Transformations of diallylsilanes under the action of electrophilic reagents

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ABSTRACT

Reactions of dimethyl-, diphenyl-, and (chloromethyl)methyldiallylsilanes with acetic, trifluoroacetic, triflic acids and complex $BF_3 \cdot 2AcOH$ are studied. Depending on the structure of the starting diallylsilane and the nature of the electrophilic reagent the following processes are realized: addition of an electrophile to one C=C bond; expulsion of one or two molecules of propene with addition of the electrophile residue to the silicon atom; and rearrangement with elimination of one allyl group from silicon and its attachment to the second allyl group of diallylsilane. Quantum chemical calculations of all three types of transformations are performed on the example of the reactions of dimethyl- and bis(chloromethyl)diallylsilanes with HF, CF_3COOH, CF_3SO_3H, as well as of the intermediate carbenium and silicenium cations.

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1. Introduction

Recently we have shown that the reaction of diallyl(diphenyl)-silane (**1**) with complex $BF_3 \cdot 2AcOH$ gives the product of rearrangement, fluoro(2-methyl-4-pentenyl)diphenylsilane [1]. It was of interest to analyze the dependence of the reaction course on the structure of the silane and electrophilic reagent as well as on the reaction conditions. A priori, based on the literature data, one could assume three routes, namely, (i) addition of the acid to allyl group, (ii) elimination of one or two molecules of propene, and (iii) rearrangement with rupture of the $Si–CH_2CH=CH_2$ bond followed by addition of the eliminated allyl group to the second allyl group of diallylsilane.

All three types of the reactions are known in the literature. Electrophilic addition to allyl group in allylsilanes was thoroughly studied [2–4]; they obey the Markovnikov rule due to stabilization of the initially formed carbocation by the $\sigma(CH_2–Si) \rightarrow p(C^+)$ electrondonating effect [5]. Elimination of the allyl group under acidic conditions (protodesilylation reactions) was also actively studied (see, e.g., a comprehensive review [6]); owing to these reactions allylsilanes became effective synthons for preparation of various organic compounds [6–9]. Special mentioning deserves elimination of one allyl group from mono- and diallylsilanes $Me_nAll_{3-n}SiCH_2Cl$ ($n = 0–2$) under the action of Lewis acids ($FeCl_3$, $AlCl_3$) occurring under mild conditions (25–40 °C) to afford $Me_nAll_{2-n}Si(Cl)CH_2Cl$ [10]. No further elimination was detected, as the authors believe, due to mild conditions used. Rearrange-

ments similar to that described in [1] are also known. They proceed either for diallylsilanes as in the reaction of $R_2Si(CH_2CH=CH_2)_2$ with α,β-unsaturated ketones and $BF_3 \cdot OEt_2$ occurring at room temperature and resulting in $R_2Si(F)CH_2CH(Me)CH_2CH=CH_2$ as by-products [11] or during thermolysis of silanes $R_2Si(CH_2CH=CH_2)$-$(CH_2CHClCH_3)$, apparently, initiated by dehydrochlorination and eventually giving rise to the products of elimination $R_2Si(Cl)$-$(CH_2CH=CH_2)$ and rearrangement $R_2Si(F)CH_2CH(Me)CH_2CH=CH_2$ [12].

In spite of abundance of the literature dealing with each type of these reactions, the number of works concerning diallylsilanes is rather limited, although the presence of two allyl groups provides a possibility for new transformations, like the aforementioned rearrangement with both allyl groups being involved. We also failed to find studies reporting the effect of the structure of the silane and electrophilic reagent on the reaction course and the reasons directing the reaction in favor of this or that mechanism. In order to fill in this gap we have undertaken this study and examined the behaviour of diallyl(diphenyl)silane (**1**), diallyl(di-methyl)silane (**2**) and diallyl(chloromethyl)methylsilane (**3**) under the action of different electrophiles – acetic, trifluoroacetic and triflic acids, and complex $BF_3 \cdot 2AcOH$. All reactions were carried out in boiling methylene chloride or upon cooling to −20 °C. It turned out that depending on the structure of the reagents all the aformentioned reaction routes are realized.

2. Results and discussion

We have found that diallyl(diphenyl)silane (**1**) does not react with acetic acid but with trifluoroacetic acid it forms the adduct to one allyl group **4** in 70% yield. With more strong triflic acid

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the reaction proceeds similar to that with complex $BF_3 \cdot 2AcOH$[1] to afford the rearrangement products **5** and **6** in 80% and 63% yield, respectively (Scheme 1).

