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Acid-catalyzed reactions of (3-(naphthalen-2-yl)-2,2-bis(trimethylsilyl)oxiran. A new synthesis of functional-group-substituted vinylsilanes

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ABSTRACT

The magnesium bromide-diethyl etherate-catalyzed ring-opening of (3-(naphthalen-2-yl)-2,2-bis(trimethylsilyl)oxiran **2** with thiophenols affords (1-trimethylsilylvinyl)sulfides **3** and the (1-bromovinyl) silane **4**. Nucleophilic attack occurs regioselectively at the position α- to silicon. The compound **2** has been converted into the (1-trimethylsilylvinyl)amide **5** with an excess of acetonitrile and into the (1-trimethylsilylvinyl)acetate **6** with acetic acid/acetic anhydride. These reactions proceed with catalytic amounts of boron trifluoride-diethylether. Treatment of **2** with acetic acid alone gives naphthaldehyde. The epoxide **2** reacts also with $MgBr_2 \cdot OEt_2$, MeLi/CuI, HX (X=Br or Cl) and $LiAlH_4$ with nucleophilic attack at the bis(trimethylsilyl)-substituted carbon.

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1. Introduction

2,2-Bis(trimethylsilyl)oxirans [1] are valuable reagents for the production of organosilicon compounds [2]. Ring-opening of epoxides with thiols is used widely in pharmaceutical and natural product chemistry [3]. Recent approaches for the synthesis of vinylsulfides have involved nucleophilic ring-opening of epoxysilanes with lithium thiophenolate, in a solvent and in the presence of a Lewis acid [4]. Although the behavior of trimethylsilylepoxides toward nucleophiles has been widely studied [5–7], there have been fewer references to the reactivity of bis(trimethylsilyl)epoxides. These are versatile intermediates that react with a wide variety of reagents via ring-opening α- to silicon. We have recently reported the synthesis and reactivity of 1,4-bis[2,2-bis(trimethylsilyl)ethenyl]benzene and a 2,2-bis(trimethylsilyl)oxiran [8].

Given the utility of vinylsilylsulfides in synthesis [9] and the availability of 1,1-bis(trimethylsilyl)ethenes, the development of a method for conversion of bis(trimethylsilyl)ethenes into vinylsilylsulfides via bis(trimethylsilyl)epoxides would be of value. In this paper we describe the ring-opening of (3-(naphthalen-2-yl)-2,2-bis(trimethylsilyl)oxiran **2** with ArSH/$MgBr_2 \cdot OEt_2$ to give (1-trimethylsilylvinyl)sulfides. Treatment of **2** with $CH_3CN/BF_3.Et_2O$, AcOH/$Ac_2O/BF_3.Et_2O$, HX (X=Br or Cl), MeLi/CuI or $LiAlH_4$ led to the formation of (1-trimethylsilylvinyl)acetamide, (1-trimethylsilylvinyl) acetate, (1-halovinyl)silanes and alkenylsilanes, respectively.

2. Results and discussion

The Peterson reaction gives 1,1-disilylalkenes with non-enolisable aldehydes and ketones. In previous work, we prepared various 1,1-disilylalkenes from aldehydes and treated them with electrophilic reagents. 1,1-Bis(trimethylsilyl)-2-(2-naphthyl)ethene **1** was prepared from the reaction of [tris(trimethylsilyl)methyl]lithium, $(Me_3Si)_3CLi$, with 2-naphthaldehyde via the Peterson protocol [10–12]. Epoxidation of this compound with *m*-chloroperoxybenzoic acid (MCPBA) in CH_2Cl_2 at room temperature gave (3-(naphthalen-2-yl)-2,2-bis(trimethylsilyl)oxiran **2** (Scheme 1).

