

Hydrosilylation of unsaturated (hetero)aromatic aldehydes and related compounds catalyzed by transition metal complexes

Irina Iovel, Juris Popelis, Alexander Gaukhman, Edmunds Lukevics *

Latvian Institute of Organic Synthesis, 21 Aizkraukles str, Riga, LV-1006, Latvia

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Abstract

[Rh(COD)Cl]₂ has been found to be a more active catalyst than Ir, Ru, Pt and Pd complexes for the hydrosilylation of unsaturated furan and aromatic aldehydes with HSiEt₃. 1,4- and 1,2-addition reactions giving unsaturated silyl ethers in *cis*- and *trans*-configurations occurred as well as the hydrogenation reactions which produce the corresponding saturated silyl ethers. The migration of the ethyl group was observed in the hydrosilylation of 3-ethyl-3-(5-nitrofuryl)acrolein. The dehydrogenative silylation occurred in the reactions of cinnamyl alcohol and furan-2-acrylic acid. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hydrosilylation; Complex catalysis; Rhodium(I); (Hetero)aromatic aldehydes

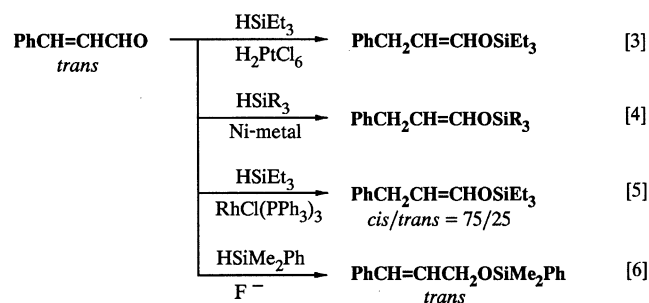
1. Introduction

The hydrosilylation of a large number of various unsaturated compounds with alkylsilanes has been successfully carried out during the last decades [1]. The investigations of this reaction are still continuing [2]. Nevertheless, up to now the hydrosilylation of unsaturated (hetero)aromatic aldehydes (and related alcohols and acids) has not been investigated in detail. The pool of catalysts used for these processes is very limited.

The hydrosilylation of cinnamaldehyde (*trans*-3-phenyl-2-propenal) with various trialkyl(aryl)silanes was studied in the presence of homogeneous and heterogeneous catalysts. The reaction directions depend on a catalyst nature. In the presence of Speier's and Wilkinson's catalysts (H₂PtCl₆ · 6H₂O solution in 2-propanol and RhCl(PPh₃)₃, respectively) and metallic nickel the 1,4-addition occurs giving the corresponding silyl ethers [3–5]. The ratio of the product stereo isomers *cis*/*trans* = 75/25 was determined in [5]. The reaction catalyzed by fluoride ion gives the *trans*-product of 1,2-addition to the carbonyl group [6] (Scheme 1).

The dehydrogenative silylation to unsaturated silyl ethers occurs as the main process in the reactions of cinnamic (*trans*-3-phenylacrylic) acid with thienyl silanes in the presence of Speier's catalyst [7]. The hydrosilylation of methyl cinnamate with HSiEt₃ catalyzed by RhCl(PPh₃)₃ proceeds as 1,4-addition, giving the corresponding silyl ether [8].

To our knowledge, the hydrosilylation of heterocyclic unsaturated carbonyl and carboxyl functionalized compounds has been reported only in our previous work [9]. *trans*-3-(2-Furyl)acrolein and *trans*-3-(2-furyl)acrylic acid were studied in the hydrosilylation



Scheme 1.

* Corresponding author. Fax: + 371 7821038.

with trialkylsilanes in the presence of Speier's catalyst, which was not enough effective, therefore, reactions were carried out at prolonged reflux. The corresponding silyl ethers were obtained from the aldehyde in the result of 1,4 addition. Their configurations were not detected. The saturated compounds were prepared from the acid via dehydrogenative silylation accompanied by hydrogenation.

The studies of such objects in the hydrosilylation are intriguing from both scientific and practical points of view: as for determination of the reaction regio- and stereoselectivity and other phenomena as well as for the preparation of biologically active compounds [10,11].

Recently we investigated the hydrosilylation of O-, S- and N-heterocyclic aldehydes in the presence of various metal complex catalysts [12,13], and the asymmetric hydrosilylation and hydrogen transfer reduction of heteroaromatic ketones [14]. A number of complexes has been shown to be efficient in these processes. In the present paper we are reporting the hydrosilylation of (hetero)aromatic compounds, containing two reactive sites in the side chain, with HSiEt_3 in the presence of various metal complexes (some results were reported in [15]).

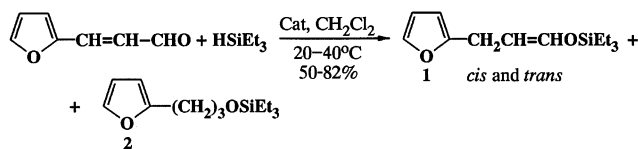
2. Results and discussion

2.1. Hydrosilylation of furylacrolein

3-(2-Furyl)acrolein (FA) is known only as a *trans*-isomer. The hydrosilylation of this compound with triethylsilane was studied in the presence of a number of transition metal complexes: $[\text{Rh}(\text{COD})\text{Cl}]_2$ (COD = *cis,cis*-1,5-cyclooctadiene), $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$, $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$, as well as in the presence of Speier's catalyst for a comparison. The complexes of bivalent Pd(II) and Pt(II) have been found to be absolutely inactive in this process at ambient temperature. $[\text{Rh}(\text{COD})\text{Cl}]_2$ catalyzed the addition reaction at the room temperature. The studied complexes can be arranged according to their activity in the order: $[\text{Rh}(\text{COD})\text{Cl}]_2 \gg \text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl} > \text{Ru}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2 > \text{H}_2\text{PtCl}_6 \gg \text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$.