It is known from the literature that the reaction of diallyl(dimethyl)silane (**2**) with triflic acid at −40 °C gives rise to the product of elimination of one molecule of propene $Me_2Si(CH_2CH=CH_2)$-OSO_2CF_3 (**7**) [13]. At room temperature the reaction occurs similarly except for 25% of the bis-triflate $Me_2Si(OSO_2CF_3)_2$ is formed as a by-product due to elimination of two molecules of propene [13]. We have found that silane **2** does not react with acetic acid at room temperature, whereas with trifluoroacetic acid it gives the product of elimination **8** in 51% yield. With more strong electrophile, complex $BF_3 \cdot 2AcOH$, difluoro(dimethyl)silane (**9**) is formed as a result of elimination of two molecules of propene. Both products [difluoro(dimethyl)silane and propene] are gaseous, so, they were trapped by bubbling the evolved gases into CCl_4 in a cooled trap. Formation of difluoro(dimethyl)silane is unequivocally proved by the presence of a septet with $^3J_{HF}$ 6.1 Hz and a doublet of septets on the ^{29}Si satellite signals with $^1J_{HF}$ 290.7 Hz in the ^{19}F NMR spectrum. The formation of propene is proved by the presence in the ^1H NMR spectrum a doublet of the methyl group, two doublets of the $=CH_2$ group with characteristic coupling constants J_{cis} and J_{trans}, and a multiplet of CH= proton, in the ratio of 3:1:1:1, as well as the corresponding signals in the ^{13}C NMR spectrum. Therefore, combining our and the Uhlig's [13] results, the following scheme can be written for silane **2** (Scheme 2).

No formation of other products for the reactions of silanes **1** and **2** with electrophiles when carrying out at low temperature (−20 °C) or upon large dilution and slow addition of the reagents was detected.

Diallyl(chloromethyl)methylsilane (**3**) does not react with acetic acid, either. Trifluoroacetic acid in methylene chloride adds to one allyl group giving rise to the adduct **10** in good yield. In the reaction of silane **3** with complex $BF_3 \cdot 2AcOH$, similar to silane **1**, the only isolated product was the product of rearrangement **11**. However, the ^{29}Si NMR spectrum of the crude product, apart from the two close doublets at 24 ppm corresponding to two diastereomers of compound **11**, contained another doublet (~14%) at

20 ppm with J 291 Hz, that completely coincided with that in the independently synthesized allyl(chloromethyl)fluoro(methyl)-silane **12**. Therefore, the reaction proceeds by 86% as rearrangement and by 14% as elimination. With the most strong electrophile, triflic acid, at room temperature the products of rearrangement **13** and elimination of one molecule of propene **14** are formed in the ratio of 1:1. When the reaction is carried out at −20 °C this ratio changes to 1:1.5 in favor of the elimination product **14** (Scheme 3).

The structure of all products was confirmed by ^1H, ^{13}C, ^{19}F, ^{29}Si NMR spectroscopy. The presence of a chiral carbon atom in molecules **4**, **5**, **6** causes diastereotopism of the methylene protons, and in the proton spectra of compounds **10**, **11**, **13** due to the presence of two chiral centers (silicon and carbon atoms) the multiplet signals of two diastereomers (R,S) and (R,R) presenting in a close to 1:1 ratio are superimposed so that it does not allow to determine the fine structure of the multiplets.

Table 1 summarizes the results of investigation of the reactions of diallylsilanes with different electrophilic reagents. As follows from these data, the course of the reaction and the ratio of the products formed depend both on the strength of the acid and the structure of the original diallylsilane.

Dependence of the ease of the reaction of allylsilanes with acids on the acid strength is well known in the literature. Thus, isomeric allylsilanes $Me_3SiCH_2CH=CHSiMe_2Ph$ and $PhMe_2SiCH_2CH=CH-SiMe_3$ do not suffer any changes in acetic acid after 5 days at room temperature but react with more strong halogenoacetic acids, the time of the reaction being drastically decreased with the strength of the acid: from 10.5 h for $ClCH_2COOH$ to <1 min for CF_3COOH [14]. That means that the first step of the reaction is protonation of the substrate. Possible routes for the formation of the products of addition, elimination and rearrangement for diallylsilanes are shown in Scheme 4. Depending on the stability of the silicenium cations, the process may be either stepwise or concerted (vide infra).

Such a weak acid as acetic acid cannot protonate the double bond, therefore, no reaction occurs with none of the investigated substrates in this medium. No reaction is observed also for silane
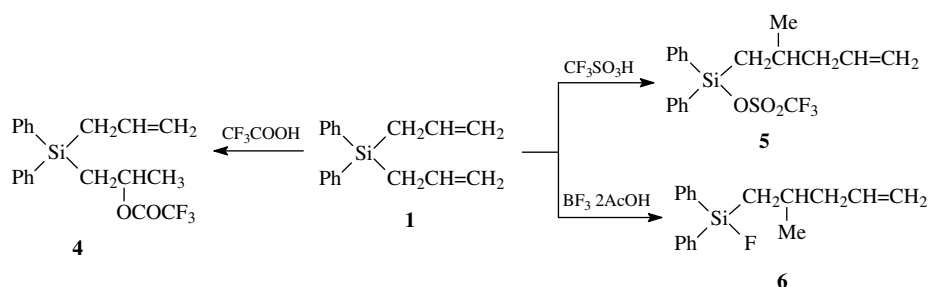
Scheme 1.
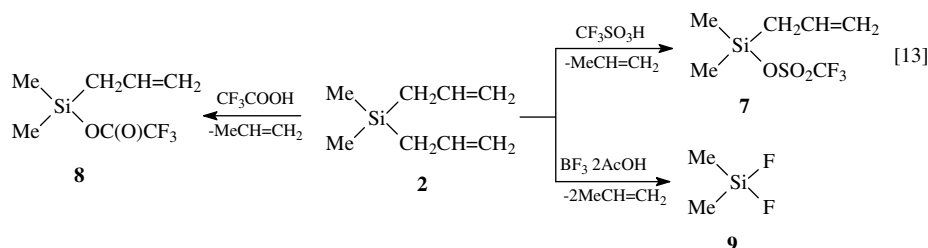
Scheme 2.

