NUCLEOPHILIC REACTIONS OF HETERYLSILANES AND HETERYLGERMANES* (REVIEW)

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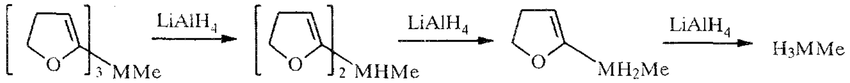
We generalize data on the reactivity of furyl-, dihydrofuryl-, tetrahydrofuryl-, dihydropyranyl-, and tetrahydropyranylsilanes and -germanes in reactions with nucleophilic reagents. We show that upon reaction of heterosilanes and heterogermanes with O-, N-, C-, and H-nucleophiles, sequential substitution of the heterocycles occurs at the nucleophilic group. We consider the rearrangement of (2-tetrahydrofuryl)- and (2-tetrahydropyranyl) hydrosilanes with ring expansion, and also rearrangement of linear acyloxymethyl- and halomethylhydrosilanes to the corresponding acyloxy- and halosilanes.

Furyl-, dihydrofuryl-, tetrahydrofuryl-, dihydropyranyl-, and tetrahydropyranylhydrosilanes and -germanes can be considered as unique systems simultaneously containing vinyl ether, vinylsilane, and silyl ester moieties. The presence of these fragments in the heterylsilane or -germane molecule exert an effect on the reactivity of the M – C and M – H bonds. In reactions with nucleophilic reagents, such compounds are ambident substrates, which opens up prospects for creating new classes of compounds which cannot be obtained by other methods. In turn, reactions of heterylsilanes and heterogermanes containing alkyl and aryl substituents at the metal atom with H-, C-, O-, and N-nucleophiles can serve as convenient methods for synthesis of new silanes and germanes. Accordingly, we studied nucleophilic reactions of heterylsilanes and heterylgermanes.

REACTIONS WITH H-NUCLEOPHILES

Lithium aluminum hydride can substitute a hydrogen atom for the dihydrofuryl group in *tris*-[2-(4,5-dihydrofuryl)]-methylsilane and -germane [1]:



1, 2 *3, 4* *5, 6* *7, 8*

1,3,5,7 M = Si; *2,4,6,8* M = Ge

This reaction occurs in stages. In tetrahydrofuran (25°C/30 min) and diethyl ether (25°C/3 h), generally we observe exhaustive substitution and the sole product is methylsilane (or methylgermane), not containing the heterocyclic group. In less polar benzene, pentane, or hexane under phase transfer catalysis conditions [2, 3], we can obtain the product of substitution of the two heteryl groups: the monoheterylsilane 5. Upon boiling silane 1 in pentane with LiAlH$_4$ in the presence of 18-crown-6, we obtain [2-(4,5-dihydrofuryl)]methylsilane (5) in 53% yield.

In the case of germane 2, there are no important differences in reactivity between the starting *tris*-dihydrofurylgermane 2 and subsequent hydrogermanes 3 and 4 relative LiAlH$_4$, since even in nonpolar pentane or benzene, all the components are present in the reaction mixture to an equal extent (the monoheterylgermane 4 was characterized only by chromatography/mass spectrometry) and when the reaction is carried out for a longer time (24 h), the sole product is methylgermane (6).

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*Dedicated to Professor A. R. Katritsky on the occasion of his 65th birthday.

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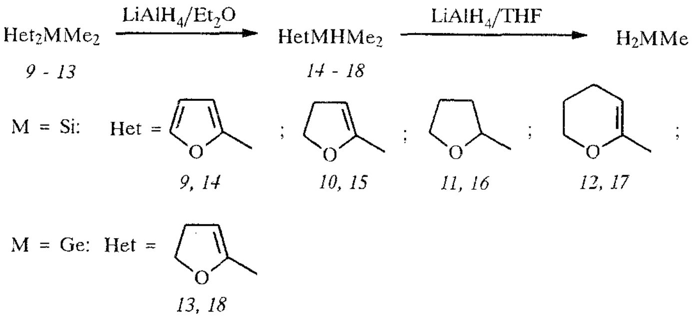
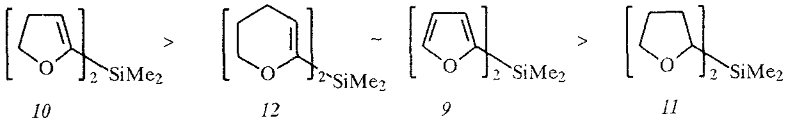
Lithium aluminum hydride can substitute a hydrogen atom for the furyl, dihydrofuryl, tetrahydrofuryl, and dihydropyranyl groups in *bis*-heterylsilanes 9-12 and -germane 13. In this case, we could easily (25-80°C) and in good yield (60-100%) obtain the difficultly accessible and previously unknown monoheterylsilanes 14-17 and -germane 18 [1, 4]:



