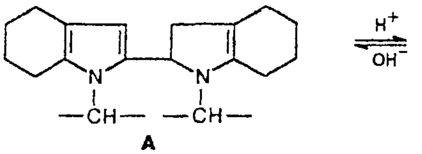
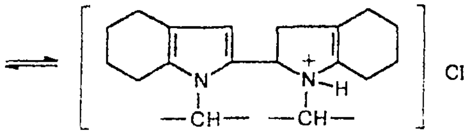
The intensities of the absorption band corresponding to the stretching vibrations of the CH=CH fragment (1640 cm^{-1}) and bands of the δ(CH) (1415 cm^{-1}) and ω(CH) (830 cm^{-1}) vibrations decrease sharply.

The reaction of the immonium cation with the pyrrole fragment of VTHI results in the formation of structure A. The subsequent protonation of the nitrogen atom of the nonaromatic heterocycle affords the ammonium cation **B** with the absorption band at 2400—3600 cm^{-1} (NH^+) in the IR spectrum.[2]



A



B

In the copolymers of VC with VTHI, the immonium cation predominates, while the copolymers of VDC with VTHI contain predominantly the ammonium cation. The treatment of the copolymer of VDC with VTHI with a solution of potassium hydroxide results in the deprotonation of the ammonium cation (**B** → **A**). In the IR spectra of the copolymer of VDC with VTHI, the "ammonium" band $\nu(NH^+)$ disappears, while the long-wave band with λ_{max} 360 nm disappears in the UV spectra.

The copolymerization of the monomers was carried out in sealed tubes at 80 °C in the presence of azoisobutyronitrile in an argon atmosphere. The reaction mass was dissolved in benzene, and the copolymer was precipitated with heptane. The copolymers were reprecipitated from a benzene solution with heptane. IR spectra were recorded on a Specord IR-75 spectrometer (pellets with KBr and suspensions in Vaseline oil). UV spectra were recorded on a Specord UV-VIS spectrometer (EtOH, l = 0.5—2.0 cm).

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Aluminacyclopropenes, a novel series of organoaluminum compounds

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Cycloalumination of disubstituted derivatives of acetylene with Et_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 leads to 2,3-disubstituted aluminacyclopentenes.[1–4]

To determine the possibility of synthesis of aluminacyclopropenes, we studied the interaction of acetylene derivatives with $EtAlCl_2$ under the action of Ti and Zr complexes, which are widely used as catalysts of hydro-, carbo-, and cyclometallation[2–6] of olefins.

The formation of molecules of zirconacyclopentanes from olefins and zirconacene proceeds[7–12] through the stage of formation of zirconacyclopropenes, while titanacyclopropenes obtained from low-valence Ti complexes and acetylene derivatives are stable. These data allowed us to assume that aluminacyclopropenes can be synthesized by cycloalumination of acetylene derivatives with alkylaluminum dihalides in the presence of Cp_2TiCl_2 and activated magnesium powder as an acceptor of chloride ions according to Scheme 1.

To verify the above assumption, we studied the interaction of 1,2-diphenylacetylene (**1**) and oct-4-yne (**2**) with $EtAlCl_2$, catalyzed by Ti and Zr compounds in the

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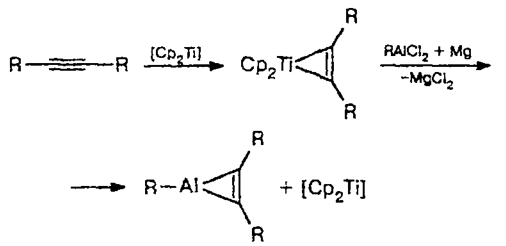
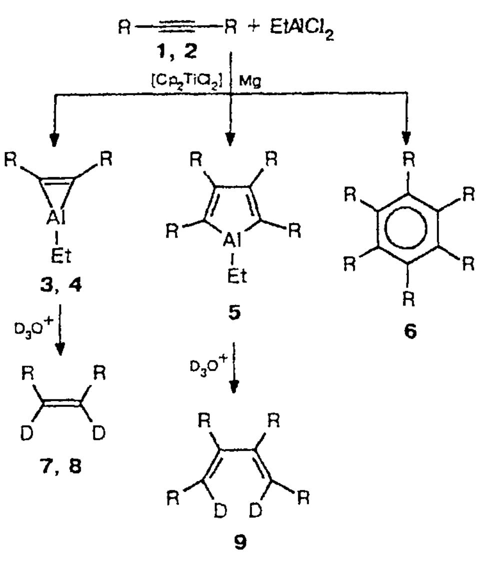
Scheme 1



presence of activated magnesium (a molar ratio of $RC\equiv CR : EtAlCl_2 : Mg : Cp_2TiCl_2$ = 100 : 150 : 100 : 5), in THF at ~20 °C for 8—10 h.

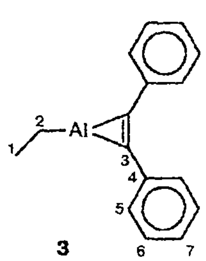
It turned out that using Zr complexes leads to the predominant formation of substituted aluminacyclopentadienes, and only in the case of catalysts based on titanium compounds, Cp_2TiCl_2 or the less selective $Ti(OPr^i)_4$ and $Ti(OBu^n)_4$, we did obtain the corresponding aluminacyclopropenes **3** and **4** in 65—90% yields (Scheme 2).

