°C. Under these conditions, the ratio of cyclic organoaluminum compounds **IIa**, **IIIa**, and **IVa** was 7:3:2 (overall yield ~80%; GLC data). We also tried to improve the procedure by reacting internal

Scheme 1.



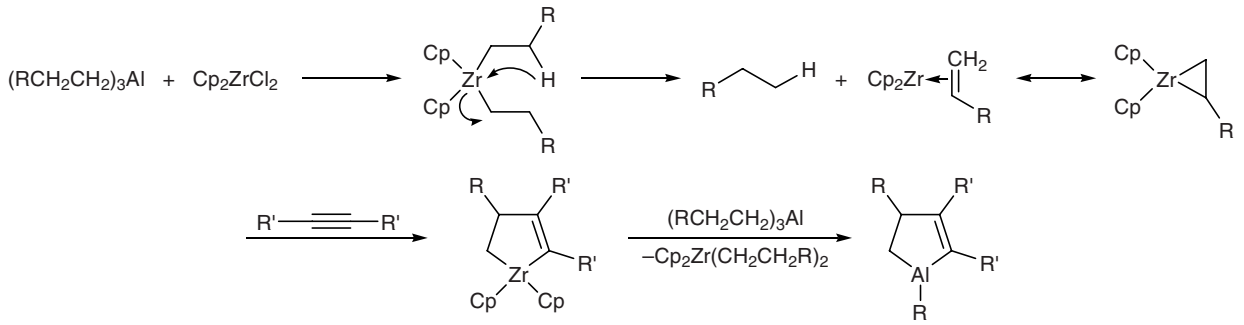
I

Scheme 2.



$R^1 = C_6H_{13}$, $R^2 = R^3 = Et$ (**a**); $R^1 = Bu$, $R^2 = R^3 = Pr$ (**b**); $R^1 = Bu$, $R^2 = Ph$, $R^3 = Me$ (**c**); $R^1 = Bu$, $R^2 = Me$, $R^3 = Ph$ (**d**).

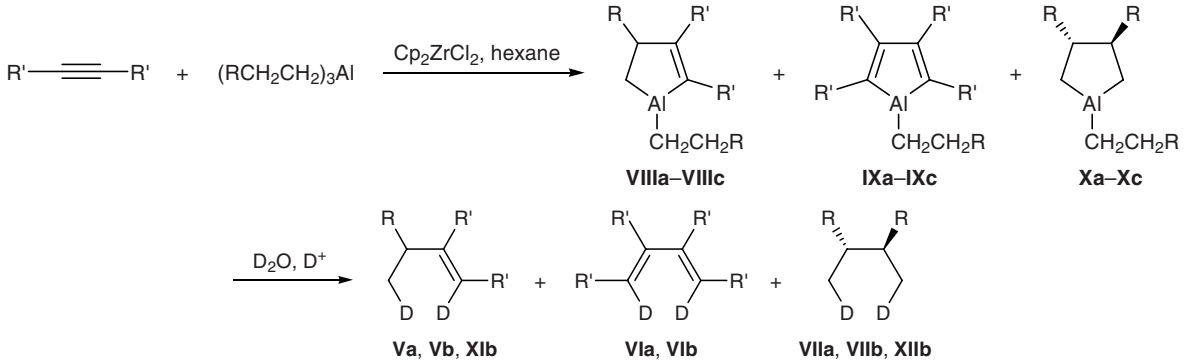
Scheme 3.



alkynes with higher trialkylalanes in the presence of Cp_2ZrCl_2. In doing so we relied upon published data [10–12], according to which the required terminal olefin should be generated *in situ* as shown in Scheme 3. We presumed that the terminal olefin will be involved in joint cycloalumination of acetylenes to provide the target aluminacyclopentenes. As higher trialkylalanes we used trihexylaluminum, trioctylaluminum, and tris(undecyl)aluminum.