The main product in all cases was the corresponding unsaturated silyl ether (**1**) in *cis*- and *trans*-configurations. In the presence of monovalent Rh(I) and Ir(I) complexes the 1,4-addition was accompanied by hydrogenation giving saturated silyl ether (**2**) (Scheme 2, Table 1).

The hydrosilylation of a number of (hetero)aromatic unsaturated aldehydes and related compounds with HSiEt_3 (molar ratio 1:1.2) has been studied in the presence of the most active catalyst $[\text{Rh}(\text{COD})\text{Cl}]_2$. The reactions were carried out at various temperatures until complete conversion of the starting substrate (control



Scheme 2.

by GC and GC-MS). The hydrosilylation of 3-(4-pyridyl)acrolein, nitrofuryl derivatives and cinnamyl alcohol was undertaken for the first time.

2.2. Hydrosilylation of six-membered α,β -unsaturated(hetero)aromatic aldehydes

The hydrosilylation of cinnamaldehyde (*trans*-3-phenyl-2-propenal, CA) and 3-(4-pyridyl)acrolein (*trans*-configuration, PA) with HSiEt_3 were studied in the presence of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (1–2 mol.%). The reactivity of CA was considerably higher than that of PA. CA reacted at ambient temperature reaching the complete conversion after 15 h; the product was isolated in 82% yield. According to $^1\text{H-NMR}$ data triethyl[(3-phenyl-2-propenyl)oxy]silane (**3**) in *cis*- and *trans*-configurations (isomer ratio: 77/23) was obtained.

The hydrosilylation of PA occurred only under more vigorous conditions (at 120°C for 48 h). It proceeded also as 1,4-addition yielding triethyl[3-(4-pyridyl)-2-propenyl]oxy]silane (**4**) but in *cis*-configuration only. However, the main product in this case was the saturated silyl ether **5**. GC reaction control showed that the hydrogenation occurred consecutively to the 1,4-hydrosilylation (Scheme 3).

The low reactivity of PA may be explained by the formation of stable complexes of a catalyst with the electron-donor pyridine derivatives (substrate and products) hindering the reaction. This phenomenon has been also observed in the hydrosilylation of pyridine-carbaldehydes [12,13].

2.3. Hydrosilylation of nitrofurylacroleins

The hydrosilylation of *trans*-3-(5-nitro-2-furyl)acrolein (NFA1) and *E*-3-ethyl-3-(5-nitro-2-furyl)acrolein (NFA2) was carried out at 40°C for 20 h. Very complicated mixtures of the products were obtained for these substrates. They have been separated by column chromatography. It has been found that 1,4-addition as well as 1,2-addition took place giving the corresponding unsaturated silyl ethers (Scheme 4). The subsequent hydrogenation accompanied the hydrosilylation of NFA1 yielding saturated silyl derivative. Unusual migration of Et group was observed in the reaction of NFA2. Perhaps the complex of the substrate with a catalyst caused such migration.

Table 1
Hydrosilylation of *trans*-3-(2-furyl)acrolein with HSiEt₃ in the presence of metal complexes

Complex	Conversion ^a (%) (GC)		Total yield ^b (%)	Products ratios ^c (%)		
	r.t., 24 h	40°C		<i>cis</i> - 1	<i>trans</i> - 1	2
[Rh(COD)Cl] ₂	100	—	82	51	37	12
Ir(CO)(PPh ₃) ₂ Cl	41	68 (48 h)	54	35	42	23
Ru(Co)(PPh ₃) ₂ Cl ₂	30	70 (60 h)	50	63	37	0
H ₂ PtCl ₆ · 6H ₂ O ^d	12	56 (60 h)	50	59	41	0
Pd(PPh ₃) ₂ Cl ₂	≈0					
Pt(PPh ₃) ₂ Cl ₂	≈0					

^a The reactions were carried out under argon in a solvent—0.61 g (5 mmol) of FA in 2 ml CH₂Cl₂; molar ratio of FA to HSiEt₃ = 1:1.2; catalyst amounts of [Rh(COD)Cl]₂ was 1 mol.%, for others were 5 mol.%.

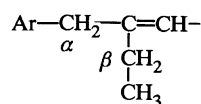
^b Products were isolated by vacuum distillation (69–72°C/0.1–0.2 mm).

^c Determined by means of ¹H-NMR.

^d Used as 1 mol.% solution in 2-propanol.

The formation of the compounds **6–10** was confirmed by ¹H-NMR and GC-MS spectra (see Experimental). In ¹H-NMR spectrum of compound **6** the additional coupling of doublets of the furan ring protons to triplets was found, that evidenced for the existence of CH₂ group in 2 position of the furan ring. The values of *J*_{HC-CH} stipulated *cis*- and *trans*-forms for compounds **6** and **7**. In the second case these values were higher than in the first (5.7 Hz (*cis*) and 11.8 Hz (*trans*) for **6** and 15.7 Hz (*trans*) for **7**).

