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Synthesis and reactions of silanes containing two triflate groups *

K. Matyjaszewski* **and Y.L. Chen**

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213 (U.S.A.)

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Abstract

1,2-Bis(trifluoromethanesulfonyloxy)tetramethyldisilane (**1**) and dimethylsilylbis-(trifluoromethanesulfonate) (**2**) have been prepared via displacement of phenyl, chloro, and methyl groups in the corresponding mono- and di-silanes. Phenyl groups are displaced more rapidly than chloro and methyl groups. The unreacted groups are strongly deactivated by the presence of a triflate group at the same silicon atom. The deactivation is much weaker when a triflate group is present at the adjacent silicon atom. Alcohols and amines react more rapidly with ditriflates than with monotriflates.

Introduction

We report the preparation and some chemical reactions of a new compound, a disilane containing two triflate groups, 1,2-bis(trifluoromethanesulfonyloxy)tetramethyldisilane (**1**) and a simple synthesis of dimethylsilyl-bis(trifluoromethanesulfonate) (**2**).

We are interested in the preparation of new high molecular weight polysilanes [1]. The severe reaction conditions of a typical reductive coupling of dichlorosilanes with sodium allow only alkyl and aryl substituents at the silicon atom [2]. The studies reported below describe our model reactions with mono- and di-silanes which lead to the incorporation of reactive trifluoromethanesulfonate (triflate) groups. These groups could be quantitatively replaced by any nucleophilic reagents providing new polysilanes.

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Results and discussion

1. Relative rates of displacement of chloro and phenyl groups

Trimethylsilyl triflate is the most versatile silylating reagent [3] and is a few orders of magnitude more reactive than the classical silylating reagent, trimethylsilyl chloride [4]. Trimethylsilyl triflate was initially prepared from silver triflate and trimethylchlorosilane [5]. Later, trifluoromethanesulfonic acid was used for the preparation of triflated silanes and found to react readily with chloro [6,7], aryl [8], and alkyl [9] groups.

Rapid and quantitative formation of trimethylsilyl triflate from trimethylchlorosilane and trimethylphenylsilane indicates higher reactivity of chloro and phenyl than methyl groups towards triflic acid. The relative rates of displacement of phenyl and chloro substituents were not known.

We have studied by ^{1}H NMR the reaction of a mixture of chloro- and phenyl-trimethylsilane (10/1 molar ratio) with 1 equivalent of triflic acid in CH_2Cl_2 solvent at 20 °C. After 1 min the complete disappearance of the trimethylphenylsilane signal (0.299 ppm) and the formation of trimethylsilyl triflate (0.526 ppm) was found. The signal of the chloride (0.467 ppm) remained unchanged. Taking into account the accuracy of integration (not more than 5% of chloride could react) and molar ratio, we can estimate that the reactivity of the phenyl group in comparison with the chloro derivative is at least 200 times higher. Phenyl groups are usually displaced by protonic acids via benzenonium cation intermediates [10].

The prediction of the pathway of the reaction between triflic acid and dimethylphenylchlorosilane is more difficult because displacement of a phenyl group would lead to a silane with two electron-withdrawing groups (dichlorosilanes are more reactive and less stable than monochlorosilanes). In the ^{1}H NMR spectrum of the reaction mixture of dimethylphenylchlorosilane with one equivalent of triflic acid, the sharp singlet of benzene (7.4 ppm; A_2B_2C pattern in the initial silane) and a new singlet of methyl groups in dimethylchlorosilyl triflate at 0.861 ppm was found. No signal of the dimethylphenylsilyl triflate (0.823 ppm) was observed. This result indicates that the phenyl group is displaced much more rapidly than the chlorine atom:

$$PhSiMe_2Cl + HOSO_2CF_3 \rightarrow CF_3SO_2OSiMe_2Cl + C_6H_6 \qquad (1)$$

Formation of the dimethylchlorosilyl triflate is probably kinetically controlled. Similar results were found in the reaction of triflic acid with methylphenyldichlorosilane. In that case, the phenyl group was again preferentially displaced in spite of the presence of two chloro atoms and methyldichlorosilyl triflate (1.176 ppm) was formed.

2. Preparation of dimethylsilylbis(trifluoromethanesulfonate) (2)

Reaction of diphenyldimethylsilane (0.609 ppm) with 1 equivalent of triflic acid yielded phenyldimethylsilyl triflate (0.823 ppm) immediately. Addition of the second equivalent of the acid led to the formation of **2**. The displacement of the second phenyl group was much slower and the reaction was completed after 1 h at room temperature ($[HOSO_2CF_3]_0$ 0.40 mol/l). After 2 min nearly equal proportions of mono- and di-triflate were observed.

