Silyl Triflates – Valuable Synthetic Materials in Organosilicon Chemistry

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The highly reactive silyl triflates $R_{4-n}Si(OSO_2CF_3)_n$ are valuable materials in organosilicon chemistry. Numerous new triflate derivatives of mono-, oligo-, and polysilanes were prepared by stepwise substitution of trifluoromethylsulfonyl groups for phenyl groups or other leaving groups. Conversions of silyl triflates with nucleophiles proceed regioselectively and, in most cases, quantitatively at low temperatures with short reaction times. Therefore, silyl triflates are suitable reagents for the synthesis and functionalization of linear and cyclic oligosilanes. Novel polycarbosilanes, polysilylalkynes, and polysilylphenylenes, which show a regular alternating arrangement of silylene groups and organic units, were prepared from α,ω-bis[(trifluoromethylsulfonyloxy)silyl]-substituted compounds and dinucleophiles. Branched polysilanes and polysilynes were obtained by reductive coupling of polymeric silyl triflates with potassium-graphite.

Introduction

In recent years, much attention has been directed to silicon-containing oligomers and polymers as sources of novel materials. The development of organosilicon oligomer and polymer chemistry[1–5] requires new synthetic methods not only for the generation of specific chains and rings but also for the manipulation of functional groups on the molecules without silicon-silicon bond cleavage. One such useful group for building new systems is the trifluoromethanesulfonate (triflate) group (CF_3SO_3=TfO). In an earlier review[6] Simchen and coworkers demonstrated that trialkylsilyl triflates take an exceptional position with regard to their silylation potentials in organic chemistry. The extremely high reactivity of these compounds and of the less stable iodotrimethylsilane was confirmed by kinetic investigation. The determination of the rate constants of the silylation reactions of ketones with various silylating agents R_3SiX in the presence of triethylamine gave the following sequence of relative rate constants k_{rel} (silylation potential)[7] (Table 1).

Table 1. Silylation potential of various silylating agents R_3SiX

X	k_{rel}	X	k_{rel}
Cl	1	$CF_3CH_2SO_3$	$1.4 \cdot 10^4$
CH_3SO_3	40	Br	$7.9 \cdot 10^4$
$C_6H_5SO_3$	160	CF_3SO_3	$6.7 \cdot 10^8$
Me_3SiOSO_3	270	I	$7.0 \cdot 10^9$

Silylation reactions of organic compounds with silyl triflates proceed rapidly at 0–20°C. Thus, side reactions are

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suppressed and yields are generally high. Triethylamine appears to be the most efficient auxiliary base, because triethylammonium triflate, which is insoluble in nonpolar solvents, separates in liquid form. The progress and end of the rection may, therefore, be observed by the increase in the degree of evolution of the second (salt) phase.

Up to the eighties, only a limited number of silyl triflates R_3SiOTf and $R_2Si(OTf)_2$ had been synthesized, and only those with R=alkyl or aryl reported[6,8–15]. For a broad utilization of these derivatives in organosilicon chemistry it was necessary to elaborate efficient syntheses for monomeric silyl triflates with variable substitution patterns. In a second step these synthetic principles should be transferred to oligomeric and polymeric organosilicon compounds. This procedure allowed the synthesis of numerous new organosilicon oligomers and polymers and the modification of known polymer chains. In this microreview the development of the silyl triflate chemistry from the monomers to the oligomeric and polymeric structures is documented.

Synthesis and Selected Reactions of Monomeric Silyl Triflates

Systematic investigations of the reaction of compounds of the type R_2SiXY (R=alkyl) with triflic acid (Scheme 1) have shown that compounds $R_2SiXOTf$ can be synthesized readily by highly selective cleavages. The ease of replacement of Y by OTf decreases in the order $Y=NEt_2$ > allyl > *p*-anisyl > α-naphthyl > *p*-tolyl > phenyl > Cl > ethynyl > H ≫ alkyl[16–21]. In no case were competitive cleavages of Si–X or Si–R observed. This reaction has the double advantages of avoiding expensive reagents, such as silver triflate[22], and of using readily available starting materials.

