ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 6, pp. 781–784. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © I.R. Ramazanov, A.G. Ibragimov, U.M. Dzhemilev, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 6, pp. 793–796.

New Method for Cycloalumination of Disubstituted Acetylenes with 1,2-Dichloroethane

I. R. Ramazanov, A. G. Ibragimov, and U. M. Dzhemilev

Institute of Petroleum Chemistry and Catalysis, Russian Academy of Sciences, pr. Oktyabrya 141, Ufa, 450075 Bashkortostan, Russia
e-mail: ink@anrb.ru

Received October 30, 2007

Abstract—A new procedure has been developed for the synthesis of 2,3-dialkyl(phenyl)aluminacyclopent-2-enes by Cp_2TiCl_2-catalyzed cycloalumination of disubstituted acetylenes with $EtAlCl_2$ in the presence of ethylene generated *in situ* from 1,2-dichloroethane and activated magnesium.

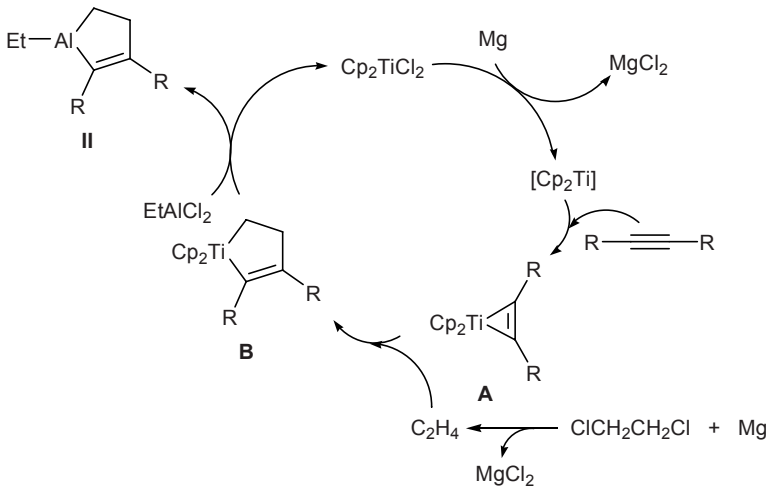
DOI: 10.1134/S1070428008060018

We previously discovered a new class of cyclic organoaluminum compounds, aluminacyclopropenes **I**, that are formed by cycloalumination of disubstituted acetylenes with $EtAlCl_2$ in the presence of magnesium and a catalytic amount of Cp_2TiCl_2 in tetrahydrofuran [1]. A probable reaction mechanism includes reduction of Cp_2TiCl_2 to coordinatively unsaturated $[Cp_2Ti]$ species, complex formation of the latter with disubstituted acetylene, and transmetalation of titanacyclopropene intermediate thus formed with $EtAlCl_2$. Aluminacyclopropenes show a weaker reactivity than do titanacyclopropenes **A**, so that it is difficult to involve them in subsequent transformations.

Therefore, we tried to effect some chemical transformations, e.g., ring expansion, at the stage of formation of titanacyclopropene intermediate **A** via insertion into the Ti–C bond of an unsaturated molecule which is inert toward the initial organoaluminum compound. Such unsaturated compound may be ethylene which can be readily generated *in situ* by reaction of 1,2-dichloroethane with magnesium, the latter being used in the cyclometalation process. Insertion of ethylene molecule into the Ti–C bond should give titanacyclopentene **B** whose transmetalation with initial dihaloalane could produce the target aluminacyclopentenes **II** (Scheme 1).

The efficiency of this approach was demonstrated by us previously while developing a new procedure for the synthesis of aluminacyclopentanes [2] and 1,2-diphenyl-1,4-dialuminabut-1-ene [3] and intermolecular

Scheme 1.