Previously vinylsulfides were synthesized from epoxysilanes; we now report the synthesis of (1-trimethylsilylvinyl)sulfides by the magnesium bromide-diethyl etherate-catalyzed ring-opening of bis(trimethylsilyl)epoxides. Magnesium bromide-diethyl etherate has found many applications as a mild Lewis acid to facilitate various synthetic organic transformations including ring-opening of epoxides with thiols under mild conditions [3]. The epoxide **2** reacted with various thiophenols (Table 1) in the presence of $MgBr_2 \cdot OEt_2$ in CH_2Cl_2 at room temperature via α-ring opening and subsequent elimination of the silyl group and oxygen to give the (1-trimethylsilylvinyl)sulfides **3**. In these reactions both isomers (Z and E) have been formed. The formation of Z-alkene is most likely favored due to pronounced differences in eclipsing interactions between the two possible conformations for syn elimination [5,13]. However, in the presence of two bulky groups $-SiMe_3$ and $-SAr$ approximately equal amounts of E and Z isomers are formed. To prove the above results, we attributed the phenylthio

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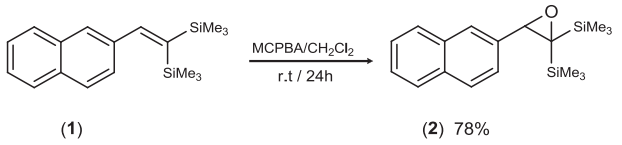


(**1**) (**2**) 78%

Scheme 1. Preparation of (3-(naphthalen-2-yl)-2,2-bis(trimethylsilyl)oxiran (**2**).

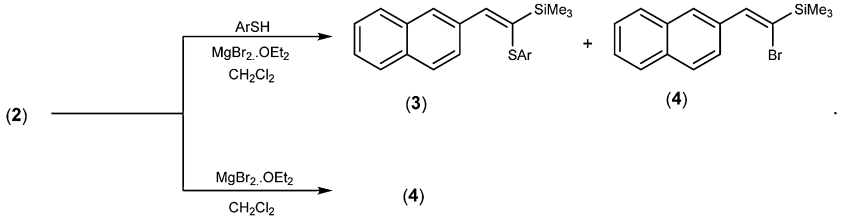
group elimination reaction in **3a** (Scheme 2) [14]. The elimination of the phenylthio from a mixture of the (Z) and (E)-1-phenylthio-1-trimethylsilyl-2-naphthylethene (**3a**) proceeded smoothly with lithium naphthalenide to give the corresponding vinylsilane (**9**). In this elimination reaction, the yield of trans isomer was 56%. Namely the Z isomer is more than the E isomer. These results have been confirmed by ^{1}H NMR and GC-mass spectra (Table 2).

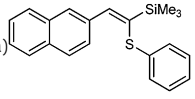
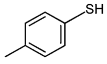
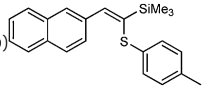
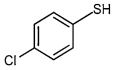
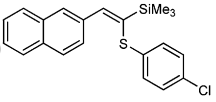
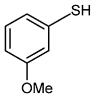
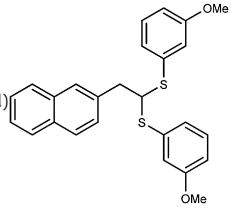
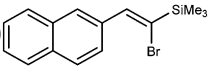
Compound **2** reacted with 3-methoxythiophenol in the presence of $MgBr_2 \cdot OEt_2$ for 18 h to give the unexpected product **3d** (Table 1). In this reaction, the yield of the (1-bromovinyl)silane **4**, itself a valuable reagent in organic chemistry, is more than that of compound **3d**. Treatment of **2** with $MgBr_2 \cdot OEt_2$ led to the formation of **4**.

Acid-catalyzed reactions yielded products derived from cleavage of the C—O bond in the direction expected to produce the more stable cation. The products in these reactions were consistent with α-cleavage of the α,β-epoxides and only bromohydrins were obtained from epoxysilanes [15]. However treatment of the epoxide **2** with $MgBr_2 \cdot OEt_2$ at room temperature produced the (1-bromovinyl)silane **4** directly (Table 1). Formation of **4** showed that Peterson olefination took place after or concurrently with the addition of Lewis acid.