Scheme 1

$$R_2SiXY + TfOH \rightarrow R_2SiX(OTf) + HY$$

$$R_2SiX(NEt_2) + 2\ TfOH \rightarrow R_2SiX(OTf) + Et_2NH_2OTf$$

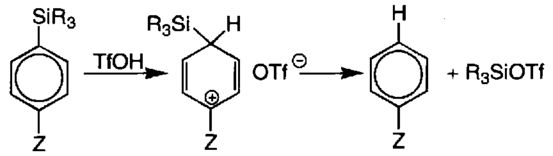
X,Y = NEt_2, allyl, *p*-anisyl, α-naphthyl, *p*-tolyl, phenyl, Cl,

ethynyl, H, alkyl

Phenylsilanes, which are highly reactive towards the protodesilylation reaction (Scheme 2), are ideal starting materials for the synthesis of novel silyl triflates. Eaborn and coworkers[23] studied the effects of the substituents Z and R on the rate of acid cleavage of $p\text{-}Z\text{-}C_6H_4SiR_3$ and obtained the following results[24,25]:

- The relative reactivities of the compounds with different substituents Z indicates that electron release from Z facilitates the reaction. The reaction rates fall in the order (Z =) OCH_3 > H > Cl.
- The presence of phenyl groups at the silicon atom leads to a strong decrease of the reaction rate. The reaction rates fall in the order (R_3 =) Me_3 > Me_2Ph > $MePh_2$ > Ph_3. The electron-withdrawing halogen substituents (R=Cl, Br) also extend the reaction times.

Scheme 2



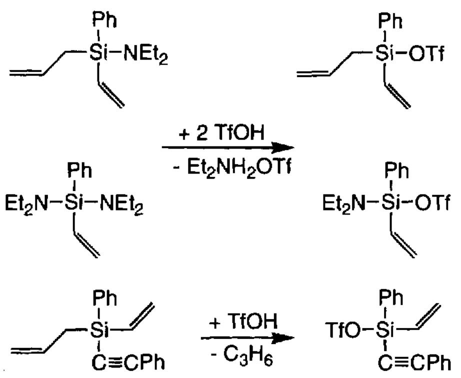
The second observation implies that a triflate group causes a strong deactivation of the other substituents on the silicon atom, and the displacement of a second phenyl group on the same silicon atom is much slower than that of the first. Therefore, bis- and tris(triflate)-substituted silanes can be obtained by the stepwise reaction of di- and triphenylsilanes with two and three equivalents of triflic acid. Schemes 3 and 4 illustrate the broad synthetic potential of the cleavage of silicon-element bonds by triflic acid on selected examples[16,18–20,26]. It should be emphasized that reactions in the molar ratio 1:1 proceed quantitatively within a few minutes. The stepwise cleavage of two phenyl groups on the silicon atom requires 30–60 minutes, and the cleavage of three phenyl groups 2–4 hours. Progress and end of the reactions may be followed by ^{29}Si-NMR spectroscopy. The silyl triflates can be used for following reaction without further purification.

Scheme 3

$H_2MeSiPh$		$H_2MeSi(OTf)$
		$HMeSi(OTf)_2$
$HMeSiPh_2$		$HMeSiPh(OTf)$
		$HMeSi(OTf)_2$
		$MeSi(OTf)_3$
$HClSiPh_2$	$\xrightarrow[-\,n\,C_6H_6\ \ -\,m\,H_2]{(n+m)\ TfOH}$	$HClSiPh(OTf)$
		$HClSi(OTf)_2$
H_3SiPh		$H_3Si(OTf)$
Cl_3SiPh		$Cl_3Si(OTf)$
$t\text{-}Bu_3SiH$		$t\text{-}Bu_3SiOTf$

All functionally substituted silyl triflates as well as silyl bis(triflates) and silyl tris(triflates) show excellent silylation properties because of their high electrophilicity. They react with many organic nucleophiles as described for trialkylsilyl triflates[6]. Only one example, which demonstrates the high reactivity of the compounds at low temperatures, is worthy of mention here: Dimethylsilylbis(triflate) reacts with two equivalents of diazomethane[27] (at −60°C) or diazoacetic ester[28] to give the silylated derivatives in high yields (Scheme 5). Silyl triflates also react rapidly and completely with active hydrogen compounds of group-14 to group-17 elements or with the corresponding lithium derivatives. Exchange processes analogous to metal/halogen exchange are

Scheme 4



not observed. This unambiguous reaction pathway prompted us to elaborate an interesting method for the formation of silicon-phosphorus bonds: Thus, we synthesized $P(SiMe_3)_3$ and other silyl-phosphanes in high yields[29,30], Becker reported on the synthesis of H_3SiPH_2[31], and Wiberg successfully prepared t-Bu_3SiPH_2[26] (Scheme 5).