Cycloalumination of disubstituted acetylenes with $EtAlCl_2$ in the presence of magnesium and 1,2-dichloroethane using Cp_2TiCl_2 as catalyst

Run no.	Initial acetylene	Yield,[a] %			Conversion of acetylene, %
		II	**I**	**III**	
1	Oct-4-yne	55	20	20	100
2	Dec-5-yne	65	15	20	100
3	Dec-1-en-4-yne	50	20	10	80
4	1,2-Diphenylethyne	45	5	–	50
5	Pent-4-en-1-yn-1-ylbenzene	50	10	–	70
6	Pent-1-yn-1-ylbenzene	55	15	5	75

[a] The yields were determined for the corresponding hydrolysis products.

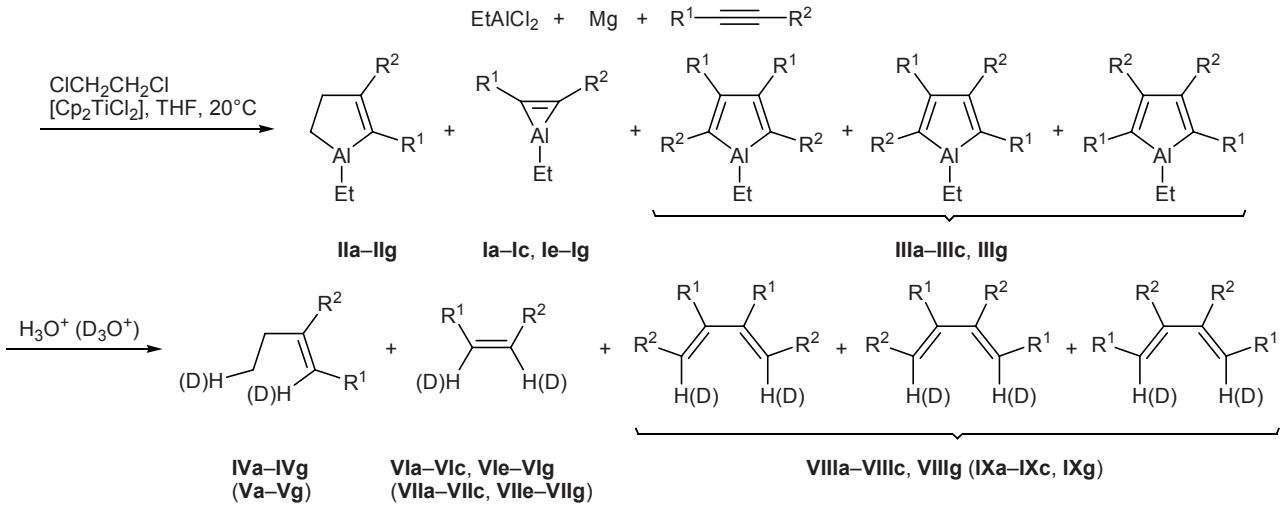
cycloalumination of disubstituted acetylenes and terminal olefins [4].

Taking into account the above stated, we performed cycloalumination of a series of disubstituted acetylenes with $EtAlCl_2$ in the presence of activated magnesium and Cp_2TiCl_2 as catalyst. The reactions were carried out by slowly adding a mixture of 1,2-dichloroethane and disubstituted acetylene to a solution of $EtAlCl_2$ in THF (molar ratio acetylene–$C_2H_4Cl_2$–$EtAlCl_2$–Mg–Cp_2TiCl_2 = 1:2:4:3:0.05). The process was complete in 10 h at room temperature. Apart from aluminacyclopentenes **II**, the reaction mixture contained aluminacyclopropenes **I** and aluminacyclopentadienes **III**; their yields and ratios depended on the substituent nature in the acetylenic substrate. The reactions with dialkyl-substituted acetylenes (oct-4-yne and dec-5-yne) and 1-allyl-2-pentylacetylene (dec-1-en-4-yne) were not selective, and the fraction of by-products **I** and **III** was fairly large (up to 40% for oct-4-yne; see table, run nos. 1–3). Moreover, cycloalumination of dec-1-en-4-yne gave a mixture of regioisomeric aluminacyclopentenes **IIf** and **IIg** at a ratio of 1:1.

