Catalytic reactions of hydrosiloxanes with allyl chloride

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Abstract

Catalytic reactivity of Si–H bond of di-, trisiloxanes with allyl chloride in the presence of platinum catalyst has been examined. Hydrosilylation process competes with hydrogen substitution by chlorine and/or propenyl group. The effect of the reaction conditions as well as structure of siloxane on the yield and selectivity of the number of products has been discussed. Several consecutive-competitive processes have been identified. The results obtained can be helpful in the study of the catalytic hydropolysiloxanes reactions with allyl derivatives–systems of great practical importance, to produce commercial functionalized silicones.
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1. Introduction

Catalytic hydrosilylation of organic substrates possessing both unsaturated carbon–carbon bond and other organic functionalities is an effective and still attractive way of synthesis of carbofunctional silanes, siloxanes and oligo(poly)siloxanes [1–6]. The resulting addition products show the reactivity originating from the presence of organic functional groups and substituents at silicon atom(s) – e.g. $\equiv$Si–H, $\equiv$Si–OR, $\equiv$SiX, etc., preserving some hydrophobic properties due to the presence of far less reactive $\equiv$Si–R or $\equiv$Si–O–Si$\equiv$groups [2–4]. Widely applied and recently explored hydrosilylation of polymeric systems [2,4] and especially hydrosilylation curing of polyvinylsiloxanes by polyhydrosiloxanes have been attracting increasing attention due to the practical outcome and recent development in silicon-containing polymeric systems. The open literature and patent descriptions are generally limited in scope to systems involving well-known or modified catalysts (in particular Karstedt's and other Pt complexes) not only in the synthesis of macromolecular compounds but also in catalytic cure of polysiloxanes [5].

Hydrosilylation of allyl derivatives seems to be of great practical importance [1,2]. Introduction of the $XCH_2CH_2CH_2$ group at terminal or internal position of siloxane chain via hydrosilylation of allyl derivative ($XCH_2CH=CH_2$, X = Cl, NH_2, OR, CN, CF_3, etc.) modifies both siloxane reactivity and physicochemical properties. Allyl chloride, due to its availability and characteristic easy conversion of chlorine atom to other functionalities should be a good choice although the literature on its reactivity toward hydro(poly)siloxanes is very limited [7–9] and there is a lack of thorough investigation of the above-mentioned reaction process. Pt(0), H_2PtCl_6 (cyclohexanone) and $Ru_3(CO)_{12}$ have been effectively applied to the hydrosilylation of allyl derivatives by oligosiloxanes having Si–H bonds [7,8]. The conversion of siloxane has been studied using a quantitative IR method (based on Si–H bond frequency) and under the optimum conditions functionalization proceeded smoothly, however, no detailed data on allyl chloride runs are available [7].

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The reaction of allyl chloride with polydimethylsiloxane having hydrogen bonded to silicon at one end in the presence of Pt catalyst (50 °C, 5 h, toluene as a solvent) yielded effectively polydimethylsiloxane chlorinated at one end [9]. In this reaction the Si–H substitution by chlorine dominates over the addition process. Besides, it has been established that a significant percentage of the allyl groups undergo isomerization under the addition reaction conditions to propenyl groups [10]. This isomerization can be depicted by the following equation:

$$\text{(1)}$$
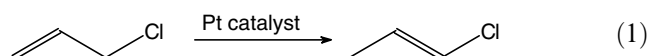
It has become accepted practice in industry, to use stoichiometric excesses (20% mole or more) of the allyl group to ensure complete reaction of all silanic hydrogen atoms.

On the other hand, chloropropyl substituted siloxanes (both terminal and internal ones) are very good substrates for tertiary aminopropylsiloxane derivatives of practical use [11,12]. Thiol and amino-terminated silicones may be prepared by reacting chloropropyl substituted siloxane with ammonia, an amine or H$_2$S to provide a primary amine, secondary amine or thiol ended oligomer, respectively [13].

Di- and trisiloxanes with one or two terminal Si–H bonds can be model compounds of α-hydro, α,ω-dihydro or polyhydrosiloxanes with the Si–H bond at all silicon atoms in the polysiloxane backbone – chemical models for polyhydrosiloxane fluids of market importance.

In this paper, we would like to present the results of our study on pentamethyldisiloxane (I), 1,1,1,3,5,5,5-heptamethyltrisiloxane (II) and 1,1,3,3-tetramethyldisiloxane (III) reactions with allyl chloride in the presence of platinum complexes and to compare the reactivity of Si–H bond in terminal and internal position.

2. Results and discussion

2.1. Reaction of pentamethyldisiloxane (I) with allyl chloride

Siloxane (I) represents siloxanes and/or oligo-(poly)siloxanes with one terminal Si–H bond. First attempts were carried out in the presence of Karstedt's catalyst Pt$_2${[CH$_2$=CHSi(CH$_3$)$_2$]$_2$O}$_3$. It was found that typically three products 1–3 were observed with only traces of some other ones (GC):

$$\text{(2)}$$
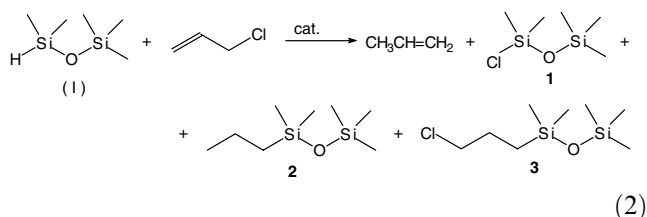
The addition product 3 is accompanied by chlorodisiloxane 1 and propyldisiloxane 2. Other products, found in minor quantities, could be the result of specific catalytic rearrangements of siloxane substrate [14], leading to Si–H redistribution products, e.g.:

$$\text{(3)}$$
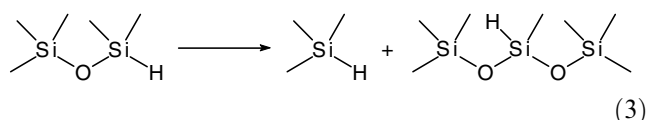
and their consecutive reactions products. Under mild conditions several catalytic reactions runs have been performed to determine the effect of the substrate molar ratio and reaction temperature on the substrate conversion, yield and selectivity of the reaction products (see Table 1).