The product **9** was identified as *E*-isomer because CH₂ protons of Et group had not the long range coupling with proton of C=CH group. The ¹H-NMR spectra of **10** (*Z*- and *E*-) indicated the Et group migration from C-4 to C-3 in the side chain. In the spectra of *Z*-**10** and *E*-**10** there have appeared the signals of two CH₂-group protons with chemical shifts δ = 3.51 and 3.29 which are close to those in spectra of *cis*-**6** and *trans*-**6** (3.54 and 3.33). Besides, the additional coupling (*J* = 0.8–1 Hz) of doublet to triplet of the proton in 3 position of the furan ring was observed. The similar values of δ and coupling constants were found for the compound **6**, thus confirming the presence of CH₂ group in the 2 position of the furan ring. The assignment of *Z*- and *E*-conformers of the **10** is based on the analysis of the proton chemical shifts of the α - and β -CH₂ groups in the system:

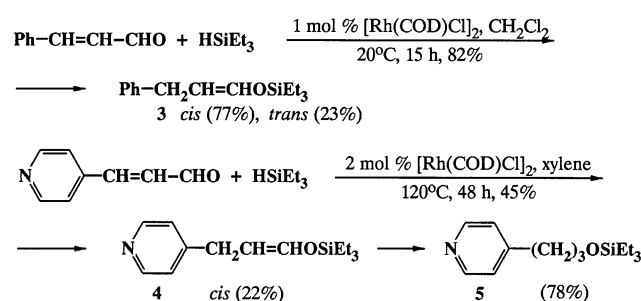


It is known [16], that the change of the cisoidal position to the transoidal one causes the decrease by ~0.2 ppm in the chemical shift of the α -methylene protons and slight increase in δ of β -CH₂ protons. The comparison of the chemical shifts of both CH₂ groups (α - and β -) showed that *Z*-**10** α -CH₂ protons resonate in lower field ($\Delta\delta$ = 0.22 ppm) than protons of *E*-**10**

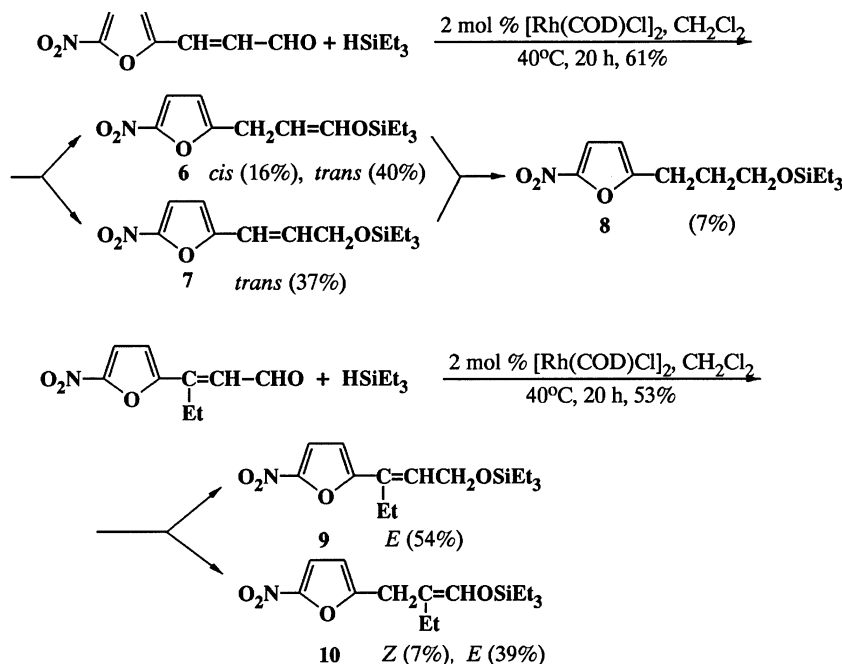
(δ = 3.51 and 3.29 ppm, respectively). At the same time the signals of β -CH₂ protons for *E*-**10** are shifted downfield (by more than 0.15 ppm).

2.4. Hydrosilylation of unsaturated hydroxy derivatives

The hydrosilylation of furan-2-acrylic acid (FAC) and cinnamyl alcohol (CAL), the *trans*-isomers both, was studied in the presence of 1 mol.% [Rh(COD)Cl]₂ in dichloromethane. The complete conversions were reached for 15 h at 40°C and after 46 h without heating, respectively (Scheme 5). In the reaction of FAC the products were isolated by vacuum distillation (70–80°C/0.1 mm) in 68% yield. The reaction products of CAL hydrosilylation were isolated by filtration over silica gel in 75% yield. The mixtures of the unsaturated (in *trans*-configurations) and saturated compounds were detected by the ¹H-NMR and GC-MS analysis of the reaction products. The dehydrogenative silylation took place in the reactions of these starting substrates yielding the corresponding silyl ether of alcohol and ester of acid (**11** and **13**). The processes of complete additions also occurred giving the saturated products (**12** and **14**).



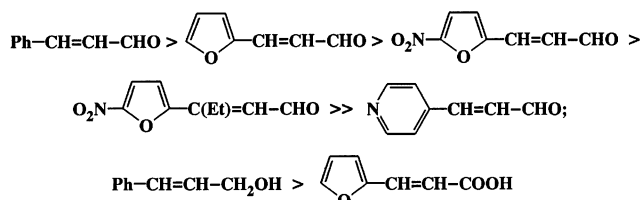
Scheme 3.



Scheme 4.