The reactions were more selective when 1-alkyl-(allyl)-2-phenylacetylenes and diphenylacetylene were used as substrates. In these cases, the yield of the corresponding aluminacyclopentenes **II** was 45–65%, and the amount of aluminacyclopropenes **I** was as small as 5–15% (see table, run nos. 4–6). The presence of a phenyl group at the triple bond favors regioselective process with predominant formation of one isomer (~9:1) in which the phenyl group occupies the α-position with respect to the aluminum atom (compounds **IIf** and **IIg**).

Unsymmetrically substituted acetylenes (dec-1-en-4-yne, pent-1-yn-1-ylbenzene) gave rise to 10% of a mixture of regioisomeric aluminacyclopentadienes

Scheme 2.



$R^1 = R^2$ = Pr (**a**), Bu (**b**), Ph (**d**); $R^1 = C_5H_{11}$, $R^2 = CH_2{=}CHCH_2$ (**c**); $R^1 = CH_2{=}CHCH_2$, C_5H_{11} (**d**); R^1 = Ph, $R^2 = CH_2{=}CHCH_2$ (**f**), Pr (**g**).

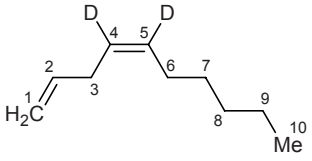
III at a ratio of 1 : 1 : 1 (for dec-1-en-4-yne) or to 5% of preferentially one isomer (for pent-1-yn-1-ylbenzene).

The configuration of the double bond in cyclic organoaluminum compounds **I**–**III** does not change upon hydrolysis or deuterolysis. The cycloalumination of disubstituted acetylenes was found to occur with high stereoselectivity (>95%, according to the ^{1}H and ^{13}C NMR data). Thus the hydrolysis of the products resulted in the formation of *cis*-olefins **IVa**–**IVg**, **VIa**–**VIc**, and **VIe**–**VIg** and *trans*,*trans*-dienes **VIIIa**–**VIIIc** and **VIIIg** (Scheme 2). The reactions with dec-1-en-4-yne and pent-1-yn-1-ylbenzene under the given conditions were not accompanied by cycloalumination involving the double bond in the substrate.

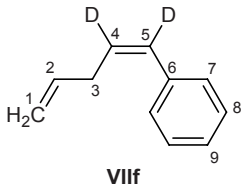
Qualitative analysis of steric factors affecting the formation of titanacyclopentene intermediate **B** and the observed ratio of regioisomers obtained from 1-alkyl-2-phenyl-substituted acetylenes suggest that the reaction regioselectivity is determined mainly by electronic factors. The rate of catalytic cycloalumination of phenylacetylenes is lower due mainly to steric hindrances related to approach of the titanacene fragment to bulky phenyl substituent. Steric factors are also responsible for the reduced fraction of aluminacyclopentadienes **III** formed in the reactions with 1-alkyl(allyl)-2-phenylacetylene as a result of coordination of the second acetylene molecule by titanacyclopropene intermediate **A** and subsequent transmetalation of titanacyclopentadiene with $EtAlCl_2$. Our results indicate higher reactivity of titanacyclopropene intermediate **A** generated *in situ* toward ethylene derived from 1,2-dichloroethane rather than toward initial disubstituted acetylene.

A very important condition is slow addition of a mixture of 1,2-dichloroethane and disubstituted acetylene to the reaction system. The presence of excess 1,2-dichloroethane induces strong heat evolution which favors side processes leading to aluminacyclopentadienes **III** and cyclotrimerization products of initial acetylene.