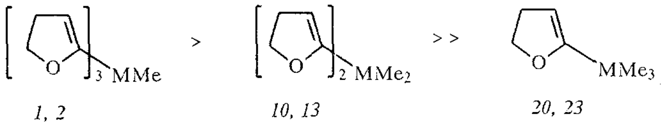
In diethyl ether, the reaction proceeds selectively with formation of exclusively the heterylsilanes 14-17 and the germane 18. In the more polar tetrahydrofuran, the extent of reaction is greater and the reaction is significantly faster, as a result of which the sole product is dimethylsilane (or dimethylgermane). Substitution of the dihydrofuryl groups in the germane proceeds more slowly than in its silyl analog.

We can arrange the silanes 9-12 in the following series according to ease of removal of the heteryl group:



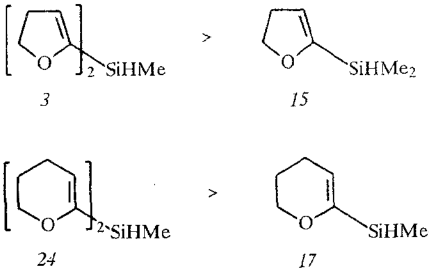
The monoheterylsilanes and -germanes containing three alkyl substituents at the metal atom [(2-furyl)trimethylsilane (19), [2-(4,5-dihydrofuryl)]trimethylsilane (20), (2-tetrahydrofuryl)trimethylsilane (21), [2-(5,6-dihydro-4H-pyranyl)]-trimethylsilane (22) and [2-(4,5-dihyrofuryl)]trimethylgermane (23)] are stable relative to $LiAlH_4$ and do not lose the heterocycle even upon prolonged boiling in tetrahydrofuran [1].

As a result of our reactions of heterylsilanes and -germanes with $LiAlH_4$, we established some characteristics of the reactivity of the studied compounds as a function of the number and nature of the heteryl groups at the Si or Ge atom. A general trend is reduction of the reactivity of silanes and germanes as the number of the indicated groups decreases.



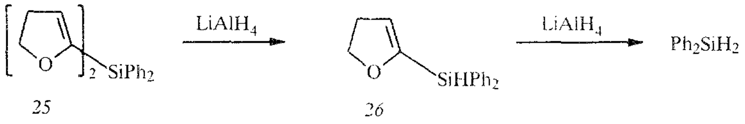
1, 10, 20 M = Si; *2, 13, 23* M = Ge

Heterylsilanes containing a single Si—H bond behave analogously [1, 5]:



We have studied the analogous reactions of phenyl-containing heterylsilanes.

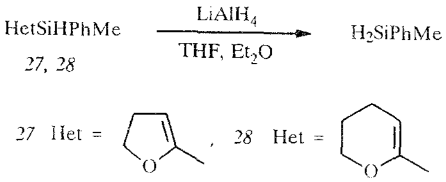
Bis-[2-(4,5-dihydrofuryl)diphenylsilane (25) reacts with $LiAlH_4$ significantly faster than its methyl analog *bis*[2-(4,5-dihydrofuryl)]dimethylsilane (10): in either, even after 1 h the sole product is diphenylsilane 26. In benzene, the reaction proceeds in stages, but not selectively; consequently we cannot stop the process at the stage of formation of hydrosilane 26.



A control experiment with hydrosilane 26 indicates close reactivity of silanes 25 and 26 in this reaction.

