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Joint Cycloalumination of Ethylene and Other Unsaturated Compounds with $EtAlCl_2$ in the Presence of Cp_2ZrCl_2. Synthesis of Aluminacarbocycles

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Abstract—A procedure has been developed for the selective synthesis of five-membered aluminum-containing heterocycles, 2,3-dialkyl-1-ethylaluminacyclopent-2-enes, 3-alkyl-1-ethylaluminacyclopentanes, 2-alkylidene-1-ethylaluminacyclopentanes, and 3-alkyl-1-ethyl-2-methylidenealuminacyclopentanes, via joint cycloalumination of ethylene and other unsaturated compounds (acetylenes, olefins, and allenes) with $EtAlCl_2$ in the presence of Cp_2ZrCl_2 as catalyst.

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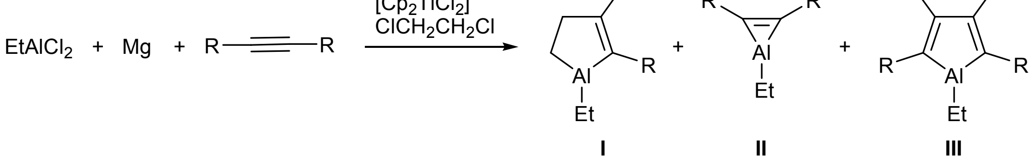
Increased interest in Cp_2ZrCl_2-catalyzed cycloalumination of unsaturated compounds (acetylenes [1, 2], olefins [3, 4], and allenes [5]) with Et_3Al is related to the possibility for synthesizing novel aluminacarbocycles, such as aluminacyclopent-2-enes and aluminacyclopentanes. The subsequent one-pot transformations of aluminacarbocycles generated *in situ* [6, 7] into alcohols [8–10], including optically active ones [11], ethers [12], 1,3-dienes [13], carbo- [14–17] and heterocycles [18–20], cyclopentenones [21], and biologically active compounds [22, 23] stimulated further studies on cycloalumination reactions with a view to replace explosive triethylaluminum by less pyrophoric organoaluminum compounds. These studies resulted in the development of a new synthetic approach [24] to 2,3-dialkyl-1-ethylaluminacyclopent-2-enes **I** based on cycloalumination of acetylenes with $EtAlCl_2$ in the presence of ethylene generated from 1,2-dichloroethane and magnesium using Cp_2TiCl_2 as catalyst. Apart from 2,3-dialkyl-1-ethylaluminacyclopent-2-enes **I**, this reaction led to the formation of considerable amounts (up to ~40%) of 2,3-dialkyl-1-ethylaluminacycloprop-2-enes **II** and 2,3,4,5-tetraalkyl-1-ethylaluminacyclopenta-2,4-dienes **III** [24] (Scheme 1).

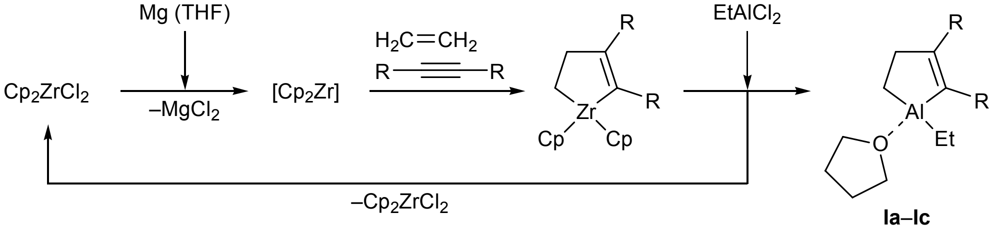
Drawbacks of this procedure include the necessity of generating ethylene (for building up molecule **I**) from 1,2-dichloroethane with the aid of magnesium and low chemoselectivity of the reaction due to formation of intermediate titanium-containing heterocycles (titanacyclopropenes and titanacyclopenta-2,4-dienes [25]) whose transmetalation with $EtAlCl_2$ yields byproducts **II** and **III**.

The goal of the present work was to develop a procedure for selective synthesis of substituted aluminacarbocycles (aluminacyclopent-2-enes and aluminacyclopentanes) with the use of relatively fire-safe reagents ($EtAlCl_2$, $AlCl_3$) and accessible ethylene with participation of other unsaturated compounds (acetylenes, olefins, allenes). While choosing the catalyst, as well as conditions for the synthesis of aluminacarbocycles, we presumed [26] that zirconocene gener-

Scheme 1.