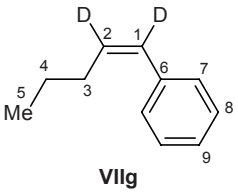
By studying cyclometalation of dec-5-yne with $EtAlCl_2$ using chloride ion acceptor (Mg) and ethylene donor (1,2-dichloroethane) in the presence of Ti, Zr, and Hf complexes we found that Cp_2TiCl_2 showed the highest catalytic activity. Titanium(IV) alkoxides like $Ti(OBu)_4$ and $Ti(OPr\text{-}i)_4$ ensured considerably lower selectivity. Dicyclopentadienylzirconium dichloride Cp_2ZrCl_2 favored predominant formation of aluminacyclopentadiene **III** (the yield of compound **IVa** was 17% according to the GLC data), while Cp_2HfCl_2 turned out to be almost inactive (the concentration of **IVa** in the hydrolysis products was as low as 5%). The reaction successfully occurs in ethers (THF, diethyl ether). Aliphatic (hexane, cyclohexane) and aromatic solvents (benzene, toluene) promoted oligomerization of disubstituted acetylenes.



VIIc



VIIf



VIIg

The structure of cyclic organoaluminum compounds **I**–**III** was determined on the basis of the ^{1}H and ^{13}C NMR and mass spectra of the corresponding deuterolysis products. The ^{1}H and ^{13}C NMR parameters of compounds **V**, **VII**, and **IX** were compared with previously reported data for **Va**, **Vb**, **Ve** [5], **Vc**, **Vd**, **Vf**, **Vg** [6], **VIIa**, **VIIe** [1], **VIIb** [3], **IXa** [1], and **IXb** [7]. Signals in the ^{13}C NMR spectra of **VIIc**, **VIIf**, and **VIIg** were assigned taking into account known spectral parameters of their undeuterated analogs [8]. Compounds **IXc**, **IXd**, and **IXg** were identified by mass spectrometry and GLC (by comparing with retention times of dienes **VIIIc** and **VIIIg** obtained by hydrolysis of aluminacyclopentadienes which were formed in the cycloalumination of the corresponding acetylenes with $EtAlCl_2$ in the presence of Cp_2ZrCl_2 [7]).

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were measured from solutions in $CDCl_3$ on a Jeol FX-90Q spectrometer at 90 and 22.5 MHz, respectively, using tetramethylsilane (^{1}H) or the solvent (^{13}C) as internal reference. The ^{13}C NMR spectra were recorded with complete decoupling from protons and using INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) pulse sequence. The products were analyzed by gas–liquid chromatography on a Carlo Erba instrument equipped with a flame ionization detector and an Ultra-1 (25 m × 0.2 mm) glass capillary column; oven temperature 50–170°C; carrier gas helium. The mass spectra (electron

impact, 70 eV) were obtained on a Finnigan 4021 mass spectrometer (ion source temperature 200°C). The elemental compositions were determined using a Carlo Erba 1106 analyzer. The boiling points were determined according to Sivolobov [9].

General procedure for the cycloalumination of disubstituted acetylenes. A glass reactor was filled with argon and charged with 5 ml of THF, 8 mmol of magnesium powder, and 4 mmol of $EtAlCl_2$. The reactor was cooled in an ice bath, 2.5 mg (0.1 mmol) of Cp_2TiCl_2 was added, the cooling bath was removed, and a mixture of 4 mmol of 1,2-dichloroethane and 2 mmol of disubstituted acetylene in 5 ml of THF was added dropwise under stirring over a period of 4 h. When the reaction was complete, 5 ml of hexane was added, and the mixture was treated with 10% hydrochloric acid or a 7% solution of DCl in D_2O. The organic phase was separated, the aqueous phase was extracted with diethyl ether, and the extract was combined with the organic phase, washed with a solution of Na_2CO_3 until neutral reaction, and dried over $CaCl_2$. Individual products were isolated by vacuum distillation.

(4*Z*)-(4,5-$^2H_2$)Deca-1,4-diene (VIIc). Yield 50%, bp 170°C. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, 10-H), 1.1–1.55 m (6H, 7-H, 8-H, 9-H), 1.85–2.15 m (2H, 6-H), 2.55–3.0 m (2H, 3-H), 4.9–5.15 m (2H, 1-H), 5.6–6.05 m (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 14.15 (C^{10}), 22.67 (C^9), 27.09 (C^3), 27.09 (C^6), 29.37 (C^7), 31.58 (C^8), 114.56 (C^1), 126.31 (C^4, $^1J_{CD}$ = 23.8 Hz), 130.93 (C^5, $^1J_{CD}$ = 23.6 Hz), 137.25 (C^2). Mass spectrum: *m*/*z* 140 $[M]^+$. Found, %: C 85.72; H+D 14.28. $C_{10}H_{16}D_2$. Calculated, %: C 85.64; H 11.50; D 2.87.