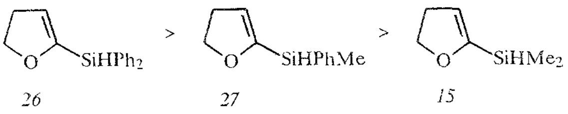
[2-(4,5-Dihydrofuryl)]dimethylphenylsilane is more inert to $LiAlH_4$ than heterylsilanes 25 and 26. Removal of the dihydrofuryl group occurs only in tetrahydrofuran after 4 h at room temperature.

The dihydropyranylhydrosilane 28 also loses the heterocycle in reaction with $LiAlH_4$:



Compound 28 is more stable than its dihydrofuryl analog 27 (in tetrahydrofuran, after 1 h we observe complete conversion of silane 27 after 1 h and of silane 28 after 4 h; in Et_2O, complete conversion of silane 27 after 4 h and of silane 28 after 24 h).

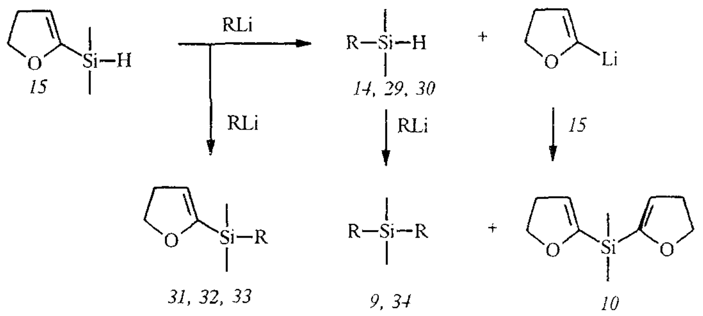
In a number of phenyl-containing dihydrofurylsilanes, it has been claimed that the stability of the silane to the action of $LiAlH_4$ increases with a decrease in the number of phenyl groups in the molecule:



To study the possibility of removal of the heteryl groups in heterylsilanes by other metal hydrides (LiH, NaH, $LiBH_4$, $NaBH_4$), as the object of investigation we chose the most reactive in reactions with $LiAlH_4$: *bis*[2-(4,5-dihydrofuryl)]methylsilane (3). We established that the listed metal hydrides can remove a dihydrofuryl group in hydrosilane 3, but they are less reactive and less selective than $LiAlH_4$ [1].

Bis[2-(4,5-dihydrofuryl)]methylsilane (3) does not undergo any changes in reactions with $LiBH_4$ and $NaBH_4$ under phase transfer catalysis conditions (0.1 M solution in benzene, 5% 18-crown-6, [3]: [metal hydride] = 1:2, 5 h, 80°C). The product of substitution of one dihydrofuryl group (hydrosilane 5) was obtained in slight amounts ($\approx$5%) under the indicated conditions only in reactions with LiH and NaH. Reactions with NaH, $LiBH_4$, and $NaBH_4$ in more polar tetrahydrofuran at room temperature after 24 h lead to the product of exhaustion substitution of the dihydrofuryl groups in silane 3: methylsilane in 20%, 75%, and 59% yield respectively. Under the same conditions for substitution of the dihydrofuryl groups, the reaction with LiH proceeds in stages and after 24 h the reaction mixture consists only of the products of substitution of one and two dihydrofuryl groups by hydride ion in 1:1.4 ratio.

The fact that cleavage of the Si−C bond in furylsilanes by *n*-butyllithium and furyllithium occurs is well known [6]. With the goal of further studying the possibility of cleavage of the Si−C bond by organolithium reagents, we carried out reactions of dihydrofurylhydrosilane 15 with (2-furyl)lithium, [2-(5,6-dihydro-4H-pyranyl)]lithium, phenyllithium, and *n*-butyllithium [7,8]:



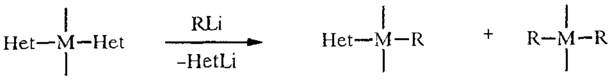
9, 14, 31 R = furyl. 29, 32, 34 R = Ph; 30, 33 R = Bu

(2-[4,5-Dihydrofuryl])dimethylsilane (15) was treated with equimolar amounts of organolithium compounds in a 1:8 hexane-tetrahydrofuran mixture at -30°C and held at this temperature for 30 min. After spontaneous heating up to room temperature, the reaction mixture was stirred for 30 min, then the organolithium compounds (the organolithium reagent and the heteryllithium formed in the reaction) were neutralized by additional of a calculated amount of Me_3SiCl.

