SYNTHESIS AND CONVERSIONS OF METALLOCYCLES.

7.* A NOVEL APPROACH TO THE SYNTHESIS OF 3,4-DIALKYL-SUBSTITUTED ALUMINACYCLOPENTANES IN THE PRESENCE OF Cp_2TrCl_

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A novel approach was developed for the stereoselective synthesis of trans-3,4dialkyl-substituted aluminacyclopentanes from α -olefins, metallic magnesium, and EtAlCl₂ in the presence of catalytic amounts of Cp₂ZrCl₂. The hydrolysis and deuterolysis products of the 3,4-dialkyl-substituted aluminacyclopentanes obtained are only in the trans configuration.

Recently we proposed a method for producing 3,4-dialkyl substituted aluminacyclopentanes (ACP) by cyclometallation of α -olefins with trialkylalanes (R₃Al) with Cp₂ZrCl₂ as catalyst [1] using the following scheme:



 $R = \Lambda lk$.

In order to develop a new preparative method for synthesis of available reagents as well as to seek effective approaches to the synthesis of aluminacyclopentane compounds we studied the reaction of α -olefins with EtAlCl₂ and metallic magnesium in the presence of catalytic amounts of Cp₂ZrCl₂.

We proceeded from the premise that during the reduction of Cp_2ZrCl_2 using active Mg, Cp_2Zr is generated in situ [2, 3], which cyclometallates α -olefins giving the corresponding zirconacyclopentanes. Remetallation of the latter, as we proposed, should have led to 3,4-diallyl-substituted ACP.



 $R = C_{3}H_{7}$ (a), $C_{5}H_{11}$ (b), $C_{8}H_{17}$ (c), Ph (d).

*For previous communication, see [1].

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In order to realize the above hypothesis we carried out reactions of a series of aliphatic α -olefins with EtAlCl₂ and metallic magnesium in a molar ratio of 2:1:1 in a solution of tetrahydrofuran (THF) at 23-25°C (6-8 h) in the presence of 5 mole % Cp₂ZrCl₂. Under these conditions 1-ethyl-trans-3,4-dialkyl-substituted ACP were obtained in 70-85% yields.

ACP (Ia-d) containing two asymmetric carbon atoms (C³ and C⁴) upon hydrolysis or deuterolysis yield the corresponding conversion products exclusively in the three configuration. The stereochemistry of the compounds obtained was determined uniquely via ¹³C NMR [1, 4].

On the basis of the results obtained we can conclude that the key intermediate in the synthesis of trans-3,4-dialkyl-substituted ACP is zirconocene formed from Cp_2ZrCl_2 and metallic magnesium. The catalytic cycle is completed by cyclometallation of an α -olefin followed by remetallation of the zirconacyclopentane intermediate using EtAlCl₂ and regeneration of the initial Cp_2ZrCl_2 .



EXPERIMENTAL

The reaction was carried out in dry argon. THF was distilled over LiAlH₄ immediately prior to use. Gas-liquid chromatography was done with a Khrom-5 chromatograph in a stream of He on a 1200 \times 3 mm column with 5% SE-30 or 15% PEG-6000 on N-AW. IR spectra were recorded on a UR-20 (film) spectrometer and mass spectra were obtained on an MX-1306 spectrometer at 70 eV and 130°C. ¹H NMR were recorded in CDCl₃ on Tesla BS-567 (100 MHz) and Tesla BS-467 (60 MHz) spectrometers with TMS as internal standard. ¹³C NMR spectra were taken on a JEOL FX-90Q spectrometer (22.5 MHz) with wideband and extra resonance quenching with respect to protons. The yields of aluminacyclopentanes were determined by gas-liquid chromatography of the hydrolysis or deuterolysis products. Compounds (IIa) and (IIIa-c) were identified by comparison with previously synthesized samples [1].

Synthesis of Ethyl trans-3,4-Dialkyl-Substituted Aluminacyclopentanes. A glass 50 ml reactor on a magnetic stirrer in an atmosphere of dry argon at -5 to 0°C was charged with 0.0876 g (0.3 mmole) Cp_2ZrCl_2 , 0.24 g (10 mmoles) magnesium powder, 2.24 g (20 mmoles) 1-octane, 10 ml THF, and 1.27 g (10 mmoles) ETAlCl₂. The temperature was slowly raised to 23-25°C and the mixture stirred for 10 h. Hydrolysis of the organoaluminum compound obtained gives 7,8-dimethyltetradecane in a yield of 1.72 g (76%).