[(1*Z*)-(1,2-$^2H_2$)Penta-1,4-dien-1-yl]benzene (VIIf). Yield 50%, bp 85°C (15 mm). ^{1}H NMR spectrum, δ, ppm: 2.75–2.85 m (2H, CH_2), 4.9–6.05 m (3H, CH_2=CH), 7.25–7.45 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 31.82 (C^3), 115.40 (C^1), 125.93 (C^4, $^1J_{CD}$ = 23.6 Hz), 126.31 (C^7), 127.41 (C^8), 128.51 (C^5, $^1J_{CD}$ = 23.6 Hz), 135.23 (C^2), 136.76 (C^9), 139.10 (C^6). Mass spectrum: *m*/*z* 146 $[M]^+$. Found, %: C 90.89; H+D 9.11. $C_{11}H_{10}D_2$. Calculated, %: C 90.36; H 6.89; D 2.75.

[(1*Z*)-(1,2-$^2H_2$)Pent-1-en-1-yl]benzene (VIIg). Yield 55%, bp 94°C (14 mm). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 7 Hz), 1.2–1.45 m (2H, CH_2), 1.85–2.1 m (2H, CH_2), 7.25–7.5 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 13.03 (C^5), 21.54 (C^4), 28.90 (C^3), 129.91 (C^1, $^1J_{CD}$ = 23.8 Hz), 118.02 (C^2, $^1J_{CD}$ = 23.8 Hz), 126.70 (C^7), 128.10 (C^8), 132.60 (C^9), 137.03 (C^6). Mass spectrum: *m*/*z* 148 $[M]^+$. Found, %: C 88.89; H+D 11.11. $C_{11}H_{12}D_2$. Calculated, %: C 89.13; H 8.16; D 2.71.

This study was performed under financial support by the Ministry of Science and Education of the Russian Federation (project no. NSh-7470.2006.3).

REFERENCES

1. Dzhemilev, U.M., Ibragimov, A.G., Ramazanov, I.R., and Khalilov, L.M., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1997, no. 12, p. 2269.
2. Ibragimov, A.G., Khafizova, L.O., Yakovleva, L.G., Nikitina, E.V., Satenov, K.G., Khalilov, L.M., and Dzhemilev, U.M., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1999, no. 4, p. 778.
3. Dzhemilev, U.M., Ibragimov, A.G., Yakovleva, L.G., Khafizova, L.O., Borisova, A.L., and Yakupova, L.R., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2003, no. 7, p. 1490.
4. Khafizova, L.O., Yakupova, L.R., Ibragimov, A.G., and Dzhemilev, U.M., *Russ. J. Org. Chem*., 2007, vol. 43, p. 1804.
5. Dzhemilev, U.M., Ibragimov, A.G., and Zolotarev, A.P., *Mendeleev Commun*., 1992, p. 135.
6. Dzhemilev, U.M., Ibragimov, A.G., Ramazanov, I.R., Luk'yanova, M.P., and Sharipova, A.Z., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2001, no. 3, p. 465.
7. Dzhemilev, U.M., Ibragimov, A.G., Khafizova, L.O., Yakupova, L.R., and Khalilov, L.M., *Russ. J. Org. Chem*., 2005, vol. 41, p. 673.
8. Gimaeva, A.R., *Cand. Sci. (Chem.) Dissertation*, Ufa, 1999.
9. Agronomov, A.E. and Shabarov, E.S., *Laboratornye raboty v organicheskom praktikume* (Laboratory Works in Organic Practicum), Moscow: Khimiya, 1974.