



*Citation for published version:*

Baker, T & Lewis, SE 2010, 'Bifunctional silyl triflates in synthesis. Part 1: Synthesis and characterization of novel alkane-, -diyl-bis(silyl triflates)', *Synthetic Communications*, vol. 40, no. 18, pp. 2747-2752.  
<https://doi.org/10.1080/00397910903318724>

*DOI:*

[10.1080/00397910903318724](https://doi.org/10.1080/00397910903318724)

*Publication date:*

2010

[Link to publication](#)

This is an electronic version of an article published in: Baker, T., Lewis, S. E., 2010. Bifunctional silyl triflates in synthesis. Part 1: Synthesis and characterization of novel alkane-, -diyl-bis(silyl triflates). *Synthetic Communications*, 40 (18), pp. 2747-2752. *Synthetic Communications* is available online at: <http://www.informaworld.com/openurl?genre=article&issn=0039%2d7911&spage=2747>

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## **Bifunctional Silyl Triflates in Synthesis. Part 1: Synthesis and Characterisation of Novel Alkane- $\alpha,\omega$ -diyl-bis(silyl triflates)**

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**Abstract:** We report the preparation of two bifunctional silyl triflates, 1,1,4,4-tetramethyl-1,4-disila-1,4-butanediyl-bis(trifluoromethanesulfonate) and 1,1,5,5-tetramethyl-1,5-disila-1,5-pentane-diyl-bis(trifluoromethanesulfonate). Detailed synthetic procedures and characterisation data are described.

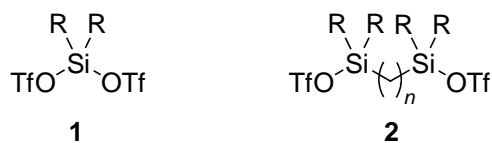
**Keywords:** silyl triflates, organometallic reagents, metathesis, protonations, arenes

### **INTRODUCTION**

Silyl triflates were first reported in 1970, with independent reports from Schmei $\beta$ er<sup>[1]</sup> and Roesky<sup>[2]</sup> of the preparation of trimethylsilyl triflate. In the ensuing period, silyl triflates have found numerous uses in organic synthesis.<sup>[3]</sup> In the area of protecting group chemistry, they are often superior to the corresponding silyl chlorides for the formation of a silyl ether from a sterically hindered or otherwise unreactive alcohol.<sup>[4]</sup> They are able to effect the formation of silyl enol ethers from the corresponding aldehydes and ketones and of silyl ketene acetals from the corresponding esters.<sup>[5]</sup> Also, silyl triflates are non-metal Lewis acids and as such have found applications as

mediators of diverse carbon-carbon<sup>[6]</sup> and carbon-heteroatom<sup>[7]</sup> bond-forming reactions. This diverse array of synthetic applications therefore provides a significant impetus for the synthesis of novel silyl triflates.

As part of an ongoing project developing new synthetic methodology, we wished to synthesise unreported bifunctional silyl triflates. 1,1-Silyl ditriflates of type **1** are well known<sup>[1]</sup> and were first utilized in organic synthesis by Corey for diol protection.<sup>[8]</sup> Rather than such geminal ditriflates, however, we sought to access compounds of type **2**, possessing two discrete silyl triflate functional groups connected by an alkyl linker (Figure 1). In the field of organosilicon polymers, related bifunctional silyl triflates have proven to be highly versatile monomers; many such triflates have been reported by Uhlig, who has recently reviewed the field.<sup>[9]</sup> So far, bifunctional silyl triflates such as **2** have yet to be exploited in organic synthesis.



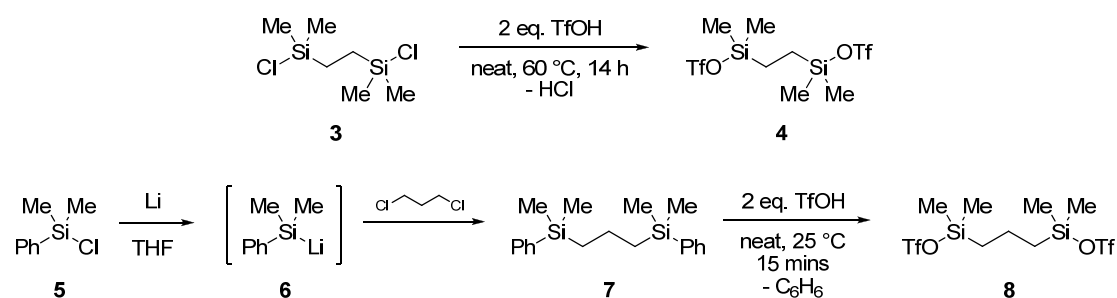
### Scheme 1.

