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Synthesis and transformations of metallocycles
15.* A novel method for β-vinylation of α-olefins with $AlEt_3$ under the action of Ni- and Zr-containing catalysts

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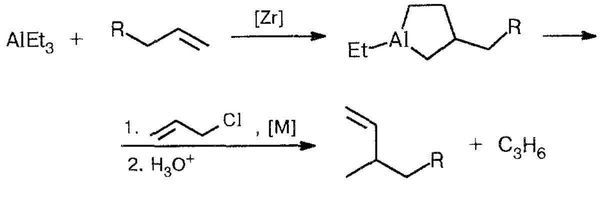
A novel regioselective method has been developed for the synthesis of 2-substituted 1,3-butadienes by β-vinylation of α-olefins with $AlEt_3$ in the presence of Ni- and Zr-containing catalysts.

Key words: dienes, synthesis; nickel complexes, catalysts; allyl compounds; organoaluminum compounds.

Recently[2] we described an efficient one-pot method for the synthesis of 2-vinylalkanes from α-olefins and $AlEt_3$ involving Zr-, Ni-, and Co-containing metallocomplex catalysts. The method is based on the one-stage reaction of cycloalumination of α-olefins by $AlEt_3$ in the presence of catalytic amounts of Cp_2ZrCl_2 developed by us. The reaction results in the formation of 3-substituted alumocyclopentanes (ACP).[3—6]

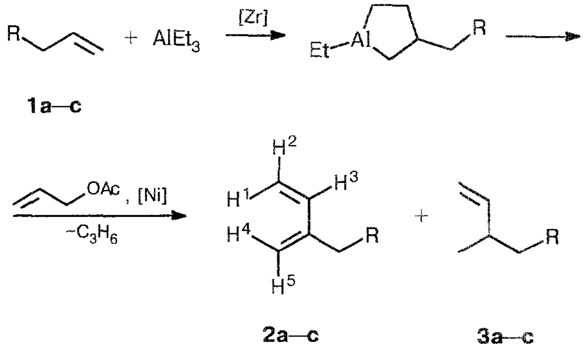
Subsequent transformations of ACP obtained *in situ* under the action of complexes of low-valence Ni and Co in the presence of allyl chloride, which acts as a reoxidant,[2] result in 2-vinylalkanes in one technological stage.



M = Ni, Co; R = Alk

While studying the scope of the application of this reaction we found that 2-alkyl-substituted 1,3-butadienes are formed in the course of transformations of ACP under the action of catalytic amounts of the $Ni(acac)_2$ complex in the presence of allyl acetate. To choose the optimum conditions for the synthesis of conjugated dienes, we studied the effects of the nature of the solvent, the ratio of the components of the catalyst and initial reagents, as well as the temperature and the duration of the reaction on the selectivity of transformations of ACP to the corresponding 2-substituted 1,3-butadienes. It was found that the highest yields of the products are obtained when $Ni(acac)_2$ in a THF solution (the molar ratio $Ni(acac)_2$: ACP : allyl acetate is 5 : 100 : 360) is used as the catalyst.

Thus, α-olefins **1a—c** produce 2-alkyl-1,3-butadienes **2a—c**, respectively (the yields are 71—76 %) in the presence of 5 mol. % $Ni(acac)_2$ at the ratio ACP/CH_2CHCH_2OAc = 1 : 3.6 after 10 h in a THF solution at 21—23 °C after the hydrolysis of the reaction mass with a 5 % aqueous HCl. In each experiment, the reaction is accompanied by the liberation of an equimolar amount of propylene and the formation of 3-methyl-1-alkenes[2] **3a—c** (the yields are 10—25 %).



a: R = Pr
b: R = C_5H_{11}
c: R = C_8H_{17}

Using 1-undecene (**1c**) as an example, it was shown that the yield of diene **2c** decreases from 71 to 63 % when the reaction is carried out in ether and decreases

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* For Part 14, see Ref. 1.