Along with substitution at the Si−H bond, (2-furyllithium, phenyllithium and *n*-butyllithium can cleave the Si−C bond in the starting hydrosilane 15 with substitution of the dihydrofuryl group by a residue of the organolithium reagent (yield of products 31, 32, 33 is 27%, 34%, and 35% respectively). [2-(5,6-Dihydro-4H-pyranyl)]lithium is not very active in this reaction: in the reaction mixture, we detected only slight amounts (8%) of *bis*-dihydrofuryl derivative 10.

We investigated the possibility of carrying out analogous reactions with C-nucleophiles for the example of *bis*(2-furyl)dimethylsilane (9), bis [2-(4,5-dihydrofuryl)]dimethylsilane (10), *bis*[2-(5,6-dihydro-4H-pyranyl)]dimethylsilane (12), and *bis*[2-4,5-dihydrofuryl)]dimethylgermane (13) [8].

As the C-nucleophiles (R-Li), we considered 2-furyllithium, [2-(4,5-dihydrofuryl)]lithium, [2-(5,6-dihydro-4H-pyranyl)]lithium, phenyllithium, and *n*-butyllithium:



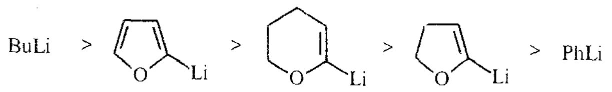
$$\text{Het}-\text{M}-\text{Het} \xrightarrow[\text{-HetLi}]{\text{RLi}} \text{Het}-\text{M}-\text{R} + \text{R}-\text{M}-\text{R}$$

M = Si, Ge; Het = furyl, 4,5-dihydrofuryl, 5,6-dihydro-4H-pyranyl

The most active of the selected C-nucleophiles is the hardest nucleophile, *n*-BuLi. In this case, reactions with all the starting heteryl derivatives are characterized by a high extent of conversion of the latter (67-89%) and proceed the most selectively: only monosubstituted products are formed (yield 37-86%).

Reactions of 9-13 with heteryllithium derivatives are characterized by a lower extent of conversion of the starting compounds (35-60%). In all cases, in the reaction mixture there are slight amounts (3-12%) of products of exhaustive substitution of the heteryl group of the starting compounds by the heteryl group of the organolithium reagent. The weakest reagent is phenyllithium, which can enter into the reaction under study only with the most active substrate: *bis*-dihydrofurylsilane 10.

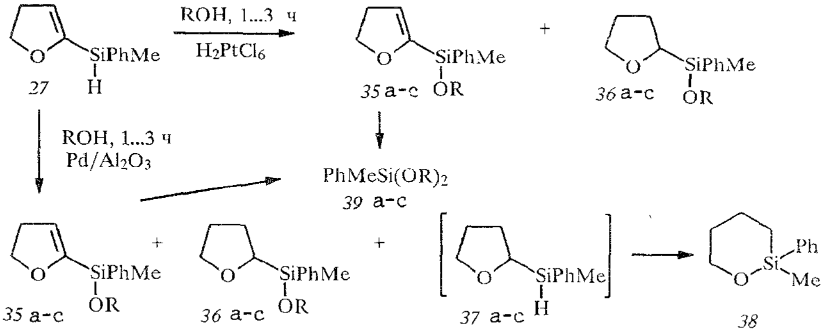
All the investigated organolithium reagents can be arranged in the following series according to decreasing reactivity:



For the example of *bis*[2-(4,5-dihydrofuryl)]-dimethylsilane (10), the most active in reactions with C-nucleophiles, we have shown that methylmagnesium iodide cannot substitute the easiest leaving dihydrofuryl group in *bis*(dihydrofuryl)silane (10) even upon prolonged boiling in tetrahydrofuran.