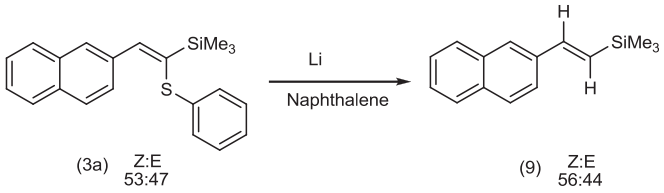
It has been reported [16–18] that when epoxides were treated with CH_3CN in the presence of $BF_3 \cdot Et_2O$ the initial products were oxazolines and that subsequent hydrolysis yielded hydroxyamides. Treatment of these hydroxyamides with KH in THF gave the enamides. However, in the case of **2**, Peterson-type olefination after or concurrently with the addition of $CH_3CN/BF_3 \cdot OEt_2$ gave the (1-trimethylsilylvinyl)amide **5** regioselectively in one step without addition of KH or other reagents (Scheme 3). This reaction was carried out by stirring equimolar amounts of the epoxide **2** and boron trifluoride-ether, with an excess of acetonitrile as solvent, for 24 h at room temperature.

Table 1
Reaction of **2** with thiophenols and summary of experimental conditions and yields.



Entry	ArSH	Product	Time(h)	Yield [a](%)	
				(3) (Z:E)	(4) (Z)
1		(**3a**) 	2	76 (53:47)	24
2		(**3b**) 	4	70 (50.4:49.6)	30
3		(**3c**) 	4	65 (55:45)	35
4		(**3d**) 	18	40	60
5	_	(**4**) 	18	_	69

[a] Yields obtained by GC-Mass spectrometry.



Scheme 2. Elimination reaction of compound **3a**.

Treatment of **2** with acetic acid containing 20% acetic anhydride and 1% $BF_3 \cdot OEt_2$ at room temperature gave the acetate **6** directly. In this system, trimethylsilanol was eliminated spontaneously with BF_3-catalyzed oxide ring opening to yield the vinyl ester in a single step. However when **2** was treated with acetic acid in the absence of $BF_3 \cdot OEt_2$ and acetic anhydride, only the unexpected product naphthaldehyde was observed at 80 °C. Thus Lewis acid BF_3 catalyzed the cleavage of a silicon-carbon bond and the formation of a positive charge in position α- to the trimethylsilyl groups for the nucleophilic attack [19,20].

Treatment of the epoxide **2** with MeLi/CuI gave the methylation product **7** (Scheme 4, Table 2). But the major product was identified by FTIR, NMR (^1H and ^{13}C) and mass spectrometry as the bis(trimethylsilyl)-derivative **1**.

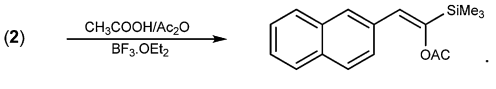
As pointed out above the (1-bromovinyl)silane **4** could be prepared by the reaction of **2** with the magnesium bromide-diethyl etherate. An alternative method for synthesis of (halovinyl)silanes is by reactions of epoxides with hydrogen halides [1]. Reaction of **2** with HX (X=Br or Cl) in aq. THF under reflux gave the (1-halovinyl) silanes **4** and **8** (Scheme 5). The mechanism of this reaction has been discussed [5,8,21].

We wished to prepare the β-hydroxysilane from the reduction of **2** with lithium aluminum hydride in diethyl ether but Peterson olefination was found to occur concurrently to give the vinylsilane **9** (Scheme 6). The extremely high stereoselectivity of the reaction (only *trans* was formed) is noteworthy.

3. Conclusion

This work demonstrates that ring opening of the bis(trimethylsilyl)epoxide **2** in the presence of catalytic amounts of Lewis acids occurred regioselectively at the position α- to the trimethylsilyl groups. Epoxidation of 1,1-bis(trimethylsilyl)-2-(2-naphthyl)ethene **1** with MCPBA in CH_2Cl_2 gave (3-(naphthalen-2-yl)-2,2-bis(trimethylsilyl)oxiran **2** that served as precursor for the preparation of a series of valuable compounds. Treatment of **2** with thiols in the presence of $MgBr_2 \cdot OEt_2$ led to the preparation of (1-trimethylsilylvinyl)sulfides **3** and (1-bromovinyl)silane **4**. These reactions provide a general regioselective method for preparation of (1-halovinyl)silanes.