Table 1
Routes of the reactions of diallylsilanes R'R''Si(CH₂CH=CH₂)₂ with electrophiles.

HX R', R''	AcOH	CF₃COOH	BF₃ · 2AcOH	CF3SO₃H
Ph, Ph	No reaction	Addition	Rearrangement	Rearrangement
Me, Me	No reaction	Elimination	Double elimination[a]	Elimination [13][b]
Me, ClCH₂	No reaction	Addition	Rearrangement + elimination	Elimination + rearrangement

[a] At 25–40 °C.
[b] At −40 °C.

3 with trifluoroacetic acid in methanol, unlike the reaction in methylene chloride (vide supra). Different behaviour of dial-lyl(chloromethyl)methylsilane (**3**) with respect to trifluoroacetic acid in methanol and methylene chloride is in good compliance with the determining role of protonation as the first step of the process. The protonating ability of trifluoroacetic acid in methanol is lower than in methylene chloride due to strong specific solvation of the carboxylic group, that accounts for the absence of any transformations in methanol.

Formation of adducts is observed only in the reaction with tri-fluoroacetic acid that apparently is due to higher nucleophilicity of the anion CF₃COO⁻ as compared to that of the triflate anion CF₃SO₃⁻. As to complex BF₃ · 2AcOH, there are no data on the nucle-ophilicity of the conjugated anion but it evidently should be low due to interactions of the HBF₂(OAc)–F···H–OAc type.

More complicated is the situation with the competition be-tween the processes of rearrangement and elimination. According to Scheme 2, it is determined by the interaction of the carbocation center with orbitals π(C=C) and σ(CH₂–Si), routes a and b in Scheme 3, respectively. Therefore, it could be anticipated that elec-trondonating substituents at the silicon atom will, first of all, favor the elimination reaction due to the enhanced σ(CH₂–Si) → p(C⁺) interaction. Comparison of the results presented in Table 1 for dial-lylsilanes **2** and **3** confirms this conclusion.

The competition between the two processes could also have been affected by steric effects of the group R. However, the steric effects of R should be similar, if not to say identical, for the two silicenium cations depicted in Scheme 4, diorganyl(2-methyl-4-pentenyl)silicenium cation and diorganyl(allyl)silicenium cation, since the surrounding of the silicon atom is nearly the same. This
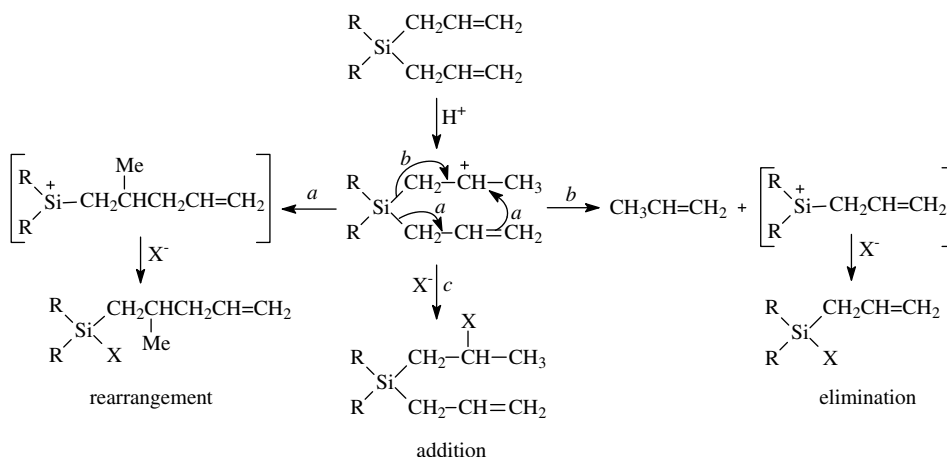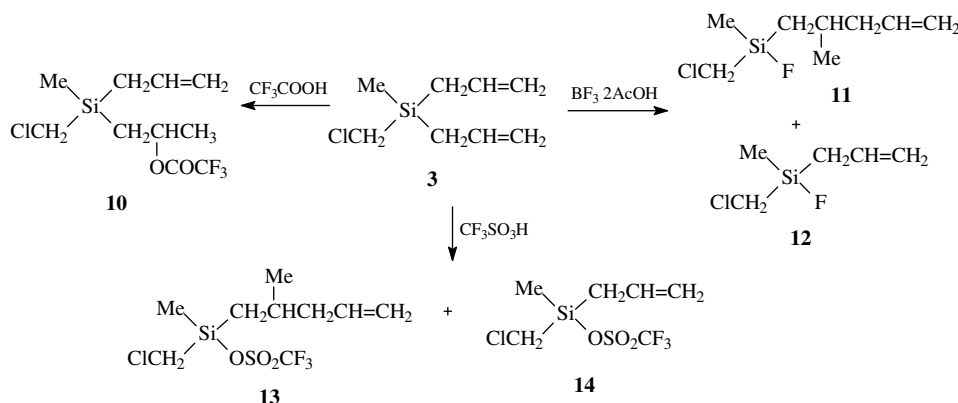

Scheme 3.

Scheme 4.