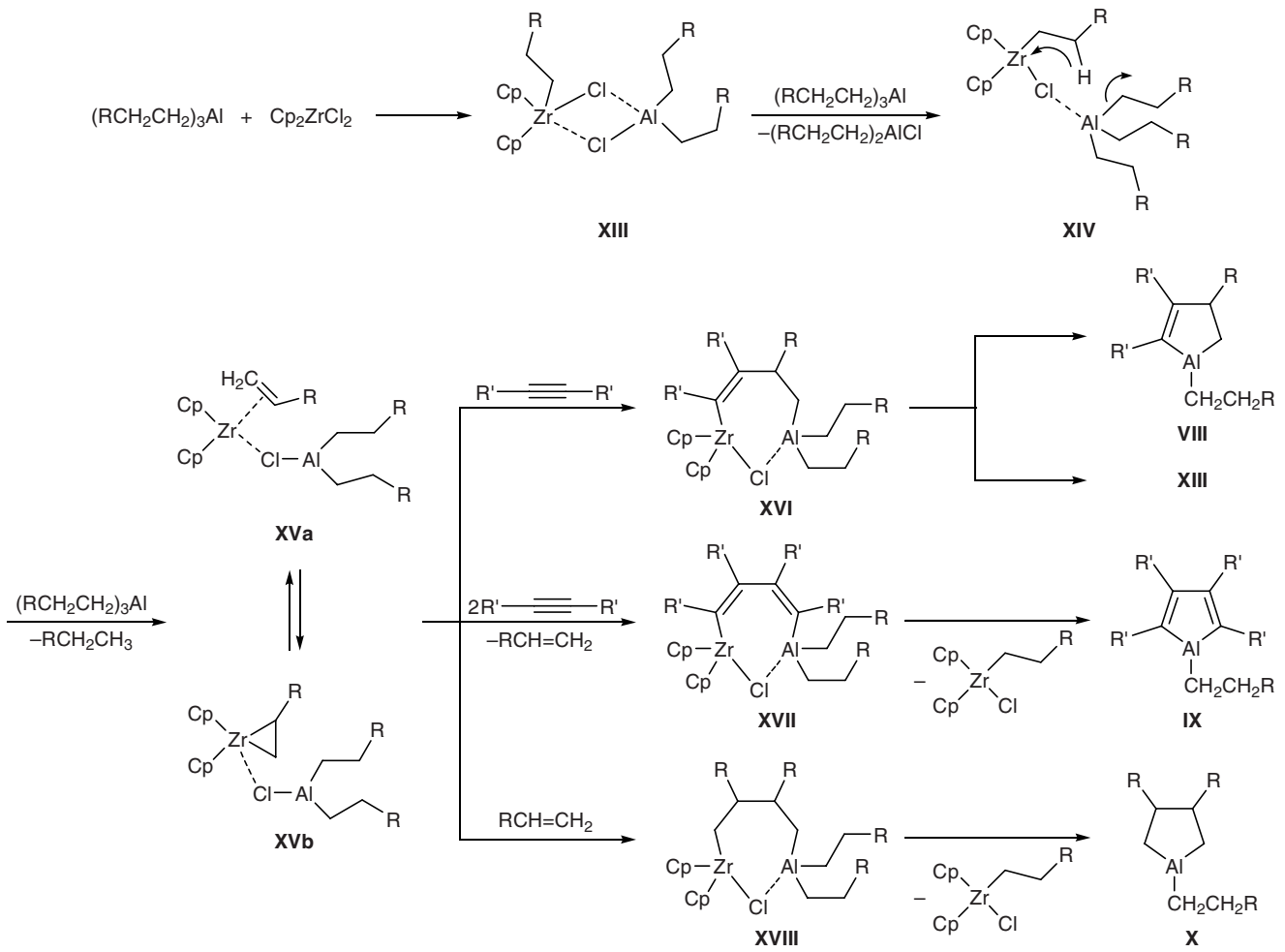
Cycloalumination of hex-3-yne and oct-4-yne) with the above trialkylalanes gave 50–55% of the corresponding 1,2,3,4-tetrasubstituted aluminacyclopent-2-enes **VIII**. In all cases, 1,2,3,4,5-pentasubstituted aluminacyclopenta-2,4-dienes **IX** and 1-alkyl-*trans*-3,4-dialkylaluminacyclopentanes **X** were formed as minor products (10–15%; Scheme 4). On the basis of published data [13–15] and our experimental results we proposed Scheme 5 for the formation of tetrasubstituted aluminacyclopent-2-enes from internal alkynes and higher trialkylalanes in the presence of Cp_2ZrCl_2. Initial alkylation of Cp_2ZrCl_2 with trialkylalane gives intermediate **XIII** in which the zirconium and alumi-

Scheme 4.