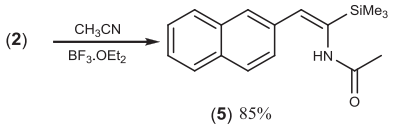
Table 2
Treatment of **2** with acetic acid under various conditions.



(**6**)

Entry	Reagents	Temperature (°C)	Time (h)	Product	Yield [a](%)
1	CH_3COOH	80	2	Naphthaldehyde	62
2	CH_3COOH	0	24	–	–
3	CH_3COOH/Ac_2O $BF_3 \cdot OEt_2$	r.t	2	(**6**)	70

[a] Yields obtained by PTLC.



Scheme 3. Treatment of compound **2** with acetonitrile.

4. Experimental

4.1. Solvents and reagents

The reactions were carried out under dry argon. Solvents were dried by standard methods. Substrates for the preparation of tris (trimethylsilyl)methyllithium, viz. Me_3SiCl (Merck), Li (Merck), $CHCl_3$ (Merck), and for the preparation of (3-(naphthalen-2-yl)-2,2-bis(trimethylsilyl)oxiran **2**, viz. 2-naphthaldehyde (Merck) and MCPBA (Acros) were used as received.

4.2. Spectra

The ^1H and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz instrument at room temperature and $CDCl_3$ as a solvent. The mass spectra were obtained with a GC-mass Agilent quadrupole mode 5973N instrument, operating at 70 eV. FTIR spectra were recorded on a Bruker-Tensor 270 spectrometer. Elemental analyses were carried out with an elementar vario EL III instrument.

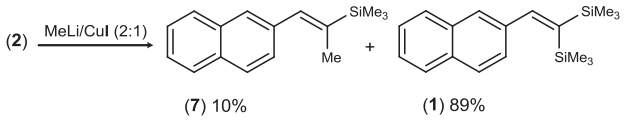
4.3. Synthesis of products *1*–*9*

4.3.1. Synthesis of (3-(naphthalen-2-yl)-2,2-bis(trimethylsilyl)) oxiran (*2*)

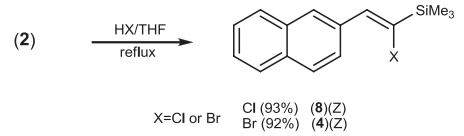
A mixture of vinylsilane **1** (2.00 g, 6.71 mmol), MCPBA (75% w/w pure) and CH_2Cl_2 (75 ml) was stirred at room temperature for 24 h. The mixture was washed with aq. $NaHCO_3$ (5 × 40 ml), water (40 ml), brine (40 ml) and the organic layer was dried ($MgSO_4$). Solvent was evaporated and the residue purified by column chromatography (1:4 n-hexane:ethyl acetate) to give **2** as a yellow liquid. Yield 78%. $R_f = 0.6$. FTIR (KBr, cm^{-1}): 3054 (CH, Ar), 2957 (CH), 1506 and 1388 (Ar), 1252, 930 and 846 (C—Si), 1107 (C—O); ^1H NMR (400 MHz, $CDCl_3$):δ −0.21 and 0.20 (s, 18 H, $SiMe_3$), 4.33 (s, 1H, HC—O), 7.45–7.84 (m, 7H, Ar); ^{13}C NMR ($CDCl_3$): δ −3.01 and −1.33 ($SiMe_3$), 54.67 and 60.77 (C—O), 123.91–134.90 (Ar); *m/z* (EI): 314 (41%, $[M]^+$), 147 (100%), 148 (16%), 198 (31%), 73 (64%, $[SiMe_3]^+$). Anal. Calc. for $C_{18}H_{26}OSi_2$: C, 68.8; H, 8.2. Found: C, 68.9; H, 7.9%.