Higher temperature and/or catalyst concentration lead obviously to higher substrate conversion, however for the equimolar ratio (see runs 1–4), the conversion of siloxane is drastically higher than that of the second

Table 1
The effect of reaction conditions on the selectivity of the products of the reaction of the siloxane (I) with allyl chloride in the presence of Karstedt's catalyst (0.2 ml of siloxane, vials/glass ampoules, reaction time 24 h)

No.	Siloxane conv. (%)	AllCl conv. (%)	$\frac{[\text{siloxane}]}{[\text{AllCl}]}$	$\frac{[\text{siloxane}]}{[\text{catalyst}]}$	T (°C)	Products selectivity (%)			
						1	**2**	**3**	Others
1	34	27	1	10^5	45	55	10	31	4
2	97	77	1	10^5	85	62	9	25	4
3	100	62	1	10^4	45	59	11	28	2
4	100	68	1	10^4	85	67	8	21	5
5	27	66	2	10^5	45	46	9	41	4
6	60	100	2	10^5	85	40	25	30	5
7	100	100	2	10^4	45	32	38	24	6
8	67	97	2	10^4	85	41	21	27	11
9	44	10	0.5	10^5	45	59	11	26	4
10	62	23	0.5	10^5	85	66	13	18	3
11	100	35	0.5	10^4	45	64	9	25	2
12	94	46	0.5	10^4	85	77	6	13	4

substrate. The Si–H/Si–Cl exchange process dominates over addition and the Si–H/Si–R exchange. The double excess of siloxane (see runs 5–8 in Table 1) influences the ratio of addition product **3** but in all cases chlorodisiloxane **1** predominates and is accompanied by traces of propenyldisiloxane (see Section 4). In the excess of allyl chloride (2:1) its conversion is even lower (comparing to equimolar ratio). Both addition product **3** as well chlorodisiloxane derivative **1** have been isolated from reaction mixture and fully characterized (see Section 4). Identification of **2** is based on GC-MS measurements. The results discussed above show that under the reaction conditions chlorine substitutes hydrogen at the silicon atom. Some propene is evolved and partially hydrosilylated toward product **2**. It is known that addition of siloxane (I) to β-methallyl chloride has resulted in 97% yield of typical adduct (H_2PtCl_6, reflux, 2 h) or 96% of chlorodisiloxane (Pd/C, reflux, 2 h) [15], providing evidence that both catalyst and organic substrate nature determine the reaction mode.

2.2. Reactions of 1,1,1,3,5,5,5-heptamethyltrisiloxane (II) with allyl chloride

Trisiloxane (II) can be another model of oligo(poly)siloxanes with isolated [$HSiO(CH_3)$] units. Under the conditions comparable to described previously, reaction of trisiloxane (II) with allyl chloride led to addition product **7**, accompanied by chloro **4**, propyl **5** and propenyl **6** substituted trisiloxane (Eq. (4))

$$(4)$$
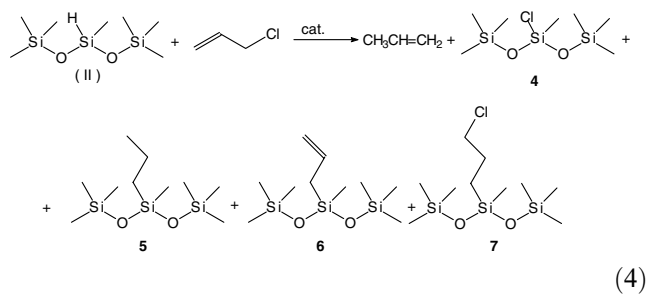
The use of standard Pt catalyst allows us to achieve high conversion of substrates, however, in all cases the process is unselective. The effect of

the reaction conditions on the conversion of substrates and products selectivity is illustrated in Table 2.

For equimolar reagents mixture at 85 °C almost 100% conversion of substrates is observed (see run 2) with chlorotrisiloxane **4** dominating over other products. In the excess of siloxane (II) conversions remain high, however, for lower catalyst concentrations (see run 4) adduct **7** is not formed at all. The H/Cl exchange product seems to be the main one despite the reaction conditions applied, especially in the higher excess of allyl chloride in the reaction mixture (see runs 6–8) which may even allow an isolation of **4** (see Section 4). Hydrosilylation competes with H/Cl and H/propenyl exchange reactions, the highest amount of product **7** has been found for run 6. All the products have been isolated and their structures have been confirmed by GC and spectroscopic analyses (see Section 4). Propene can undergo hydrosilylation towards propyl derivative **5**, especially in the excess of siloxane (II). It is known from literature that the hydrosilylation of allyl chloride by heptamethyltrisiloxane (Pt catalyst, 120 °C, 40 min) yielded 15 % of addition product as one of several products [16]. $MeCl_2SiH$ added at the equimolar level effectively enhanced the yield, but not the rate, of the hydrosilylation reaction product up to 44%. The use of Cl_3SiH enhanced both the rate (3 min reaction time!) and adduct yield (40%). Unfortunately, there is no data on other products selectivity. On the other hand, hydrosilylation of β-methallyl chloride by $(Me_3SiO)_2Si$-(Me)H in the presence of H_2PtCl_6 (reflux, 1 h) leads to a mixture of adduct (34%), SiH/Cl exchange product – chlorosiloxane (18%) and β-methylpropenyl derivative of trisiloxane (9%) as substitution product [15]. Pt/C catalyst has shown a very similar selectivity of the products, but in the presence of Pd/C and Ru/C chlorotrisiloxane has been the only product observed (with yield 74% and 60%, respectively).