Table 2
Thermal effects (ΔE, kcal/mol) for reactions of diallylsilanes $R_2Si(CH_2CH=CH_2)_2$ with electrophiles HX.

No.	Reaction	R	X	$-\Delta E$
1		Me	CF$_3$COO	13.0
2			CF$_3$SO$_2$O	14.7
3	$R_2SiAll_2 + HX \rightarrow R_2Si(All)CH_2CH(X)CH_3$		F	15.1
4		ClCH$_2$	CF$_3$COO	12.9
5			CF$_3$SO$_2$O	13.8
6			F	13.3
7		Me	CF$_3$COO	28.1
8			CF$_3$SO$_2$O	32.2
9	$R_2SiAll_2 + HX \rightarrow R_2Si(X)CH_2CH=CH_2 + CH_3CH=CH_2$		F	37.7
10		ClCH$_2$	CF$_3$COO	22.9
11			CF$_3$SO$_2$O	26.6
12			F	29.2
13		Me	CF$_3$COO	43.0
14			CF$_3$SO$_2$O	46.0
15	$R_2SiAll_2 + HX \rightarrow R_2Si(X)CH_2CH(CH_3)CH_2CH=CH_2$		F	52.3
16		ClCH$_2$	CF$_3$COO	38.3
17			CF$_3$SO$_2$O	42.0
18			F	47.6
19	$R_2Si(CH_2CH=CH_2)(CH_2CHCH_3)^+ \rightarrow R_2SiCH_2CH=CH_2^+ + CH_3CH=CH_2$	Me		−17.3
20		ClCH$_2$		−25.0

is true also for the two final products for the rearrangement and elimination processes. Therefore, it is the electronic effects that are responsible for the result of the competition between the rearrangement and elimination. Lowering the stability of the silicenium cations leading, in the limit, to a concerted transformation of the carbocation into the final products by routes *a* and *b* does not change this conclusion.

To get a better insight into the understanding of the dependence of the course of the reaction on the structure of the reagents we have performed quantum chemical calculations of the reagents, products, and intermediate carbenium and silicenium cations. Thermal effects of the reactions of addition, elimination and rearrangement were calculated for dimethyl- and bis(chloromethyl)diallylsilane simulating the behaviour of substrates with electrondonating and electronwithdrawing substituents at the

by 10–20 kcal/mol. Such an order is clear enough since the products of rearrangement and elimination have the Si–X bond (X = O, F) which is much stronger than the Si–C bond in the products of addition, especially for X = F. A larger exothermicity of rearrangement as compared to elimination is explained by the fact that formally the product of rearrangement is formed by addition of propene to the product of elimination, that is, by rupture of one C=C bond and formation of two C–C bonds.

Calculation of the initially formed carbenium cations $[R_2Si(All)CH_2CHCH_3]^+$ (R = Me, ClCH$_2$) suggests the presence of very strong interaction of the $\sigma(CH_2–Si) \rightarrow p(C^+)$ type, leading to elongation of the Si–C bond and transfer of the electron density to the formed molecule of propene. As a result, their structure virtually corresponds to a silicenium cation interacting with the molecule of propene:
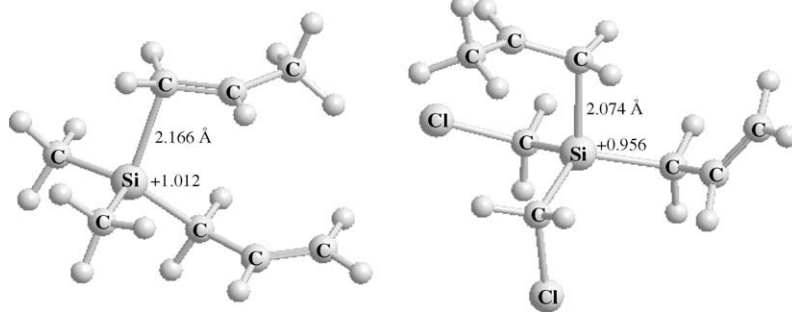
silicon atom. HF, CF$_3$COOH, and CF$_3$SO$_3$H were chosen as electrophiles. Besides, the reactions of conversion of the initially formed carbenium cation to the silicenium cation as a result of elimination of the molecule of propene from dimethyl- and bis(chloromethyl)allylsilyl propenylium cations have also been calculated. The results are represented in Table 2.

Obviously, being obtained without taking into account solvent effects and entropy factors, these data can be considered as giving only an estimation of the *relative* preferability of different reaction routes for different substrates and electrophiles. As follows from Table 2, all three processes are exothermic, the rearrangement being the most and the addition the least thermodynamically favorable. Elimination is less exothermic as compared to rearrangement by ~15 kcal/mol, but more exothermic than addition

That means that the transition state for the reaction of elimination of propene (reactions (19) and (20) in Table 2) is late, that is, close in structure to the product of the reaction, silicenium cation. With this, for the dimethylsubstituted cation it is more late than in the bis(chloromethyl)substituted cation, and hyperconjugation $\sigma(CH_2–Si) \rightarrow p(C^+)$ for R = Me is notably stronger, as witnessed by much larger Si–C distance (2.166 Å and 2.074 Å), a larger charge on the silicon atom (+1.012 and +0.956), and more developed double bond in the eliminated fragment ($l_{C=C}$ 1.376 Å and 1.388 Å, ∠HCCH 169.3° and 160.2°). All this is indicative of the predominance of elimination for R = Me.

