## SYNTHESIS AND CONVERSIONS OF METALLOCYCLES. 8.\* REGIOSELECTIVE $\beta$ -HYDROVINYLATION OF $\alpha$ -OLEFINS WITH THE PARTICIPATION OF METALLOCOMPLEX CATALYSTS

U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, and R. R. Muslukhov

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A new method is proposed for the synthesis of 2-vinylalkanes by the reactions of aluminocyclopentanes with allyl halides or ethers in presence of catalytic amounts of nickel or cobalt complexes.

<u>Keywords</u>: synthesis, olefins, nickel complexes, cobalt complexes, catalysts, allyl compounds, phosphines, organoaluminum compounds, reduction, elimination.

We recently carried out the conversion of 3-alkyl-substituted aluminocyclopentanes (ACP) [2] into cyclobutanes under the action of phosphine complexes of Pd [3], and also into 1,1-disubstituted cyclopropanes in the presence of catalytic amounts of Ni(acac)<sub>2</sub> [4].

In the present work we studied the new reaction of 3-alkyl-substituted ACP with allyl compounds. The ACP used (Ia-d) were prepared by the cycloalumination of 1-hexene, 1-heptane, 1-hexadecene, and 2,7-octadien-1-ol by AlEt<sub>3</sub> in the presence of catalytic amounts of  $Cp_2ZrCl_2$  ( $Cp = \eta^5-C_5H_5$ ) [2]. It was found that the resulting ACP in the presence of a three-fold excess of allyl chloride or an allyl ether under the action of three-component catalysts Ni(acac)\_2-Ph\_3P-i-Bu\_2AlH or Co(acac)\_3-Ph\_3P-i-Bu\_2AlH (1:4:8) are converted after hydrolysis into 2-vinylalkanes. For example, the ACP (Ia-d) in the presence of 5 mole % of a phosphine complex of Ni or CO react with allyl chloride (ACP:allyl chloride = 1:3) over the course of 10 h at ~20°C, and the hydrolysis of the reaction mixture with aqueous HCl then gives the 3-methyl-1-alkenes (2a-d) in yields of ~75%. In the course of the reaction an equimolecular amount of propene is liberated. In each experiment, apart from 3-methyl-1-alkenes, their structural isomers (2-methylenealkanes) are formed (content in the mixture of hydrocarbons 5-8%).

AlEt<sub>3</sub> + R  $\xrightarrow{[Zr]}$  Et -A1  $\xrightarrow{[M]}$  R  $\xrightarrow{[M]}$ (1a-d) (2a-d) R = C<sub>3</sub>H<sub>7</sub> (a), C<sub>4</sub>H<sub>9</sub> (b), C<sub>13</sub>H<sub>27</sub> (c), CH<sub>2</sub>-CH<sub>2</sub>-CH=CH-CH<sub>2</sub>OH (d); M = Ni, Co.

In the absence of a complex catalyst or an allyl compound, the reaction does not proceed. The nature of the solvent has scarcely any influence on the yields of the vinylalkanes (2a-d), but the latter depend greatly on the structure of the allyl compound used (Table 1). Of the catalysts tried in this reaction, which were based on complexes of Fe, Co, Ni, Pd, Rh, and Ir, the Ni- and Co-containing systems gave the highest yields of vinylalkanes.

It may be supposed that the formation of molecules of 2-vinylalkanes from 3-alkylsubstituted ACP proceeds through intramolecular  $\beta$ -hydride transfer of a hydrogen atom in the original ACP under the action of low-valence complexes of Ni and Co, leading to hydride

\*For previous communication, see [1].