3. Conclusions

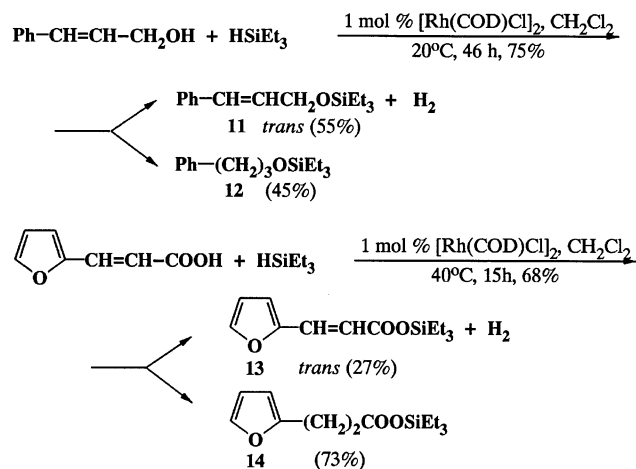
1. $[\text{Rh}(\text{COD})\text{Cl}]_2$ has been found to be effective in the hydrosilylation of unsaturated furan and benzene aldehydes, acid and carbinol.
2. The hydrosilylation of aldehydes proceeds mainly as an 1,4-addition reaction yielding the corresponding *Z*- and *E*-silyl ethers.
3. The hydrosilylation of the nitro derivatives of 3-(2-furyl)acrolein yields moreover the products of corresponding to a 1,2-addition.
4. The subsequent hydrogenation accompanies the hydrosilylation of 3-(2-furyl)acrolein, 3-(5-nitro-2-furyl)acrolein and 3-(4-pyridyl)acrolein.
5. The migration of α -ethyl group to β -position was found in the hydrosilylation of 3-ethyl-3-(5-nitro-2-furyl)acrolein.
6. The products of dehydrogenative silylation were obtained in the reactions of cinnamyl alcohol and furan-2-acrylic acid.
7. The order of the substrates reactivity in the hydrosilylation catalyzed by $[\text{Rh}(\text{COD})\text{Cl}]_2$ is as follows:



4. Experimental

4.1. Measurement

^1H -NMR spectra were registered on a Bruker AC-360 (360 MHz) spectrometer using CDCl_3 as a solvent and Me_4Si as an internal standard. The mass spectra were obtained on a Kratos MS-25 (70 eV) GC-MS instrument. The GC analyses of the reaction mixtures were performed on a chromatograph Chrom-4 equipped with a flame-ionization detector and glass column (2.4 m $\times$ 3 mm) packed with 10% SE-30 and 2.5% Reoplex 400 on Chromosorb W-AW (60–80 mesh); the carrier gas was nitrogen (60 ml min $^{-1}$). The temperature was programmed from 60 to 270°C (10°C min $^{-1}$).



Scheme 5.

4.2. Materials

Dichloromethane was dried over P_2O_5 and distilled; xylene was distilled from $LiAlH_4$ prior to use. $[Rh(COD)Cl]_2$ was synthesized according to procedure given in [17]. The other transition metal complexes were obtained from Fluka. Triethylsilane, cinnamaldehyde, cinnamyl alcohol, furylacrolein and furylacrylic acid were purchased from commercial sources (Fluka, Aldrich). Silica gel (Kieselgel 60, 0.063–0.200 mm, Merck) was used for column chromatography. 4-Pyridylacrolein and two nitrofuryl derivatives were synthesized following the methods [18,19].

4.3. General procedure for hydrosilylation of unsaturated (hetero)aromatic aldehydes, acid and alcohol

In a typical procedure 0.05–0.25 mmol of the metal complex catalyst was placed in a 5-cm³ Pierce reaction vial under an argon atmosphere and was dissolved in 2 ml of dry dichloromethane (or xylene in a case of PA). Then 5 mmol of substrate and 1.2 equivalents (6 mmol, 1.0 ml) of triethylsilane were added and stirred at ambient temperature (either at 40, or 120°C) until almost complete conversion of the substrate (monitoring by GC and GC-MS). The resulting reaction mixture was filtered off from the catalyst over silica gel, the solvent was removed under reduced pressure to obtain a mixture of the reaction products-silyl derivatives, which were analyzed by means of ¹H-NMR and GC-MS. Some reaction mixtures were distilled in vacuum, some of them were separated by column chromatography (silica gel 60, eluents: hexane–ethyl ether 9:1 or benzene–hexane 9:1).

4.4. Reaction of 3-(2-furyl)acrolein (FA)

In a Pierce vial the catalyst $[Rh(COD)Cl]_2$ (25 mg, 0.05 mmol), dichloromethane (2 ml), FA (0.61 g, 5 mmol), $HSiEt_3$ (1 ml, 6 mmol) were placed and stirred at ambient temperature. The complete conversion was reached after 24 h (analysis by GC and GC-MS). The reaction mixture was filtered over silica gel and the solvent was removed. The product was isolated by vacuum distillation at 69–72°C/0.1–0.2 mm in yield 1.05 g (87%). The mixture of silyl ethers **1** (in *cis*- and *trans*-configurations) and **2** (in ratio 51/37/12) was detected in this product by means of ¹H-NMR and GC-MS analysis.