2.3. Reactions of 1,1,3,3-tetramethyldisiloxane (III) with allyl chloride

Tetramethyldisiloxane can produce both mono- and diadducts, however, it is practically impossible to

Table 2
The effect of reaction conditions on the selectivity of the products of the reaction of the siloxane (II) with allyl chloride in the presence of Karstedt's catalyst (0.2 ml of siloxane, vials/glass ampoules, reaction time 24 h)

No.	Siloxane conv. (%)	AllCl conv. (%)	$\frac{[\text{siloxane}]}{[\text{AllCl}]}$	$\frac{[\text{siloxane}]}{[\text{catalyst}]}$	T (°C)	Products selectivity (%)			
						4	**5 + 6**	**7**	Others
1	33	59	1	10^5	45	45	9	26	0
2	98	100	1	10^5	85	70	11	18	1
3	100	93	1	10^4	45	67	14	19	0
4	42	100	2	10^5	85	69	30	0	1
5	56	100	2	10^4	85	51	23	25	1
6	97	60	0.5	10^5	85	37	4	59	0
7	100	52	0.5	10^4	85	85	7	8	0
8	97	33	0.25	10^5	85	90	5	4	1

achieve monoadduct with high selectivity and yield [17]. The patent literature describes the reaction of tetramethyldisiloxane with allyl chloride in the presence of Pt(0)/divinylsiloxane (80 °C, 18 h) leading only toward monoadduct with the yield up to 24% using iPr$_3$SiO-SO$_2$CF$_3$ and ethyltriacetoxysilane as catalyst promoters [17]. The autoclave reaction in the molar excess of allyl chloride (3:1) in the presence of 5% Pt/C (120 °C, 12 h) led only to 1-chloro-3-chloropropyl-1,1,3,3-tetramethyldisiloxane (34% yield) [18]. Typically, in the presence of Karstedt's catalyst, the post-reaction mixture shows complex composition (see Fig. 1 – GC analysis) due to the presence of nine identified products (Eq. (5)).

$$(5)$$
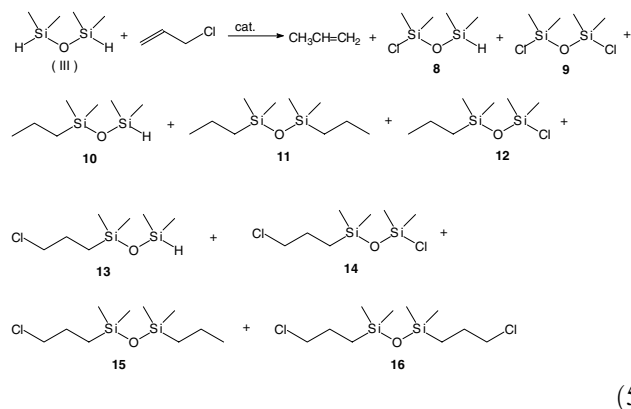
Mono- and diaddition products **13** and **16** are accompanied by chloro- and alkyl derivatives of **13** **14** and **15** and several chloro- and propyldisiloxanes **8**–**12**. Monoadduct **13** could be of great interest as a potential candidate for substrate of diorganofunctional disiloxanes of the mixed functionality. Diorganofuctional disiloxanes are interesting substrates for modification of a multitude of organic and inorganic polymers and oligomers, including chemical curing processes and synthesis of block organic-inorganic polymers [2,4]. All the products were identified; six of them were isolated from reaction mixture and four of them **8**, **9**, **11** and **16** were synthesized independently (details in Section 4). Separation of reaction mixture was a difficult task since low quantity of products and very close boiling points of several of them. Manipulation of reaction conditions and sacrificing the yield led us to isolation most of the products, including hydrosilylation products. There was some evidence of the presence (in minor quantity) of mono- and di- propenyldisiloxanes in the reaction mixtures studied. Independent syntheses of mixture of **8** and **9** (via chlorination of siloxane (III) with PCl$_5$ [19]), alcoholysis of ClSiMe$_2$Pr leading to bis-propyldisiloxane **11** and more complex synthesis of diadduct **16** (via dimethylchlorosilane addition to allyl
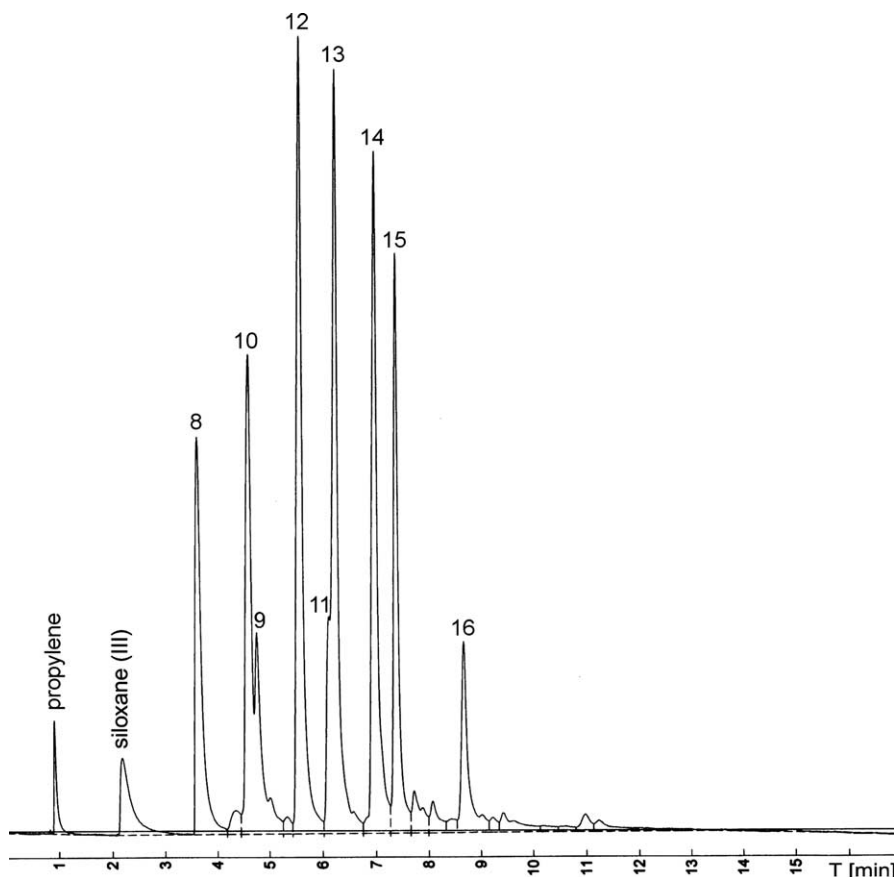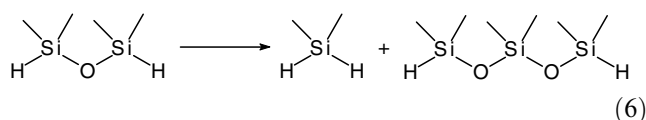

