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Metathesis of silicon-containing olefins

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Abstract

The behaviour of various olefins containing Si–C, Ge–C, Si–Si, Si–H, Si–O–Si and Si–O–C bonds has been studied in the presence of rhenium on alumina metathesis catalysts. Monovinyl-, allyl-, and butenylsilanes bearing alkyl, alkenyl, aryl, aralkyl, silacycloalkyl, siloxane and hydride substituents, as well as unsaturated silacarbon heterocycles, mono- and diallylgermanes, were used as substrates. Heterogeneous Re_2O_7/Al_2O_3–$SnBu_4$ and Re_2O_7/Al_2O_3–$PbEt_4$ catalysts showing good activity in metathesis were examined. Except for hydrides, allyl- and butenylsilanes or germanes were active in metathesis regardless of the nature of the substituents at the metal atom. On the other hand, all of the vinylsilanes used were practically inactive in the reaction. Except for vinyl derivatives, metathesis of di- and polyalkenylsilanes, disilanes, disiloxanes and germanes occurred via both intermolecular and intramolecular pathways. These were used to develop a novel effective synthetic method for producing linear 1,4-bis(triorganylsilyl)- (or germyl-) but-2-enes (including those with ferrocenyl substituents at the silicon) and six-membered mono- and disilacycloalkenes, as well as silaspirane structures. It was shown that α-olefin co-metathesis with allylsilanes (followed by protodesilylation) is a convenient method for increasing the length of an α-olefin hydrocarbon chain.

Introduction

The chemical properties and transformations of olefins and cycloolefins containing silicon form an original area of organic and organosilicon chemistry, attractive from a theoretical point of view and with good prospects for application in synthesis. These properties are mainly determined by the specific features and influence of silicon atoms on the neighbouring atoms and groups. In many aspects they are different from the properties of their hydrocarbon analogues.

It should be noted that the proximity of Si and C in the periodic table does not ensure a similarity in the chemical behaviours of the corresponding structural analogues. This is especially true when Si atoms are in the vicinity of fragments with lone pairs of electrons (halogens, O-, N-, S-containing groups) or multiple bonds. The silicon atom has a large covalent radius and, accordingly, forms longer chemical bonds, has decreased electronegativity and has low-lying 3d orbitals [1], resulting in

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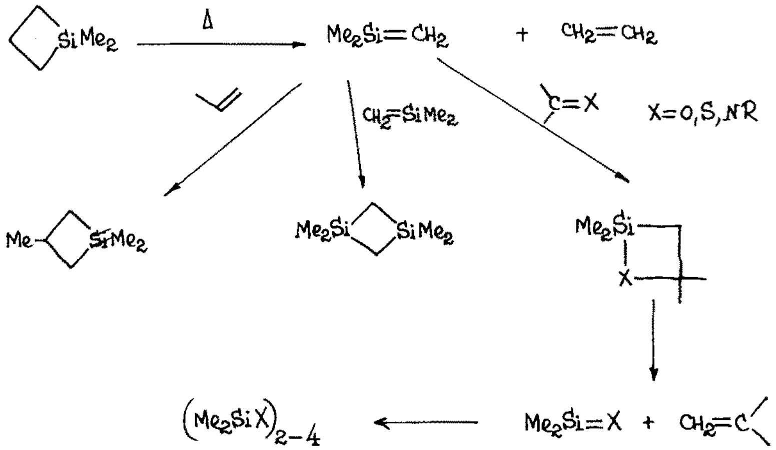
the high reactivity of Si–H, Si–Si and Si–X bonds. The same holds for Si–C bonds in unsaturated compounds bearing C(sp^2) or C(sp) atoms in α- or β-positions relative to the silicon atom.