Scheme 5

$$Me_2Si(OTf)_2 + 2\,CHR^1N_2 \xrightarrow[-\,2\,R_3NHOTf]{+\,2\,R_3N} Me_2Si(CR^1N_2)_2$$

R^1 = H, COOEt

$$3\,Me_3Si(OTf) + PH_3 \xrightarrow[-\,3\,Et_3NHOTf]{+\,3\,Et_3N} P(SiMe_3)_3\ \ (95\%)$$

$$4\,H_3Si(OTf) \xrightarrow[-\,Na[Al(OTf)_4]]{+\,Na[Al(PH_2)_4]} 4\,H_3SiPH_2$$

$$t\text{-}Bu_3Si(OTf) \xrightarrow[-\,LiOTf]{+\,LiPH_2} t\text{-}Bu_3SiPH_2$$

The commercially available t-$Bu_2Si(OTf)_2$ is particularly important for the synthesis of sterically hindered silanes. Firstly, this compound was used as a protecting group for 1,2- and 1,3-diols[15]. Furthermore, we obtained *tert*-butyl-substituted silylphosphanes at low temperatures in quantitative yields[32] and showed that the conversion of t-$Bu_2Si(OTf)_2$ with nucleophiles in the stoichiometric ratio 1:1 leads to novel functionally substituted silyl triflates[33] (Scheme 6).

Scheme 6

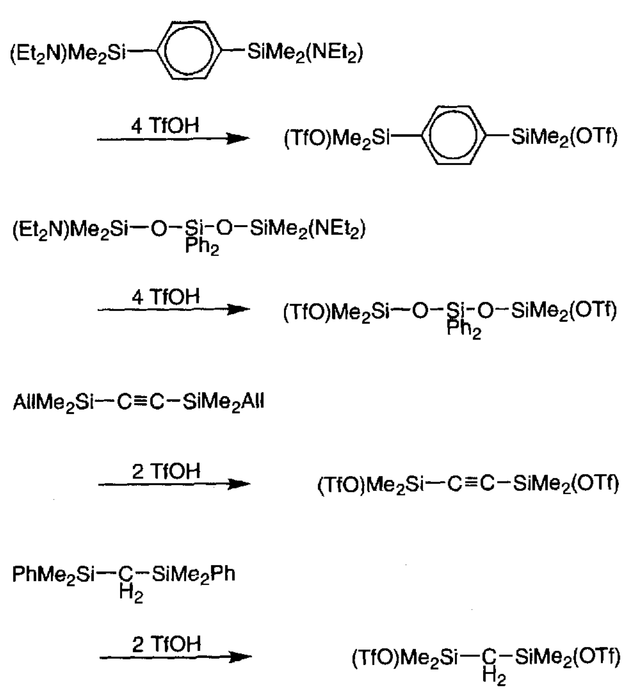
$$t\text{-}Bu_2Si(OTf)_2 + 2\,LiPHPh \xrightarrow[-\,2\,LiOTf]{-78^\circ C} t\text{-}Bu_2Si(PHPh)_2\ \ (98\%)$$

$$t\text{-}Bu_2Si(OTf)_2 + LiX \xrightarrow[-\,LiOTf]{-78^\circ C} t\text{-}Bu_2Si(OTf)X$$

X = PPh_2, PHPh, C≡CPh, $SiPh_2Me$, $GePh_3$, $SnPh_3$, NMe_2

A large number of different α,ω-bis[(trifluoromethylsulfonyloxy)silyl]-substituted compounds can be obtained from the corresponding amino-, allyl-, or phenylsilanes by relatively simple methods[21,34–37]. Moreover, it is remarkable that these triflate derivatives are often easily formed, when the synthesis of the corresponding chloro- or bromosilanes is difficult or does not appear to have been attempted. Scheme 7 shows selected examples of these reactions. The resulting products are useful synthetic materials for polycondensations with dinucleophiles leading to new organosilicon polymers.