For appraisal of the relative probability of the elimination and addition reactions from the data of Table 2, the values $\Delta\Delta E = \Delta E_{elim} - \Delta E_{add}$ for R = Me and ClCH$_2$ should be compared. For all

electrophiles the values of $|\Delta\Delta E|$ for R = Me are by 5–7 kcal/mol larger than for R = ClCH$_2$, that is, the relative probability of elimination is higher for R = Me. Therefore, the analysis of both the structure of the intermediate carbenium cations and the thermal effects of the corresponding reactions testifies to preferability of elimination for diallylsilanes with electrondonating substituents at the silicon atom, in compliance with the experimental observations (Table 1). The largest $\Delta\Delta E$ value is observed for the reaction with HF and, indeed, in the reaction of diallyl(dimethyl)silane (**2**) with complex BF$_3$ · 2AcOH double elimination occurs, that is, two molecules of propene are expelled and difluoro(dimethyl)silane (**9**) is formed (Table 1).

Now let us compare the values of $\Delta\Delta E' = \Delta E_{\text{rearr}} - \Delta E_{\text{elim}}$ for R = Me and ClCH$_2$. Following the same logic, they may be used for appraisal of the relative probability of the elimination and rearrangement reactions. First, the $|\Delta\Delta E'|$ values for R = ClCH$_2$ are larger than for R = Me, that is, the relative probability of rearrangement for R = ClCH$_2$ is higher. Indeed, in the reaction of silane **3** with complex BF$_3$ · 2AcOH the rearrangement is the main process whereas with silane **2** only the product of elimination is observed. In the reaction with CF$_3$SO$_3$H, silane **2** gives only elimination product whereas silane **3** gives rise to both products (Table 1). Second, the $\Delta\Delta E'$ value for silane **3** is by 3.0 kcal/mol larger for HF than for CF$_3$SO$_3$H, which is also in agreement with the experimental observation of lower percentage of elimination in the reaction with complex BF$_3$ · 2AcOH than with CF$_3$SO$_3$H (14% and 50–60%, respectively). Third, the $\Delta\Delta E'$ values are substantially smaller than $\Delta\Delta E$ ($-\Delta\Delta E' = 0.5$, 1.6 and 3.8 kcal/mol for CF$_3$COOH, CF$_3$SO$_3$H, HF, respectively). This comply with the possibility of parallel formation of the products of rearrangement and elimination and the absence of simultaneous formation of the products of elimination and addition (Table 1).

3. Conclusion

The above experimental and theoretical investigation allows us to conclude that reactions of diallylsilanes with electrophiles can proceed in three principal directions – addition of electrophile, elimination of the molecule of propene, and rearrangement including elimination of one allyl group and its addition to the second allyl group of the same molecule. The course of the reaction and the composition of the reaction products depend on the acidity of the electrophile and the nature of the substituents at silicon, and are rather insensitive to the reaction conditions.

4. Experimental

4.1. General remarks

Reaction of silane **1** with complex BF$_3$ · 2AcOH is described in our previous work [1]. All reactions were carried out in argon atmosphere. Flash chromatography was performed on silica gel 60 purchased from Merck.

4.2. Theoretical calculations

All calculations were performed at the B3LYP/6-311+G(d,p) level of theory with the basis set augmented with polarization functions on heavy atoms with full optimization of all variables using the GAUSSIAN 03 suite of programs [15].

4.3. Spectroscopic measurements

IR spectra were taken on a Specord IR-75 instrument. ^{1}H, ^{13}C, ^{19}F, ^{29}Si NMR spectra were recorded on a Bruker DPX 400 spec-trometer for CDCl$_3$ solutions at working frequencies 400.13 (^{1}H), 100.62 (^{13}C), 376.50 (^{19}F) and 79.50 (^{29}Si) MHz; ^{1}H, ^{13}C and ^{29}Si NMR chemical shifts are reported in parts per million downfield to TMS, and ^{19}F NMR in parts per million downfield to CFCl$_3$.

4.4. Reactions of diallylsilanes with electrophiles

4.4.1. 2-[Allyl(diphenyl)silyl]-1-methylethyl trifluoroacetate (**4**)

To diallyl(diphenyl)silane (**1**) (1.45 g, 5.49 mmol) in absolute CH$_2$Cl$_2$ (5 mL) the solution of trifluoroacetic acid (0.63 g, 5.49 mmol) in CH$_2$Cl$_2$ (5 mL) was added dropwise at room temperature in the course of 15 min. The reaction mixture was refluxed for 4 h, washed with cold water (3 × 25 mL), dried over CaCl$_2$. After removal of solvent the *title compound* **4** (1.45 g, 70%) was obtained. Analytically pure sample was isolated by flash chromatography (hexane/ether 80:1–8:1, R_f 0.61) as a colorless oil. Anal. Calc. for C$_{20}$H$_{21}$F$_3$SiO$_2$: C, 63.48; H, 5.59; F, 15.06; Si, 7.41. Found: C, 63.54; H, 5.98; F, 15.28; Si, 6.96%. ν_{max}(liquid film): 3080, 2995, 1785, 1620, 1600, 1420, 1390, 1160, 1110, 790, 695 cm^{-1}; δ_{H} 7.54–7.42 (10H, m, Ph); 5.80 (1H, m, CH=); 5.25 (1H, m, CMe); 4.98 (1H, d, *J* 15.8 Hz, CH$_2$=); 4.95 (1H, d, *J* 9.3 Hz, CH$_2$=); 2.20 (2H, d, *J* 8.0 Hz, CH$_2$C=); 1.85 (1H, dd, *J* 14.7, 8.31 Hz, SiCH$_a$H$_b$C); 1.62 (1H, dd, *J* 14.7, 6.0 Hz, SiCH$_a$H$_b$C); 1.28 (3H, d, *J* 6.0 Hz, CH$_3$C); δ_{C} 156.76 (q, *J* 41.5 Hz, C=O); 128.22, 129.96, 133.99, 134.98 (Ph); 115.44 (CH$_2$=); 114.77 (q, *J* 286 Hz, CF$_3$); 75.70 (CH); 22.56 (Me); 21.06, 20.80 (SiCH$_2$); δ_{F} −75.28; δ_{Si} 12.01.