4.3.2. General procedure for the preparation of (1-trimethylsilylvinyl) sulfides *3*

A mixture of the epoxide **2** (0.5 mmol), thiol (0.6 mmol), anhydrous dichloromethane (2–3 ml) and $MgBr_2 \cdot OEt_2$ (0.2 mmol) was stirred and the course of the reaction was monitored by TLC until the starting materials had completely disappeared. The mixture was diluted in dichloromethane (10 ml) and washed twice with water (10 ml). The organic phase was dried over Na_2SO_4, the



Scheme 4. Reaction of **2** with MeLi/CuI.



Scheme 5. Reaction of **2** with HX (X=Cl or Br).

solvent was removed at reduced pressure, and the product was purified by preparative TLC on silica gel.

*4.3.2.1. Analytical data for **3a**.* White solid (76%): (R_f = 0.17 n-hexane, m.p. 84–86 °C), FTIR (KBr, cm^{-1}): 3053 (CH, vinyl), 2954 (CH, Ar), 2924 (CH), 1649-1471 (C=C, Ar), 1243, 930 and 837 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.14 (s, 9H, $SiMe_3$), 7.20–8.08 (1H, vinyl, 12H, Ar); ^{13}C NMR ($CDCl_3$): δ −1.65 ($SiMe_3$), 124.75–135.95 (C=C, Ar), 145.13 (C–S); *m/z* (EI): 335 (28% $[M+1]^+$), 334 (100% $[M]^+$), 167 (60%), 73 (53%, $[SiMe_3]^+$). Anal. Calc. For $C_{21}H_{22}SSi$: C, 75.4; H, 6.6. Found: C, 75.1; H, 6.8%.

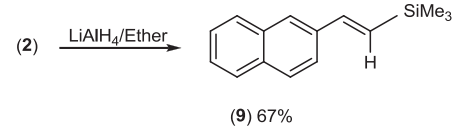
*4.3.2.2. Analytical data for **3b**.* Colorless oil (70%): (R_f = 0.16 n-hexane), FTIR (KBr, cm^{-1}): 3054 (CH, vinyl), 3018 (CH, Ar), 2957 and 2925 (CH), 1629–1462 (C=C, Ar), 1248, 933 and 840 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.09 (s, 9H, $SiMe_3$), 2.36 (s, 3H, CH_3) 7.19–7.88 (1H, vinyl, 11H, Ar); ^{13}C NMR ($CDCl_3$): δ −1.53 ($SiMe_3$), 20.19 (CH_3), 124.76–132.67 (C=C, Ar), 144.05 (C–S); *m/z* (EI): 349 (29% $[M+1]^+$), 348 (100% $[M]^+$), 275 (24% $[M-SiMe_3]^+$), 181 (46%), 73(59%, $[SiMe_3]^+$). Anal. Calc. For $C_{22}H_{24}SSi$: C, 75.9; H, 6.9. Found: C, 76.1; H, 6.9%.

*4.3.2.3. Analytical data for **3c**.* Yellow oil (65%): (R_f = 0.4 n-hexane), FTIR (KBr, cm^{-1}): 3045 (CH, vinyl), 2924 (CH, Ar), 2853 (CH), 1633–1467 (C=C, Ar), 1256, 967 and 841 (C–Si), 812 (C–Cl); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.06 (s, 9H, $SiMe_3$), 7.15–8.04 (1H, vinyl, 11H, Ar); ^{13}C NMR ($CDCl_3$): δ −1.71 ($SiMe_3$), 122.46–132.75 (C=C, Ar), 143.31 (C–S); *m/z* (EI): 370 (43% $[M+2]^+$), 369(29% $[M+1]^+$), 368 (100% $[M]^+$), 201 (32%), 73(59%, $[SiMe_3]^+$). Anal. Calc. For $C_{21}H_{21}ClSSi$: C, 68.4; H, 5.7. Found: C, 68.1; H, 5.5%.