Scheme 7

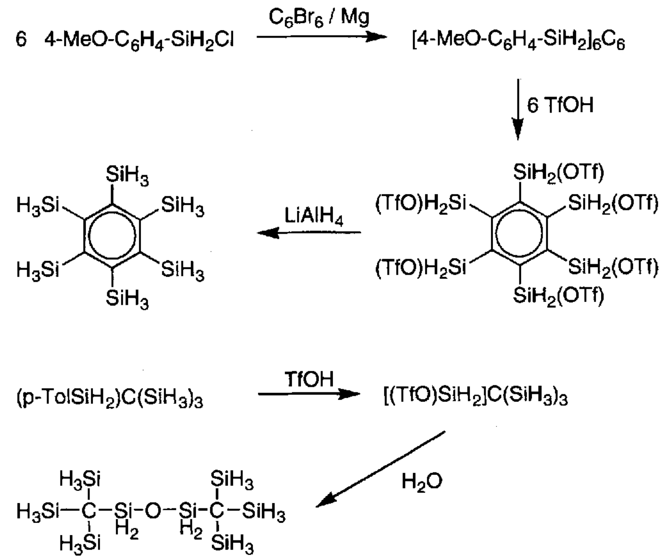


The selective cleavage of silicon-carbon bonds by triflic acid also plays an important role in the synthesis of polysilylated hydrocarbons which can be interesting starting materials for the preparation of organosilicon polymers by thermal or catalytic dehydrogenative coupling reactions. Schmidbaur obtained polysilylmethanes[38,39] and polysilylarenes[40–42] by using p-tolyl and p-anisyl substituents as leaving groups (Scheme 8). The silyl triflates were reduced with $LiAlH_4$ to SiH_3 derivatives. Solvolysis with water gave the corresponding siloxanes.

Synthesis and Reactivity of Triflate-Substituted Oligosilanes

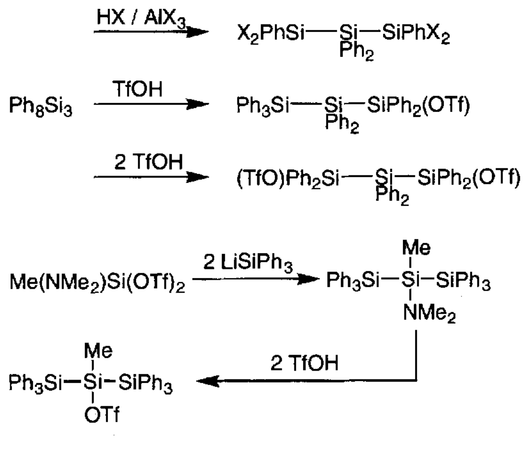
Two methods were developed to introduce functional groups into organic oligosilanes $R_{2n+2}Si_n$ both of which rely on electrophilic cleavage of phenyl groups from the silicon atom. The use of $HX/AlCl_3$ does not appear to discriminate between the different positions of the phenyl group[43]. More recently, triflic acid was used to remove phenyl groups, and it was shown that the reaction of phenylated oligosilanes with one or two equivalents of TfOH leads to a stepwise protodesilylation on the terminal silicon atoms[18,44–51]. It appears that replacement of one phenyl