A typical example shows the principal limitations that exist in organosilicon chemistry. The systematic investigations, performed mainly in the 1970s and 1980s, established that silicon is unable to form stable multiple bonds, either with carbon or with any other element [2]. Numerous attempts by many researchers to obtain silicon analogues of ethylene, acetylene, butadiene, cyclopropane, benzene and their simple derivatives failed. Some representatives of this series have been synthesized, but only at low temperature by means of matrix isolation techniques. Using special gas-phase methods, noncatalyzed chemical reactions of short-lived silaalkene molecules can be performed according to schemes similar to those of olefin metathesis (Scheme 1). In our opinion, the use of catalysis for effective realization of these reactions, especially for cross-metathesis involving unstable particles such as



Scheme 1.

$>\mathrm{Si{=}C}<$ and $>\mathrm{Si{=}Si}<$

would be promising.

It is quite natural that unsaturated organsilicon compounds bearing C=C bonds and silicon-containing groups as substituents (alkenylsilanes, sila- and silylcycloolefins) can be used as objects for catalytic metathesis. However, it should be emphasized that because of the reasons mentioned above, they do not duplicate their carbon analogues in chemical properties and differ significantly from their neighbours in a homologous series. For example, vinyltrimethylsilane can be smoothly polymerized by an anionic mechanism, in contrast to its structural analogue neohexene [3, 4]. On the other hand, allyltrimethylsilanes are inactive with anionic catalysts but can be polymerized by metal complex systems of the Ziegler type [5]. The distribution of electron density in double bonds of vinyl derivatives of silicon ensures the alkylation of aromatic compounds to produce normal structures [6]. This behaviour is unlike that of olefin hydrocarbons, which always form branched adducts. In contrast, allyl derivatives react similarly to their carbon analogues [7]. Using catalysts one should take into account the enhanced ability of Si–C bonds in alkenyl groups to interact with active sites.

Bearing this in mind, we cannot expect the complete duplication of the behaviour of olefin hydrocarbons by silicon-containing analogues in metathesis, since silyl groups can significantly influence the properties of four-membered metallacycles and metallacarbene intermediates and their precursors.

This paper is devoted to the study of the behaviour of various mono- and dialkenylsilanes bearing C=C bonds in α-, β- and γ-positions to Si under the influence of rhenium-on-alumina metathesis catalysts, to establish the influence of various Si-containing groups on metathesis and to extend the scope of this reaction to the important field of organosilicon chemistry.

Experimental

The ^{1}H NMR spectra were recorded on Varian T-60 and Bruker MSL-300 spectrometers for 5% samples in CCl_4 using TMS as the internal standard.

The IR spectra were taken on a UR-20 instrument. For the MS studies, LKB-2091 and Kratos MS-80 mass spectrometers were used.

GC analyses were carried out on a LKhM-8MD chromatograph fitted with a thermal conductivity detector (a 25 m × 0.2 mm steel column packed with SE-30 or OV-101 or a 50 m × 0.2 mm steel column packed with SKFT (polytrifluoropropyl)methylsilicon, 50% trifluoropropyl, with H_2 and He as carrier gases).

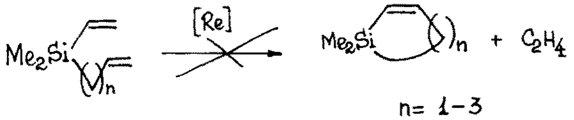
Substrates and solvents were purified by adsorption on thermoactivated γ-Al_2O_3 and distilled under Ar atmosphere.

Very significant in the implementation of the metathesis reaction of silicon and germanium derivatives is their degree of purity. In the present study most of the synthesized substrates were subjected to chromatography in columns with Al_2O_3, in addition to thorough drying and rectification.

10% Re_2O_7/Al_2O_3–$SnBu_4$ and 10% Re_2O_7/Al_2O_3–$PbEt_4$ catalysts were prepared according to reported techniques [8–12]. Reactions were carried out in the liquid phase over a temperature range of 25–70 °C in a thermostatted reactor equipped with a magnetic stirrer, a dropping funnel and a condenser, connected with a gas burette to collect the evolved ethylene. Metathesis of silicon-containing olefins was done according to a technique that allowed removal of reaction products from contact with the catalyst. The apparatus consisted of a flask connected to a pipe reactor that had a condenser in its upper part. Substrate and solvent were placed in the flask under Ar atomsphere. The activated rhenium/alumina catalyst was placed in the pipe reactor. When the substrate and solvent were boiled, their vapors reached the catalyst. The liquid reaction products were washed away to the still, and the gaseous products were removed through the condenser.

