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Unusual Pt-catalyzed stereo and regioselective intramolecular hydrosilylation of propargyl alcohols to (*E*,*E*)-1,6-dioxa-2,7-disila-3,8-ecidienes

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Abstract

Stereo- and regioselective functionalization of propargyl alcohols have been achieved via intramolecular hydrosilylation reaction promoted by solvated Pt-atoms. © 1998 Elsevier Science S.A. All rights reserved.

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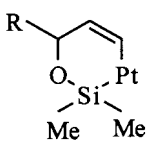
There is a great deal of attention in catalytic intramolecular hydrosilylation reactions as new powerful approach to regiocontrolled syntheses [1,2].

Hydrodimethylsilylethers derived from homopropargyl alcohols have been reported to rapidly undergo chloroplatinic acid catalyzed *cis*-intramolecular hydrosilylation to penta-cyclovinyl silanes, while propargyl alcohol silyl ether derivatives gave only polymeric materials under similar reaction conditions [2].

We found that mesitylene solvated platinum atoms, already reported [3] as remarkable catalysts for the hydrosilylation of dienes and acetylenes, are able to promote the intramolecular hydrosilylation of hydrodimethylsilylethers of propargyl alcohols to ten membered rings as illustrated in Scheme 1.

Propargyl alcohols **1**, quantitatively converted to hydrodimethylsilylethers **2** by reaction with tetramethyldisilazane at r.t., rapidly undergoes, in the presence of mesitylene solvated Pt atoms ($3-5 \times 10^{-3}$ g atom% based on the hydrosilyl ether **2**), a selective cyclodimerization to (*E*,*E*)-5,10-dialkyl-2,2,7,7-tetramethyl-1,6-dioxa-2,7-disila-3,8-ecidienes, **3**. Compounds **3** have been fully characterised by MS, ^{1}H- and ^{13}C-NMR; the *trans* configuration of the double bonds has been also confirmed by a bromine cleavage of the silicon–carbon bonds of **3a**, which proceeds with complete inversion of stereochemistry [4], achieving the *cis* bromide **4a** (Scheme 1).

It is worth noting that, using H_2PtCl_6 as catalytic precursor, we found that compounds **3** are formed only in traces; in this reaction polymeric materials are the main reaction product, as observed with other propargyl alcohol silyl ether derivatives [2]. The different behaviour found using solvated Pt-atoms and H_2PtCl_6 as catalysts could be rationalized considering that in the platinum catalyzed hydrosilylation the true catalytic species are likely to be Pt colloids [5]; their formation from H_2PtCl_6 will require an induction period which could overtake, for some substrates, by reactions, such as polymerization; on the contrary solvated Pt-atoms can be regarded as already reactive 'naked' Pt clusters, able to rapidly promote hydrosilylation reactions [3].



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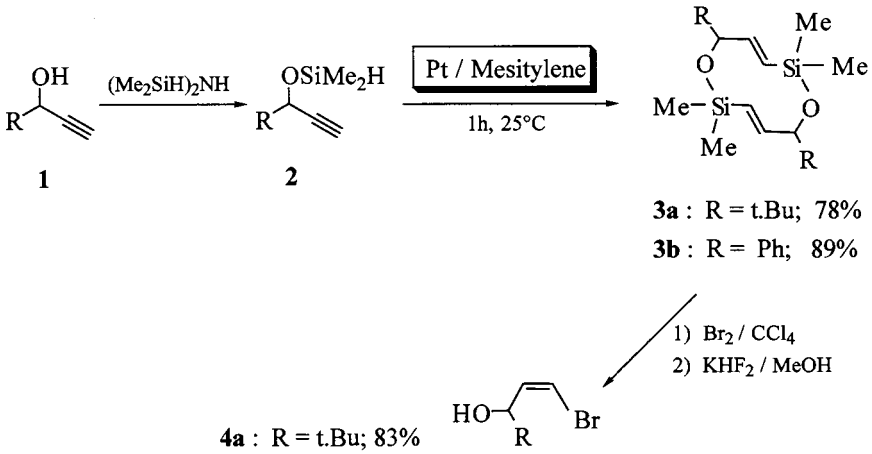


Scheme 1.

The reaction pathway to **3** is probably complicated; a likely first step of the reaction could be the formation of a six membered intermediate **5** deriving from a 6-endo-dig ring clousure involving the Pt atom. It will then appear that a further reductive elimination should afford a strained pentacyclo product, making more favoured a dimerization process, as also observed in the cyclohydrosilylation of allyl alcohols [6].