$R = C_6H_{13}$, $R' = Et$ (**a**); $R = C_9H_{19}$, $R' = Et$ (**b**); $R = Bu$, $R' = Pr$ (**c**).

Scheme 5.



num atoms are linked through bridging chlorine atoms. The reaction of **XIII** with the second molecule of trialkylalane (which is a stronger base that dialkilaluminum chloride formed in the first step) involves β-hydride transfer in intermediate **XIV** with elimination of alkane and formation of olefin–zirconocene complex **XVa**. Insertion of initial alkyne molecule into the Zr–C bond of zirconacyclopropane intermediate **XVb** leads to dinuclear complex **XVI** which is transformed into tetrasubstituted aluminacyclopent-2-ene **VIII** with regeneration of bridged complex **XIII**. Replacement of olefin molecule from the coordination sphere of zirconium in complex **XVa** by internal alkyne gives intermediate **XVII** as precursor of minor aluminacyclopentadiene **IX**. The replaced α-olefin molecule is trapped by zirconacyclopropane intermediate **XVb**, and dinuclear complex **XVIII** thus formed is converted into minor aluminacyclopentane **X**.

We can conclude that we have developed convenient and effective procedures for the synthesis of tetrasubstituted aluminacyclopent-2-enes via intermolecular cycloalumination of α-olefins and internal alkynes with $EtAlCl_2$ and cycloalumination of acetylenes with higher trialkylalanes in the presence of Cp_2ZrCl_2 as catalyst.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a JEOL FX-90Q spectrometer (89.55 MHz for ^1H and 22.5 MHz for ^{13}C). The hydrolysis and deuterolysis products were analyzed by GLC on a Chrom-5 chromatograph (1200×3-mm column packed with 5% of SE-30 or 15% of PEG-6000 on Chromaton N-AW; carrier gas helium). The mass spectra (electron impact, 70 eV) were obtained on an MKh-1306 spectrometer (ion source temperature 200°C). The yields of organoaluminum compounds were determined by GLC analysis of the hydrolysis products. All reactions with organometallic compounds

were carried out in a stream of dry argon. Tetrahydrofuran was dried by heating under reflux over metallic sodium and subsequent distillation just before use. Dichloroethylaluminum was commercial product with a purity of 86%. Higher trialkylalanes were synthesized according to the procedure described in [16]. Compounds **VIa**–**VId**, **VIIa**, **VIIb**, and **XIIb** were reported previously [4, 17–19]. Regioisomers **Vc** and **Vd** were separated using a Carlo Erba Fractovap Mod.GW preparative gas chromatograph (4000×6-mm column, stationary phase SE-30, carrier gas helium).

Joint cycloalumination of terminal olefins and internal alkynes with $EtAlCl_2$ in the presence of Cp_2ZrCl_2 (*general procedure*). A glass reactor was charged under dry argon with 1 mmol of Cp_2ZrCl_2, 12 mmol of magnesium powder, 5 ml of THF, and 10 mmol of the corresponding alkyne, and a mixture of 10 mmol of the corresponding terminal olefin and 12 mmol of $EtAlCl_2$ in 10 ml of THF was added dropwise over a period of ~6 h under stirring. The mixture was stirred for 4 h, treated with 10% D_2O, and extracted with diethyl ether or hexane. The extract was dried over magnesium sulfate, and the products were isolated by fractional distillation under reduced pressure. A mixture of isomeric deuterolysis products **Vc** and **Vd** isolated by distillation was separated by preparative GLC.