Results and discussion

In complete contrast to α-olefins, the first representative of the alkenylsilane series — trimethylvinylsilane — turned out to be inactive in the metathesis reaction in the presence of several different catalysts (WCl_6–SnR_4, Re_2O_7/Al_2O_3–MR_4). Earlier it was reported that trimethylvinyl- and trimethylallylsilanes give corresponding α,ω-bis (trimethylsilyl)alkenes with yields of 10–13% on Re_2O_7/Al_2O_3 and MoO_3/Al_2O_3 [8, 9]. Our conversions of trimethylvinyl- and dimethyl(vinyl)-alkenylsilanes did not exceed 3–4% in the presence of Re_2O_7/Al_2O_3 promoted by $SnBu_4$ or $PbEt_4$ at 20–45°. The metathesis reaction was basically not observed, even in the case of $n = 3$, *i.e.*, when the formation of thermodynamically stable six-membered ring was possible (Scheme 2).



Scheme 2.

This example clearly indicates that vinyl groups on the silicon atom are inactive in self-metathesis and co-metathesis with the pentenyl group. It also shows that vinyl groups of this type prevent self-metathesis of pentenyl groups where the double bond is shifted from the silicon atom and has almost the same properties as one in common α-olefins.

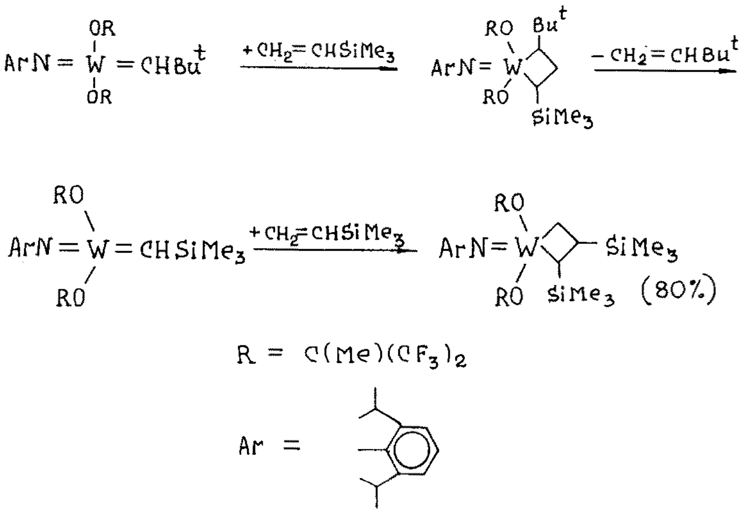
Similar results have been obtained [13] for the reaction of trimethylvinylsilane in the presence of homogeneous W-containing catalysts. It was shown that this silicon-containing olefin did not undergo metathesis, but inhibited the metathesis polymerization of cyclopentene. These phenomena are apparently related to the formation of metal–carbene complexes stabilized by vacant 3d orbitals of the Si atom, which is in the α-position relative to the carbene center (Scheme 3):

$$Me_3SiCH{=}CH_2 \xrightarrow{ML_n} Me_3SiCH{=}ML_n$$

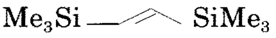
Scheme 3.

These silyl–methylene complexes seem to be unable to participate in chain-propagation reactions or the exchange of alkylidene groups to form new double bonds.