Several different synthetic approaches to silyl triflates have been established. The superacidity of trifluoromethanesulfonic acid<sup>[10]</sup> allows for the synthesis of silyl triflates by direct metathesis with an appropriate silane. Thus, combination of a chlorosilane with trifluoromethanesulfonic acid furnishes the required silyl triflate, with extrusion of hydrogen chloride.<sup>[11,12,13]</sup> Similarly, reaction of a phenylsilane with trifluoromethanesulfonic acid affords the required silyl triflate with extrusion of benzene.<sup>[14,15]</sup> Allyl silanes may be similarly employed<sup>[16,17]</sup> and simple silane Si-H bonds are also able to undergo this metathesis, with concomitant formation of hydrogen gas.<sup>[18,19]</sup> Alternative approaches include metathesis of silyl halides with silver triflate, but the prohibitive cost of this reagent has limited use of this method to

cases where silicon possesses extremely bulky substituents<sup>[20,21,22,23]</sup> or where the halide would not be the most easily removed silyl substituent in direct metathesis with trifluoromethanesulfonic acid.<sup>[24]</sup>

## RESULTS AND DISCUSSION

We targeted bifunctional triflates **4** and **8** (Scheme 2) via two contrasting synthetic routes. Bifunctional triflate **4**, possessing an ethylene linker, was accessible in one step from commercially available 1,2-bis(chlorodimethylsilyl)ethane **3**. This starting material has been introduced for STABASE protection of primary amines.<sup>[25]</sup> We found that it readily undergoes metathesis with two equivalents of trifluoromethanesulfonic acid to furnish **4** in good yield (87%). The reaction is performed neat and requires heating to above the melting point of **3** to permit efficient mixing. The product **4** is then isolated by distillation under reduced pressure. One noteworthy point is that **4** is a solid at room temperature, in contrast to **5**. This is all the more surprising when it is considered that the corresponding bis(nonaflate) synthesised from **3** is reported to be a liquid.<sup>[26]</sup> As a solid, **4** is less susceptible to hydrolysis by atmospheric moisture than analogous liquid silyl triflates; we have found it most convenient to prepare stock solutions in dry dichloromethane (in which it is readily soluble) for subsequent dispensing.



## Scheme 2.

For the synthesis of bifunctional triflate **8** we adopted a multistep procedure, since the corresponding bis(chlorosilane), although commercially available, is much more expensive. Therefore, we instead effected the lithiation of **5**,<sup>[27]</sup> giving silyllithium **6** which was reacted *in situ* with 1,3-dichloropropane to give bis(phenylsilane) **7**, purified by distillation. This then underwent treatment with two equivalents of trifluoromethanesulfonic acid to furnish the desired **8** in good yield (68%) after distillation. In this instance much milder reaction conditions could be employed than those used in the synthesis of **4**, since the metathesis of a phenylsilane is known to be more facile than that of a chlorosilane.<sup>[7]</sup> It should be noted that the modular strategy employed to access **8** would be equally applicable to linkers of varying length or with additional substitution.

Both **4** and **8** were stable upon storage for several months at  $-20\text{ }^{\circ}\text{C}$  in an inert atmosphere. These novel silyl triflates were characterised by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{29}\text{Si}$  NMR and by IR spectroscopy. The  $^{29}\text{Si}$  resonances were observed in the downfield region ( $\delta = 42.6$  and  $42.0$  for **4** and **8** respectively), confirming the highly electrophilic character of the silicon.<sup>[11]</sup> Mass spectrometric characterisation proved more challenging. Neither **4** nor **7** gave observable parent ions under a variety of ionisation techniques,<sup>[28]</sup> but the mass spectrum of **8** exhibited a parent ion signal of low intensity under APCI conditions.

In summary, we have synthesised two novel silyl triflates via operationally simple procedures that permit preparation of multigram quantities. The silyl triflates **4** and **8** are anticipated to find numerous applications in organic synthesis; further studies on these are underway and will be reported in due course.

## EXPERIMENTAL

**General Procedures and Instrumentation.** Reactions were carried out under an atmosphere of nitrogen. THF was dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. 1,2-bis(chlorodimethylsilyl)ethane and lithium wire were purchased from Sigma-Aldrich, 1,3-dichloropropane was purchased from Acros and chlorodimethylphenylsilane and trifluoromethanesulfonic acid were purchased from Fluorochem; all reagents were used as received. IR spectra were recorded on Perkin-Elmer 1600 FT IR spectrometer with absorbances quoted as  $\nu$  in  $\text{cm}^{-1}$ . NMR spectra were run in  $\text{CDCl}_3$  on either a Bruker Avance 300 MHz or Bruker Avance 400 MHz instrument at 298 K. Mass spectra were recorded with a micrOTOF mass spectrometer (Bruker Daltonik) under APCI and ESI ionisation conditions. Elemental analyses were performed using an Exeter Analytical CE 440 analyzer.