Dimethyldichlorosilane reacted with triflic acid much more slowly than diphenyldimethylsilane. Under similar conditions the reaction of the second equivalent of the acid with dimethylchlorosilyl triflate was completed after 24 h. Displacement of the methyl group in trimethylsilyl triflate was not observed after a few days at room temperature. However, at higher temperatures dimethylsilylbis(fluorosulfonate) was found in a similar reaction [11].

3. Synthesis of 1,2-bis(trifluoromethanesulfonyloxy)tetramethyldisilane (1)

Reaction of 1 equivalent of triflic acid with 1,2-diphenyltetramethyldisilane led to a mixture of the unreacted disilane, **1**, and monotriflate. This result indicates that the second phenyl group in the disilane is deactivated less by the triflate group than the second group in the monosilane. In Fig. 1 the dependence of the composition of the reaction mixture on the ratio of the acid to the initial disilane is shown. The experimental points fit very well with the theoretically calculated curves for $k_1/k_2 = 8$:

$$CF_3SO_2OH + PhSiMe_2SiMe_2Ph \xrightarrow{k_1} CF_3SO_2OSiMe_2SiMe_2Ph + PhH \qquad (2)$$

$$CF_3SO_2OH + CF_3SO_2OSiMe_2SiMe_2Ph \xrightarrow{k_2} CF_3SO_2OSiMe_2SiMe_2OSO_2CF_3 + PhH$$

For the monosilane the reaction proceeds as a two-step process, allowing the separation of the monotriflate after addition of 1 equivalent of the acid. Under similar conditions 13% of the unreacted disilane and 13% of the ditriflate are present in the reaction with the disilane. Thus, taking into account the statistical factor (two phenyl groups in the diphenyldisilane) the presence of the triflate group at the neighboring silicon atom weakly deactivates the adjacent phenyl group (4 times).

Deactivation is stronger in the reaction with hexamethyldisilane and 1,2-dichlorotetramethyldisilane. In both systems reaction with one equivalent of the acid leads to the monotriflate while the second triflate group is incorporated only at higher

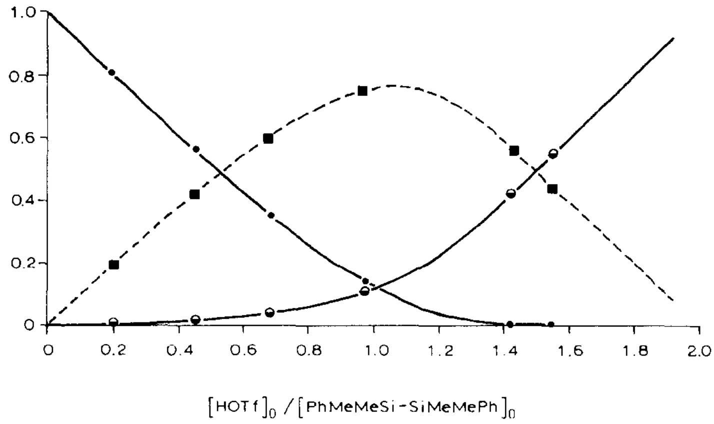

Fig. 1. Calculated (curves) and experimental proportions of 1,2-diphenyltetramethyldisilane (●), monotriflate (■) and ditriflate (⊖) at different $[acid]_0/[disilane]_0$ ratios. Calculations were performed assuming $k_1/k_2 = 8$.

temperature. Pentamethyldisilyl triflate has been recently described in the literature [12]. The first methyl group was displaced rapidly at 0 °C. We found that the second group is removed only at 60 °C.

1 was separated by vacuum distillation (b.p. 92 °C/10 Torr). The preparative yield was above 70% in the reaction with all discussed disilanes.

4. Reactions of ditriflates

Silyl triflates are powerful silylating reagents. We have studied the reactions of ditriflates with different nucleophilic reagents such as alcohols and amines. Ditriflates react rapidly with methyl, ethyl, isopropyl, t-butyl, allyl, and 2,2,2-trifluoroethyl alcohols:

$$\mathrm{CF_3SO_2OSiMe_2SiMe_2OSO_2CF_3 + 2\ ROH + 2B: \rightarrow}$$
$$\mathrm{ROSiMe_2SiMe_2OR + 2BH^+\ OSO_2CF_3^-} \qquad (3)$$

$$\mathrm{(R = CH_3,\ C_2H_5,\ (CH_3)_3C,\ CH_2{=}CHCH_2,\ CF_3CH_2)}$$

The reactivity of ditriflates is higher than that of monotriflates. Thus, when the mixture of trimethylsilyl triflate and **2** (3/1) reacted with 1 equivalent of methanol in the presence of triethylamine only dimethylmethoxysilyl triflate (0.514 ppm) was formed. **1** has also been found to be more reactive than disilylmonotriflate.