Schrock's investigations [14] also supported the observation that trimethylvinylsilane is inactive in metathesis. Imido alkylidene tungsten complexes were shown to react with trimethylvinylsilane to form stable tungstacyclobutanes and silylmethylene complexes (Scheme 4). No products of catalytic metathesis of trimethylvinylsilane (25°) were found. Both disubstituted metallacycles decompose with the formation of the initial trimethylvinylsilane and neohexene, but not the product of metathesis



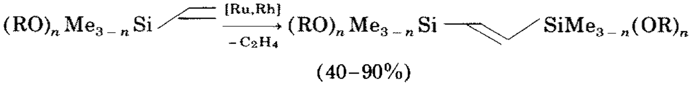
Scheme 4.



or co-metathesis

Schrock attributes this to steric effects.

Remarkable results were obtained by the Polish scientists headed by Marciniec in their study of alkoxyvinylsilane metathesis [15–19]. It was shown that at 80–140°, homogeneous catalysts based on Ru and Rh complexes actively initiate the reaction to form the appropriate 1,2-bis(silylethylene) (Scheme 5):

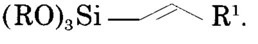


R = Me, Et, n-Pr, i-Pr; $n = 1-3$

Scheme 5.

Ru and Rh chlorides in combination with Lewis acids and hydride donors such as $(RO)_3SiH$, R_3SiH, $LiAlH_4$ and $NaBH_4$ as co-catalysts, were highly active. Traces of oxygen also promoted the process. Rh-based systems were inactive in the case of trialkoxy derivatives, but effectively caused metathesis of methyl(dialkoxy)vinylsilanes.

The results of the study of co-metathesis of triethoxyvinylsilane and olefins turned out to be attractive for synthetic applications. These results offer an effective synthetic approach for producing a number of vinyl derivatives of silicon not available by other methods, *e.g.* [17, 19],

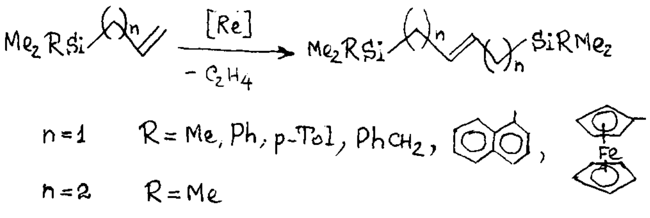


Metathesis of monoallyl- and butenylsilanes and germanes

Metathesis of monoallyl- and butenylsilanes and germanes was studied in the presence of rhenium/alumina systems $Re_2O_7/Al_2O_3-MR_4(M = Sn, Pb, R = Et, Bu^n)$, which are known to be active catalysts for metathesis of olefins and their functional derivatives under mild conditions at ambient temperatures [8–12, 20–22]. This is especially important because the $Si-C_{allyl}$ bond is sensitive to both nucleophilic and electrophilic agents [1, 23]. Examples of these agents include many components of common metathesis catalysts.

We observed that MoO_3/Al_2O_3 and WO_3/Al_2O_3, which are active with α-olefins at 150–200° and 300–350°, respectively, are unable to cause metathesis of allylsilanes because of elimination of allyl groups.

We have shown that at 35–75° rhenium/alumina catalysts initiate selective metathesis and co-metathesis of allyl- and butenylsilanes containing different substituents at the Si atom (Scheme 6) [24–30]. The metathesis of allyltrimethyl-, allyldimethylphenyl-, allyldimethyl-*p*-tolyl- and allyldimethylbenzylsilanes proceeds with high conversions (72–86%) and is not complicated by side reactions. We noted above that $Si-C_{allyl}$, $Si-C_{aryl}$ and $Si-C_{benzyl}$ bonds are known to be more active than the corresponding C–C bonds [1, 23]. Thus, from the preparative viewpoint, it is of great importance that under these conditions ($Re_2O_7/Al_2O_3-SnBu_4$ or $PbEt_4$, 45–75°) the presence of these bonds in the substrate did not lead to catalytic poisoning or side reactions.

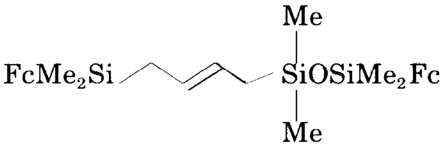


Scheme 6.