REACTIONS OF DIHYDROFURYLSILANES WITH O-NUCLEOPHILES

We know that [2-(4,5-dihydrofuryl)]dimethylsilane (15) reacts with methanol in the presence of a Speier catalyst with formation of the corresponding methoxysilane [9]. In the side reaction with [2-(4,5-dihydrofuryl)]methylphenylsilane (27), tetrahydrofuryl derivatives (36a-c) are formed (sometimes in an overwhelming amount) along with the expected dehydrocondensation products [5, 8]:



a R = Me, b R = Pr, c R = Bu

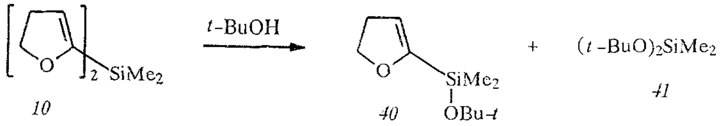
As a result of dehydrocondensation of the starting hydrosilane 27 with alcohol, hydrogen is evolved, which in the presence of $H_2PtCl_6{\cdot}6H_2O$ is capable of hydrogenating both the alkoxydihydrofurylsilane molecule 35a and the starting hydrosilane 27 present in the reaction mixture. The latter process leads to (2-tetrahydrofuryl)methylphenylsilane 37, which upon subsequent reaction with alcohol forms the alkoxy derivative 36.

Since (2-tetrahydrofuryl)dimethylsilane in the presence of supported palladium catalyst is rearranged with ring expansion to the six membered 1-oxa-2-silacyclohexane [9], in order to establish the formation of the tetrahydrofuryl derivative 36a we carried out the reaction of methanolysis of [2-(4,5-dihydrofuryl)] methylphenylsilane (27) in the presence of Pd/Al_2O_3. In this case, in fact along with 35a and 36a, the product of rearrangement of 38 was formed in appreciable amounts. Based on this fact, and also on the fact that the dihydrofurylsilane 35 is also obtained in the reaction, we can conclude that both alternative routes are realized for dehydrocondensation of the starting hydrosilane 27 with alcohol.

Alkoxysilanes 39a-c are also present in the reaction mixture, formed exclusively as a result of rupture of the Si-$C_{dihydrofuryl}$ bond by the alcohol in [2-(4,5-dihydrofuryl)]alkoxysilanes 35a-c, which was shown by control experiments.

For the sample of *bis*[2-(4,5-tetrahydrofuryl)dimethylsilane (10), we studied the possibility of carrying out the analogous reaction with silanes containing other unsaturated substituents instead of the phenyl group [8]. We have shown that compound 10 in a mixture with ethanol instantaneously becomes tarry even in the absence of catalyst. Analogous conversions are also observed when carrying out the reaction in hexane for 6 h.

In the reaction mixture of *bis*[2-(4,5-dihydrofuryl)]dimethylsilane (10) and the more highly branched *tert*-butanol, at room temperature in the absence of solvent we can detect the product of substitution of one dihydrofuryl group by a *tert*-butoxyl group: [2-(4,5-dihydrofuryl)]dimethyl(*tert*-butoxy)silane (40). However, the major component in this mixture is the product of exhaustive heterolysis of *bis*(dihydrofuryl)silane (10) by *tert*-butanol: di(*tert*-butoxy)dimethylsilane (41).



The reaction was carried out with equimolar amounts of compound 10 and *t*-BuOH; in this case, we obtained a mixture of products 40 and 41 in 1:11 ratio.

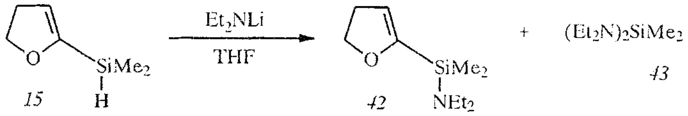
We studied the possibility of addition of alcohols at the double bond of the heterocycle in [2-(4,5-dihydrofuryl)]-trimethylsilane and [2-(5,6-dihydro-4H-pyranyl)]trimethylsilane, which if successful could be one more approach to dihydrofuryl and dihydropyranyl protection of alcohols [8].