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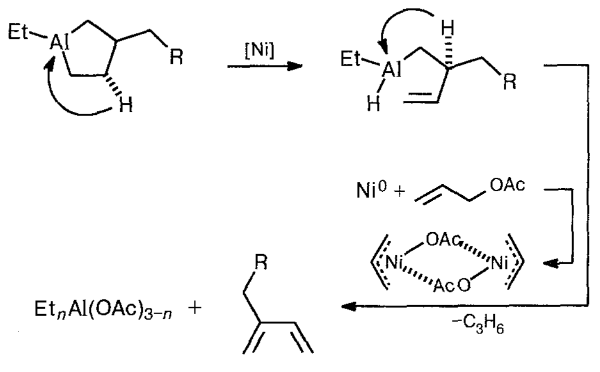
to 43 % when pentane is used. All other conditions being equal, replacing allyl acetate with allyl propionate results in desired product **2c** in a yield of 51 %. The use of $Ni(PPh_3)_2$ prepared *in situ* instead of $Ni(acac)_2$ results in a decrease in the yield of diene **2c** to 52 %. No 2-substituted 1,3-butadienes are formed in the absence of Ni-containing compounds or allyl acetate.

It can be assumed that 2-substituted 1,3-butadienes are formed *via* the intramolecular β-hydride detachment of the H atom in the initial ACP through the action of low-valence Ni complexes to form alkenyl hydridalanes, which reduce π-allyl Ni complexes to Ni^0. The role of allyl acetate is probably to generate the catalytically active binuclear π-allyl complexes formed as the result of their oxidative addition to Ni^0.

The subsequent catalytic β-hydride detachment of the H atom in the alkene hydridalanes formed results in the formation of 2-substituted 1,3-butadienes.



It was established using β-vinylation of allylbenzene and 4-vinylcyclohexene as an example (Scheme 1) that an aryl substituent or an additional double bond in the initial α-olefin exerts virtually no effect on the direction of the reaction, however, the yield of substituted 1,3-butadienes decreases.

The method developed is promising for the synthesis of useful 2-substituted 1,3-butadienes of the given structures from accessible α-olefins and $AlEt_3$ under mild conditions and in rather high yields.