Fig. 1. GC-spectrum of the reaction mixture: [siloxane (III)]:[allyl chloride]:[Karstedt's catalyst] = 1:1:5 × 10^{-5}, 85 °C.

chloride and consecutive methanolysis) allowed us to identify all the main products of the studied siloxane – allyl chloride system. Catalytic redistribution of the substrate (III):


(6)

was not observed. The effect of reaction conditions on the conversion of substrates and products selectivity is illustrated by the data in Table 3.

For the equimolar ratio of substrates, higher reaction temperatures for both catalyst concentrations prefer higher ratios of monochloro **8** and monopropylo **10** derivatives and monoadduct **13** in reaction mixture and lower ratios of "chlorinated" adduct **14** (see runs 1–4 in Table 3). In the excess of disiloxane (III) the amounts of **10** and adduct **13** are significantly higher (see runs 5–6 in Table 3) relative to their presence in the equimolar reaction mixture. On the contrary, in the excess of allyl chloride (see runs 7–9), the monoadduct is missing (some amounts of diadduct **16** are detected) as well as chloro- and propylsiloxanes **8** and **10** but chlorosubstituted adduct **14** predominates. Interestingly, high conversion of allyl chloride (up to 100%) is observed for its two-fold excess in the reaction mixture but lower than 40% conversion has been observed for a four-fold one. In the latter case significantly higher amount of dichlorodisiloxanes **9** has been detected (see runs 9–10) however, at higher temperatures the amount of **14** is diminished due to a higher concentration of **12**.

To understand this complexity, some preliminary experiments were conducted to follow the composition of the reaction mixture in the course of the reaction progress. Fig. 2 represents relative amounts of the reaction substrates and products in the course of the reaction for the chosen experiment ([siloxane]:[allyl chloride]:[Karstedt's catalyst] = $1:2:5 \times 10^{-5}$, 85 °C).

The amount of chlorosiloxane **8** increased in the first 72 h of the reaction progress and then rapidly decreased. In the very same time dichlorodisiloxane **9** appeared in the reaction mixture. A similar situation has been observed in the presence of monoadduct **13** and diadduct **16**. After the first 24 h, adduct **13** and chlorodisiloxane **8** are the main products, accompanied by chlorosubstituted adduct **14** after another 24 h. H/Cl exchange for **13** yields high amount of 14 after 72 and 96 h. Monoadduct **13** undergoes addition leading to high amount of product **15**. The analysis of the curves presented in Fig. 2 allows us to propose a general scheme of the reaction progress. In the first step hydrosilylation and H/Cl exchange lead to the appropriate products **13** and **8**

(7)
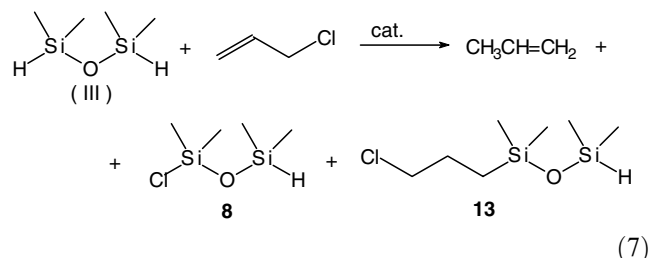
Then product **13**, beside further addition leading to synthesis of diadduct **16**, undergoes mainly H/Cl exchange yielding **14**:

(8)
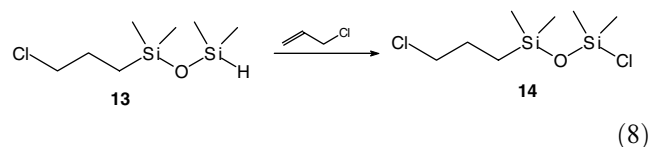
and, to a much less extent, hydrosilylation of propene. In the very same manner **8** is converted to **9**, however part of **8** yields **12**. Under the prolonged reaction time (96 h and more) only traces of product **8** and substrates can be determined. Consecutive-competitive set of hydrosilylation, H/Cl and H/propenyl exchange processes occurs leading to number of products, presented in Eq. (5).

Table 3
The effect of reaction conditions on the selectivity of the products of the reaction of the siloxane (III) with allyl chloride in the presence of Karstedt's catalyst (0.2 ml of siloxane, vials/glass ampoules, reaction time 24 h)