*4.3.2.4. Analytical data for **3d**.* Yellowish liquid (40%): (R_f = 0.24 10:1 n-hexane:ethyl acetate), FTIR (KBr, cm^{-1}): 3054 (CH, vinyl), 2956 (CH, Ar), 2924 (CH), 1636 and 1470 (C=C, Ar); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.33 (d, 2H, J = 7.04 Hz, CH_2), 3.71 (s, 6H, CH_3), 4.71 (t, 1H, J = 8 Hz, CH), 6.79–7.80 (m, 15H, Ar); ^{13}C NMR ($CDCl_3$): δ 41.52 (CH_2), 54.22 (CH), 58.38 (CH_3), 112.75–158.68 (Ar); *m/z* (EI): 432 (7%, $[M]^+$), 293 (78%, $[M-SC_6H_4OMe]^+$), 153 (28%, $[CH_2SC_6H_4OMe]^+$), 139 (28%, $[SC_6H_4OMe]^+$). Anal. Calc. For $C_{26}H_{24}O_2S_2$: C, 72.2; H, 5.5. Found: C, 72.4; H, 5.8%.

*4.3.3. Reaction of **2** with $MgBr_2 \cdot OEt_2$*

A mixture of bis(trimethylsilyl)epoxide **2** (0.5 mmol), anhydrous dichloromethane (2–3 ml) and $MgBr_2 \cdot OEt_2$ (0.2 mmol) was stirred for 18 h. TLC showed that by this time the reaction was complete. Further dichloromethane (10 ml) was added and the mixture was washed twice with water (10 ml). The organic phase was dried over Na_2SO_4, the solvent was removed at reduced pressure, and the residue was purified by preparative TLC on silica gel to give yellow solid (69%). The NMR and GC-mass spectra of **4** have been shown in 4.3.8.2.



Scheme 6. Reduction of **2** with $LiAlH_4$.

*4.3.4. Elimination reaction of **3a***

Li (10 mg, 3 mmol) and naphthalene (50 mg, 0.8 mmol) were mixed under argon atmosphere in THF (2 ml) and the mixture was stirred at 0 °C for 2 h. Then (1-trimethylsilylvinyl)sulfide **3a** (34 mg, 0.1 mmol) in THF (1 ml) was added, and the mixture was stirred for 1 h. Ether (20 ml) and water (3 drops) were added and the mixture was washed with water. The organic layer was dried ($MgSO_4$) and the solvent was evaporated to give crude product. The crude product was purified by TLC on silica gel to give a yellow oil (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.19 (s, 9H, $SiMe_3$), 6.58 (d, 1H, J = 19.12 Hz, vinyl), 7.02 (d, 1H, J = 19.12 Hz, vinyl), 7.41–7.82 (m, 7H, Ar).

*4.3.5. Reaction of **2** with CH_3CN*

Equimolar amounts (0.32 mmol) of **2** and boron trifluoride-ether in acetonitrile as solvent (2–3 ml) were stirred at room temperature for 24 h. The mixture was poured into aqueous sodium hydrogen carbonate and the dichloromethane extract was washed, then dried (Na_2SO_4). Solvent was evaporated and the residue separated by preparative TLC on silica gel (10:1 n-hexane:ethyl acetate) to give a yellow solid **5** (85%, R_f = 0.34, m.p.117–119 °C). FTIR (KBr, cm^{-1}): 3245 (NH), 3050 (CH, vinyl), 2924 (CH, Ar), 2853 (CH), 1644 (C=O), 1597 and 1523 (C=C, Ar),1241, 992 and 840 (C–Si), 1130 (CN); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.32 (s, 9H, $SiMe_3$), 1.98 (s, 3H, methyl), 6.31 (s, 1H, vinyl), 7.31–7.87 (m, 7H, Ar, 1H, NH); ^{13}C NMR ($CDCl_3$): δ −0.51 ($SiMe_3$), 22.12 (CH_3), 122.13–138.72 (C=C, Ar), 166.73 (C=O); *m/z* (EI): 283 (5%, $[M]^+$), 268 (100%, $[M-Me]^+$), 116 (13%), 209(9%), 73(7%, $[SiMe_3]^+$). Anal. Calc. for $C_{17}H_{21}NOSi$: C, 72.0; H, 7.4;N, 4.9. Found: C, 72.0; H, 7.3;N, 5.1%.