Scheme 2.



Ia–Ic

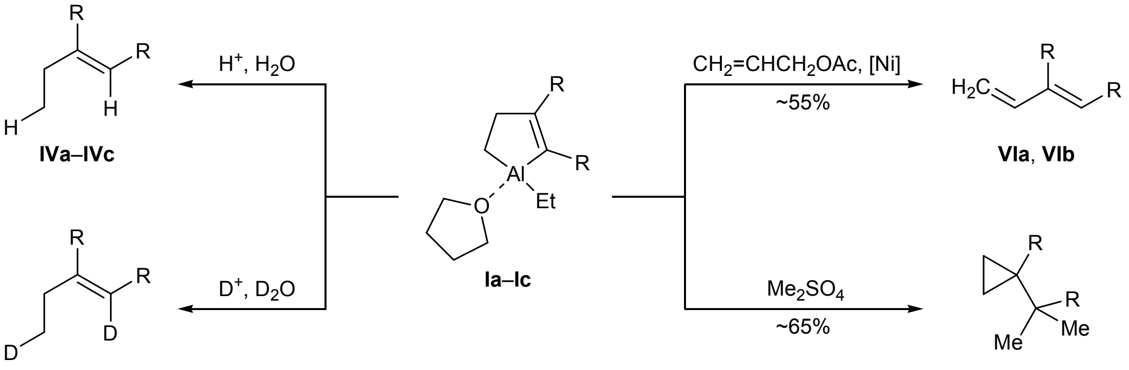
R = Pr (**a**), Bu (**b**), Ph (**c**).

ated, e.g., from Cp_2ZrCl_2 and BuLi [27] is capable of taking up alkynes in the presence of ethylene, yielding up to 98% of 2,3-disubstituted zirconacyclopent-2-enes. These transformations [26] are characterized by complete absence in the reaction mixture of tetrasubstituted zirconacyclopentadienes that are formed as the major products in the absence of ethylene [28]. Therefore, a necessary condition for selective formation of 2,3-disubstituted zirconacyclopent-2-enes (precursors of aluminacyclopent-2-enes) is generation of $[Cp_2Zr]$ in the presence of ethylene taken in excess with respect to disubstituted acetylene. Metallic magnesium was used to generate $[Cp_2Zr]$ from Cp_2ZrCl_2 [29], and transmetalation of zirconacyclopent-2-enes generated *in situ* was performed using $EtAlCl_2$ or $AlCl_3$ according to Scheme 2.

As shown in Scheme 2, cycloalumination of dialkyl(phenyl)acetylenes (oct-4-yne, dec-5-yne, and diphenylacetylene) with $EtAlCl_2$ in ethylene atmosphere (excess pressure 0.02 MPa) in the presence of magnesium powder and Cp_2ZrCl_2 as catalyst (molar ratio alkyne–$EtAlCl_2$–Mg–Cp_2ZrCl_2 10:15:12:0.1, THF, ~20°C, 6 h) gave aluminacyclopent-2-enes **Ia**–**Ic** in 65–80% yield. Analysis of their hydrolysis and deuterolysis products **IVa**–**IVc** and **Va**–**Vc** showed that the yield of by-products like **II** and **III** did not exceed 3%. An important condition for selective formation of targeted compounds **Ia**–**Ic** is slow (portionwise) addition of alkyne to the reaction mixture in the presence of ethylene. When the reaction was carried out with the use of more accessible aluminum(III) chloride instead of $EtAlCl_2$, other conditions being equal, aluminacyclopent-2-enes **Ia**–**Ic** were formed in 50–65% yield. As follows from Scheme 2, ethylene and alkyne molecule are involved in construction of the carbon skeleton of compounds **Ia**–**Ic**. In the cycloalumination with Et_3Al [1, 2], the aluminacyclopent-2-ene fragment is formed from alkyne molecule and ethyl substituent in the initial triethylaluminum [30].