Scheme 8



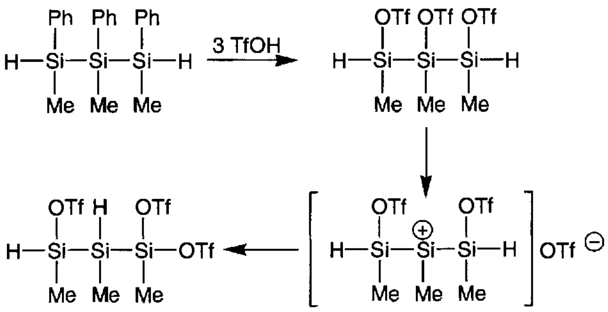
substituent at a silicon center by a triflate group deactivates that center towards additional substitution. Both methods of electrophilic cleavage are compared by using Ph_8Si_3 as example. Moreover, a selective cleavage at the centrally located silicon atom was observed only if this atom possesses a more efficient leaving group, for instance an amino substituent (Scheme 9). A similar deactivation was demonstrated by the rates of removal of one or two phenyl groups in $PhMe_2Si(SiMe_2)_nSiMe_2Ph$ ($n=0-3$)[52,53]. The cleavage of both internal and terminal Si–Ph groups by TfOH was only found by Corey in the case of the trisilane $H(MePhSi)_3H$, but the major product is the terminally substituted trisilane. A rearrangement by migration of a triflate group was observed during the reaction of $H(MePhSi)_3H$ with two or three equivalents of TfOH[54]. A cationic intermediate was proposed for the process (Scheme 10).

Scheme 9



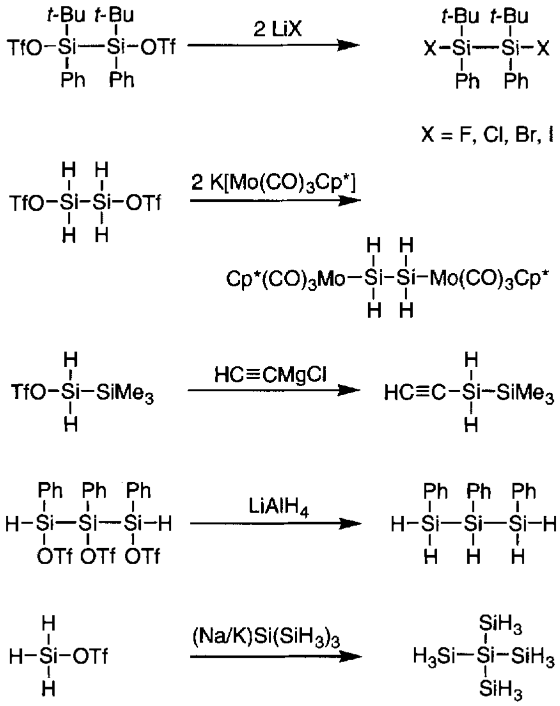
Triflate-substituted oligosilanes are important starting materials for the preparation of numerous other oligosilane derivatives. Conversions with lithium halides[48,55,56], $LiAlH_4$[46,47] and $K[Mo(CO)_3Cp^*]$[49] were described mainly by Hengge, Hassler and coworkers. Furthermore,

Scheme 10



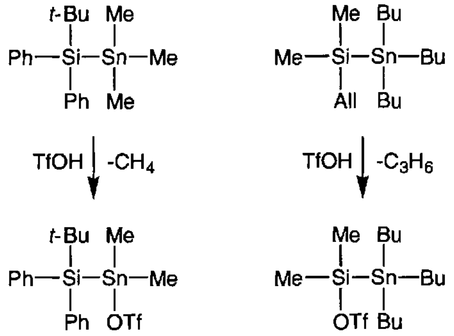
Maier reported on reactions with vinyl- and ethynylmagnesium chloride[57,58] and Sundermeyer found an interesting trapping reaction of $(Na/K)Si(SiH_3)_3$ with H_3SiOTf[59]. Scheme 11 shows some typical examples of nucleophilic substitutions.

Scheme 11



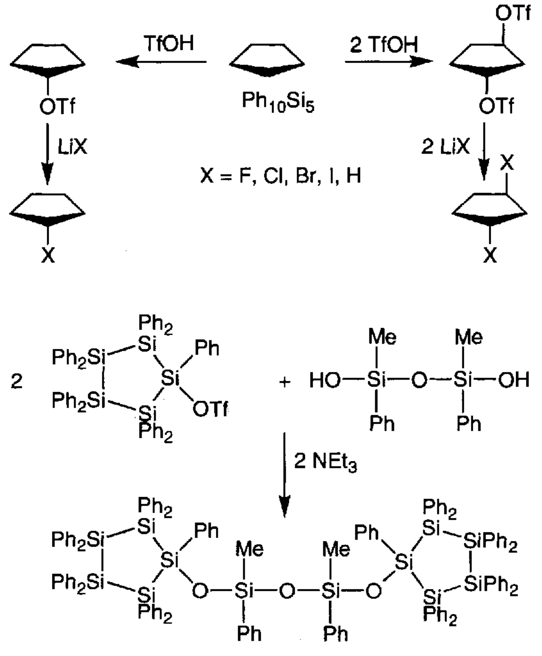
The reactions of stannyl- and germylsilanes with triflic acid were also studied. Normally, the relative ease of cleavage of the element-carbon bonds increases in the sequence (E =) Si < Ge ≪ Sn and reflects the strength of these bonds even though these remain intact in the rate-determining step[60]. These results are in agreement with the investigations of Eaborn[23], who studied the cleavage of element-carbon bonds by perchloric acid. Moreover, the cleavage of the Si–C bond in stannylsilanes is possible by using an allyl substituent as leaving group[61]. We found similar results for germylsilanes[62].