| No.	Siloxane conv. (%)	AllCl conv. (%)	$\frac{[siloxane]}{[AllCl]}$	$\frac{[siloxane]}{[catalyst]}$	T (°C)	Products selectivity (%)								
						8	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
1	89	100	1	10^4	45	9	5	14	2	15	17	15	9	5
2	94	100	1	10^4	85	15	5	17	6	23	21	2	14	6
3	95	98	1	10^5	45	11	5	12	3	19	17	16	11	5
4	88	100	1	10^5	85	16	5	17	0	19	25	2	11	6
5	68	100	2	10^5	45	21	0	30	0	9	31	2	5	2
6	69	100	2	10^5	85	15	0	34	0	3	32	4	9	4
7	98	100	0.5	10^5	45	0	18	0	3	23	0	37	10	9
8	84	100	0.5	10^4	45	0	21	0	3	21	0	38	9	8
9	100	39	0.25	10^4	45	0	31	0	3	24	0	31	6	5
10	100	34	0.25	10^4	85	0	34	0	5	31	0	10	11	8
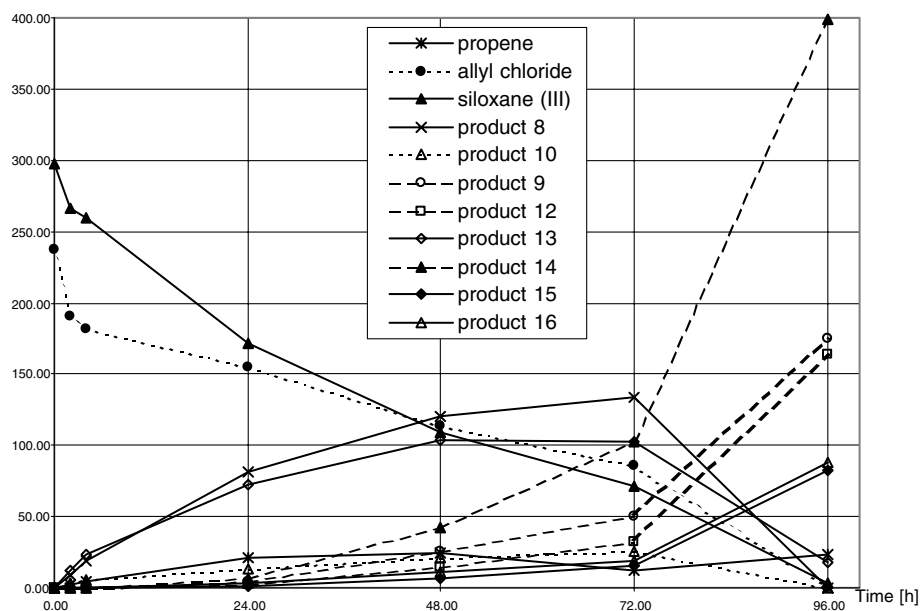
Fig. 2. Relative amounts of the reagents in the course of reaction (III) with allyl chloride in the presence of Karstedt's catalyst.

3. Conclusions

It is obvious that addition of di(tri)siloxanes to allyl chloride leads to several products and that the reaction conditions influence the process selectivity. All the results discussed above lead to a conclusion that the reaction of di- and trisiloxanes with allyl chloride involves several processes (mainly substitution and addition). The amounts of specific products depend on the reaction temperature and the ratio of substrates, due to consecutive addition and/or substitution reactions of several products.

Fig. 3 shows generalized reaction pathways in the systems studied:

Moreover, both substrates and primary products, especially that having SiH groups **8**, **13**, undergo hydrosilylation processes leading to a number of final products **12**, **14**, **15**.

In the series of siloxanes studied, the increasing electron-withdrawing effect of Me_3SiO substitutes increases the strength of the Si–H bond in the order $(Me_3SiO)_2SiMeH > Me_3SiOSiMe_2H$, steric shielding seems to change in the same order. Probably both factors affect destabilization of olefin–Pt complex and hence the formation of chlorosiloxanes dominates over addition. Besides, there is a striking similarity between the behavior of siloxane (I) and (II) in the studied processes.

There are published evidences that $\equiv SiCH_2CH_2CH_2Cl$ group does not undergo decomposition to $\equiv SiCl$ and $CH_2=CHCH_3$ [20] or hydrosilanes SiH are not chlorinated by $ClCH_2CH_2CH_2Si\equiv$ leading to $\equiv SiCl$ and $CH_3CH_2CH_2Si\equiv$ [21]. Additionally, it is known that for all allyl compounds, in the presence of silanes containing SiH group, propene is formed in considerable quantities [22].

From such a point of view, the structure of the reaction product of polyhydrosiloxane reaction with allylchloride, reported in a recent US patent [8], seems to reflect the results of our study. Addition of oligosiloxane $Me_3SiO[HSiMeO]_{40}SiMe_3$ to allyl chloride (Karstedt's catalyst, 100–140 °C, 2.5 h) produced a modified siloxane of formula:
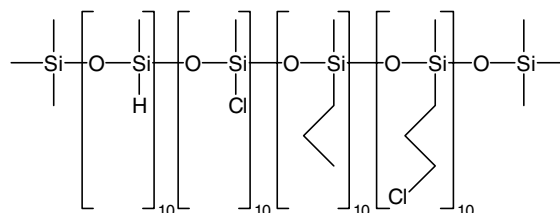
supported by NMR data. The product obtained in the second step after Na_2S_4 treatment leads to sulfur functional polyorganosiloxanes for rubber mixtures. The typical use of excess of allyl chloride (to cover its losses due to catalytic isomerization toward unreactive propenylchloride (1)) additionally push the competitive Si–H substitution resulting in the low yield of chloropropyl-substituted siloxane units in both monomeric (di- and trisiloxanes) and oligomeric (polymeric) products.

4. Experimental

4.1. Chemicals

1,1,3,3-tetramethyldisiloxane (Aldrich), 1,1,1,3,5,5,5-heptamethyltrisiloxane (Aldrich). Pentamethyldisilox-
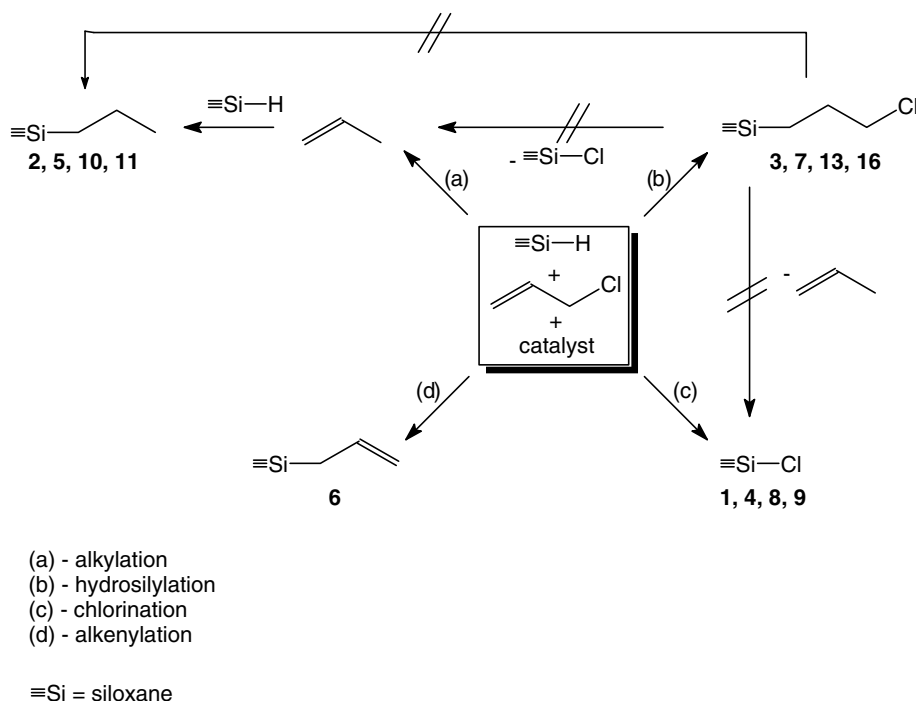
Fig. 3. Generalized reaction pathways of hydrosiloxanes with allyl chloride.