Reactions of ditriflates with alcohols are catalyzed by amines which act as proton traps. Best results were obtained with the hindered pyridines 2,6-di-t-butylpyridine and 2,6-di-t-butyl-4-methylpyridine. Owing to steric hindrance they do not react with the silyl group directly. The unsubstituted pyridine reacted with triflates forming *N*-silylated pyridinium salts which were insoluble in methylene chloride and chloroform. This resembles the behavior of a monotriflate [13]. The pyridinium salts of **1** were soluble in nitromethane. The ^{1}H NMR spectra of the mixture of pyridine and ditriflate (1/1 molar ratio) showed a broad singlet of all methyl groups in ditriflate at 0.3 ppm and signals of pyridine shifted downfield by approximately 0.2 ppm. This indicates a rapid exchange of the pyridine between all silyl triflate groups. The signal of methyl groups shifted downfield with an increasing concentration of pyridine and at a ratio larger than 2/1, a narrow singlet at 0.21 ppm was found. At still higher concentration of pyridine, the aromatic signals move upfield which might indicate a rapid exchange between free and complexed pyridine.

The addition of two equivalents of diethylamine to ditriflate (1/1 molar ratio) yields an equimolar mixture of protonated amine and 1-diethylamino-2-trifluoromethanesulfonyloxytetramethyldisilane:

$$\mathrm{CF_3SO_2OSiMe_2SiMe_2OSO_2CF_3 + 2HNEt_2 \rightarrow}$$
$$\mathrm{Et_2NSiMe_2SiMe_2OSO_2CF_3 + Et_2NH_2^+\ CF_3SO_3^-} \qquad (4)$$

The excess of diethylamine leads to 1,2-diaminodisilane:

$$\mathrm{CF_3SO_2OSiMe_2SiMe_2OSO_2CF_3 + 4HNEt_2 \rightarrow}$$
$$\mathrm{Et_2NSiMe_2SiMe_2NEt_2 + 2\ Et_2NH_2^+\ CF_3SO_3}$$

Methyl groups bound to the silicon atoms in the diamine absorb at a higher field (0.154 ppm) than in the monotriflate (0.322 and 0.587 ppm). The excess diethylamine exchanges with the protonated amine. Secondary amines are more basic than pyridines since no protonated pyridine is observed in equimolar mixtures of **2**, diethylamine, and hindered pyridine.

Experimental

All reactions were carried out in an argon atmosphere in flame-dried glassware. All the reagents were freshly distilled and dried over CaH_2 in an argon atmosphere. ^1H NMR spectra were recorded using 300 MHz GE and 80 MHz IBM instruments in $CDCl_3$, CD_3NO_2 and CD_2Cl_2 solutions using the signal of CH_2Cl_2 (5.32 ppm) as the reference. Elemental analysis were performed by MicAnal (Tuscon, Arizona).

Synthesis of 1

A. From 1,2-dichlorotetramethyldisilane and triflic acid. Trifluoromethanesulfonic acid (5.09 g, 34 mmol) was added dropwise to 1,2-dichlorotetramethyldisilane (3.16 g, 17 mmol) at room temperature. The reaction mixture was heated to 60 °C for 12 h. After that time no further HCl was evolved. The product was distilled directly from the reaction mixture to afford 5.65 g (80% yield) of **1**, b.p. 92 °C/10 Torr. ^1H NMR: singlet at 0.771 ppm, ^{13}C NMR: -0.5, and 119.2 ppm. Anal. Found: C, 17.01; H, 2.98; S, 15.16. $C_6H_{12}F_6O_6S_2Si_2$ calcd.: C, 17.39; H, 2.92; S, 15.47%.

B. From 1,2-diphenyltetramethyldisilane and triflic acid. Trifluoromethanesulfonic acid (3.39 g, 23 mmol) was added dropwise at -23 °C to 1,2-diphenyltetramethyldisilane (3.06 g, 11.5 mmol) dissolved in 15 ml of CCl_4. After the addition was completed the reaction mixture was stirred for 2 h at room temperature and distilled using a Vigreaux column to yield 72% (3.37 g) of **1**.

C. From hexamethyldisilane and triflic acid. The reaction was performed in the way analogous to *A* yielding 81% of **1**.