 $\frac{\text{Ethyl} (\text{trans-3,4-Dibutyl}) \text{aluminacyclopentane (Ia)}}{(C^2, C^5), 43.95 \text{ d} (C^3, C^4), 0.52 \text{ t} (C^6), 8.80 \text{ q} (C^7), 37.66 \text{ t} (C^8), 30.21 \text{ t} (C^9), 23.54 \text{ t} (C^{10}), 14.52 \text{ q} (C^{11}).}$

<u>Ethyl (trans-3,4-Dibenzyl)aluminacyclopentane (Id)</u>. ¹³C NMR spectrum (δ , ppm): 11.05 t (C², C⁵), 45.59 t (C³, C⁴), 0.86 t (C⁶), 8.93 q (C⁷), 44.69 t (C⁹), 143.60 s (C⁹), 128.08 d (C¹⁰, C¹⁴), 129.56 d (C¹¹, C¹³), 125.43 d (C¹²).

 $\frac{\text{threo-10,ll-Dimethyleicosane (IIb)}}{(6H, CH_3), 0.88 \text{ t} (6H, CH_3), 1.05-1.44 \text{ m} (34H, CH, CH_2).$ ¹³C NMR spectrum (δ , ppm): 14.17 q (C¹), 36.71 d (C²), 35.11 t (C³), 27.87 t (C⁴), 30.17 t (C⁵), 29.52 t (C⁶), 29.82 t (C⁷), 29.91 t (C⁸), 32.08 t (C⁹), 22.80 t (C¹⁰), 14.48 q (C¹¹).

 $\frac{\text{threo-2,3-Dibenzylbutane (IId)}}{\text{IR spectrum }(\nu, \text{ cm}^{-1}): 2980, 1600, 1495, 1443, 1365, 740, 700. PMR spectrum (ô, ppm): 0.83 d}$

(6H, CH₃), 1.80 m (2H, CH), 2.43-2.71 m (4H, CH₂), 7.03-7.34 m (10H, Ph). ¹³C NMR spectrum (δ_{\odot} ppm): 13.92 (C¹), 38.09 d (C²), 41.34 t (C³), 141.36 s (C⁴), 128.02 d (C⁵), 128.84 d (C⁶), 125.51 d (C⁷). M⁺ 238.

 $\frac{1,4-\text{Dideutero-threo-2,3-dibenzylbutane (IIId)}{132-135^{\circ}C (1 \text{ mm})}. \text{ IR spectrum (v, cm^{-1}): } 3022, 2943, 2865, 2200, 1605, 1510, 1464, 762, 720. PMR spectrum (\delta, ppm): 0.76-0.92 m (4H, CH_2D), 1.73-1.86 m (2H, CH), 2.35-2.72 m (4H, CH_2Ph), 7.05-7.37 m (10H, Ph). ^{13}C NMR spectrum (\delta, ppm): 12.83 t (C¹), 38.06 d (C²), 41.31 t (C³), 141.48 s (C⁴), 128.04 d (C⁵), 128.90 d (C⁶), 125.53 d (C⁷). M⁺ 240.$

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SYNTHESIS OF STERICALLY HINDERED AROMATIC ALDEHYDES

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Formylation of mesitylene, durene, and m-xylene derivatives containing electrondonor and electron-acceptor substituents by dichloromethyl methyl ether was studied in the presence of TiCl₄. A series of functionally substituted sterically hindered benzaldehydes was prepared from the products of these reactions.

Previously, in studying the formylation of mesitylene by dichloromethyl methyl ether (DCME) in the presence of $AlCl_3$ and $TiCl_4$, we observed an unknown direction of this reaction, leading to the formation of dichloromethyl derivatives [1]. Here we identified among the reaction products not only (dichloromethyl)mesitylene (Ia), but also 2,4,6-trimethyl-3-(dichloromethyl)benzaldehyde (IIa), whose formation was due to the formylation of chloride (Ia) under the reaction conditions. In the present paper, this assumption was confirmed experimentally. In addition to attempting to elucidate the range of use of this reaction, we studied the reaction of DCME in the presence of $TiCl_4$ with substituted mesitylenes and also with durene, m-xylene, and their dichloromethyl-substituted compounds.

From among substituted mesitylenes, we studied the dichloride (Ia), acetylmesitylene (Ie), (chloromethyl)mesitylene (Ib), mesitol (Ic), (trichloromethyl)mesitylene (Id), bis-(chloromethyl)mesitylene (IIIa), and also bis(dichloromethyl)mesitylene (IIIb) and formyl-mesitylene. The conditions under which formylation of these mesitylene derivatives occurs depend on the electron-acceptor ability of the substituent. Thus, formylation of compounds (Ia-c) occurs at -20°C, whereas less active compounds (Id), (Ie), and (IIIa) are formylated at 40°C, and compound (IIIb), strongly deactivated by two dichloromethyl groups, does not react, even during long-term boiling in methylene chloride, used as a solvent. The products of formylation of compounds (Ia-e) and (IIIa) are the corresponding aldehydes (IIa-e) and (IVa) (Table 1) (see scheme on top of following page).

Because dichloromethyl-substituted compounds are facilely prepared by the reaction of PCl; with the appropriate aldehydes, the dichloromethyl group can be considered as a unique shielding group, making it possible to carry out the successive introduction of two aldehyde groups into aromatic compounds. Thus, the above-described conversion of dichloride

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