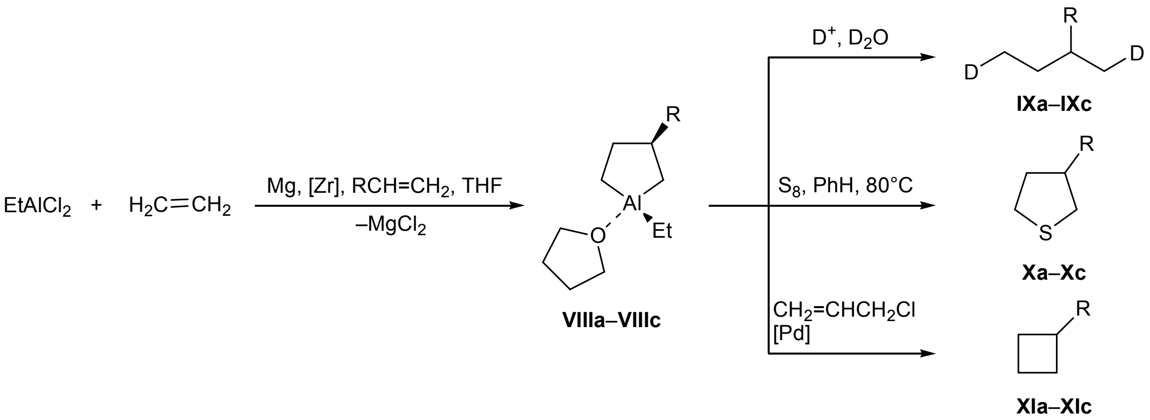
The ^{13}C NMR spectrum of aluminacyclopent-2-ene **Ia** contained two signals in the region corresponding to double-bonded carbon atoms, at δ_C 159.6 and 149.9 ppm. The chemical shifts of sp^3-hybridized carbon atoms in molecule **Ia** were similar to those reported in [31] for the same compound in an ether solvent. An additional support to cyclic structure of compounds **Ia** and **Ib** is provided by their transformation into 1,2-dialkylbuta-1,3-dienes **VIa** and **VIb** [15] or 1,1-disubstituted cyclopropanes **VIIa** and **VIIb** [16] (Scheme 3).

Scheme 3.



R = Pr (**a**), Bu (**b**), Ph (**c**).

Scheme 4.

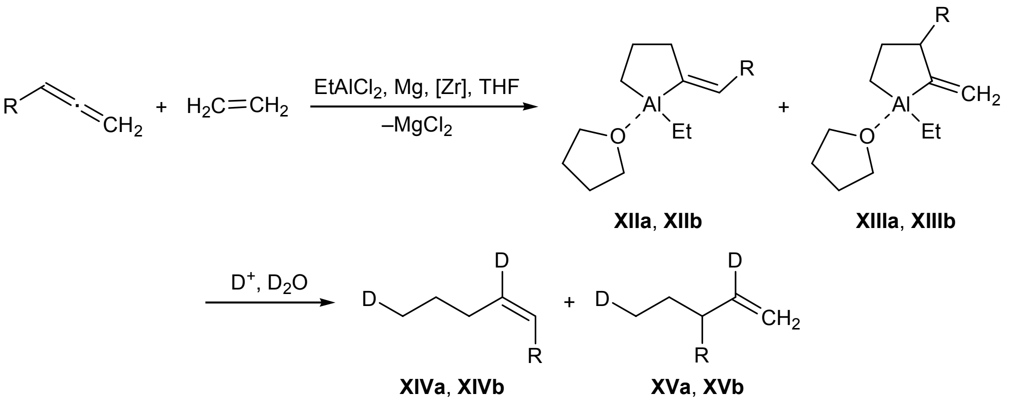


R = C_4H_9 (**a**), C_6H_{13} (**b**), C_8H_{17} (**c**).