Reactions of 1 with different nucleophiles

A. Allyl alcohol. To a mixture of 0.95 g (16 mmol) of allyl alcohol and 1.65 g (16 mmol) of triethylamine in 10 ml of CH_2Cl_2 3.37 g (8 mmol) of **1** was added at 0 °C. The mixture was stirred for 1 h at 0 °C and for an additional 12 h at room temperature. After aqueous work-up and drying, the residue was distilled (b.p. 58 °C/4 Torr to yield 1,2-diallyloxytetramethyldisilane [14] in 46% yield. ^1H NMR: 0.2 (s, 6H), 4.1 (d, 2H), 5.1 to 5.3 (m, 2H), and 5.9 to 6.0 ppm (m, 1H)

B. Methanol. This reaction was performed in the identical way as described above. The preparative yield of 1,2-dimethoxytetramethyldisilane [15] was only 34%. However, the NMR spectra of the reaction mixture using triethylamine or 2,6-di-t-butylpyridine show only the presence of 1,2-dialkoxytetramethyldisilane. ^1H NMR: 0.25 (s,12H) and 3.40 ppm (s, 6H) (b.p. 87 °C/100 Torr).

C. Diethylamine. This reaction was carried out in an NMR tube in the presence of 2,6-di-t-butylpyridine. The chemical shift of **1** (0.76 ppm) did not change after addition of two equivalents of the pyridine. Two new signals at 0.59 and 0.32 ppm (1/1 ratio) ascribed to the monotriflated amine were found after addition of the first equivalent of the diethylamine. After addition of the second equivalent of the diethylamine, half of **1** was converted to the monoamine (no diamine was found). Two triplets at 1.05 and 1.39 and two quartets at 2.85 and 3.05 ppm were assigned to methyl and methylene groups in the monoamine and the protonated diethylamine. After addition of four equivalents of diethylamine, 1,2-bis(diethylamino)tetramethyldisilane 0.15 (s), 1.00(t), and 2.80(q) ppm was found. Triflic acid was exclusively complexed by the diethylamine (3.05 and 1.39 ppm). The hindered pyridine was not protonated under these reaction conditions.

D. Pyridine. Addition of one equivalent of the unsubstituted pyridine to **1** in $CDCl_3$ led to the precipitation of the complex with pyridine. In CD_3NO_2 the complex is soluble and the broad singlet at 0.27 ppm indicates the rapid exchange of pyridine with **1**. This signal shifts upfield to 0.21 ppm after addition of a second equivalent of pyridine. Pyridine absorbs at approximately 0.2 ppm downfield indicating complexation.

Synthesis of **2**

A. From dichlorodimethylsilane and triflic acid. Trifluoromethanesulfonic acid (5.09 g, 34 mmol) was added dropwise to dichlorodimethylsilane (2.101 g, 17 mmol) at room temperature. The resulting mixture was heated to 60 °C for 12 h until no further hydrogen chloride was evolved. The product was distilled at 66–68 °C (10 Torr) to afford 5.11 g (85%) of **2**. ^{1}H NMR: 0.91 (s) ppm.

B. From diphenyldimethylsilane and triflic acid. Trifluoromethanesulfonic acid (0.070 g, 0.47 mmol) was added dropwise to diphenyldimethylsilane (0.050 g, 0. 235 mmol) dissolved in 1 ml of $CDCl_3$. ^{1}H NMR showed quantitative formation of **2** (0.91 ppm) and complete disappearance of diphenyldimethylsilane (0.61 ppm).

Acknowledgments

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References

1 K. Matyjaszewski, Y.L. Chen, and H.K. Kim, ACS Symposium Series, in press, F. Yenca, Y.L. Chen, and K. Matyjaszewski, ACS Polymer Preprints 28(2) (1987) 222.

2 R. West, J. Organomet. Chem., 300 (1986) 327.

3 H. Emde, D. Domsch, H. Feger, U. Frick, A. Gotz, H.H. Hergott, K. Hofmann, W. Kober, K. Krageloh, T. Oesterle, W. Steppan, W. West, and G. Simchen, Synthesis (1982) 1.

4 H.H. Hergott and G. Simchen, Justus Liebigs Ann. Chem., (1980) 1781.

5 M. Schmeiser, P. Sartori and B. Lippsmeier, Chem. Ber., 103 (1970) 868.

6 H.C. Marsmann and H.G. Horn, Z. Naturforsch., 27 (1972) 1448.

7 E.J. Corey, H. Cho, C. Rucker, D.H. Hua, Tetrahedron Lett., 22 (1981) 3455.

8 D. Habich and F. Effenberger, Synthesis, (1978) 755.

9 M. Demuth and G. Mikhail, Synthesis, (1982) 827.

10 C. Eaborn, J. Organomet. Chem., 100 (1975) 43.

11 D.H. O'Brien and C.M. Hardbordt, J. Organomet. Chem., 21 (1970) 321.

12 R.F. Cunico, Synth. React. Inorg. Met.-Org. Chem., 16 (1986) 33.

13 A.R. Bassindale and T. Stout, Tetrahedron Lett., 26 (1985) 3403.

14 A. Hosomi, H. Hashimoto, and H. Sakurai, J. Organomet. Chem., 175 (1979) C1.

15 W.H. Atwell and D.R. Weynberg, J. Organomet. Chem., 3 (1965) 489.