Scheme 12

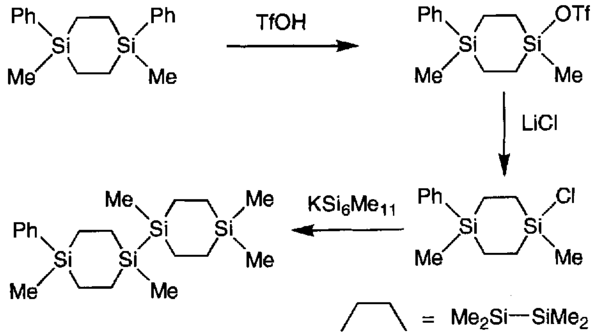


The dearylation of perphenylated cyclosilanes was intensively studied in the last few years. The reaction with HX/AlX_3 allows only the preparation of $(SiX_2)_m$ (m = 4–6, X=Cl, Br, I); otherwise the reaction products are mixtures of partially halogenated products. In contrast, dearylation reactions with triflic acid proceed more selectively. Matyjaszewski prepared $Ph_3Me_4Si_4(OTf)$[63] and $Ph_{8-n}Si_4(OTf)_n$ (n = 2–4)[64], while Hassler obtained $Ph_4(p\text{-Tol})_3Si_4(OTf)$ and numerous related products[65]. We reported on the selective mono- and 1,3-difunctionalization of $Ph_{10}Si_5$[17,18,66]. $Ph_9Si_5(OTf)$ reacts with silanols to furnish siloxanes containing cyclopentasilane rings[67]. The conversion of $Ph_8Si_5(OTf)_2$ with LiF leads to the *trans*-1,3-isomer in yields up to 70%. The structure of this compound was proved by X-ray crystal structure analysis[68] (Scheme 13). Triflate-substituted cyclohexasilanes were described by Hengge[69,70] and our group[71]. Scheme 14 shows the use of these derivatives for the coupling of cyclosilanes.