The synthesis of 2,3-dialkyl(phenyl)aluminacyclopent-2-enes **I** with the use of $EtAlCl_2$ and $AlCl_3$ underlay an efficient procedure for the preparation of 3-alkylaluminacyclopentanes **VIII**. A necessary condition for selective formation of compounds **VIII** is intermediate generation of 3-alkylzirconacyclopentane complex from ethylene and terminal olefin [32]. We expected that transmetalation of 3-alkylzirconacyclopentane with $EtAlCl_2$ or $AlCl_3$ should lead to aluminacyclopentanes. By slowly (portionwise) adding terminal olefin (hex-1-ene, oct-1-ene, or dec-1-ene) to $EtAlCl_2$ under an ethylene pressure of 0.02 MPa in THF in the presence of magnesium and Cp_2ZrCl_2 as catalyst (molar ratio olefin–$EtAlCl_2$–Mg–Cp_2ZrCl_2 10 : 15 : 12 : 0.1, ~20°C, 6 h) we obtained 3-alkyl-1-ethylaluminacyclopentanes **VIIIa**–**VIIIc** in 55–70% yield (Scheme 4). Here, the yield of by-products (3,4-dialkylaluminacyclopentanes [32, 33]) did not exceed 3–5%. In the reaction with $AlCl_3$ instead of $EtAlCl_2$, the yields of aluminacyclopentanes **VIII** were 45–60%. The reaction was less selective when the reaction mixture contained insufficient amount of ethylene, for example, if the latter was bubbled through the mixture under atmospheric pressure or generated from 1,2-dichloroethane by the action of magnesium [34].

The structure of 3-alkylaluminacyclopentanes **VIIIa**–**VIIIc** was confirmed by ^1H, ^{13}C, and ^{27}Al NMR spectroscopy (tetrahydrofuran was used as solvent), including two-dimensional homo- and heteronuclear correlation techniques (COSYHH, HSQC, HMBC). In the ^{13}C NMR spectra, the chemical shifts of the C_8-cyclic structure appear in a weaker field relative to the corresponding carbon signal of dialuminum compound [35]; therefore, compounds **VIII** were preliminarily identified as 3-substituted aluminacyclopentanes. In the ^{27}Al NMR spectrum of **VIIIa**, recorded in an electron-donating solvent (THF), a signal at δ_{Al} 176.8 ppm was observed ($\omega_{1/2}$ = 6000 Hz). For comparison, the ^{27}Al NMR spectrum of the same aluminacyclopentane synthesized according to the procedure described in [36] was recorded in toluene-d_8 (δ_C 153.0 ppm, $\omega_{1/2}$ = 5600 Hz). Displacement of the aluminum signal in going to polar solvent indicates formation of a complex of aluminacyclopentane with tetrahydrofuran (solvent) molecule via Al···O interaction. The complex was also characterized by ^1H and ^{13}C NMR data. Coordination of a THF molecule to the aluminum atom could give rise to two stereoisomeric structures with 1,3-*cis* and 1,3-*trans* configurations of alkyl substituents due to appearance of asymmetric center at the four-coordinate aluminum atom (as in the complex with pyridine [36]). However, compound **VIIIa** displayed in the ^{13}C NMR spectrum only one set of signals. This means that only one stereoisomer is formed preferentially. As noted previously [36], one stereoisomer also prevailed in excess deuteropyridine, whereas by portionwise addition of deuteropyridine we succeeded in detecting splitting (~1 : 1) of signals from carbon atoms in molecule **VIIIa**. Presumably, electron-donating solvent gives rise to the equilibrium *cis*-**VIIIa**···THF $\rightleftarrows$ *trans*-**VIIIa**···THF, which is displaced toward thermodynamically more stable stereoisomer in the presence of excess solvent. The results of molecular mechanics calculations (MM2) of the pyridine complex showed that its *cis* stereoisomer is more stable (by 3.0 kcal/mol). According to DFT calculations (PBE/3z functional) with account taken of electron correlation (Priroda 6.0 program), stereoisomer *cis*-**VIIIa** is more energetically favorable (by 3.2 kcal/mol).

Scheme 5.



R = C_6H_{13} (**a**), C_8H_{17} (**b**).

The chemical shifts of the α-carbon atoms (C^2 and C^5) in complex **VIIIa**···THF are smaller by 3 and 0.5 ppm, respectively, than those of the complex of **VIIIa** with pyridine. The doublet signal at δ_C 43.0 ppm was assigned to C^3, and it displayed correlation with proton signal at δ 1.12 ppm in the HSQC spectrum. The COSYHH spectrum showed two couples of geminal diastereotopic protons which resonated in the upfield region, from δ 0.1 to –1.0 ppm, and were assigned to methylene groups in the five-membered ring, neighboring to the aluminum atom. According to the HSQC data, the couple of protons resonating at δ 0.00 and –0.98 ppm (Δδ = 0.98 ppm) gives a cross peak with C^2 (δ_C 13.6 ppm), while the other couple is attached to C^5 (δ_C 5.7 ppm). The difference in the chemical shifts of the latter is somewhat smaller and is Δδ = 0.38 ppm, which is consistent with the longer distance to the C^3 chiral center. Owing to the presence of an asymmetric center, protons on C^4 and C^6 are also diastereotopic. The presence of cross peaks in the COSYHH spectrum between the methylene protons on C^2 and C^3, as well as on C^4 and C^5, is consistent with the expected spin–spin couplings in the aluminacyclopentane molecule.