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TABLE 1. Influence of the Solvent and the Nature of the Catalyst and Allyl Substrate on the Yield of 3-Methyl-1-heptadecene (2c) ( $[M] = 5 \mod \%$ , 10 h, ~20°C),

Solvent *	Yield of (2c), %	Allyl <sup>†</sup> substrate	Yield of (2c), %	Catalyst ‡	Yield of (2c), %
Hexane Pentane Cyclohexane Benzene THF Ether	75 74 74 72 70 68	Cl CH <sub>3</sub> O Ph_O BuO N() <sub>3</sub>	75 64 58 56 5 0	Ni $(acac)_2$ : Ph <sub>3</sub> P: : <i>i</i> -Bu <sub>2</sub> AlH=1:4:8 Co $(acac)_3$ : Ph <sub>3</sub> P : : <i>i</i> -Bu <sub>2</sub> AlH=1:4:8 Pd $(acac)_2$ : Ph <sub>3</sub> P : : <i>i</i> -Bu <sub>2</sub> AlH=1:4:8 Cu $(acac)_2$ : Ph <sub>3</sub> P= =1:2	75 68 0 0

\* Ni(acac)<sub>2</sub>: Ph<sub>3</sub>P:*i*-Bu<sub>2</sub>A1H = 1:4:8, / Cl:A1Et<sub>3</sub> = 3:1.

<sup>†</sup> Ni(acac)<sub>2</sub>: Ph<sub>3</sub>P:*i*-Bu<sub>2</sub>AlH = 1:4:8, allyl substrate AlEt<sub>3</sub> = 3:1.

 $\pm$  Cl:A1Et<sub>3</sub> = 3:1.

derivatives of aluminum (3) [6]. These derivatives reduce the allyl compounds (allyl chloride, allyl ethers) to propene [7] and are converted into the corresponding aluminum halides or alkoxides (4). The hydrolysis of the latter leads to 2-vinylalkanes (2), while deuterolysis leads to the corresponding 1-deutero-2-vinylalkanes (5) by the following scheme:



 $\mathbf{X} = \mathbf{Cl}, \mathbf{OR}.$ 

Analysis of the <sup>13</sup>C NMR spectra of the unsaturated organoaluminum compound (4a,  $R = C_3H_7$ , X = Cl) indicates that the diamagnetic influence of the Al atom causes an upfield shift of the signal of C<sup>1</sup> and downfield shifts of the signals of C<sup>2</sup> and C<sup>3</sup> relative to the chemical shifts of the corresponding atoms of the hydrocarbon analog (2a). The difference in the chemical shifts of the olefinic carbon atoms of (4a) and of (2a), attaining 4.6 and 9.8 ppm respectively, indicates the presence of intramolecular p-m interaction [11] of the Al atom with the m electrons of the double bond.

The method developed opens up a new promising route to the synthesis of 3-methyl-1alkenes by the  $\beta$ -hydrovinylation of  $\alpha$  olefins through the stage of the in situ preparation of 3-alkyl-substituted ACP.

## EXPERIMENTAL

The reactions were conducted in an atmosphere of dry argon; solvents were distilled over LiAlH<sub>4</sub> immediately before use. The GLC analysis was conducted in a Chrom 5 chromatograph in a stream of He; column 1200  $\times$  3 mm, 5% SE 30 or 15% PEG 6000 on Chromaton N-AW. The IR spectra were run on a UR 20 spectrometer (sample as film). The mass spectra (EI) were run on an MKh 1306 spectrometer with ionizing electrons of 70 eV energy and a source temperature of 130°C. The <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a Tesla BS 567 (100 MHz) and BS 467 (60 MHz) spectrometers, internal standard TMS. The <sup>13</sup>C NMR spectra were run on a Jeol FX 90Q spectrometer (22.5 MHz) with broad-band and out-of-resonance decoupling of protons. The constants of the hydrocarbons (2a) and (2b) agree with published data [8-10]. Synthesis of 2-Vinylalkanes. A 50 ml glass reactor provided with a magnetic stirrer and filled with an inert gas was charged with 0.0524 g (0.2 mmole) of  $Cp_2ZrCl_2$ , 1.368 g (12 mmoles) of AlEt<sub>3</sub>, and then 10 mmoles of the corresponding  $\alpha$  olefin (Table 1). The mixture was stirred for 10 h at ~20°C and then brought to -5°C, when successive additions were made of 36 mmoles of the allyl compound (Table 1) and the catalyst, prepared by mixing 0.1285 g (0.5 mmole) of Ni(acac)<sub>2</sub>, 0.524 g (2 mmoles) of Ph<sub>3</sub>P, 0.568 g (4 mmoles) of i-Bu<sub>2</sub>AlH, and hexane; the mixture was heated to ~20°C and stirred for 10 h. The reaction was accompanied by the liberation of propene. The reaction mixture was cautiously treated with 2 N HCl at 0°C and extracted with ether. The individual products were isolated by vacuum fractionation.