Although the mechanistic problems require further investigations, the reported results indicate that the MVS catalytic precursor [3] provides an efficient and general way for the functionalization of acetylenic carbinols with high stereo- and regioselectivity.

Actually, mesitylene solvated Pt-atoms are extremely effective also in promoting the intramolecular hydrosilylation of homopropargyl hydrodimethylsilyl ethers affording a practical tool for the selective preparation of a wide range of polyfunctionalized intermediates such as compounds **7** (Scheme 2).

1. Experimental details

All experiments were carried out under exclusion of air and moisture.-NMR spectra were determined with a Varian Gemini 200 instrument (200 MHz for ^{1}H, 50.3 MHz for ^{13}C); mass spectra were obtained at 70 eV on a VG Analitical 7070 mass spectrometer.

*1.1. General procedure for the synthesis of **3a**,**b***

Typically, in a 25 ml Pyrex Carius tube, 5 mmol of the propargyl carbinol **1** were treated with 1,1,3,3-tetramethyldisilazane (1.07 g, 8.0 mmol) and anhydrous NH_4Cl (ca. 5 mg). After stirring at r.t. for 15 h, the excess of tetramethyldisilazane was removed in vacuo and 3 ml of a Pt/Mesitylene solution, containing 0.015 mg atom of platinum [3], were added to the crude oil obtained. The mixture was stirred at 25°C for 1 h. The mesitylene was removed in vacuo and the crude product was dissolved in diethyl ether and filtered on celite. Pure ecidiene **3** was isolated as an oil by simple solvent evaporation.

*1.1.1. (E,E)-5,10-di(tertbutyl)-2,2,7,7-tetramethyl-1,6-dioxa-2,7-disila-3,8-ecidiene (**3a**)*

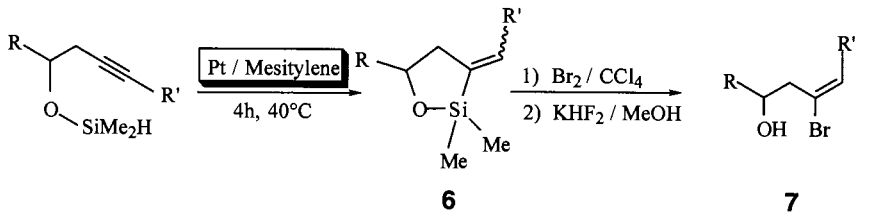
^{1}H-NMR ($CDCl_3$, δ ppm): 0.06 (6H, s, CH_3Si), 0.11 (6H, s, CH_3Si), 0.82 (18H, s, CH_3), 3.68 (2H, d, $J = 6.2$ Hz, CH–O), 5.70 (2H, d, $J = 18.9$ Hz, =CH–Si), 6.11 (2H, dd, $J = 18.9$ and 6.2 Hz, =CH). ^{13}C-NMR ($CDCl_3$, δ ppm): -0.98, -0.51, 25.9, 29.7, 83.5, 129.0, 148.4. MS m/z: 340 (M^+), 57 (100%). Anal. Found: C, 63.34; H, 10.64. $C_{18}H_{36}O_2Si_2$ Calc.: C, 63.49; H, 10.66

*1.1.2. (E,E)-5,10-diphenyl-2,2,7,7-tetramethyl-1,6-dioxa-2,7-disila-3,8-ecidiene (**3b**)*

^{1}H-NMR ($CDCl_3$, δ ppm): 0.10 (6H, s, CH_3Si), 0.13 (6H, s, CH_3Si), 5.06 (2H, d, $J = 5.0$ Hz, CH–O), 5.78 (2H, dd, $J = 18.7$ Hz, =CH–Si), 6.15 (2H, dd, $J = 18.7$ and 5.0 Hz, =CH), 7.23 (10H, m, PhH). ^{13}C-NMR ($CDCl_3$, δ ppm): -1.16, -1.01, 77.2, 125.7, 126.4, 127.1, 142.7, 150.5. MS m/z: 380 (M^+), 77 (100%). Anal. Found: C, 69.30; H, 7.39. $C_{22}H_{28}O_2Si_2$ Calc.: C, 69.44; H, 7.42.