ane (ABCR) were distilled and kept over molecular sieves 4A. Chlorodimethylsilane (ABCR), and chlorodimethylpropylsilane (ABCR) were used as purchased. Allyl chloride (Zachem Bydgoszcz) was distilled over calcium oxide and kept over molecular sieves 4A. 3-chloropropyldimethylchlorosilane was synthesized according to the literature [6]. 1,3-dichloro-tetramethyldisiloxane was purchased from Fluka. Phosphorous pentachloride (POCH Gliwice), trimethyl orthoformate (Aldrich) and tetrahydrofuran (POCH Gliwice) were used as purchased. Toluene (POCh Gliwice) was distilled over sodium and kept over molecular sieves 4A. Karstedt catalyst solution was prepared by dissolving 0.343 g of original catalyst (ABCR, 3–3.5% Pt solution in vinyl-terminatedpolidimethylsiloxanes) in 5.5 ml of dried and distilled toluene. Dichloro(1,5-cyclooctadiene)palladium (II) (Strem) was used as purchased.

4.2. Typical procedures of catalytic processes and products isolation

4.2.1. General procedure for reactions of di(tri)siloxanes with allyl chloride in the presence of Pt catalyst

In 2 ml vials equipped with PTFE/rubber septa 200 μl of appropriate siloxane, appropriate amount of allyl chloride and Karstedt's catalyst were placed. In some cases, due to high overpressure glass ampoules were used instead of vials. Reactors were sealed, put into drier thermostated at a given temperature and shaken occasionally. GC analysis was carried out at the beginning and at the reaction completion. In the case of examing

of reaction progress, GC analysis was carried out periodically.

4.2.2. General procedure for products isolation from the di(tri)siloxanes with allyl chloride reaction mixtures

Most reactions were performed in 50 ml glass flask equipped with a reflux condenser, thermometer and magnetic stirrer (10 ml of siloxane, appropriate amount of allyl chloride and catalyst). These ones which required temperatures above boiling point of the reactants were carried out in 10 ml vials sealed with aluminum caps and PTFE/rubber septa (2ml of siloxane, appropriate amount of allyl chloride and catalyst). GC analysis was carried out periodically. Evaporation of volatile matters and products distillation were performed on an Aldrich micro short-path distillation apparatus with jacketed head. Products were collected in liquid nitrogen cooled trap. Distillation pressures varied from ambient to 1 mmHg.

4.2.3. Synthesis of chloropentamethyldisiloxane 1

1 ml of pentamethyldisiloxane, 1.724 ml of allyl chloride and 47 μl ml of Karstedt's catalyst solution in toluene were mixed. Vial was sealed and kept at 85 °C for one day, then **1** was distilled from the reaction mixture.

Chloropentamethyldisiloxane **1**, b.p. 117–120 °C/760 mmHg.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.147 (s, 9H), 0.482 (s, 6H); ^{13}C NMR (CDCl$_3$): δ (ppm) = 1.602, 4.168; ^{29}Si NMR (CDCl$_3$): δ (ppm) = 4.107, 12.033; IR (neat film on KBr, cm^{-1}): 2.960(m), 2902(w), 1259(s), 1071(s),

876(m), 844(s), 812(s), 801(s), 755(m), 545(w), 465(w); Spectroscopic data evidenced the presence of trace amounts of propenylpentamethyldisiloxane,, b.p. 140–143 °C/740 mmHg: ^{1}H NMR (CDCl$_3$): δ (ppm) = 0.067 (s, 15H), 1.563 (m, 2H), 4.90 (m, 2H), 5.78 (m, 1H); ^{13}C NMR (CDCl$_3$): δ (ppm) = −0.146, 26.432, 113.179, 129.029; ^{29}Si NMR (CDCl$_3$): δ (ppm) = 31.062, 7.233–8.416; IR (neat film on KBr, cm^{-1}): 1589–1665(w).

4.2.4. Synthesis of (3-chloropropyl)pentamethyl-disiloxane 3

1 ml of pentamethyldisiloxane, 215 µl of allyl chloride and 4.7 µl ml of Karstedt's catalyst solution in toluene were mixed in a vial. The vial was sealed and kept at 45 °C for one day, then **3** was distilled from the reaction mixture.

(3-chloropropyl)Pentamethyldisiloxane **3**, b.p. 96–99 °C/40 mmHg.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.065 (s, 15H), 0.608 (m, 2H), 1.785 (m, 2H), 3.506 (t, 2H, J = 6.862); ^{13}C NMR (CDCl$_3$): δ (ppm) = 0.238, 1.913, 15.914, 27.080, 47.888; IR (neat film on KBr, cm^{-1}): 2957(s), 1255(s), 1067(s), 842(s), 804(s).

4.2.5. Synthesis of 3-chloro-1,1,1,3,5,5,5-heptamethyltrisiloxane 4 and 3-(3-chloropropyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane 7

1 ml of 1,1,1,3,5,5,5-heptamethyltrisiloxane, 602 µl of allyl chloride and 3.3 µl ml of Karstedt catalyst solution in toluene were mixed. Vial was sealed and kept at 85 °C for one day. Distillation led to isolation of **4** and **7**.