Reactions with methanol and *n*-butanol without solvent in the presence of *para*-toluenesulfonic acid or the cation exchanger Amberlist A-15 prove that dihydropyranylsilane does not undergo any changes even upon prolonged heating. [2-(4,5-Dihydrofuryl)]trimethylsilane turns into a tar upon reaction with methanol. Upon reaction with *n*-butanol, according to chromatography/mass spectrometry data, the adduct of *n*-butanol and [2-(4,5-dihydrofuryl)]trimethylsilane is detected in trace amounts, but the major reaction product is the product of heterolysis of the Si-C$_{\text{dihydrofuryl}}$ bond: butoxytrimethylsilane.

REACTIONS WITH N-NUCLEOPHILES

We studied the reactions of *bis*[2-(4,5-dihydrofuryl)]dimethylsilane (10) with N-nucleophiles. We found that N,N-dimethylamine does not react with compound 10 upon prolonged heating in the presence of base or metallic lithium [8]. Substitution of the dihydrofuryl group in *bis*[2-(4,5-dihydrofuryl)]dimethylsilane could be achieved when carrying out the reaction with lithium N,N-diethylamide:

Under mild conditions (−30°C, +25°C, 2 h, [10]: [Et_2NLi] = 1:1, we obtained [2-(4,5-dihydrofuryl)]dimethyl-N,N-diethylaminosilane (42) in quantitative yield. Aminosilane 42 was identified by chromatography/mass spectrometry, and also by an alternative synthesis from hydrosilane 15:

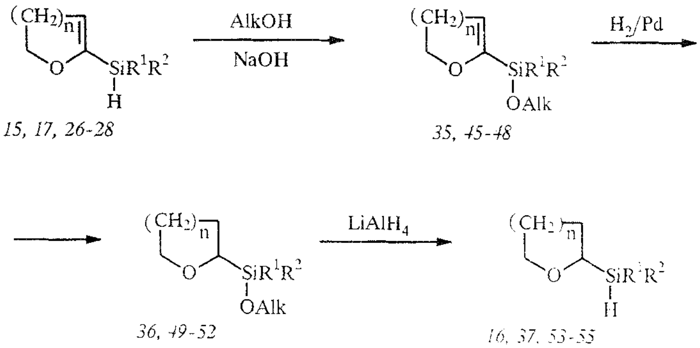


In the reaction mixture, we also observed dimethyl-*bis*(N,N-diethylamino)silane (43), formed as a result of removal of the dihydrofuryl group from silane 15 (ratio of [42]:[43] = 0.68).

REARRANGEMENT OF HETERYLHYDROSILANES

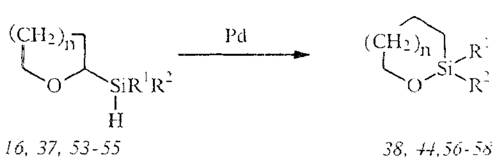
With the goal of studying the effect of substituents at the silicon atom on rearrangement of (2-tetrahydrofuryl)-dimethylsilane (16) to oxasilacyclohexane (17), occurring in the presence of palladium catalyst [10], and also the possibility of accomplishing this reaction with six-membered analogs, we synthesized a series of (2-tetrahydrofuryl)-hydrosilanes (16, 37, 53) and (2-tetrahydropyranyl) (54, 55) [5, 8, 10-12].

Obviously, hydrogenation of dihydrofuryl- and dihydropyranylhydrosilanes cannot be a convenient method for synthesis of tetrahydrofuryl- and tetrahydropyranyl- hydrosilanes, since the latter may rearrange under the reaction conditions [10]. Therefore we used the following synthesis scheme: conversion of dihydrofurylhydrosilanes (15, 26, 27) and dihydropyranylhydrosilanes (17, 28) (obtained by the familiar techniques in [1]) to alkoxysilanes 35, 45-48, followed by hydrogenation in the presence of Pd/Al_2O_3 to the tetrahydro derivatives 36, 49-52 and reduction by lithium aluminum hydride to hydrosilanes 16, 37, 53-55:



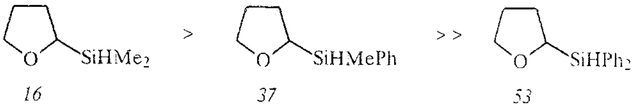
Alk = Me, Et; n = 1 *15, 16, 45, 49* $R^1 = R^2$ = Me; *27, 35, 36, 37* R^1 = Me, R^2 = Ph; *26, 46, 50, 53* $R^1 = R^2$ = Ph; n = 2 *17, 47, 51, 54* $R^1 = R^2$ = Me; *28, 48, 52, 55* R^1 = Me, R^2 = Ph

As shown by the experiment, all the synthesized tetrahydrofurylhydrosilanes (16, 37, 53) and also tetrahydropyranylhydrosilanes (54, 55) in the presence of 5% Pd/Al_2O_3 undergo rearrangement with ring expansion as a result of insertion of a silicon atom into the ring, with formation of the corresponding oxasilacyclohexanes 38, 44, 56 and oxasilacycloheptanes 57, 58 in high yield (70-100%).

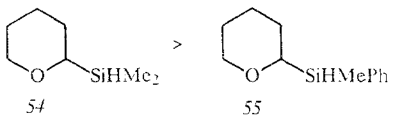


n = 1 *16, 44* R = R^1 = Me; *37, 38* R = Me, R^1 = Ph; *53, 56* R = R^1 = Ph
n = 2 *54, 57* $R^1 = R^2$ = Me; *55, 58* R^1 = Me, R^2 = Ph

The reaction rate increases with a decrease in the number of phenyl groups at the silicon atom. Thus, under typical reaction conditions (0.1 M solution of substrate in tetrahydrofuran, 25°C, [substrate]:[Pd] = 100:1), rearrangement of the dimethyl derivative 16 occurs in 20 min; 6 h for the methylphenyl derivative 37; and complete conversion of the diphenyl derivatives 53 requires boiling the reaction mixture for 72 h. We established that the tetrahydrofurylhydrosilanes 16, 37, 53 can be arranged in the following series according to the decrease in the reactivity:



An analogous correlation also holds for the six-membered analogs 54 and 55 (the reaction occurs in 6 and 48 h respectively):



Conversions of tetrahydropyranylhydrosilanes 54 → 57 and 55 → 58 occur significantly more slowly than conversions of tetrahydrofuryl analogs 16 → 44 and 37 → 38, which is probably connected with the greater stability of six-membered cyclic systems compared with the five-membered analogs.

The rate of the rearrangement 16 → 44 depends on the solvent used, but at the same time we do not observe a correlation between the polarity of the solvent and the reaction rate (Fig. 1). The reaction goes most rapidly in tetrahydrofuran and hexane, the lowest rearrangement rate is observed when the reaction is carried out in solvents containing multiple bonds

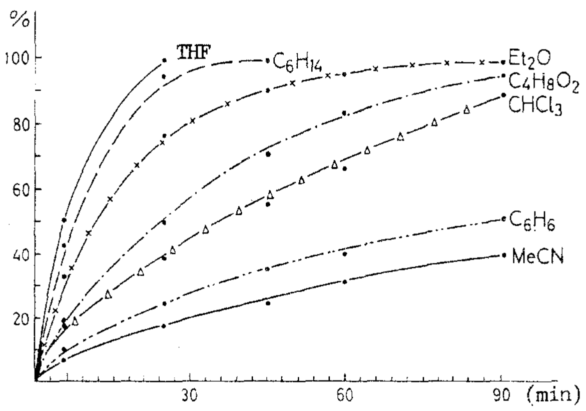


Fig. 1. Effect of the solvent on the rate of formation of oxasilacyclohexane 44.

(C_6H_6, MeCN). We can hypothesize that in this case a reaction occurs between palladium and the multiple bonds of the solvent, which competes with adsorption of hydrosilane 16 on the surface of the active palladium, slowing down the rearrangement.

We established that the most active catalysts of the studied rearrangement are palladium-containing catalysts. In the presence of PD/Al_2O_3, the yield of 44 after 45 min was 95%. Palladium black proved to be more active, and the product yield was 95% after 15 min. The reaction catalyzed by palladium (II) chloride after 1 h leads to 40% 44 with complete conversion of the starting hydrosilane 16.