With the insertion of the α-naphthyl radical, which causes considerable steric hindrance, the resulting Si–C_{aryl} bond is more labile than in the case of the phenyl substituent, and the conversion decreases to *ca.* 45%.

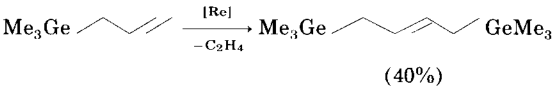
It should be noted that rhenium/alumina catalysts are stable during contact with such non-benzene aromatic systems as ferrocene. In the metathesis of allylferrocenyldimethylsilane, the yield of 1,4-bis(ferrocenyldimethylsilyl)but-2-ene (by measurement of the byproduct ethylene) was 56% (the yield of the compound isolated after recrystallization was 30%). These studies open up a new route for forming various ferrocenyl derivatives that are hard to obtain by other methods.

Nevertheless, mass spectrometry detected siloxane-type products in the reaction mixture, resulting from the rupture of Si–C_{allyl} and Si–C_{Fc} bonds, including $FcMe_2SiOSiMe_2Fc$ and



The total content of these products in the solid residue was 5–6% (^1H NMR data).

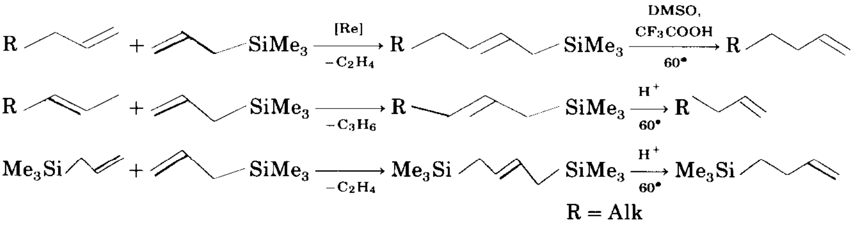
The metathesis of trimethylallylgermane proceeded in accordance with the same scheme (Scheme 7):



Scheme 7.

It was accompanied by the side reactions to a noticeable extent. As a result, the selectivity decreased to 80% (from *ca.* 95% in the case of trimethylallylsilane). In the final mixture, besides the desired 1,4-bis(trimethylgermyl)but-2-ene, oligomers were found, including two compounds that are dimers of the initial allylgermane.

The ability of allylsilanes to take part in metathesis on one end and the rupture of the Si–C_{allyl} bond on the other was used by us to elaborate upon the original two-step method of α-olefin homologization and isomer-

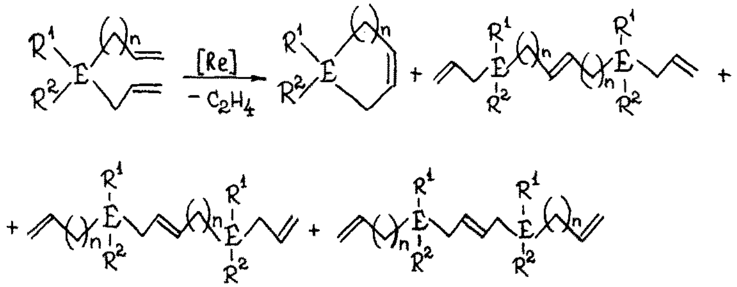


Scheme 8.

ization of the double bond from the β- to the α-position. Co-metathesis of allylsilane with the olefin substrate is the first stage, and the second is desilylation. Thus the metathesis of monoallylsilanes, irrespective of the nature of the alkyl or aryl substituents, proceeds quite effectively, with a high selectivity. It is a convenient preparative method for the synthesis of 1,4-bis(triorganosilyl)but-2-enes.

Metathesis of dialkenylsilanes and germanes

Metathesis of dialkenyl derivatives can proceed along two routes: intramolecular or intermolecular. In the former case, sila- (or germa-) cycloalkenes are formed. Intermolecular metathesis gives linear heterochain trienes. The reactions we observed corresponded to the general pathways shown in Schemes 9 and 10.