4.4.1. *cis*-triethyl{[3-(2-furyl)-2-propenyl]oxy}silane (*cis*-**1**)

MS: *m/z* [rel. int. (%)] 238 (100, M^+), 209 (93, $M^+ - Et$), 179 (12), 153 (55), 151 (29, $M^+ - 3Et$), 125 (50), 115 (22), 107 (93, $M^+ - OSiEt_3$), 103 (15), 97 (20),

87 (65), 81 (21), 77 (15), 75 (23). ¹H-NMR: δ (ppm), *J* (Hz) 0.55–0.75 (6H, q, *J* = 8.2, $MeCH_2$), 0.98 (9 H, t, *J* = 8.2, CH_3), 3.46 (2 H, m, *J*₁ = 7.4, *J*₂ = 1.4, $FurCH_2$), 4.65 (1H, dt, *J*₁ = 7.4, *J*₂ = 5.5, CH_2CH), 6.33 (1 H, dt, *J*₁ = 5.5, *J*₂ = 1.4, $CHOSi$), protons of Fur: 5.97 (1H, m, H-3), 6.27 (1H, m, H-4), 7.3 (1H, m, H-5).

4.4.2. *trans*-triethyl{[3-(2-furyl)-2-propenyl]oxy}silane (*trans*-**1**)

MS: *m/z* [rel. int. (%)] 238 (100, M^+), 209 (86, $M^+ - Et$), 179 (18), 153 (47), 151 (28, $M^+ - 3Et$), 125 (45), 115 (18), 107 (71, $M^+ - OSiEt_3$), 103 (11), 97 (15), 87 (50), 81 (22), 75 (15). ¹H-NMR: δ (ppm), *J* (Hz) 0.55–0.75 (6 H, q, *J* = 8.2, $MeCH_2$), 0.98 (9H, t, *J* = 8.2, CH_3), 3.22 (2H, m, *J*₁ = 7.6, *J*₂ = 1.2, $FurCH_2$); 5.12 (1H, dt, *J*₁ = 10.6, *J*₂ = 7.6, CH_2CH), 6.37 (1H, dt, *J*₁ = 10.6, *J*₂ = 1.2, $CHOSi$), protons of Fur: 6.0 (1 H, m, H-3), 6.3 (1 H, m, H-4), 7.3 (1 H, m, H-5).

4.4.3. Triethyl[3-(2-furyl)propoxy]silane (**2**)

MS: *m/z* [rel. int. (%)] 240 (53, M^+), 211 (70, $M^+ - Et$), 181 (10), 155 (10), 153 (18, $M^+ - 3Et$), 125 (10), 117 (12), 108 (100, $M^+ - HOSiEt_3$), 91 (14), 77 (13). ¹H-NMR: δ (ppm), *J* (Hz) 0.55–0.75 (6 H, q, *J* = 8.2, $MeCH_2$), 0.98 (9H, t, *J* = 8.2, CH_3), 2.78 (2H, m, *J*₁ = 7.4, *J*₂ = 6.4, $CH_2CH_2CH_2$), 2.98 (2H, t, *J* = 7.4, $FurCH_2$), 3.65 (2H, t, *J* = 6.4, CH_2OSi), protons of Fur: 6.0 (1H, m, H-3), 6.3 (1H, m, H-4), 7.3 (1H, m, H-5).

4.5. Reaction of cinnamaldehyde (CA)

In a Pierce vial the catalyst $[Rh(COD)Cl]_2$ (25 mg, 0.05 mmol), dichloromethane (2 ml), CA (0.66 g, 5 mmol), $HSiEt_3$ (1 ml, 6 mmol) were placed and stirred at room temperature. The complete conversion was reached after 15 h (analysis by GC and GC-MS). The reaction mixture was filtered over silica gel, and the solvent was removed. The obtained product (1.02 g, 82% yield) was analyzed by means of ¹H-NMR and GC-MS, and the silyl ether **3** (in *cis*- and *trans*-configurations, ratio 77/23) was found.

4.5.1. *cis*-triethyl[(3-phenyl-2-propenyl)oxy]silane (*cis*-**3**)

MS: *m/z* [rel. int. (%)] 248 (42, M^+), 219 (100, $M^+ - Et$), 163 (29), 135 (25), 117 (59, $M^+ - OSiEt_3$), 115 (20), 103 (20), 91 (18), 87 (19), 77 (5). ¹H-NMR: δ (ppm), *J* (Hz) 0.68(6H, q, *J* = 8.0, $MeCH_2$), 1.00 (9H, t, *J* = 8.0, CH_3), 3.45 (2H, dd, *J*₁ = 7.5, *J*₂ = 1.7, $PhCH_2$), 4.66 (1 H, dt, *J*₁ = 7.5, *J*₂ = 5.8, CH_2CH), 6.33 (1H, dt, *J*₁ = 5.8, *J*₂ = 1.7, $CHOSi$), 7.22–7.26 (5H, m, Ph).

4.5.2. *trans*-triethyl[(3-phenyl-2-propenyl)oxy]silane (*trans*-**3**)

MS: *m/z* [rel. int. (%)] 248 (40, M^+), 219 (100, $M^+ - Et$), 194 (10), 163 (28), 135 (28), 117 (67, $M^+ -$

OSiEt₃), 115 (20), 103 (18), 91 (18), 87 (20), 77 (2). ¹H-NMR: δ (ppm), J (Hz) 0.67 (6 H, q, J = 8.2, MeCH₂), 0.98 (9H, t, J = 8.2, CH₃), 3.23 (2 H, dd, J_1 = 7.5, J_2 = 1.4, PhCH₂), 5.16 (1H, dt, J_1 = 11.5, J_2 = 7.5, CH₂CH), 6.34 (1H, dt, J_1 = 11.5, J_2 = 1.4, CHOSi), 7.15–7.20 (5H, m, Ph).