4.4.2. (2-Methyl-4-pentenyl)(diphenyl)silyl trifluoromethanesulfonate (**5**)

To silane **1** (1.06 g, 4.0 mmol) in absolute CH$_2$Cl$_2$ (5 mL) the solution of triflic acid (0.60 g, 4.0 mmol) in CH$_2$Cl$_2$ (1 mL) was added dropwise at room temperature in the course of 10 min and stirred upon reflux during 4 h. After removal of solvent and vacuum distillation of the residue the *title compound* **5** (0.78 g, 50%) was obtained as a colorless oil, b.p. 158–160 °C/1 mm Hg. Anal. Calc. for C$_{19}$H$_{21}$F$_3$O$_3$SSi: C, 55.07; H, 5.07; F, 13.77; S, 7.73 Si, 6.76. Found: C, 54.60; H, 4.55; F, 13.20; S, 8.17; Si, 6.47%. δ_{H} 7.69 (4 H, m, H$_o$); 7.59 (2H, m, H$_p$); 7.50 (4H, m, H$_m$); 5.73 (1H, ddt, *J* 17.0, 10.0, 7.1 Hz, CH=); 5.05 (1H, d, *J* 17.1 Hz, =CH$_{\text{trans}}$); 4.99 (1H, d, *J* 10.0 Hz, =CH$_{\text{cis}}$); 2.09, 2.02 (1H, dt, *J* 7.0, 13.6 Hz, CH$_2$C=); 1.92 (1H, m, CH); 1.70 (1H, dd, *J* 15.4, 8.9 Hz, SiCH$_a$H$_b$C); 1.43 (1H, dd, *J* 15.4, 4.8 Hz, SiCH$_a$H$_b$C); 0.95 (3H, d, *J* 6.6 Hz, CH$_3$C); δ_{C} 136.30 (CH=); 134.79 (C$_m$); 131.73 (C$_p$); 129.59 (C^1); 128.38 (C$_o$); 118.30 (q, *J* 318 Hz, CF$_3$); 116.79 (CH$_2$); 44.30 (CH$_2$Vi); 28.24 (CH); 22.23 (Me); 21.19 (SiCH$_2$); δ_{F} −76.52; δ_{Si} 13.12.

4.4.3. Allyl(dimethyl)silyl trifluoroacetate (**8**)

To silane **2** (1.0 g, 7.1 mmol) in absolute CH$_2$Cl$_2$ (10 mL) the solution of trifluoroacetic acid (0.81 g, 7.1 mmol) in CH$_2$Cl$_2$ (5 mL) was added dropwise at room temperature in the course of 40 min. The reaction mixture was refluxed for 1 h until evolution of propene ceased. After removal of solvent and vacuum distillation of the residue the *title compound* **8** (0.77 g, 51%) was obtained as a colorless liquid, b.p. 57–57.5 °C/115 mm Hg. Anal. Calc. for C$_7$H$_{11}$F$_3$O$_2$Si: C, 39.62; H, 5.22. Found: C, 39.05; H, 5.15%. ν_{max}(liquid film) 2970, 1780, 1640, 1390, 1230, 1180, 1070, 805 cm^{-1}; δ_{H} 5.74 (1H, ddt, *J* 8.2, 9.2, 17.5 Hz, CH=); 4.99 (2H, m, CH$_2$=); 1.87 (2H, d, *J* 7.9 Hz, SiCH$_2$); 0.41 (6H, s, SiCH$_3$); δ_{C} 156.66 (q, *J* 42.6 Hz, CO); 130.93 (CH=); 115.87 (=CH$_2$); 114.59 (q, *J* 285.9 Hz, CF$_3$); 22.83 (SiCH$_2$Vi); −2.85 (SiCH$_3$); δ_{F} −75.73; δ_{Si} 28.48.

4.4.4. Reaction of diallyl(dimethyl)silane (**2**) with complex BF$_3$ · 2AcOH

To silane **2** (0.815 g, 5.8 mmol) in CH$_2$Cl$_2$ (50 mL) the solution of complex BF$_3$ · 2AcOH (1.09 g, 5.8 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise at room temperature during 1.5 h; the tempera-

ture rised to 32 °C. The gaseous products evolved were trapped in bubbler with CCl$_4$ cooled to −20 °C. After the reaction was completed the reaction mixture was stirred for 30 min at room temperature and refluxed until the gas evolution ceased (∼30 min). The solution of the evolved gaseous products in CCl$_4$, judged from the data of ^{1}H, ^{13}C and ^{19}F NMR spectroscopy with cyclohexane as an internal standard, contained the mixture of difluoro(dimethyl)silane (**9**) and propene.

