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Hydrogenation of ethyl 12-trimethylsilyl-9-dodecyn-11-enoate by isocyanide polymer-bound $Rh(PPh_3)_3Cl$

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Abstract

The *E*-isomer of the title substrate has been hydrogenated with 75% selectivity to the corresponding *Z,E*-diene at 4.5 bar H_2 and room temperature in the presence of catalytic amounts of a polymer bound rhodium complex. © 1998 Published by Elsevier Science B.V. All rights reserved.

Keywords: Selective hydrogenation; Cross-linked polymer; Isocyanide polymer; Supported catalyst; Rhodium; Alkyne; Alkene

1. Introduction

We have recently reported on the catalytic activity of a supported rhodium complex obtained by anchoring $RhCl(PPh_3)_3$ to a macromolecular ligand via isonitrile functionalities [1]. The material obtained upon activation of the supported complex under 1 bar H_2 at 50°C was shown to catalyse the hydrogenation of various unsaturated organic substrates such as alkenes, alkynes, α,β-unsaturated aldehydes and ketones, cyano- and nitro-compounds, the reduction of polyfunctional substrates such as carvone or citral being quite selective, leading in the first case to carvotanacetone, in the second case to citronellal.

We decided to test the chemoselectivity of our catalyst submitting to reductive conditions the enyne **2** whose hydrogenation at the triple bond affords a molecule that can be considered a useful intermediate in the synthesis of (*S*)-(9*Z*, 11*E*) coriolic acid, a natural compound which has recently shown to exhibit interesting physiological properties [2].

The overall synthesis design is summarized in retroanalytical fashion in Scheme 1.

Thus, a double disconnection on the dienyl moiety reveals the building block **1**, a monosilylated iodoenyne.

Accordingly, a cross-coupling reaction between the key compound **1** and an appropriate organometallic reagent leads to compound **2**. The subsequent selective reduction of the triple bond affords compound **3**, which, after a simple electrophilic substitution of the silyl group [3]

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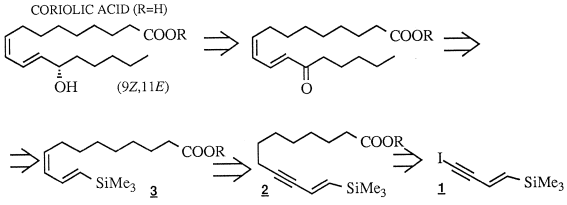


Scheme 1.

with an appropriate acyl chloride, followed by the enantioselective reduction of the carbonyl group, leads to the target molecule.

2. Results and discussion

According to the retrosynthetic scheme, the synthesis of the polyfunctional compound **2** was performed as depicted in Scheme 2.

The appropriate desilylation of the bis-silylated compound **4** [4] and the reaction of the resulting monosilylated enyne with molecular iodine in the presence of morpholine afforded compound **1**. The subsequent coupling reaction of **1** with the organozinc reagent, in the presence of CuCN and LiCl [5] led to **2** in 42% yield (E:Z = 85:15).

The tests of hydrogenation were carried out on the isomers mixture, so that minor amounts of the reaction products deriving from the reduction of (Z)-**2** were detected as byproducts in the reaction mixture. However, the following discussion, aimed to put in light the performance of our catalyst, will be centered on the reaction of the major substrate (in terms of conversion and selectivity) giving in the experimental part the data concerning the real mixture. [1]

Scheme 3 shows the hydrogenation products of **2**.

The first tests were performed at hydrogen pressure as high as 1 atm and in the temperature interval 21–70°C, but in these conditions, the hydrogenation rate was negligible.

Successive tests were carried out at 10 bar H_2 and room temperature (21°C). In this case, the rate of hydrogenation was high, but the selectivity was quite low. After 1-h reaction, the conversion was 58%, the selectivity towards **3** was 67%, and the reaction mixture revealed the presence of 9% of **7**. When the reaction time was prolonged up to 8 h, the conversion was quantitative but the major product (69%) was found to be the less interesting compound **7** coming from the overall reduction of the triple and of the double bond.