 $\frac{3-\text{Methyl-1-heptadecene}(2c)}{(1.4437)}, \text{ IR spectrum } (\nu, \text{ cm}^{-1}); 3090, 2930, 2860, 1650, 1470, 1385, 1010, 925, 740, 700. PMR spectrum <math>(\delta, \text{ ppm}); 0.90 \text{ m } (6H, \text{ CH}_3), 1.22 \text{ m}}$ (27H, CH, CH<sub>2</sub>), 4.80-5.66 m (3H, CH=CH<sub>2</sub>). <sup>13</sup>C NMR spectrum  $(\delta, \text{ ppm}); 112.13 \text{ t } (C^1), 145.03 \text{ d } (C^2), 37.75 \text{ d } (C^3), 36.71 \text{ t } (c^4), 27.26 \text{ t } (C^5), 29.38 \text{ t } (C^6), 26.69 \text{ t } (C^7-C^{14}), 31.94 \text{ t } (C^{15}), 22.11 \text{ t } (C^{16}), 14.13 \text{ q } (C^{17}), 20.20 \text{ q } (C^{18}). Mass spectrum, m/z; 252 [M<sup>+</sup>].$ 

 $\frac{7-\text{Methyl-2,8-nonadien-1-ol} (2d)}{112.78 \text{ t} (C^1), 131.25 \text{ d} (C^8), 63.02 \text{ t} (C^9), 20.46 \text{ q} (C^{10}).$ 

<u>Chloroethyl(2-vinylhexyl)aluminum (4a)</u>. <sup>13</sup>C NMR spectrum ( $\delta$ , mm, Et<sub>2</sub>O, internal standard TMS): 17.62 t (C<sup>1</sup>), 37.73 d (c<sup>2</sup>), 39.42 t (C<sup>3</sup>), 29.73 t (C<sup>4</sup>), 23.45 t (C<sup>5</sup>), 14.41 q (C<sup>6</sup>), 133.76 d (C<sup>7</sup>), 118.25 t (C<sup>8</sup>), 1.47 t (C<sup>9</sup>-A1), 8.24 q (C<sup>10</sup>).

 $\frac{3-(\text{Methyl-d})-1-\text{heptadecene (5c), nD}^{21} 1.4433. \text{ IR spectrum (v, cm}^{-1}): 2960, 2925, 2225, 1640, 1460, 1085, 1000, 995, 715, 620. PMR spectrum (\delta, ppm): 0.87-0.98 m (5H, CH<sub>3</sub>, CH<sub>2</sub>D), 1.25 m (26H, CH<sub>2</sub>), 1.72-1.98 m (1H, CH), 4.83-5.69 m (3H, CH=CH<sub>2</sub>). <sup>13</sup>C NMR spectrum (\delta, ppm): 19.69 t (C<sup>1</sup>, <sup>1</sup>J<sub>13</sub>C-D = 19.12 Hz), 36.68 d (C<sup>2</sup>), 37.43 t (C<sup>3</sup>), 27.29 t (C<sup>4</sup>), 29.70 t (C<sup>5</sup>-C<sup>12</sup>), 29.37 t (C<sup>13</sup>), 31.92 t (C<sup>14</sup>), 22.71 t (C<sup>15</sup>), 14.09 q (C<sup>16</sup>), 145.04 d (C<sup>17</sup>), 112.14 t (C<sup>18</sup>). Mass spectrum, m/z: 253 [M<sup>++</sup>].$ 

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