4.4.5. Difluoro(dimethyl)silane (**9**).

δ_H 0.27 (t, J 1.2 Hz, SiCH$_3$); δ_F −129.79 (sept, $^1J_{SiF}$ 290.7 Hz, $^3J_{HF}$ 6.1 Hz). Propene. δ_H 5.69 (1H, ddq, J 17.0, 10.1, 6.4 Hz, CH=); 4.91 (1H, d, J 17.0 Hz, =CH$_{trans}$); 4.83 (1H, d, J 10.1 Hz, =CH$_{cis}$); 1.66 (3H, d, J 6.4 Hz, CH$_3$); δ_C 132.48 (CH=); 115.39 (=CH$_2$); 18.81 (CH$_3$).

4.4.6. 2-[Allyl(chloromethyl)methylsilyl]-1-methylethyl trifluoroacetate (**10**)

Prepared similar to **4** from diallyl(chloromethyl)methylsilane (**3**) (1.245 g, 7.1 mmol) and trifluoroacetic acid (0.81 g, 7.1 mmol) as colorless liquid. Purified by flash chromatography (hexane/ether 50:3–8:1, R_f 0.42); yield 1.5 g (73%). Anal. Calc. for C$_{10}$H$_{16}$ClF$_3$O$_2$Si: C, 41.59; H, 5.54; Cl, 12.31; F, 19.76; Si, 9.71. Found: C, 41.68; H, 5.71; Cl, 12.15; F, 20.00; Si, 9.61%. ν_{max}(liquid film) 2980, 1780, 1620, 1320, 1385, 1205, 1150, 810, 715 cm^{-1}; δ_H 5.74, 5.75 (1H, ddt, J 16.9, 10.2, 8.1 Hz, CH=); 5.27 (1H, tq, J 6.5, 6.5 Hz, CHO); 4.93 (1H, ddt, J 16.9, 2.0, 1.0 Hz, =CH$_{trans}$); 4.92 (1H, ddt, J 10.2, 2.0, 1.0 Hz, =CH$_{cis}$); 2.82, 2.81 (2H, s, CH$_2$Cl); 1.69 (2H, dt, J 8.1, 1.0 Hz, SiCH$_2$C=); 1.41 (3H, d, J = 6.2 Hz, CH$_3$C); 1.314, 1.297 (1H, dd, J 5.8 Hz, SiCH$_2$C); 1.216, 1.199 (1H, dd, J 14.8, 6.7 Hz, SiCH$_2$C); 0.169, 0.168 (3H, s, SiCH$_3$); δ_C 156.96 (q, J 41 Hz, C=O); 132.66 (CH=); 115.00 (=CH$_2$); 114.47 (q, J 286 Hz, CF$_3$); 75.30 (CHO); 28.32, 28.26 (CH$_2$Cl); 22.71 (CH$_3$); 20.55, 20.52 (SiCH$_2$CHMe); 20.30, 20.26 (SiCH$_2$Vi); −6.02 (SiCH$_3$); δ_F −75.55; δ_{Si} −0.298. From the data of NMR spectroscopy, the compound is the mixture of diastereomers. The assignment of signals was made using the 2D-HSQC procedure.

4.4.7. (Chloromethyl)(fluoro)methyl(2-methyl-4-pentenyl)silane (**11**)

To silane **3** (0.529 g, 3.03 mmol) in absolute CH$_2$Cl$_2$ (3 mL) the solution of complex BF$_3$ · 2AcOH (0.57 g, 3.03 mmol) in CH$_2$Cl$_2$ (2 mL) was added dropwise during 10 min and stirred for 4 h upon reflux. Then the mixture was washed with water to neutral reaction and dried over CaCl$_2$. After removal of solvent and vacuum distillation of the residue 0.271 g of the crude product with b.p. 98–98.5 °C/37 mm Hg was obtained. The crude product containing ∼90% of the title compound **11**. Analytically pure sample of the title compound **11** (0.354 g, 60%) was obtained by flash chromatography (hexane/ether 40:1, R_f 0.77) as a colorless liquid. Anal. Calc. for C$_8$H$_{16}$ClFSi: C, 49.34; H, 8.28; Cl, 18.20; F, 9.76; Si, 14.42. Found: C, 49.48; H, 8.57; Cl, 18.31; F, 9.80; Si, 14.17%. ν_{max}(liquid film) 2920–2970, 1640, 1405, 1270, 880 cm^{-1}; δ_H 5.75 (1H, m, CH=); 5.01 (2H, m, =CH$_2$); 2.86 (2H, m, CH$_2$Cl); 2.06 (1H, dt, J 14.0, 7.2 Hz, CH$_a$H$_b$C=); 2.00 (1H, dt, J 14.0, 6.9 Hz, CH$_a$H$_b$C=); 1.84 (1H, m, CH); 0.99 (3H, d, J 6.7 Hz, CH$_3$); 0.97 (1 H, m, SiCH$_a$H$_b$); 0.72 (1H, m, SiCH$_a$H$_b$); 0.37 (3H, d, J 7.3 Hz, SiCH$_3$); δ_C 136.82 (CH=); 116.34 (=CH$_2$); 44.46, 44.42 (CH$_2$Vin); 28.37, 28.35 (CH); 28.03, 27.87 (d, J 19.1 Hz, CH$_2$Cl); 22.43, 22.38 (CCH$_3$); 21.40, 21.36 (d, J 12.1 Hz, SiCH$_2$); −3.58, −3.72 (d, J 22.5 Hz, SiCH$_3$); δ_F −163.25, −163.33 (d, J 289.9 Hz); δ_{Si} 24.14, 24.02 (d, J 288.6 Hz).