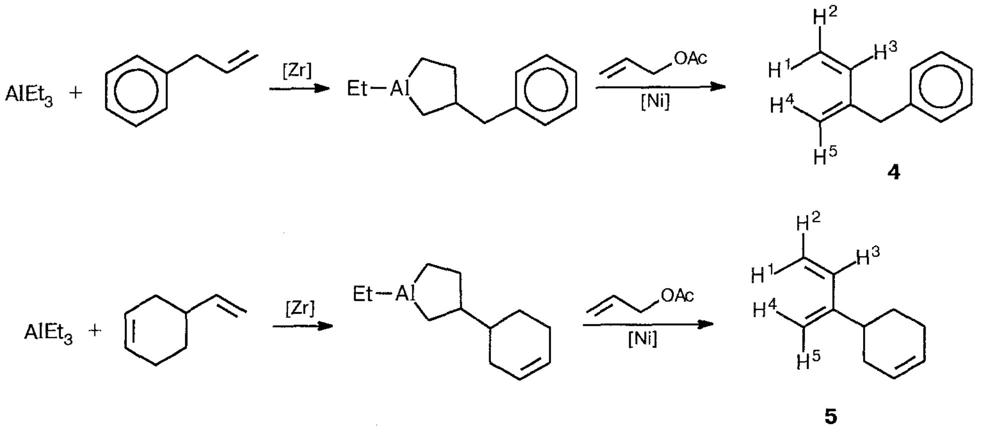
Experimental

The reactions were performed in an argon atmosphere. The solvents were distilled over $LiAlH_4$ immediately prior to use. GLC was performed on a Khrom-5 chromatograph (He as the carrier gas, column 1200×3 mm, 5 % SE-30 or 15 % PEG-6000 on Chromaton N-AW). A Perkin-Elmer F-21 chromatograph (He as the carrier gas (300 mL min^{-1}), column 5000×8 mm, 5 % SE-30 on Chromaton N-AW) was used for the preparative separation of 2-substituted 1,3-butadienes from 2-vinylalkanes. IR spectra were recorded on a UR-20 spectrophotometer (film), and mass spectra (EI) were obtained on a MKh-1306 spectrometer at 70 eV in which the temperature of the source was 130 °C. ^1H NMR spectra (in $CDCl_3$) were recorded on Tesla BS-567 (100 MHz) and Tesla BS-467 (60 MHz) spectrometers, TMS was used as the internal standard; ^{13}C NMR spectra (in $CDCl_3$) were obtained on a Jeol FX-90Q spectrometer (22.5 MHz) with the broad-band and extraresonance suppression of protons.

Synthesis of 2-substituted 1,3-butadienes (general procedure). Cp_2ZrCl_2 (0.524 g, 0.2 mmol), $AlEt_3$ (1.368 g, 12 mmol), and the corresponding α-olefin (10 mmol) were placed in an argon atmosphere in a glass reactor with a magnetic stirrer. The mixture was stirred at ~22 °C for 10 h. The reaction was accompanied by the liberation of ethane. THF (10 mL), allyl acetate (36 mmol), and $Ni(acac)_2$ (0.1285 g, 0.5 mmol) were subsequently added at −5 °C to the mixture, which was kept for 20 min, warmed to room temperature, and stirred for 10 h. The reaction was accompanied by the liberation of propylene. The reaction mass was treated with 5 % aqueous HCl at ~0 °C and was extracted with ether. Individual products were isolated by distillation *in vacuo* and preparative GLC.

2-Butyl-1,3-butadiene (2a). Yield 76 %, n_D^{22} 1.4403 (Ref. 7: n_D^{20} 1.4415). IR, ν/cm^{-1}: 3075, 2945, 2920, 2845, 1590, 1450, 1375, 990, 895, and 725. ^1H NMR, δ: 0.88 (t, 3 H, CH_3); 1.2—1.43 (m, 4 H, CH_2); 2.11—2.16 (m,

Scheme 1



2 H, CH_2—C=); 4.91 (m, 2 H, H(4), H(5)); 4.98 (d, 1 H, H(2), ^3J = 11.1 Hz); 5.15 (d, 1 H, H(1), ^3J = 17.6 Hz); 6.3 (dd, 1 H, H(3), $^3J_{H(1),H(3)}$ = 17.6 Hz, $^3J_{H(2),H(3)}$ = 10.8 Hz). ^{13}C NMR, δ: 115.5 (t, C(1)); 139.2 (d, C(2)); 144.2 (s, C(3)); 113.1 (t, C(4)); 30.5 (t, C(5)); 31.2 (t, C(6)); 22.8 (t, C(7)); 14.1 (q, C(8)).

2-Hexyl-1,3-butadiene (2b). Yield 74 %, n_D^{23} 1.4484. MS, *m/z*: 138 $[M]^+$. IR, ν/cm^{-1}: 3095, 3020, 2970, 2940, 2870, 1790, 1640, 1600, 1475, 1390, 1125, 1005, 910, and 745. UV (EtOH), λ_{max}/nm: 224 (logε 4.36). ^1H NMR, δ: 0.89 (t, 3 H, CH_3); 1.23—1.54 (m, 8 H, CH_2); 2.17—2.22 (m, 2 H, CH_2—C=); 4.98 (m, 2 H, H(4), H(5)); 5.03 (d, 1 H, H(2), ^3J = 10.9 Hz); 5.22 (d, 1 H, H(1), ^3J = 17.6 Hz (Ref. 8: ^3J = 18 Hz)); 6.36 (dd, 1 H, H(3), $^3J_{H(1),H(3)}$ = 17.6 Hz (Ref. 8: $^3J_{H(1),H(3)}$ = 18 Hz), $^3J_{H(2),H(3)}$ = 10.8 Hz (Ref. 8: $^3J_{H(2),H(3)}$ = 10 Hz)). ^{13}C NMR, δ: 115.4 (t, C(1)); 139.2 (d, C(2)); 146.8 (s, C(3)); 113.0 (t, C(4)); 31.9 (t, C(5)); 29.4 (t, C(6)); 28.3 (t, C(7)); 31.5 (t, C(8)); 22.8 (t, C(9)); 14.2 (q, C(10)).