3-Chloro-1,1,1,3,5,5,5-heptamethyltrisiloxane **4**, b.p. 170–174 °C/760 mmHg.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.156 (s, 18H), 0.375 (s, 3H); ^{13}C NMR (CDCl$_3$): δ (ppm) = 1.466, 1.662; IR (neat film on KBr, cm^{-1}): 2960(s), 2901(w), 1268(s), 1253(s), 1074(s), 870(s), 844(s), 794(s), 758(s), 559(m).

3-(3-chloropropyl)-1,1,1,3,5,5,5-Heptamethyltrisilox-ane 7, b.p. 92–95 °C/7 mmHg.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.067 (s, 3 H), 0.093 (s, 18H), 0.564 (m, 2H), 1.780 (m, 2H), 3.503 (t, 2H, J = 6.826); ^{13}C NMR (CDCl$_3$): δ (ppm) = 1.812, 1.849, 15.152, 26.870, 47.765; IR (neat film on KBr, cm^{-1}): 2959(s), 2902(w), 1260(s), 1081(s), 843(s), 797(s), 756(s).

4.2.6. Synthesis of 3-propyl-1,1,1,3,5,5,5-heptamethyltrisiloxane 5 and 3-propenyl-1,1,1,3,5,5,5-heptamethyltrisiloxane 6

2 ml of 1,1,1,3,5,5,5-heptamethyltrisiloxane, 301 µl of allyl chloride and 6.6 µl ml of Karstedt catalyst solution in toluene were mixed in a vial. The vial was sealed and kept at 85 °C for one day. Distillation led to isolation of **5** and **6** as one mixture (b.p. 54–57 °C/7 mmHg). The mixture was analyzed. Protons in ^{1}H NMR were counted separately for each compound.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.125–0.201 (m), 0.598 (CH$_3$CH$_2$**CH$_2$**Si – m, 2H), 1.022 (**CH$_3$**CH$_2$CH$_2$Si – t, 3H, J = 7.142), 1.481 (CH$_3$**CH$_2$**CH$_2$Si – m, 2H), 3.192 (CH$_2$=CHC**H$_2$**Si – t, 2H, J = 6.866), 4.996 (**CH$_2$**=CHCH$_2$Si – m, 2H), 5.885 (CH$_2$=**CH**CH$_2$Si – m, 1H); ^{13}C NMR (CDCl$_3$): δ (ppm) = 0.079(=), 0.316(–), 2.172(=), 2.242(–), 17.335(–), 18.391(–), 20.898(–), 27.475(=), 114.184(=), 134.171(=); ^{29}Si NMR (CDCl$_3$): δ (ppm) = 7.491, 8.144, 8,208; IR (neat film on KBr, cm^{-1}): 3079(w), 2959(s), 2901(m), 2872(m), 1633(w), 1259(s), 1079(s), 932(w), 895(m), 870(s), 841(s), 806(s), 792(s), 754(s), 688(w).

4.2.7. Procedure for synthesis of siloxanes 1, 4, and 9

All reactions were carried out in 2 ml vials. 400 µl of disiloxane or trisiloxane and appropriate amount of allyl chloride and PdCl$_2$(cod) catalyst were placed in them. [SiH]:[AllCl]:[PdCl$_2$(cod)] = 1:2:10^{-3}. The vials were sealed with PTFE/rubber septa and put into drier (85 °C). Reactions were monitored by GC. After quantitative consumption of siloxanes (usually 3 days) volatiles were evaporated and residue was analyzed. Chloro (di, tri)siloxanes **1**, **4** and **9** were identified, respectively. The analytical data were identical to those, described previously (see Sections 4.2.3, 4.2.5 and 4.2.8).

4.2.8. Synthesis of chlorotetramethyldisiloxane 8, 1,3-dichlorotetramethyldisiloxane 9, 1-chloro-3-(3-chloropropyl)tetramethyldisiloxane 14, 1,3-bis(3-chloropropyl)tetramethyldisiloxane 16

10 ml of 1,1,3,3-tetramethyldisiloxane, 18.4 ml of allyl chloride and 1 ml of Karstedt's catalyst solution in toluene were mixed and kept under reflux. After one day 5 ml of the reaction mixture was subjected to distillation – chlorotetramethyldisiloxane **8** was collected. The remaining part was refluxed for one more day and then distilled to other products **9**, **14**, **16**. GC analysis was carried out periodically.

Chlorotetramethyldisiloxane **8**, b.p. 104–107 °C/751 mmHg.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.281 (d, 6 H, J = 2.747), 0.481 (s, 6H), 4.763 (m, 1H); ^{13}C NMR (CDCl$_3$): δ (ppm) = 0.537, 4.026; ^{29}Si NMR (CDCl$_3$): δ (ppm) = −2.082, 6.825; IR (neat film on KBr, cm^{-1}): 2961(s), 2904(m), 2128(s), 1260(s), 1072(s), 910(s), 833(s), 805(s), 769(m), 488(m), 466(m).

1,3-Dichlorotetramethyldisiloxane **9**, b.p. 136–140 °C/760 mmHg.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.507 (s, 6 H); ^{13}C NMR (CDCl$_3$): δ (ppm) = 3.926; ^{29}Si NMR (CDCl$_3$): δ (ppm) = 8.045; IR (neat film on KBr, cm^{-1}): 2964(m), 2905(w), 1262(s), 1078(s), 830(s), 806(s), 488(m), 465(m).

1-Chloro-3-(3-chloropropyl)tetramethyldisiloxane **14**, b.p. 98–101 °C/15 mmHg.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.150 (s, 6 H), 0.432 (s, 6H), 0.696 (m, 2H), 1.810 (m, 2H), 3.519 (t, 2H, J = 7.141); ^{13}C NMR (CDCl$_3$): δ (ppm) = 0.064, 4.148, 15.511, 26.803, 47.716; ^{29}Si NMR (CDCl$_3$): δ (ppm) = 5.262, 12.455; IR (neat film on KBr, cm^{-1}): 2960(m), 2904(w), 1261(s), 1073(s), 865(m), 830(s), 803(s), 552(w), 466(m).