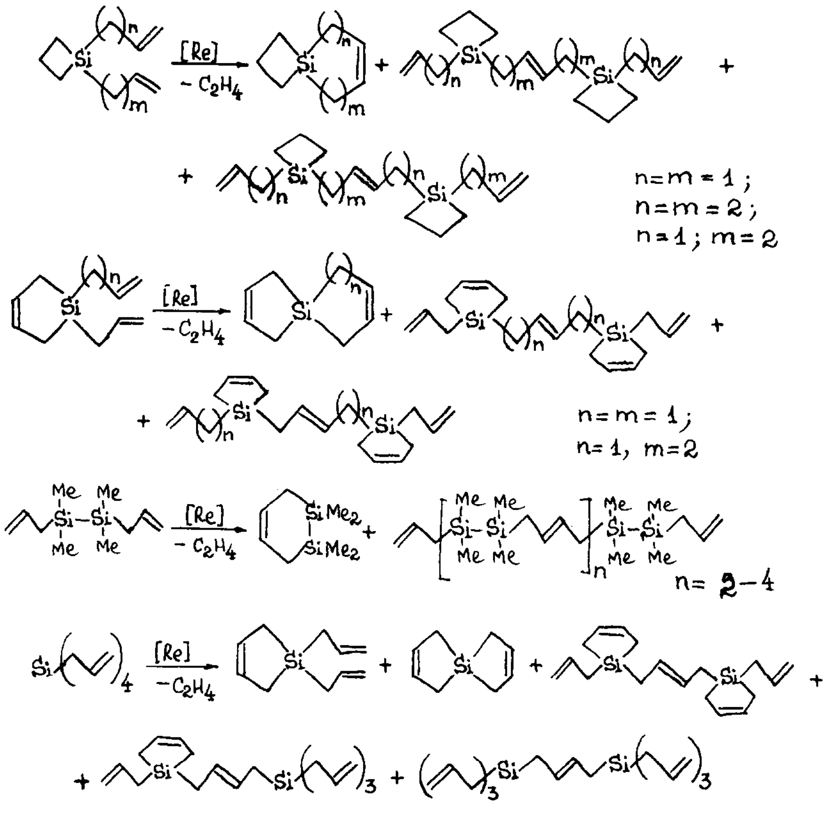


$E = Si$; $n = 1$; $R^1 = R^2 = Me, Et$
$R^1 = Me$, $R^2 = Ph$
$n = 2$; $R^1 = R^2 = Me$
$E = Ge$; $n = 1$; $R^1 = R^2 = Me$

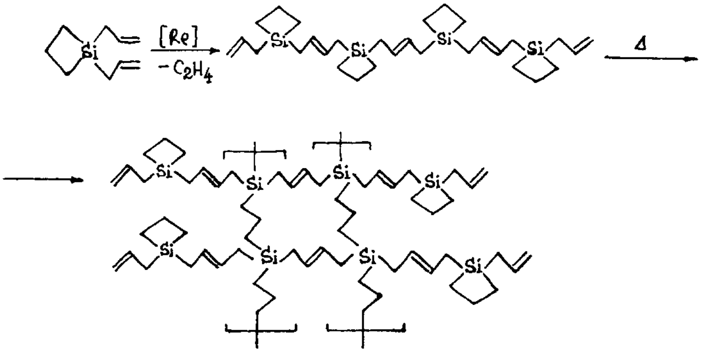
Scheme 9.

It should be noted that in most cases there is close agreement between the total conversion (by GC) and the sum of the yields of isolated end products. Therefore, as in the case of monoallyl derivatives, the main process is metathesis with ethylene formation. Exceptions are the reactions of dialkenylsilacyclobutanes and dialkenylsilacyclopentenes. In the former case, a waxlike condensation product (apparently caused by the participation of endocyclic silicon–carbon bonds of the four-membered silicon–carbon cycle) was isolated from the reaction mixture with a 35% yield (Scheme 11).