*1.2. Preparation of (Z)-1-bromo-4,4-dimethyl-1-penten-3-ol (**4a**)*

In a dry 25 ml round-bottomed flask, bromine (0.192 g, 62 μl, 1.2 mmol) was added dropwise with a microsyringe to a solution of the ecidiene **3a** (200 mg, 0.6 mmol) in CCl_4 (5 ml) at 0°C. The mixture was stirred at 0°C for 4 h. Then, KHF_2 (280 mg, 3.6 mmol) and



6 **7**

a : R = Ph , R' = H
b : R = Me , R' = Me_3Si

7a : 74%
7b : 62%

Scheme 2.

MeOH (5 ml) were added; the resulting mixture was stirred at r.t. for 12 h and filtered. The filtrate was treated with diluted aq.$Na_2S_2O_3$ and extracted with ether. The organic layer was washed with water, 6 N aq. HCl, and diluted aq.$NaHCO_3$, dried (Na_2SO_4) and concentrated in vacuo to give the crude product **4a** which was purified by bulb-to-bulb distillation (yield: 192 mg, 83%).

^{1}H-NMR ($CDCl_3$, δ ppm): 1.01 (9H, s CH_3), 2.27 (1H, s, OH), 3.65 (1H, dd, $J = 7.2$ and 1.4 Hz, CH–O), 6.18 (1H, dd, $J = 8.6$ and 7.2 Hz, =CH), 6.34 (1H, dd, $J = 8.6$ and 1.4 Hz, =CHBr). MS m/z: 194 (M^+ for ^{81}Br), 192 (M^+ for ^{79}Br), 57 (100%).

Compounds **7a** and **7b** were prepared by the above methods, with total yields noted in Scheme 2.

*1.3. 2,2-Dimethyl-3-methylene-5-phenyl-1-oxa-2-silacyclopentane (**6a**)*

^{1}H-NMR ($CDCl_3$, δ ppm): 0.29 (6H, s, CH_3Si), 2.49 (1H, dd, $J = 9.5$ and 14 Hz, CHC=), 2.68 (1H, dd, $J = 4.0$ and 14. Hz, CHC=), 4.84 (1H, m, CH–O), 5.64 (1H, d, $J = 2.0$ Hz, $=CH_2$), 5.77 (1H, m, $=CH_2$), 7.37 (5H, m, PhH). ^{13}C-NMR ($CDCl_3$, δ ppm): 0.5, 46.3, 72.7, 125.8, 127.3, 128.3, 129.1, 144.3, 148.3. MS m/z: 204 (M^+, 96%), 77 (100). Anal. Found: C, 70.37; H, 7.89. $C_{12}H_{16}OSi$ Calc.: C, 70.55; H, 7.90.

*1.4. 2,2,5-Trimethyl-3-(trimethylsilyl)methylene-1-oxa-2-silacyclopentane (**6b**)*

MS m/z: 214 (M^+, 5%), 73 (100); the compound was treated in situ with bromine without further characterization.

*1.5. 3-Bromo-1-phenyl-3-buten-1-ol (**7a**)*

^{1}H-NMR ($CDCl_3$, δ ppm): 1.97 (1H, s, OH), 2.72 (1H, ddd, $J = 1.1$, 4.8 and 14.5 Hz, CHC=), 2.84 (1H, ddd, $J = 0.8$, 8.4 and 14.5 Hz, CHC=), 5.02 (1H, dd, $J = 4.8$ and 8.4 Hz, CH–O), 5.52 (1H, m, $=CH_2$), 5.66 (1H, m, $=CH_2$), 7.30 (5H, m, PhH). ^{13}C-NMR ($CDCl_3$, δ ppm): 51.3, 71.6, 120.0, 125.8, 127.9, 128.5, 130.1, 142.8. MS m/z: 129 (M^+-Br, -H_2O, 2%), 107 (100).

*1.6. (E)-2-bromo-1-trimethylsilyl-1-penten-4-ol (**7b**)*

^{1}H-NMR ($CDCl_3$, δ ppm): 0.17 (9H, s, CH_3Si), 1.20 (3H, d, 6.2 Hz, CH_3), 1.77 (1H, s, OH), 2.58 (2H, d, $J = 6.6$ Hz, CH_2), 4.00–4.21 (1H, m, CH–O), 6.08 (1H, s, =CH). ^{13}C-NMR ($CDCl_3$, δ ppm): −0.97, 22.2, 55.5, 65.5, 132.7, 138.8. MS m/z: 223 (M^+-15, for ^{81}Br, 2%), 221 (M^+-15, for ^{79}Br, 2%), 73 (98), 45 (100). The *(E)* configuration of the double bond was determined by ^{1}H-NMR NOE experiments.

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