4.6. Reaction of 3-(4-pyridyl)acrolein (PA)

In a Pierce vial the catalyst [Rh(COD)Cl]₂ (50 mg, 0.10 mmol), xylene (2 ml), PA (0.66 g, 5 mmol), HSiEt₃ (1 ml, 6 mmol) were placed and stirred at 120°C. The complete conversion was reached after 48 h (monitoring by GC and GC-MS). The reaction mixture was filtered over silica gel, and the solvent was removed. The product (0.56 g, 45%) was analyzed by ¹H-NMR and GC-MS, and the formation of the mixture of silyl ethers **4** (in *cis*-configuration) and **5** (the ratio 22/78) was obtained.

4.6.1. *cis*-Triethyl{[3-(4-pyridyl)-2-propenyl]oxy}silane (*cis*-**4**)

MS: m/z [rel. int. (%)] 249 (45, M⁺), 220 (100, M⁺ – Et), 164 (10), 136 (25), 118 (40, M⁺ – OSiEt₃), 103 (14), 96 (13), 87 (25), 82 (14), 75 (15), 59 (32). ¹H-NMR: δ (ppm), J (Hz) 0.68 (6H, q, J = 7.9, MeCH₂), 0.98 (9H, t, J = 7.9, CH₃), 3.43 (2 H, dt, J_1 = 7.4, J_2 = 1.5, PyCH₂), 4.62 (1H, dt, J_1 = 7.4, J_2 = 5.8, CH₂CH), 6.38 (1H, dt, J_1 = 5.8, J_2 = 1.5, CHOSi), Py protons: 7.24 (2H, m, H-3, 5), 8.46 (2 H, m, H-2, 6).

4.6.2. Triethyl[3-(4-pyridyl)propoxy]silane (**5**)

MS: m/z [rel. int. (%)] 222 (100, M⁺ – Et), 194 (7), 120 (9, M⁺ – OSiEt₃), 106 (2), 97 (5), 92 (5), 83 (5), 75 (10), 47 (4). ¹H-NMR: δ (ppm), J (Hz) 0.52 (6 H, q, J = 7.7, MeCH₂), 0.93 (9H, t, J = 7.7, CH₃), 2.82 (2H, t, J = 7.2, PyCH₂), 2.95 (2H, m, CH₂CH₂CH₂), 3.65 (2H, t, J = 6.5, CH₂OSi), Py protons: 7.13 (2H, m, H-3, 5), 8.50 (2H, m, H-2, 6).

4.7. Reaction of 3-(5-nitro-2-furyl)acrolein (NFA1)

In a Pierce vial the catalyst [Rh(COD)Cl]₂ (50 mg, 0.10 mmol), dichloromethane (2 ml), NFA1 (0.83 g, 5 mmol), HSiEt₃ (1 ml, 6 mmol) were placed and stirred at 40°C. The complete conversion was reached after 20 h (analysis by GC and GC-MS). The reaction mixture was filtered over silica gel and the solvent was removed. The product was obtained by vacuum distillation at 120–130°C/0.1–0.2 mm in isolated yield 0.86 g (61%). The obtained mixture has been separated by column chromatography (silica gel 60, eluent: hexane–ethyl ether 9:1), and all four individual compounds were analyzed by means of ¹H-NMR and MS.

4.7.1. *cis*-Triethyl{[3-(5-nitro-2-furyl)-2-propenyl]oxy}silane (*cis*-**6**)

MS: m/z [rel. int. (%)] 283 (5, M⁺), 254 (100, M⁺ – Et), 195 (8), 167 (15), 151 (8), 132 (13), 115 (15), 103 (13), 91 (15), 87 (43), 75 (35), 63 (14), 59 (46), 45 (16). ¹H-NMR: δ (ppm), J (Hz) 0.67 (6 H, q, J = 8.2, MeCH₂), 0.97 (9H, t, J = 8.2, CH₃), 3.54 (2H, m, J_1 = 7.1, CH₂), 4.64 (1 H, dt, J_1 = 5.7, J_2 = 7.1, CH₂CH), 6.41 (1H, dt, J_1 = 5.7, J_2 = 1.3, CHOSi), ring protons: 6.25 (1H, dt, J_1 = 3.6, J_2 = 1.0, H-3), 7.24 (1H, dt, J_1 = 3.6, J_2 < 0.2, H-4).

4.7.2. *trans*-Triethyl{[3-(5-nitro-2-furyl)-2-propenyl]oxy}silane (*trans*-**6**)

MS: m/z [rel. int. (%)] 283 (4, M⁺), 254 (100, M⁺ – Et), 195 (8), 167 (16), 151 (8), 132 (14), 115 (16), 91 (16), 87 (44), 75 (33), 59 (45), 45 (13). ¹H-NMR: δ (ppm), J (Hz) 0.69 (6H, q, J = 8.0, MeCH₂), 0.99 (9H, t, J = 8.0, CH₃), 3.33 (2H, m, J_1 = 7.6, J_2 = 1.0, CH₂CH), 5.08 (1H, dt, J_1 = 11.8, J_2 = 7.6, CH₂CH), 6.45 (1H, dt, J_1 = 11.8, J_2 = 1.0, CHOSi), ring protons: 6.27 (1H, dt, J_1 = 3.6, J_2 = 1.0, H-3), 7.24 (1 H, dt, J_1 = 3.6, J_2 < 0.2, H-4).