In the latter case, the reaction of dialkenylsilacyclopentenes without ethylene formation may be attributed to ring-opening polymerization and dimerization by intermolecular cross-metathesis with the participation of the endocyclic and the terminal double bonds. This should lead to a dimer of the starting diallylsilacyclopentene. This product can easily be



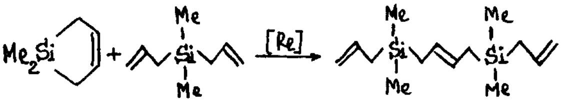
Scheme 10.



Scheme 11.

oligomerized. We succeeded in detecting it in the reaction mixture during metathesis of tetraallylsilane.

In all cases the reaction mixture contains both cyclic and linear (intra- and intermolecular) metathesis products. It might be assumed that a decrease in the concentration of the substrate would suppress the bimolecular process and facilitate the role of the intramolecular reaction. However, a tenfold and greater dilution resulted only in a slight increase in the yields of five- and seven-membered heterocycles (from 5–8 to 10–14%). At the same time, a high degree of dilution is absolutely unnecessary for obtaining high yields of six-membered heterocycles. With substrate/solvent ratios of 1:1 and 1:2 the yields of mono- and disilacyclohexenes reach 60–80%. This may be due to the fact that reactions involving six-membered rings are more energetically favourable than ones with five-membered rings, as well as the well-known fact that six-membered cycloolefins (*e.g.*, cyclohexene), unlike the highly reactive five- and seven-membered rings, are inactive in metathesis and accumulate in the reaction mixture. We cannot exclude the formation of five and seven-membered cycles; note, however, that they may easily undergo a co-metathesis reaction with the initial diallyl compound. In this case, the product formed without ethylene formation is the same as the one formed in the intermolecular self-metathesis of the initial substrate (Scheme 12).



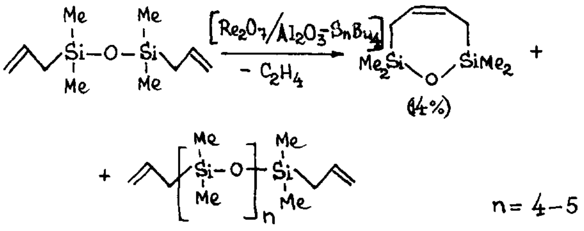
Scheme 12.

As was noted above, vinylalkenylsilanes do not undergo metathesis and co-metathesis. Even the favourability of six-membered cycle formation in intramolecular metathesis via the vinyl and pentenyl groups bonded to the silicon atom is of no help. Diallylmethylhydrosilane caused instantaneous blackening of Re_2O_7/Al_2O_3–$SnBu_4$ catalysts without ethylene formation. This is probably related to the catalyst poisoning resulting from reaction with the Si–H bond.

Vinyl- and allyl-containing siloxanes differ in their behaviour with Re_2O_7/Al_2O_3–$SnBu_4$. Tetramethyldivinyldisiloxane is practically inactive in metathesis. Its total conversion is less than 20%, and the yield of metathesis products is less than 4%. Tetramethyldiallyldisiloxane is completely consumed (total conversion 100%), the yield of the cyclic intramolecular metathesis product is *ca.* 14%, and no linear products of intermolecular metathesis were found in the reaction mixture. The reaction seems to be complicated by the rupture of $Si–C_{allyl}$ and Si–O bonds and the formation of polysiloxanes (Scheme 13).

Conclusion

The study of metathesis and co-metathesis reactions on rhenium on alumina catalysts for a series of unsaturated silicon and germanium



Scheme 13.

organic compounds has established that these reactions are effective and versatile methods for synthesis of linear silicon- and germanium-containing oligomers, heterocycles (including silaspiranes) and α-olefins. It is noteworthy that substrates with highly labile groups such as Si–C_{Fc}, Si–C_{allyl} and Si–Si bonds and silacyclobutane rings can be involved without any change in the fragments.

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