1,3-Bis(3-chloropropyl)tetramethyldisiloxane **16**, b.p. 125–129 °C/6 mmHg.

Analytical data were almost identical to that obtained in Section 5.3.

4.2.9. Synthesis of propyltetramethyldisiloxane 10 and 3-chloropropyltetramethyldisiloxane 13

6 ml of 1,1,3,3-tetramethyldisiloxane, 1.38 ml of allyl chloride and 60 µl of Karstedt's catalyst solution in toluene were mixed and kept in 45 °C for one day. GC analysis was carried out periodically to control substrate conversion. Distillation of the reaction mixture led to two main products:

Propyltetramethyldisiloxane **10**.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.064 (s, 6H), 0.166 (d, 6H, J = 2.747), 0.542 (m, 2H), 0.965 (t, 3H, J = 7.141), 1.370 (m, 2H), 4.675 (m, 1H); ^{13}C NMR (CDCl$_3$): δ (ppm) = 0.216, 1.021, 4.030, 16.831, 18.184, 20.877; ^{29}Si NMR (CDCl$_3$): δ (ppm) = −6.256, 10.432; IR (neat film on KBr, cm^{-1}): 2960(s), 2930(m), 2904(m), 2872(m), 2127(s), 1258(s), 1068(s), 911(s), 837(s), 802(s), 771(s).

3-Chloropropyltetramethyldisiloxane **13**, b.p. 62–66 °C/7 mmHg.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.088 (s, 6 H), 0.166 (d, 6H, J = 2.747), 0.639 (m, 2H), 1.792 (m, 2H), 3.502 (t, 2 H, J = 7.141), 4.686 (m, 1H); ^{13}C NMR (CDCl$_3$): δ (ppm) = 0.058, 0.961, 15.821, 27.078, 47.804; ^{29}Si NMR (CDCl$_3$): δ (ppm) = −5.530, 10.012; IR (neat film on KBr, cm^{-1}): 2959(s), 2903(m), 2125(s), 1257(s), 1061(s), 910(s), 865(m), 839(s), 801(s), 768(m).

5. Procedures for alternative syntheses

5.1. Synthesis of chlorotetramethyldisiloxane 8 and 1,3-dichlorotetramethylodisiloxane 9 [19]

In 100 ml flask equipped with a reflux condenser (with drier), thermometer and magnetic stirrer 5 ml of 1,1,3,3-tetramethylodisiloxane, 12.9 g of PCl$_5$ and 50 ml of CCl$_4$ were mixed and refluxed for one day. GC analysis was carried out periodically. Two products were observed. According to the literature these products were assigned as chlorotetramethylodisiloxane **8** and 1,3-dichlorotetramethylodisiloxane **9**. Retention times (GC) were identical to those obtained for the same products collected from the reaction mixture (see Section 4.2.8).

5.2. Synthesis of 1,3-bispropyltetramethyldisiloxane 11

In 2 ml vial equipped with PTFE/rubber septa, 400 µl (2.55 mmol) of chlorodimethylpropylsilane and 413 is µl (10.2 mmol) of methanol were placed. The reactor was sealed, put into a drier (60 °C) and shaken occasionally. GC analysis was carried out periodically. After 21 h (85% conversion of chlorodimethylpropylsilane) substrates were evaporated and product was analyzed by ^{1}H NMR.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.130 (s, 12H), 0.581 (m, 2H), 1.013 (t, 3H, J = 7.318), 1.424 (m, 2H); IR (neat film on KBr, cm^{-1}): 2957 (s), 2929 (s), 2871 (s), 1253 (s), 1203 (m), 1055 (s), 998 (m), 896 (m), 838 (s), 795 (s), 771 (s); MS: 177(17) (M-Pr + H), 175(10), 161(8) (M–Pr–Me + H), 149(65) (M–Pr–2Me + 3H), 133(100) (M–2Pr + H), 119(23) (M–2Pr–Me + 2H), 103(4), 87(2), 73(18) (OSiMe$_2$–H), 59(7), 45(4).

5.3. Synthesis of 1,3-bis(3-chloropropyl)tetramethyl-disiloxane 16

In a three-necked flask equipped with a reflux condenser, drying tube and magnetic stirrer, a portion of 100 ml (0.61 mol) of 3-chloropropyldimethylchlorosilane was placed and 74.27 ml (1.83 mol) of methanol was added by dropping funnel. Reaction proceeded in 66–70 °C for 3 h. Volatile matter was evaporated. The residue was distilled at reduced pressure (7 mmHg). Product with b.p. 126–130 °C/7 mmHg, 99% purity and 57% yield was collected.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.073 (s, 12 H), 0.616 (m, 4H), 1.770 (m, 4H), 3.509 (t, 4H, J = 7.141); ^{13}C NMR (CDCl$_3$): δ (ppm) = 0.393, 15.980, 27.129, 47.888; ^{29}Si NMR (CDCl$_3$): δ (ppm) = 8.321; IR (neat film on KBr, cm^{-1}): 3257(s), 2913(m, wide), 1258(s), 1068(s), 864(m), 838(s), 802(s).

6. Procedure for the examination of reaction (5) progress

The reaction was carried out according to the general procedure described at 4.2.1. Temp. 85 °C, [tetramethyldisiloxane]:[allyl chloride]:[Karsted's catalyst] = $1:2:5 \times 10^{-5}$. The reaction was monitored by GC at the beginning, then after 2, 4, 24 h and each next day till complete substrates conversion (4 days).

7. Analytical measurements

GC analysis was performed using an SRI 8610C gas chromatograph with TCD, Perkin Elmer elite PE-1 30 m capillary column. NMR spectroscopy (^{1}H, ^{13}C, [29]Si) was carried out on Varian XL 300 with CDCl$_3$ as solvent. The infrared spectra were recorded on Bruker

IFS 113v instrument. GC-MS spectroscopy was performed on Varian 3300 chromatograph equipped with J&W DB-1 30 m capillary column and Finnigan MAT&TD 800 spectrometer.

Acknowledgments

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