### **1,1,4,4-Tetramethyl-1,4-disila-1,4-butanediyl-bis(trifluoromethanesulfonate) (4).**

To solid 1,2-bis(chlorodimethylsilyl)ethane (5.00 g, 23.2 mmol, 1.00 equiv) stirring under a copious stream of nitrogen was added slowly trifluoromethanesulfonic acid (6.97 g, 46.5 mmol, 2.00 equiv) dropwise by glass syringe. The HCl gas evolved was neutralised via a sodium hydroxide scrubber. The resulting yellow crystals were heated to 60 °C for 14 h and subsequently distilled (bp 88 °C at 2.4 mbar) to give **4** as a white crystalline solid (8.90 g, 87%). mp 31–33 °C.  $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ) 0.90 (4H, s,  $\text{CH}_2\text{-Si}$ ), 0.52 (12H, s,  $\text{Si-CH}_3$ );  $\delta_{\text{C}}$  (75.5 MHz;  $\text{CDCl}_3$ ) 118.3 (q,  $J = 317$  Hz,  $\text{CF}_3$ ), 7.2 ( $\text{Si-CH}_2$ ), -2.0 ( $\text{Si-CH}_3$ );  $\delta_{\text{F}}$  (376 MHz;  $\text{CDCl}_3$ ) -77.0;  $\delta_{\text{Si}}$  (99.4 MHz;  $\text{CDCl}_3$ , DEPT) 42.6. HRMS-ESI, HRMS-APCI: parent ion not found. Anal. Calcd. for  $\text{C}_8\text{H}_{16}\text{F}_6\text{O}_6\text{S}_2\text{Si}_2$  C, 21.7; H, 3.64. Found: C, 21.4; H, 3.69.

**2,6-Dimethyl-2,6-diphenyl-2,6-disilaheptane (7).** To finely cut lithium wire (2.95 g, 425 mmol, 7.30 equiv) in a nitrogen purged flask was added THF (20 mL). Chlorodimethylphenylsilane (9.47 mL, 58.2 mmol, 1.00 equiv) was added dropwise. The reaction mixture was stirred at room temperature for 23 h. To remove unreacted lithium, the deep red reaction mixture was transferred via cannula to a nitrogen purged flask and washed through with 40 mL of THF. The reaction mixture was cooled to 0 °C and 1,3-dichloropropane (10.2 mL, 106 mmol, 1.82 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for a further 19 h, then concentrated under reduced pressure. The resulting yellow slurry was diluted with hexane (50 mL), added to ice and washed with distilled water (2 x 50 ml). The organic phase was dried over MgSO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure and distilled (bp 110-112 °C at 2.4 mbar) to give **7** as a light yellow oil (8.03 g, 88%).  $\delta_{\text{H}}$  (300 MHz; CDCl<sub>3</sub>) 7.51-7.47 (4H, m, Ar-H) 7.38-7.33 (6H, m, Ar-H), 1.48-1.38 (2H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 0.83 (4H, t, *J* 8.0 Hz, CH<sub>2</sub>-Si), 0.25 (12H, s, Si-CH<sub>3</sub>);  $\delta_{\text{C}}$  (75.5 MHz; CDCl<sub>3</sub>) 140.1 (4°), 133.9 (3°), 129.1 (3°), 128.1 (3°), 20.6 (Si-CH<sub>2</sub>), 18.8 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), -2.5 (Si-CH<sub>3</sub>);  $\delta_{\text{Si}}$  (99.4 MHz; CDCl<sub>3</sub>, DEPT) -3.82;  $\nu_{\text{max}}$  (film) 3096, 3022, 2954, 2912, 1427, 1336, 1248, 1140, 1112, 903, 811, 772, 728, 699 cm<sup>-1</sup>. HRMS-ESI, HRMS-APCI: parent ion not found. Anal. Calcd. for C<sub>19</sub>H<sub>28</sub>Si<sub>2</sub> C, 73.00; H, 9.03. Found: C, 72.8; H, 8.90.

**1,1,5,5-Tetramethyl-1,5-disila-1,5-pentanediy-bis(trifluoromethanesulfonate) (8).** To neat **7** (5.33 g, 17.1 mmol, 1.00 equiv) in a nitrogen purged flask was added slowly trifluoromethanesulfonic acid (5.10 g, 34.0 mmol, 1.99 equiv) by glass syringe and stirred at room temperature for 15 mins. The resulting brown oil was distilled (bp 108-120 °C at 2.7 mbar) to give **8** as a colourless oil (5.31 g, 68%).  $\delta_{\text{H}}$  (300 MHz; CDCl<sub>3</sub>) 1.64-1.54 (2H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.00 (4H, t, *J* 8.0 Hz, CH<sub>2</sub>-Si), 0.48 (12H,

s, Si-CH<sub>3</sub>);  $\delta_C$  (75.5 MHz; CDCl<sub>3</sub>) 118.3 (q,  $J = 317$  Hz, CF<sub>3</sub>) 19.9 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 15.4 (Si-CH<sub>2</sub>), -1.4 (Si-CH<sub>3</sub>);  $\delta_F$  (376 MHz; CDCl<sub>3</sub>) -76.9;  $\delta_{Si}$  (99.4 MHz; CDCl<sub>3</sub>, DEPT) 42.0;  $\nu_{max}$  (film) 2931, 1386, 1264, 1246, 1198, 1151, 959, 906, 854, 716, 683 cm<sup>-1</sup>. HRMS-APCI: [M + H]<sup>+</sup>  $m/z = 457.0037$  (theoretical  $m/z = 457.0060$ ).

**ACKNOWLEDGEMENTS.** We thank the University of Bath for funding, Dr Anneke Lubben for mass spectrometry and Dr John P. Lowe for NMR spectroscopy.

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