Cycloalumination of internal alkynes with trialkylalanes in the presence of Cp_2ZrCl_2. A glass reactor was charged under dry argon with 0.5 mmol of Cp_2ZrCl_2, 30 mmol of a terminal olefin, and 10 mmol of $(i\text{-Bu})_3Al$, and the mixture was stirred at ~60°C until 2-methylbut-1-ene no longer evolved. The mixture was then cooled to room temperature, 0.5 mmol of Cp_2ZrCl_2 and 10 mmol of the corresponding alkyne were added, and the mixture was stirred for 8 h, treated with 10% D_2O, and extracted with diethyl ether or hexane. The extract was dried over magnesium sulfate, and the products were isolated by fractional distillation under reduced pressure.

4-Ethyl-5-($^2H_1$)methyl(3-^2H)undec-3-ene (Va). Yield 47%, bp 66–68°C (5 mm). ^1H NMR spectrum, δ, ppm: 0.86–1.00 m (11H, CH_3, CH_2D), 1.05–1.28 m (11H, CH, CH_2), 1.86–2.08 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 12.34, 14.84, 14.15, 19.37 t (J_{CD} = 19.1 Hz), 22.05, 28.67, 29.87, 29.84, 31.98, 34.32, 38.64, 123.78 (J_{CD} = 22.5 Hz), 146.79. Mass spectrum: *m*/*z* 198 $[M]^+$.

6-($^2H_1$)Methyl-5-propyl(4-^2H)dec-4-ene (Vb). Yield 45%, bp 95–98°C (6 mm). ^1H NMR spectrum, δ, ppm: 0.86–1.00 m (11H, CH_3, CH_2D), 1.05–1.28 m (11H, CH, CH_2), 1.86–2.08 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 13.89, 14.00, 14.08, 18.28 t (J_{CD} = 19.1 Hz), 21.72, 22.61, 23.80, 30.36, 32.08, 35.91, 41.17, 123.98 (J_{CD} 22.5 Hz), 147.99. Mass spectrum, *m*/*z*: $[M]^+$ 198.

4-($^2H_1$)methyl-3-phenyl(2-^2H)hept-2-ene (Vc) and 2-methyl-3-($^2H_1$)methyl-1-phenyl(1-^2H)hept-1-ene (Vd) (3 : 1 isomer mixture)**.** Yield 48%, bp 120–125°C (2 mm). Compound **Vc**. Yield 36%. ^1H NMR spectrum, δ, ppm: 0.95 m (5H, CH_3, CH_2), 1.10–1.55 m (6H, CH_2), 1.80 s (3H, CH_3), 2.18 t (2H, CH), 7.10–7.50 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.09, 19.92 t (J_{CD} = 19.1 Hz), 20.63, 22.65, 32.03, 35.06, 43.65, 124.41 (J_{CD} = 19.1 Hz), 125.81, 128.05, 128.54, 137.11, 143.39. Compound **Vd**. Yield 12%. ^{13}C NMR spectrum, δ_C, ppm: 14.05, 16.89, 19.72 t (J_{CD} = 19.1 Hz), 22.26, 32.03, 37.08, 41.77, 120.21 (J_{CD} = 23.5 Hz), 126.04, 126.82, 129.04, 138.86, 143.02. Mass spectrum: *m*/*z* 204 $[M]^+$.

4-Ethyl-5-($^2H_1$)methyl-(3-^2H)tetradec-3-ene (XIb). Yield 42%, bp 127–129°C (2 mm). ^1H NMR spectrum, δ, ppm: 0.86–1.00 m (11H, CH_3, CH_2D), 1.05–1.28 m (11H, CH, CH_2), 1.86–2.08 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 12.39, 14.21, 14.83, 19.38 t (J_{CD} = 19.1 Hz), 20.78, 22.91, 28.18, 28.59, 28.65, 29.02, 29.61, 32.42, 34.22, 39.56, 124.84 (J_{CD} = 22.5 Hz), 146.29. Mass spectrum: *m*/*z* 240 $[M]^+$.

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