Deuterolysis of compounds **VIIIa**–**VIIIc** generated *in situ* gave 3-alkyl-1,4-dideuterobutanes **IXa**–**IXc**, and 3-alkyltetrahydrothiophenes **Xa**–**Xc** were obtained by heating aluminacyclopentanes **VIIIa**–**VIIIc** with elemental sulfur in boiling benzene. Carbocyclization of **VIIIa**–**VIIIc** in the presence of palladium complexes and allyl chloride as reoxidant [17] afforded monosubstituted cyclobutanes **XIa**–**XIc** (Scheme 4).

By reactions of 1,2-dienes (nona-1,2-diene and undeca-1,2-diene) with $EtAlCl_2$ in the presence of magnesium powder and Cp_2ZrCl_2 as catalyst under an ethylene pressure of 0.02 MPa (20–22°C, THF) we obtained 2-alkylidene-1-ethylaluminacyclopentanes **XIIa** and **XIIb** and 3-alkyl-1-ethyl-2-methylidenealuminacyclopentanes **XIIIa** and **XIIIb** at a ratio of ~5 : 1 (overall yield 55–75%). Under these conditions, the yield of by-products (regioisomeric aluminacyclopentanes formed from two 1,2-diene molecules [37]) did not exceed 10%. Aluminacyclopentanes **XIIa**/**XIIIa** and **XIIb**/**XIIIb** were identified by their transformation into 1,4-dideuteroolefins **XIVa**/**XVa** and **XIVb**/**XVb** (Scheme 5).

EXPERIMENTAL

The hydrolysis and deuterolysis products were analyzed 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 NMR spectra were measured on a Bruker Avance spectrometer at 400.13 MHz for ^1H, 100.62 MHz for ^{13}C, and 104.22 MHz for ^{27}Al. Two-dimensional experiments (COSYHH, HSQC, HMBC) were performed according to standard procedures. The yields of organoaluminum compounds were determined by GLC analysis of theit hydrolysis products using dodecane as internal standard. All reactions with organometallic compounds were carried out under dry argon. Tetrahydrofuran was dried by heating under reflux over metallic sodium and distilled before use. Commercially available 86% $EtAlCl_2$ was used.

Joint cycloalumination of ethylene and unsaturated compounds (dialkylacetylenes, terminal alkenes, and 1,2-dienes) with $EtAlCl_2$ ($AlCl_3$) in the presence of Cp_2ZrCl_2 as catalyst (*general procedure*). A glass reactor was charged under dry argon under stirring with 3 ml of THF, 12 mmol of magnesium powder, and 15 mmol of $EtAlCl_2$ or $AlCl_3$, 1.0 mmol of Cp_2ZrCl_2 was then added in ethylene atmosphere, excess ethylene pressure (~0.02 MPa) was supplied, and a solution of 10 mmol of the corresponding unsaturated compound in 8 ml of THF was slowly (over a period of ~2 h) added from a dropping funnel equipped with a pressure-equalization arm. The mixture was stirred for 4 h, treated with a 8–10% aqueous solution of HCl or DCl, and extracted with diethyl ether or hexane. The extract was dried over $MgSO_4$, the solvent was removed, and the products were isolated by fractional distillation. Hydrolysis and deuterolysis products **IVa**–**IVc**, **Va**–**Vc**, **IXa**–**IXc**, **XIVa**, **XIVb**, **XVa**, and **XVb** were identified by comparison with authentic samples [1–3, 5, 24].

1-Ethyl-2,3-dipropylaluminacyclopent-2-ene (Ia). Yield ~80% (according to the GLC data for the hydrolysis product). ^{13}C NMR spectrum (toluene-d_8), δ_C, ppm: 0.4 t (C^6), 3.1 t (C^5), 29.9, 32.2, 22.0, 21.62 t (C^8, C^9, C^{11}, C^{12}), 13.78, 13.81 s (C^{10}, C^{13}), 35.5 t (C^4), 149.9 s (C^2), 159.6 s (C^3).