Scheme 13



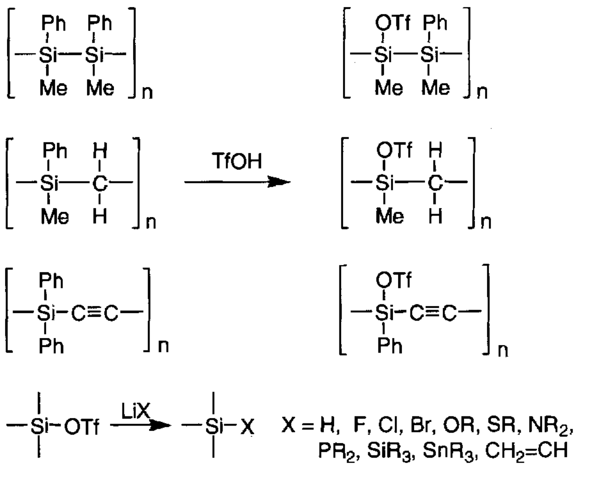
Scheme 14



Silyl Triflates in Polymer Chemistry

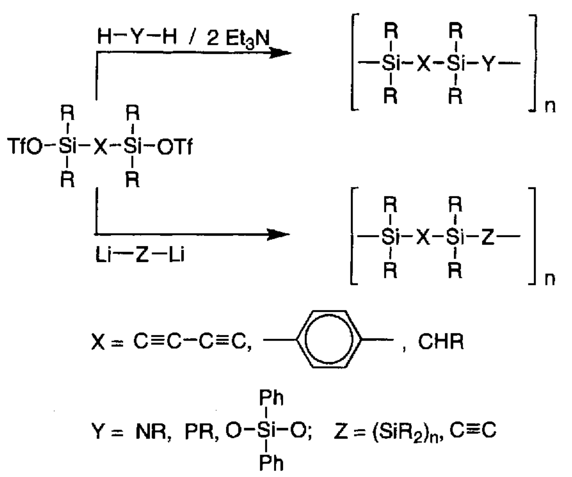
In recent years, much attention has been directed to silicon-containing polymers as sources of novel materials. Polysilanes, polysilynes and numerous polymers with alternating arrangements of organosilicon groups and π-electron-containing units were prepared[1–3,5]. In principle, two synthetic routes to new organosilicon polymers based on triflate derivatives are possible. Firstly, derivatizations can be carried out on finished polymers. Recent papers by several authors have shown the feasibility of this route in the case of polysilanes[72,73], polysilynes[74–76], polycarbosilanes[77–79], and polysilylenealkynes[21,80]. Up to 50% of the silicon atoms in polysilanes could be dearylated without cleavage of the polymer backbone. The method is illustrated in Scheme 15. Conversions of the triflate-substituted polymers with nucleophiles lead to numerous new derivatives.

Scheme 15



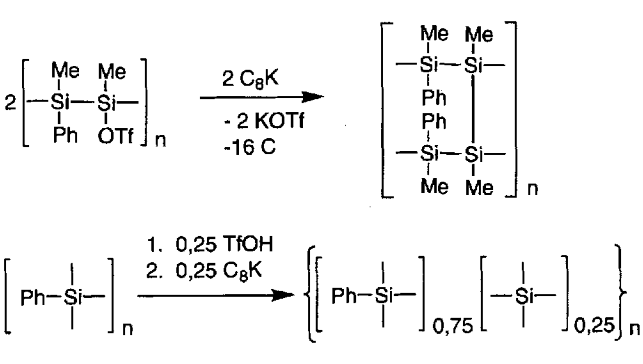
The second route consists of the formation of polymer chains by condensations of α,ω-bis(trifluoromethylsulfonyloxy)-substituted organosilicon compounds with dinucleophiles[34–36,81,82]. This synthesis is characterized by excellent yields. Therefore, the polymers prepared by this method did not contain siloxy units after hydrolysis of the reaction mixture. Exchange processes, analogous to metal/halogen exchange, were not observed. Consequently, a regular alternating arrangement of organosilicon and organic units was found in the polymers (Scheme 16).

Scheme 16



Intense research was focused on the elaboration of SiC- or Si/C/N-based materials from organosilicon precursors[3]. An idealized preceramic polymer should contain cages or rings to decrease the elimination of volatile fragments resulting from backbone cleavage. We obtained branched polysilanes[76] and polysilynes[83] by reductive coupling of the corresponding triflate-substituted polymers with potassium-graphite (C_8K) (Scheme 17). Molecular masses and polydispersities increase significantly as a consequence of this reaction. Silyl triflates are reduced quantitatively at low temperatures in short reaction times. In contrast, silyl triflates react only incompletely with alkali metals. We also used the reductive coupling with C_8K to prepare linear polymers from different α,ω-bis(trifluoromethylsulfonyloxy)-substituted organosilicon compounds[84].

Scheme 17



Conclusions

Numerous novel monomeric, oligomeric, and polymeric silyl triflates could be synthesized by protodesilylation reactions. Silylating reactions with these agents are characterized by high yields at low temperatures and short reaction times. Exchange processes analogous to metal/halogen exchange were not observed. Therefore, silyl triflates are suitable materials for the synthesis of new functionally substituted organosilanes and to construct new oligomeric and polymeric silicon networks. Obviously, the synthetic methods described here may appear to be too expensive for technical applications at the moment. However, the essential advantage of the silyl triflate chemistry consists of the possibility of preparing with relatively little efforts small amounts of numerous differently structured organosilicon oligo- and polymers for investigations in the field of materials and surface science.

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