Scheme 2



R = Ph (**1**, **3**, **7**), Pr^n (**2**, **4—6**, **8**, **9**)

It should be noted that, unlike compound **1**, experiments with compound **2** are characterized by formation of 1-ethyl-2,3,4,5-tetrapropyl-1-aluminacyclopenta-2,4-diene (**5**) and hexapropylbenzene (**6**) along with compound **4** (in the ratio of **4** : **5** : **6** ≈ 65 : 10 : 25) in an overall yield of ~90%. The structures of cyclic organoaluminum compounds obtained were determined using ^{13}C NMR spectroscopy and by their transformation into unsaturated compounds **7—9** upon deuterolysis.



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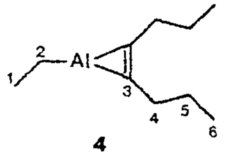

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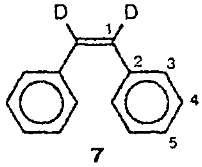

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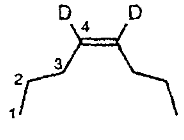

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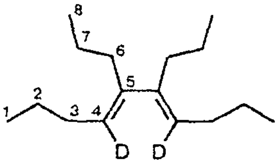

9

^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q instrument (^1H, 90 and ^{13}C, 22.5 MHz).

^{13}C NMR ($SiMe_4$, C_6D_6), δ: **1-ethyl-2,3-diphenyl-1-aluminacycloprop-2-ene (3):** 7.91 (C-1); 1.86 (C-2); 139.85 (C-3); 136.41 (C-4); 126.85 (C-5); 128.48 (C-6); 125.55 (C-7); **1-ethyl-2,3-dipropyl-1-aluminacycloprop-2-ene (4):** 8.22 (C-1); 0.60 (C-2); 128.40 (C-3); 28.46 (C-4); 24.68 (C-5); 14.36 (C-6); ***cis*-1,2-dideutero-1,2-diphenylethylene (7):** 130.08 (C-1, J_{C-D} = 23.0 Hz); 137.09 (C-2); 128.13 (C-3), 128.82 (C-4); 127.04 (C-5); ***cis*-4,5-dideuterooct-4-ene (8):** 13.81 (C-1); 22.94 (C-2); 29.34 (C-3); 129.40 (C-4, J_{C-D} = 23.8 Hz); **4,7-dideutero-5,6-dipropyldeca-4,6-diene (9):** 13.95 (C-1); 23.02 (C-2); 30.12 (C-3); 125.70 (C-4, J_{C-D} = 24.0 Hz); 141.22 (C-5); 31.31 (C-6); 22.12 (C-7); 14.13 (C-8).

Hexapropylbenzene (6) was identified by comparison with a reference compound.[13]

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Diastereoselective allylboration of carbonyl derivatives of [2.2]paracyclophane

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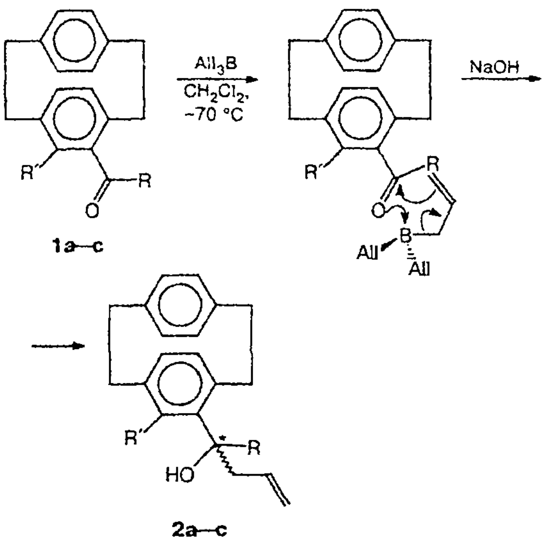
In this work, we performed for the first time the diastereoselective nucleophilic addition at the C=O bond in monosubstituted carbonyl derivatives of [2.2]paracyclophane ([2.2]PC).

Monosubstituted [2.2]PC possess planar chirality, and the thermal and conformational stability of compounds of this class make them promising as auxiliary reagents and ligands for the development of catalysts for asymmetrical synthesis.[1]

Organomagnesium and -lithium reagents react with monosubstituted carbonyl derivatives of [2.2]PC to give the corresponding alcohols; however, these reactions are not stereoselective.[2,3] It is also known[4] that β,γ-unsaturated (allylic) boron derivatives react with carbonyl compounds similarly to classical organometallic reagents, *i.e.*, *via* 1,2-addition to the C=O bond. Allylboration occurs with the 1,3-rearrangement through a chair-like six-centered transition state (2π+2π+2σ-process),[5] which allows enantio- and diastereoselective allylboration to be performed with the corresponding reagents.[6] Based on these data, we have studied for the first time the allylboration of planar chiral derivatives of [2.2]PC.

Carbonyl derivatives of [2.2]PC (4-formyl[2.2]PC (**1a**), 4-acetyl[2.2]PC (**1b**), and 4-hydroxy-5-formyl[2.2]PC (**1c**)) react with triallylborane in CH_2Cl_2 at −70 to +40 °C to give, after treatment with an aqueous solution of alkali, the corresponding homoallylic alcohols (**2a—c**) in 80—99% yields (Scheme 1). The existence of one or two signals of protons of diastereotopic groups (—C*H*(OH), —CH(O*H*), —C*H*$_2$—CH=, —C*H*=CH$_2$) in the ^{1}H NMR spectra of the reaction mixture made it possible to study the diastereoselectivity of allylboration for racemic carbonyl compounds of [2.2]PC.

Scheme 1



1a, **2a**: R = R' = H
1b, **2b**: R = Me, R' = H
1c, **2c**: R = H, R' = OH

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