*4.3.6. Reaction of **2** with CH_3COOH*

A mixture of **2** (1 mmol), 5 mmol of acetic acid, 20% anhydride acid and 1% $BF_3 \cdot OEt_2$ was stirred at room temperature for 2 h, then extracted with CH_2Cl_2. The organic phase was washed with water, then dried over Na_2SO_4. Solvent was evaporated and the product purified by preparative TLC on silica gel (10:1 n-hexane:ethyl acetate) to give a white solid **6** (70%, R_f = 0.68, m.p.65–66 °C). FTIR (KBr, cm^{-1}): 3053 (CH, vinyl), 2957 (CH, Ar), 2925 (CH), 1743 (C=O), 1621 (C=C), 1496 and 1462 (Ar), 1248, 967 and 838 (C–Si), 1208 (CO); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.27 (s, 9H, $SiMe_3$), 2.23 (s, 3H methyl), 6.44 (s, 1H, vinyl), 7.26–7.91 (m, 7H, Ar); ^{13}C NMR ($CDCl_3$): δ −2.00 ($SiMe_3$), 19.87 (CH_3), 122.96–132.33 (C=C, Ar), 155.93 (C–O), 168.10 (C=O); *m/z* (EI): 284 (30%, $[M]^+$), 269 (37%, $[M-Me]^+$), 242 (81%, $[M-CH_3CO]^+$), 73(100%, $[SiMe_3]^+$). Anal. Calc. for $C_{17}H_{20}O_2Si$: C, 71.8; H, 7.0. Found: C, 72.0; H, 7.2%.

*4.3.7. Reaction of **2** with MeLi/CuI*

To a mixture of 0.49 g (5.14 mmol) CuI in 10 ml anhydrous ether at −45 °C was added dropwise a solution of methyllithium, made by the addition of 0.32 ml (5.14 mmol) MeI in 5 ml anhydrous ether to 72 mg (10.3 mmol) Li in 10 ml ether. The mixture was stirred for 1 h at −45 °C. Then a solution of 200 mg (0.64 mmol) of **2** in ether (5 ml) was added dropwise. The mixture was stirred for 2 h at −45 °C, then for 23 h as the solution was allowed to warm to room temperature. It was treated with 20 ml saturated $NaHCO_3$ then water, and the organic layer was dried ($MgSO_4$), and concentrated. The residue was separated by preparative TLC on silica gel (n-hexane) to give the bis(trimethylsilyl)ethene **1** (89%, R_f = 0.44) and a brown oil **7** (10%, R_f = 0.12). FTIR (KBr, cm^{-1}): 3054 (CH, vinyl), 2956 (CH, Ar), 2924 (CH), 1647-1458 (C=C, Ar), 1244, 961 and 837 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.31 (s, 9H, $SiMe_3$), 1.25 (s, 3H, CH_3), 7.25 (s, 1H, vinyl), 7.44–7.87 (7H, Ar); ^{13}C

NMR ($CDCl_3$): δ −2.20 ($SiMe_3$), 28.69 (CH_3), 122.31–142.58 (C=C, Ar); *m*/*z* (EI): 240 (78%, $[M]^+$), 225 (100%, $[M-Me]^+$), 185 (95%), 165 (41%), 73 (65%, $[SiMe_3]^+$). Anal. Calc. For $C_{16}H_{20}Si$: C, 80.0; H, 8.3. Found: C, 79.7; H, 8.1%.

*4.3.8. Reaction of **2** with HX (X=Cl or Br)*

A mixture of **2** (100 mg, 0.32 mmol), HX (2 mol dm^{-3}; 5 ml) and THF (5 ml) was stirred at 70 °C. After 18 h the reaction mixture was washed with saturated aq. Na_2CO_3 (2 × 10 ml), aq. $Na_2S_2O_3$ (1 mol dm^{-3}, 10 ml), water (10 ml) and brine (10 ml). The organic layer was dried ($MgSO_4$) and solvent evaporated to give a residue which was purified by preparative TLC on silica gel (15:1 n-hexane:ethyl acetate) to give yellow solids **4** (92%) and **8** (93%).