The metal complex catalyst $(Ph_3P)_2PdCl_2$ (0.1 M solution in hexane, [16]:[catalyst] = 100:1, 25°C) also has high catalytic activity (after 24 h, the yield of 44 was 95%). Contrary to expectations, the zero-valent palladium complex $(Ph_3P)_4Pd$ does not catalyze the rearrangement 16 → 44.

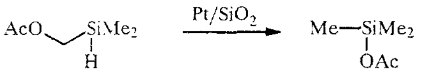
When using Pt(black), after 6 h the yield of 44 was 17%. Significantly lower catalytic activity compared with that for $(Ph_3P)_2PdCl_2$ is displayed by $(Ph_3P)_2PtCl_2$ (after 24 h, the yield is only 18%).

Rh/C and Rh(black) catalyze the rearrangement to a slight extent (5%). The rhodium catalysts $(Ph_3P)_3Rh(CO)H$ and $(Ph_3P)_2Rh(CO)Cl$ catalyze the rearrangement only upon heating to a slight extent (after 3 h at 60°C, the yield of 44 was about 20% with 100% conversion of the starting hydrosilane 16). Ruthenium, iridium, osmium, and nickel metal complex compounds do not display substantial catalytic activity in the studied reaction. No catalytic activity for this rearrangement is displayed by $H_2PtCl_6 \cdot 6H_2O$, $RhCl_3 \cdot 3H_2O$, Pt/Al_2O_3, and Lewis acids.

We have shown that both upon ultraviolet irradiation with a mercury lamp (254 nm) for 3 h and upon fast heating up to 400°C in the gas phase, hydrosilane 16 does not undergo any changes.

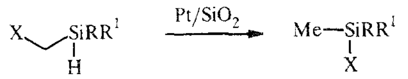
REARRANGEMENT OF ACETOXY- AND HALOMETHYLHYDROSILANES

We have observed that under mild conditions (0.1 M solution in hexane, [59]:[Pt] = 50:1, 25°C, 1 h), dimethylacetoxysilane 59 in the presence of Pt on silica gel is rearranged with migration of the acyloxy group to the silicon atom, and the yield of acyloxysilane 60 in this case is about 40%.



59 60

Trace amounts of Pd/Al_2O_3 even at −78°C turn hydrosilane 59 into tar. Palladium on Al_2O_3 can be used for rearrangement of halomethylhydrosilanes 61a-f to the corresponding methylhalosilanes (62a-f) under mild conditions (0.1 M solution in hexane or methylene chloride; [substrate]:[Pd] = 50:1, 25-80°C, 5-90 min) and in good yield (for 61a-c, 80-100%; for 61f, 40%).



61 a-f 62 a-f

a X = Cl, R = R^1 = Me; b X = Br, R = R^1 = Me; c X = Cl, R = Me, R^1 = Ph; d X = Cl, R = R^1 = Ph; e X = Cl, R = H, R^1 = n-C$_6$H$_{13}$; f X = Cl, R = H, R^1 = Ph

Upon subsequent substitution of the methyl groups by phenyl groups, as in the case with the cyclic analogs, we observe a decrease in the reactivity of the starting hydrosilanes 61 (RR^1:Me$_2$ (61a) > MePh (61b) > Ph$_2$ (61d)). Upon thermal rearrangement of AcOCH$_2$SiHRR^1, we observe the reverse order of decrease in reactivity [13]. The bromomethyldimethylsilane (61b) in turn is rearranged more slowly than its chloromethyl analog (61a).

Chloromethyldimethylsilane (61a) is easily (10 min, 25°C) rearranged also in the presence of AlCl$_3$, although the reaction does not proceed selectively and the yield of trimethylchlorosilane (62a) is about 60% for 100% conversion of the starting hydrosilane 61a.

The amino-substituted silane Me$_2$NCH$_2$SiHMe$_2$ 63 does not undergo any changes even under more vigorous conditions compared with those suggested for halomethylhydrosilanes 61a-f (boiling the reaction mixture for 100 h, [63]:[Pd] = 10:1).

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