4.4.8. Allyl(chloromethyl)fluoro(methyl) silane (**12**)

Allyl(chloro)(chloromethyl)(methyl)silane Me(ClCH$_2$)Si(Me)Cl (12.25 g, 70 mmol) was treated with 50 mL of 40% aqueous HF, organic layer separated and dried over KF. After vacuum distillation the title compound **12** (4.29 g, 35%) was obtained with b.p. 60–65 °C/55 mm Hg. Anal. Calc. for C$_5$H$_{10}$ClFSi requires C, 39.34; H,

6.60; Cl, 23.22; F, 12.44; Si, 18.40. Found: C, 39.19; H, 6.64; Cl, 23.72; F, 11.92; Si, 17.96%. δ_H 5.80 (1H, ddt, J 17.0, 10.1, 8.0 Hz, CH=); 5.05 (1H, dq, J 17.0, 1.2 Hz, =CH$_{trans}$); 5.01 (1H, d, J 10.1 Hz, =CH$_{cis}$); 2.90 (2H, dd, J 2.8, 3.1 Hz, CH$_2$Cl); 1.88 (2H, dd, J 7.5, 6.6 Hz, SiCH$_2$Vi); 0.37 (3H, d, J 7.2 Hz, SiCH$_3$); δ_C 130.76 (CH=); 116.08 (=CH$_2$); 26.79 (d, J 19.0 Hz, CH$_2$Cl); 20.83 (d, J 12.5 Hz, SiCH$_2$Vi); −4.88 (d, J 13.8 Hz, SiCH$_3$); δ_{Si} 20.31 (d, J 290.6 Hz).

4.4.9. Reaction of diallyl(chloromethyl)methylsilane (**3**) with triflic acid

To silane **3** (3.77 g, 21.6 mmol) in absolute CH$_2$Cl$_2$ (7 mL) the solution of triflic acid (3.24 g, 21.6 mmol) in CH$_2$Cl$_2$ (8 mL) was added dropwise at room temperature in the course of 50 min and stirred at reflux during 4 h. After removal of solvent and vacuum distillion of the residue 4.11 g (total yield 63%) of the mixture of products **13** and **14** in the ratio of 1:1 was obtained. After repeat vacuum distillation compound **13** (1.4 g, 20%) with b.p. 125–130 °C/35 mm Hg and compound **14** (1.6 g, 21%) with b.p. 104–108 °C/35 mm Hg were obtained as colorless oils.

4.4.10. (Chloromethyl)(methyl)(2-methyl-4-pentenyl)silyl trifluoromethanesulfonate (**13**)

Anal. Calc. for C$_9$H$_{16}$F$_3$ClO$_3$SSi requires Cl, 10.94; S, 9.86; Si, 8.63. Found: Cl, 11.61; S, 9.59; Si, 7.99%. δ_H 5.75 (1H, ddt, J 17.1, 10.2, 6.9 Hz, CH=); 5.05 (2H, m, =CH$_2$); 3.07 (2H, s, CH$_2$Cl); 2.06 (2H, t, J 6.5 Hz, CH$_2$Vi); 1.88 (1H, m, CH); 1.23 (1H, dd, J 15.5, 4.8 Hz, SiCH$_a$H$_b$); 1.03 (3H, d, J 6.6 Hz, CH$_3$); 0.94 (1H, dd, J 15.5, 9.2 Hz, SiCH$_a$H$_b$); 0.65 (3H, s, SiCH$_3$); δ_C 136.17 (CH=); 118.42 (q, J 318.5 Hz, CF$_3$); 116.94 (=CH$_2$); 44.31 (CH$_2$Vi); 28.10 (CH); 27.01 (CH$_2$Cl); 22.20 (CH$_3$); 20.89 (SiCH$_2$); −3.50 (SiCH$_3$); δ_F −76.40; δ_{Si} 29.50.

4.4.11. 2-Allyl(chloromethyl)methylsilyl trifluoromethanesulfunate (**14**)

δ_H 5.77 (1H, ddt, J 7.8, 10.0, 17.1 Hz, CH=); 5.14 (2H, m, =CH$_2$); 3.08 (2H, s, CH$_2$Cl); 2.07 (2H, d, J 7.8 Hz, SiCH$_2$Vi); 0.64 (3H, s, SiCH$_3$); δ_C 128.60 (CH=); 118.36 (q, J 318 Hz, CF$_3$); 118.06 (=CH$_2$); 25.78 (CH$_2$Cl); 20.18 (SiCH$_2$Vi); −4.82 (SiCH$_3$); δ_F −75.92. δ_{Si} 24.58.

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