2-Nonyl-1,3-butadiene (2c). Yield 71 %, n_D^{21} 1.4546. IR, ν/cm^{-1}: 3105, 2940, 1650, 1480, 1015, 920, and 750. UV (EtOH), λ_{max}/nm: 225 (logε 4.18). ^1H NMR, δ: 0.89 (t, 3 H, CH_3); 1.15—1.5 (m, 14 H, CH_2); 2.17—2.23 (m, 2 H, CH_2—C=); 4.98 (m, 2 H, H(4), H(5)); 5.05 (d, 1 H, H(2), ^3J = 10.8 Hz (Ref. 8: ^3J = 10 Hz)); 5.23 (d, 1 H, H(1), ^3J = 17.5 Hz (Ref. 8: ^3J = 18 Hz)); 6.23 (dd, 1 H, H(3), $^3J_{H(1),H(3)}$ = 16.6 Hz, $^3J_{H(2),H(3)}$ = 10.8 Hz). ^{13}C NMR, δ: 115.5 (t, C(1)); 139.1 (d, C(2)); 148.7 (s, C(3)); 113.1 (t, C(4)); 32.0 (t, C(5)); 28.6 (t, C(6)); 29.4 (t, C(7)); 29.7 (t, C(8), C(9), C(10)); 31.5 (t, C(11)); 22.8 (t, C(12)); 14.2 (q, C(13)).

2-Benzyl-1,3-butadiene (4). Yield 57 %, $n_D^{16.5}$ 1.5397 (Ref. 9: n_D^{20} 1.5407). IR, ν/cm^{-1}: 3075, 3010, 2890, 1585, 1485, 1445, 980, 890, 715, and 690. ^1H NMR, δ: 3.47 (s, 2 H, CH_2); 4.87 (m, 2 H, H(4), H(5)); 5.05 (d, 1 H, H(2), ^3J = 10.7 Hz (Ref. 8: ^3J = 10 Hz)); 5.24 (d, 1 H, H(1), ^3J = 17.4 Hz (Ref. 8: ^3J = 17 Hz)); 6.36 (dd, 1 H, H(3)); 7.07—7.19 (m, 5 H, Ph). ^{13}C NMR, δ: 114.4 (t, C(1)); 138.5 (d, C(2)); 145.3 (s, C(3)); 118.3 (t, C(4)); 38.3 (t, C(5)); 139.5 (s, C(6)); 128.4 (d, C(7), C(11)); 129.3 (d, C(8), C(10)); 126.1 (d, C(9)).

2-(4-Cyclohexenyl)-1,3-butadiene (5). Yield 61 %, $n_D^{16.5}$ 1.5023 (Ref. 10: n_D^{20} 1.5088). IR, ν/cm^{-1}: 3075, 3010, 2905, 2825, 1590, 1430, 980, 885, 715, and 640. ^1H NMR, δ: 1.28—1.90 (m, 2 H, CH_2); 1.92—2.16 (m, 4 H, CH_2C=); 2.19—2.60 (m, 1 H, CH—C=); 4.92 (m, 2 H, H(4), H(5)); 4.99 (d, 1 H, H(2), ^3J = 10.4 Hz); 5.12 (d, 1 H, H(1), ^3J = 17.3 Hz); 5.63—5.65 (m, 2 H, CH=CH); 6.29 (dd, 1 H, H(3), $^3J_{H(1),H(3)}$ = 17.3 Hz, $^3J_{H(2),H(3)}$ = 10.4 Hz). ^{13}C NMR, δ: 115.3 (t, C(1)); 138.9 (d, C(2)); 151.4 (s, C(3)); 112.3 (t, C(4)); 34.7 (d, C(5)); 31.8 (t, C(6)); 126.0 (d, C(7)); 126.7 (d, C(8)); 25.4 (t, C(9)); 29.0 (t, C(10)).

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