*4.3.8.1. Analytical data for **8**.* (R_f = 0.82 15:1 n-hexane:ethyl acetate, m.p.42–44 °C), FTIR (KBr, cm^{-1}): 3055 (CH, vinyl), 2961 (CH, Ar), 2926 (CH), 1586–1409 (C=C, Ar), 1259, 931 and 809 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.29 (s, 9H, $SiMe_3$), 7.01 (s, 1H, vinyl), 7.26–8.19 (m, 7H, Ar); ^{13}C NMR ($CDCl_3$): δ −4.15 ($SiMe_3$), 124.13–133.52 (C–Cl, C=C, Ar); *m*/*z* (EI): 262 (37%, $[M+2]^+$), 260 (100%, $[M]^+$), 93 (91%), 95 (33%,), 152 (24%). Anal. Calc. For $C_{15}H_{17}ClSi$: C, 69.2; H, 6.5. Found: C, 69.4; H, 6.7%.

*4.3.8.2. Analytical data for **4**.* (R_f = 0.83 15:1 n-hexane:ethyl acetate, m.p. 58–60 °C), FTIR (KBr, cm^{-1}): 3054 (CH, vinyl), 2951 (CH, Ar), 2859 (CH), 1586–1409 (C=C, Ar), 1249, 907 and 827 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 9H, $SiMe_3$), 7.29 (s, 1H, vinyl), 7.41–7.90 (m, 7H, Ar); ^{13}C NMR ($CDCl_3$): δ −2.79 ($SiMe_3$), 125.17–137.19 (C–Br, C=C, Ar); *m*/*z* (EI): 308 (24%, $[M+2]^+$), 306 (100%, $[M]^+$), 304 (97%, $[M-2]^+$), 209 (40%), 139 (92%), 136 (89%), 73 (30%, $[SiMe_3]^+$). Anal. Calc. for $C_{15}H_{17}BrSi$: C, 58.8; H, 5.5. Found: C, 58.5; H, 5.5%.

*4.3.9. Reduction of **2** with $LiAlH_4$*

To 100 mg (2.44 mmol) of $LiAlH_4$ in 25 ml of anhydrous ether at 0 °C was added 200 mg (0.64 mmol) of **2**. The stirred mixture was allowed to warm to room temperature during 6 h. It was then cooled in a N_2/ethyl acetate bath (−78 °C), and cold aqueous $NaHCO_3$ (10 ml) was added dropwise. The mixture was allowed to warm to room temperature. Ether was added, the organic layer was separated, and the aqueous layer was extracted with ether (2 × 20 ml). The combined organic layers were dried ($MgSO_4$) and solvent was evaporated. The residue was separated by preparative TLC on silica gel (10:1 n-hexane:ethyl acetate) to give **9** as a white solid (67%, R_f = 0.67, m.p.52–54 °C). FTIR (KBr, cm^{-1}): 3053 (CH, vinyl), 2954 (CH, Ar), 2925 (CH), 1603 (C=C), 1601 and 1405 (C=C, Ar), 1247, 985 and 833 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.19 (s, 9H, $SiMe_3$), 6.58 (d, 1H, J = 19.12 Hz, vinyl), 7.02 (d, 1H, J = 19.12 Hz, vinyl), 7.41–7.82 (m, 7H, Ar); ^{13}C NMR ($CDCl_3$): δ −2.20 ($SiMe_3$), 122.32–142.58 (C=C, Ar); *m*/*z* (EI): 226 (58%, $[M]^+$), 211 (100%, $[M-Me]^+$), 195 (48%), 59 (23% $[SiMe_2]^+$), 212 (20%). Anal. Calc. For $C_{15}H_{18}Si$: C, 79.6; H, 7.9. Found: C, 79.3; H, 8.1%.

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