3-Butyl-1-ethylaluminacyclopentane (VIIIa). Yield ~65% (GLC). ^1H NMR spectrum (THF-d_8), δ, ppm: –0.78 br.m (1H, 2-H), –0.49 br.m (1H, 5-H), –0.29 m (2H, 6-H), –0.20 br.m (1H, 5-H), 0.00 br.m (1H, 2-H), 0.79 m (3H, $C^{11}H_3$), 0.88 t (3H, C^7H_3, J = 6 Hz), 0.99 m (1H, 8-H), 1.19 m (8H, 3-H, 4-H, 8-H, 9-H, 10-H), 1.76 br.m (CH_2 in THF), 3.64 br.m (CH_2O in THF). ^{13}C NMR spectrum, δ, ppm: 0.0 t (C^6), 5.7 t (C^5), 13.6 t (C^2), 10.0 q (C^7), 14.8 q (C^{11}), 23.7 t (C^{10}), 31.5 t (C^9), 38.8 t (C^4), 42.1 t (C^8), 43.1 d (C^3), 26.5 t ($\mathbf{C}H_2$ in THF), 67.2 t ($\mathbf{C}H_2O$ in THF).

1,2-Dialkylbuta-1,3-dienes VIa and VIb (*general procedure*). Allyl acetate, 40 mmol, and $Pd(acac)_2$, 5 mol %, were added under stirring at –5°C to 2,3-dialkyl-1-ethylaluminacyclopent-2-ene **Ia** or **Ib** generated *in situ* from the corresponding dialkylacetylene, and the mixture was stirred for 10 h at room temperature, treated with 8–10% hydrochloric acid, and extracted with diethyl ether or hexane. The organic phase was separated, washed with a solution of sodium carbonate until neutral reaction, and dried over $CaCl_2$. 1,2-Dialkylbuta-1,3-dienes **VIa** and **VIb** were identified by comparison with authentic samples [15].

1,1-Disubstituted cyclopropanes VIIa and VIIb (*general procedure*). Dimethyl sulfate, 40 mmol, was added dropwise under stirring at 0°C to 2,3-dialkyl-1-ethylaluminacyclopent-2-ene **Ia** or **Ib** generated *in situ* from the corresponding dialkylacetylene, and the mixture was stirred for 12 h at ~20°C, treated with 8–10% hydrochloric acid, and extracted with hexane (3 × 5 ml). The extract was washed with a solution of Na_2CO_3 until neutral reaction and dried over $CaCl_2$. 1,1-Disubstituted cyclopropanes **VIIa** and **VIIb** were identified by comparison with authentic samples [16].

3-Alkyltetrahydrothiophenes Xa–Xc (*general procedure*). Anhydrous benzene, 10 ml, was added (after removal of THF) to 3-alkyl-1-ethylaluminacyclopentane **VIIIa**–**VIIIc** generated *in situ* from the corresponding terminal alkene, 45 mmol of cyclooctasulfane (C_8) was added, and the mixture was stirred for 6 h on heating at ~80°C. The mixture was then treated with 8–10% hydrochloric acid and extracted with diethyl ether, the extract was washed with a solution of sodium carbonate until neutral reaction and dried over $CaCl_2$, and 3-alkyltetrahydrothiophenes **Xa**–**Xc** were identified by comparison with authentic samples [18].

Alkylcyclobutanes XIa–XIc (*general procedure*). Anhydrous diethyl ether, 10 ml, was added (after removal of THF) to 3-alkyl-1-ethylaluminacyclopentane **VIIIa**–**VIIIc** generated *in situ* from the corresponding terminal alkene, the mixture was cooled to –5°C, 45 mmol of allyl chloride and 5 mol % of $Pd(acac)_2$–Ph_3P were added, and the mixture was stirred for 6 h at ~20°C, treated with 8–10% hydrochloric acid, and extracted with diethyl ether. The extract was washed with a solution of sodium carbonate until neutral reaction and dried over $CaCl_2$. Alkylcyclobutanes **XIa**–**XIc** were identified by comparison with authentic samples [17].

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