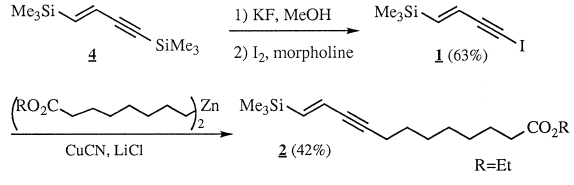
After several tests carried out in the pressure interval 1–10 bar, the best results were obtained when the reaction was performed at 4.5 bar hydrogen. The selectivity towards **3** maintains as high as 75% during all reaction which was stopped after 7 h with a conversion of **2** as high as 92%. Noteworthy, no trace of the saturated compound **7** and only 6% of **5** was found in the reaction mixture, the major byproducts being the monoenes **6a**–**b** (17%).

The time course of this reaction is reported in Fig. 1.

3. Experimental

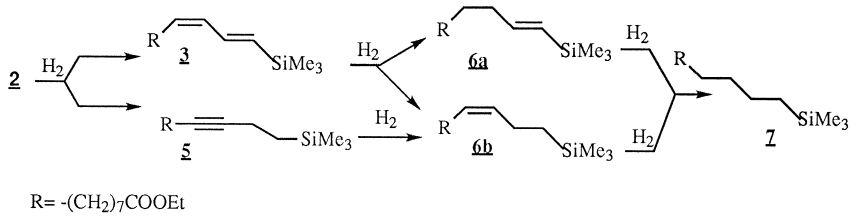
The polymeric complex was synthesized by the procedure described in Ref. [1].

Chromatographic analyses were carried out on a Hewlett Packard 5890 chromatograph using a 25-m SPB-1 capillary column. GC/MS



Scheme 2.

[1] In the data presented in the discussion, the formation of the alkyne **5** was attributed only to the hydrogenation of the major substrate although it derives also from the hydrogenation of the (Z)-**2** isomer.



Scheme 3.

analyses were performed using a HP 5890 chromatograph (30 m SE30 column) coupled with a mass selective detector HP 5970B, 70 eV. NMR spectra were recorded on Bruker AM300 or Varian XL200 instruments.

3.1. Hydrogenation reactions

3.1.1. Atmospheric pressure

A Schlenk tube was charged with the activated catalyst (15 mg, 0.011 mmol of rhodium), the substrate (1.74 mmol) and methanol (2.5 ml) and stirred under 1-atm H_2 at the desired temperature (21, 50, or 70°C).

3.1.2. Reactions under pressure

A stainless steel autoclave was charged with the activated catalyst (15 mg, 0.011 mmol of rhodium), the substrate (1.74 mmol) and 2.5 ml of methanol and pressurized with H_2 to the desired pressure. The mixture was stirred at room temperature and monitored by GLC.

After stopping the reactions, the recovered suspension was filtered and the liquid phase was analysed by GLC, GC/MS, and, after evaporation, ^{1}H NMR. The gas chromatographic composition of the solution resulting from the reaction carried out at 4.5 bar hydrogen was: 7% (*E*)-**2**, 5% (*Z*)-**2**, 59% **3**, 24% monoenes and 5% **5**.

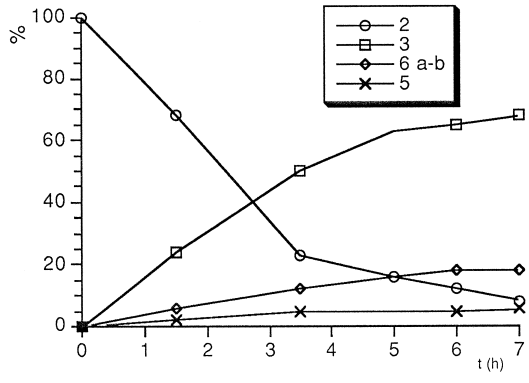


Fig. 1. Time-course of the hydrogenation of **2** carried out under 4.5 bar hydrogen.