4.7.3. *trans*-Triethyl{[3-(5-nitro-2-furyl)-3-propenyl]oxy}silane (*trans*-**7**)

MS: m/z [rel. int. (%)] 283 (27, M⁺), 254 (89, M⁺ – Et), 195 (11), 167 (6), 151 (34), 132 (100), 115 (48), 106 (24), 104 (47), 91 (16), 87 (92), 79 (12), 78 (44), 75 (51), 66 (18), 59 (48), 45 (28), 30 (30). ¹H-NMR: δ (ppm), J (Hz) 0.67 (6 H, q, J = 8.0, MeCH₂); 0.99 (9H, t, J = 8.0, CH₃), 4.39 (2H, dd, J_1 = 3.8, J_2 = 2.1, CH₂OSi), 6.54 (1H, dt, J_1 = 15.7, J_2 = 2.1, ring-CH), 6.67 (1H, dt, J_1 = 15.7, J_2 = 3.8, CHCH₂), ring protons: 6.41 (1H, d, J = 3.8, H-3), 7.30 (1H, d, J = 3.8, H-4).

4.7.4. Triethyl[3-(5-nitro-2-furyl)propoxy]silane (**8**)

MS: m/z [rel. int. (%)] 256 (100, M⁺ – Et), 169 (16), 123 (8), 115 (7), 103 (11), 91 (17), 87 (13), 75 (26), 63 (15), 59 (16), 47 (16), 45 (13). ¹H-NMR: δ (ppm), J (Hz) 0.60 (6H, q, J = 8.2, MeCH₂), 0.96 (9H, t, J = 8.2, CH₃), 1.93 (2H, m, J_1 = 7.6, J_2 = 6.0, CH₂CH₂CH₂), 2.83 (2H, bt, J = 7.6, ring-CH₂), 3.67 (2H, t, J = 6.0, CH₂OSi), ring protons: 6.27 (1H, dt, J_1 = 3.6, J_2 = 0.8, H-3), 7.24 (1H, dt, J_1 = 3.6, J_2 < 0.2, H-4).

4.8. Reaction of 3-ethyl-3-(5-nitro-2-furyl)acrolein (NFA2)

In a Pierce vial the catalyst [Rh(COD)Cl]₂ (50 mg, 0.10 mmol), dichloromethane (2 ml), NFA2 (0.97 g, 5 mmol), HSiEt₃ (1 ml, 6 mmol) were placed and stirred at 40°C. The almost complete conversion was reached

after 20 h (analysis by GC and GC-MS). The reaction mixture was filtered over silica gel and the solvent was removed. The product was prepared in isolated yield 0.82 g (53%). The mixture has been separated by column chromatography (silica gel 60, eluent: benzene–hexane 9:1).

4.8.1. *E*-Triethyl{[3-ethyl-3-(5-nitro-2-furyl)-3-propenyl]oxy}silane (**E-9**)

MS: m/z [rel. int. (%)] 311 (22, M^+), 282 (100, $M^+ - Et$), 254 (10), 238 (11), 223 (10), 179 (10), 132 (21), 115 (46), 103 (20), 91 (25), 87 (53), 75 (30), 59 (23), 47 (10). 1H -NMR: δ (ppm), J (Hz) 0.66 (6 H, q, $J = 8.2$, $MeCH_2Si$), 0.99 (9 H, t, $J = 8.2$, CH_3CH_2Si), 1.16 (3H, t, $J = 7.6$, CH_3), 2.43 (2H, q, $J = 7.6$, $MeCH_2$), 4.24 (2H, d, $J = 1.9$, CH_2OSi), 6.42 (1H, t, $J = 1.9$, $C(Et)=CH$), ring protons: 6.41 (1H, d, $J = 3.8$, $H-3$), 7.33 (1H, d, $J = 3.8$, $H-4$).

4.8.2. *Z*-Triethyl{[2-ethyl-3-(5-nitro-2-furyl)-2-propenyl]oxy}silane (**Z-10**)

MS: m/z [rel. int. (%)] 311 (45, M^+), 282 (100, $M^+ - Et$), 223 (12), 199 (12), 195 (12), 179 (10), 149 (11), 138 (18), 115 (30), 103 (18), 91 (21), 87 (62), 75 (34), 59 (49). 1H -NMR: δ (ppm), J (Hz) 0.66 (6H, q, $J = 8.2$, $MeCH_2Si$), 0.96 (9 H, t, $J = 8.2$, CH_3CH_2Si), 0.98 (3H, t, $J = 7.4$, CH_3), 1.96 (2H, dq, $J_1 = 7.4$, $J_2 = 1.3$, $MeCH_2$), 3.51 (2H, bs, ring- CH_2), 6.27 (1H, t, $J = 1.3$, $CHOSi$), ring protons: 6.22 (1H, dt, $J_1 = 3.6$, $J_2 = 1.0$, $H-3$), 7.23 (1H, d, $J = 3.6$, $H-4$).