3.2. Synthesis of compounds **1** and **2**

3.2.1. 1-Iodo-4-trimethylsilyl-3-buten-1-yne (**1**)

KF (14.82 g, 255 mmol) was added to a stirred solution of (*E*)-1,4-bis(trimethylsilyl)-3-buten-1-yne [4] (5.07 g, 25.5 mmol) in CH_3OH (48 ml). The mixture was warmed at 50–55°C for 1 h, then treated with water and extracted with ethyl ether. The organic solvent was washed with water, dried over Na_2SO_4 and evaporated at atmospheric pressure. A THF solution (40 ml) of molecular iodine (6.47 g, 25.5 mmol) was dropped into the solution of the resulting mono-silylated enyne and morpholine (2.22 g, 25.5 mmol) in THF (40 ml). After complete addition, the resulting mixture was warmed at 40°C for 4 h. Then, the reaction mixture was quenched with aqueous $Na_2S_2O_3$ 3% and extracted with ethyl acetate. The combined organic extracts were washed with water, dried (Na_2SO_4) and concentrated. The residue was purified by distillation (Kugelrohr oven temperature 75°C/1 mmHg) leading to compound **1** in 63% overall yield (4.02 g, $E:Z = 87:13$).

3.2.2. Ethyl (*E*)-12-trimethylsilyl-9-dodecyn-11-enoate (**2**)

A solution of diethyl zinc (68 ml, 1.0 M solution in hexanes) was added under nitrogen to ethyl 8-iodooctanoate (5.01 g, 16.8 mmol)

and CuI (0.095 g, 0.50 mmol). The reaction mixture was warmed at 50–55°C and stirred for 46 h at this temperature. Then, the ethyl iodide formed, and excess diethylzinc was removed in vacuum (50°C, 2 h; 0.1 mmHg). A THF solution (26 ml) of CuCN (0.75 g, 8.4 mmol) and LiCl (0.71 g, 16.8 mmol) was added at −20°C to a stirred solution of the organozinc in THF (34 ml). After complete addition, the mixture was cooled to −78°C and compound **1** (2.1 g, 8.4 mmol) was added. The reaction mixture was stirred at −78°C for 1 h, then warmed to room temperature, quenched with aqueous NaOH 10% and extracted with ethyl acetate. The combined extracts were washed with water, dried (Na_2SO_4) and concentrated. The residue was purified by distillation (Kugelrohr oven temperature 150°C/1×10^{-4} mbar) affording 1.04 g of **2** (42% yield, $E:Z = 85:15$).

3.3. Spectroscopic features

3.3.1. *1 (E-isomer)*

MS (70 eV): m/e (relative intensity): 250 (M^+, 26), 235 (68), 209 (94), 185 (58), 127 (17), 123 (100), 73 (8), 67 (8), 59 (16), 53 (10), 43 (17). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 0.05 (s, 9 H), 6.01 (d, $J = 19.3$ Hz, 1 H), 6.47 (d, $J = 19.3$ Hz, 1 H).

3.3.2. *2 (E-isomer)*

MS (70 eV): m/e (relative intensity): 294 (M^+, 2), 279 (9), 249 (7), 173 (12), 103 (85), 75 (98), 73 (100), 59 (58). ^{1}H NMR (300 MHz, CDCl3, ppm): 0.02 (s, 9 H), 1.14–1.40 (m, 9 H), 1.41–1.63 (m, 4 H), 2.17–2.32 (m, 4 H), 4.06 (q, $J = 7.2$ Hz, 2 H), 5.87 (dt, $J = 19.2$, 2.0 Hz, 1 H), 6.25 (d, $J = 19.2$ Hz, 1 H).

3.3.3. *Ethyl (9Z,11E)-12-trimethylsilyl-9,11-dodecadienoate (3)*

MS (70 eV): m/e (relative intensity): 296 (M^+, 9), 251 (4), 173 (15), 149 (4), 103 (44), 75 (61), 73 (100), 59 (63). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.04 (s, 9 H), 1.15–1.42 (m, 11 H), 1.49–1.64 (m, 2 H), 2.11–2.30 (m, 4 H), 4.07 (q, $J = 7.1$ Hz, 2 H), 5.38 (dt, $J = 10.7$, 7.7 Hz, 1 H), 5.78 (d, $J = 18.3$ Hz, 1 H), 5.95 (t, $J = 10.7$ Hz, 1 H), 6.76 (dd, $J = 18.3$, 10.7 Hz, 1 H).

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