4.8.3. *E*-Triethyl{[2-ethyl-3-(5-nitro-2-furyl)-2-propenyl]oxy}silane (**E-10**)

MS: m/z [rel. int. (%)] 311 (45, M^+), 282 (100, $M^+ - Et$), 195 (13), 132 (16), 115 (33), 103 (13), 91 (22), 87 (70), 75 (33), 59 (62). 1H -NMR: δ (ppm), J (Hz) 0.67 (6H, q, $J = 8.2$, $MeCH_2Si$), 0.99 (9H, t, $J = 8.2$, CH_3CH_2Si), 0.93 (3H, t, $J = 7.5$, CH_3), 2.11 (2H, dq, $J_1 = 7.5$, $J_2 = 0.7$, $MeCH_2$), 3.29 (2H, bs, ring- CH_2), 6.24 (1H, t, $J = 0.7$, $CHOSi$), ring protons: 6.25 (1 H, dt, $J_1 = 3.6$, $J_2 = 0.8$, $H-3$), 7.24 (1H, d, $J = 3.6$, $H-4$).

4.9. Reaction of cinnamyl alcohol (CAL)

In a Pierce vial the catalyst $[Rh(COD)Cl]_2$ (25 mg, 0.05 mmol), dichloromethane (2 ml), CAL (0.67 g, 5 mmol), $HSiEt_3$ (1 ml, 6 mmol) were placed and stirred at room temperature. The complete conversion was reached after 46 h (analysis by GC and GC-MS). The reaction mixture was filtered over silica gel, and the solvent was removed. The obtained product (0.94 g, 75% yield) was analyzed by means of 1H -NMR and GC-MS, and two silyl ethers (in ratio 55/45) were detected.

4.9.1. *trans*-Triethyl[(3-phenyl-3-propenyl)oxy]silane (**trans-11**)

MS: m/z [rel. int. (%)] 248 (28, M^+), 219 (89, $M^+ - Et$), 117 (100, $M^+ - OSiEt_3$), 115 (29), 103 (12), 91 (15), 77 (2). 1H -NMR: δ (ppm), J (Hz) 0.65 (6H, q, $J = 7.8$, $MeCH_2$), 0.99 (9H, t, $J = 7.8$, CH_3), 4.34 (2H, dd, $J_1 = 5.1$, $J_2 = 1.7$, CH_2OSi), 6.29 (1 H, dt, $J_1 = 15.9$, $J_2 = 5.1$, $CHCH_2$), 6.60 (1H, dt, $J_1 = 15.9$, $J_2 = 1.7$, $PhCH$), 7.15–7.38 (5H, m, Ph).

4.9.2. Triethyl(3-phenylpropoxy)silane (**12**)

MS: m/z [rel. int. (%)] 250 (2, M^+), 221 (100, $M^+ - Et$), 163 (2, $M^+ - 3Et$), 118 (22), 117 (18), 103 (10), 91 (35), 77 (2). 1H -NMR: δ (ppm), J (Hz) 0.60 (6 H, q, $J = 7.9$, $MeCH_2$), 0.96 (9H, t, $J = 7.9$, CH_3), 1.85 (2 H, m, $CH_2CH_2CH_2$), 2.68 (2H, dd, $J_1 = 8.0$, $J_2 = 7.8$, $PhCH_2$), 3.64 (2H, t, $J = 6.5$, CH_2OSi), 7.15–7.38 (5H, m, Ph).

4.10. Reactions of 3-(2-furyl)acrylic acid (FAC)

In a Pierce vial the catalyst $[Rh(COD)Cl]_2$ (25 mg, 0.05 mmol), dichloromethane (2 ml), FAC (0.69 g, 5 mmol), $HSiEt_3$ (1 ml, 6 mmol) were placed and stirred at 40°C. The complete conversion was reached after 15 h (analysis by GC and GC-MS). The reaction mixture was filtered over silica gel and the solvent was removed. The product was obtained by vacuum distillation at 70–80°C/0.1 mm in a yield 0.86 g (68%). The mixture of silyl esters **13** and **14** (in ratio 27/73) was found in this product by means of 1H -NMR and GC-MS analysis.

4.10.1. *trans*-Triethylsilyl ester of 3-(2-furyl)acrylic acid (**trans-13**)

MS: m/z [rel. int. (%)] 252 (6, M^+), 223 (100, $M^+ - Et$), 179 (27), 151 (12), 121 (55, $M^+ - OSiEt_3$), 103 (8), 92 (3), 75 (12), 65 (20). 1H -NMR: δ (ppm), J (Hz) 0.72–0.86 (6H, q, $J = 8.2$, $MeCH_2$), 1.00 (9H, t, $J = 8.2$, CH_3), 6.30 (1 H, d, $J = 15.6$, $CHCOO$), 7.37 (1H, d, $J = 15.6$, $FurCH$), protons of Fur: 6.60 (1H, m, $H-3$), 6.46 (1H, m, $H-4$), 7.47 (1H, m, $H-5$).

4.10.2. Triethylsilyl ester of 3-(2-furyl)propionic acid (**14**)

MS: m/z [rel. int. (%)] 254 (11, M^+), 225 (100, $M^+ - Et$), 183 (8), 115 (5), 103 (33), 94 (21), 87 (10), 81 (49), 75 (28). 1H -NMR: δ (ppm), J (Hz) 0.75–0.84 (6H, q, $J = 7.4$, $MeCH_2$), 0.96 (9 H, t, $J = 7.4$, CH_3), 2.67 (2 H, t, $J = 7.4$, $FurCH_2$), 2.94 (2H, t, $J = 7.4$, CH_2COO), protons of Fur: 6.01 (1H, m, $H-3$), 6.26 (1 H, m, $H-4$), 7.28 (1H, m, $H-5$).

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