Journal of Organometallic Chemistry 694 (2009) 1907–1911

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

1,4-bis[2,2-bis(trimethylsilyl)ethenyl]benzene: Regioselective ring opening of its α,β-epoxybis(silane) with some nucleophiles

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ARTICLE INFO

Article history:
Received 10 November 2008
Received in revised form 10 January 2009
Accepted 15 January 2009
Available online 22 January 2009

Keywords:
Vinylbis(silane)
Tris(trimethylsilyl)methyllithium
Peterson reaction
α,β-Epoxybis(silane)
Ring opening reaction

ABSTRACT

The Peterson olefination reaction of terephthalaldehyde with tris(trimethylsilyl)methyllithium, $(Me_3Si)_3$-CLi, in Et_2O gives disubstituted vinylbis(silane) **1** which reacts with MCPBA in CH_2Cl_2 at r.t. to afford mixture of mono and disubstituted epoxybis(silanes) **3** and **2**. Vinylbis(silane) **1** can be completely converted into epoxybis(silane) **2** with an excess amount of MCPBA. The compound **2** was reacted with various reagents such as HX (X = Cl, Br), H_2SO_4, $LiAlH_4$ and MeLi/CuI and give the related products.

1. Introduction

Vinylsilanes are important synthetic intermediates in stereocontrolled organic synthesis. Vinylbis(silanes) might be anticipated to possess broadly similar attributes to vinylsilanes for use in synthesis [1–3]. In contrast to vinylsilanes, however, vinylbis(silanes) are a relatively unexplored class of materials [4]. Their use as precursors for the preparation of ketones as well as variety of important organosilicon intermediates such as acylsilanes, epoxysilanes, 1-halovinylsilanes, silyl enol ethers, (E)-alkenylsilanes, silyl enol acetates, etc. stimulates interest in their synthetic availability [5,6].

We have recently reported [7] a convenient and stereoselective route for the synthesis of α-silyl-α,β-unsaturated enones from 1,1-bis(trimethylsilyl)-2-phenylethylene and some acyl chlorides in the presence of $AlCl_3$. The addition of an electrophile to a vinylsilane results in the build-up of electrophilic character β in the C–Si bond. A side from electrophilic substitution, one of the synthetically most useful transformations of vinylsilanes is epoxidation and hydrolysis of the resultant epoxysilanes with acid to reveal a carbonyl group, in which the carbonyl carbon originally bore the silyl substituent. Given the utility of acylsilanes in synthesis and the now readily availability of vinylbis(silanes), then the development of a method to convert vinylbis(silanes) into acylsilanes via epoxybis(silanes) would be of value [4].

In this paper, we wish to report the synthesis and the reactivity of 1,4-bis[2,2-bis(trimethylsilyl)ethenyl]benzene (**1**) and its epoxybis(silane) derivative **2** with hydrogen halides, lithium aluminum hydride, organocuprate and sulfuric acid in methanol.

2. Results and discussion

It has been previously shown that 1,4-bis[2,2-bis(trimethylsilyl)ethenyl]benzene (**1**) was prepared from reaction of ethylene glycol silylation-one-pot deethenative silylative coopling cyclization/Grignard reagent treatment–Heck coupling [5,8]. The Peterson olefination, the reaction of an α-silyl organometallic (usually organolithium) reagent with an aldehyde or ketone to yield an olefin, is a useful alternative to the Wittig reaction [9,10]. Herein, **1** has been prepared from Peterson olefination of terephthalaldehyde with [(trimethylsilyl)methyl]lithium, $(Me_3Si)_3CLi$ [11], (Scheme 1). This method of preparing functionalized silanes is limited by the readiness with which $(Me_3Si)_3CLi$ abstracts a proton, if one is available, rather than attacking at carbon [12].

Epoxidation of vinylsilanes furnish α,β-epoxysilanes, a class of compounds of considerable interest to the organic chemists [13]. The presence of trialkyl group provides regioselective control in the opening of epoxide by variety of nucleophiles. The compound **1** was reacted with MCPBA in CH_2Cl_2 at room temperature for 4 h and gave both mono and disubstituted epoxybis(silanes) **3** and **2**. In order to optimize conditions for the formation of **2**, we decided to investigate the reaction of **1** (1 mmol) with various amount of MCPBA (Table 1). When 2 mmol of MCPBA was used, for 18 h, the major product was **2**. In the reaction of **1** with 3 mmol of MCPBA the epoxybis(silane) **2** was the sole product formed.

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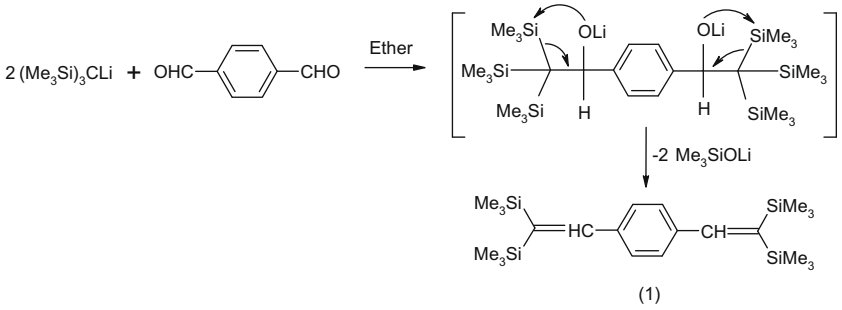
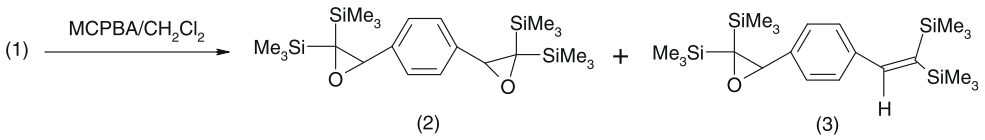
doi:10.1016/j.jorganchem.2009.01.030



Scheme 1. Preparation of 1,4-bis[2,2-bis(trimethylsilyl)ethenyl]benzene via Peterson protocol.

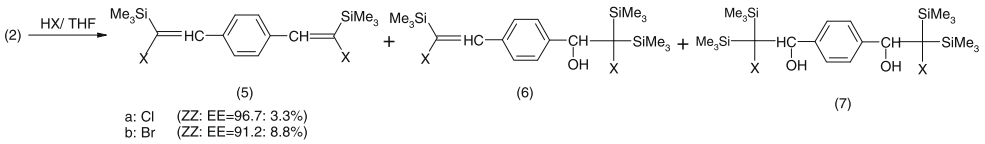
Table 1
Treatment of epoxybis(silane) **2** with MCPBA.



1:MCPBA	1:1[a]	1:2	1:3
2	25.6%	92.5%	96%
3	70.4%	3.54%	–

[a] Yields obtained by PTLC.

Table 2
Yields of the reaction of epoxybis(silane) **4** with HX (X = Cl, Br).

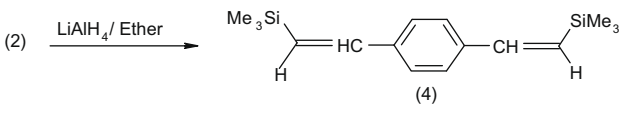


	Time/temperature		
	14 h/r.t.	14 h/reflux	24 h/reflux
5a	7.5%[a]	79.5%	96%
6a	88.5%	17%	trace
5b	5%	86%	83.5%
6b	20%	9%	12%
7b	70%	–	–

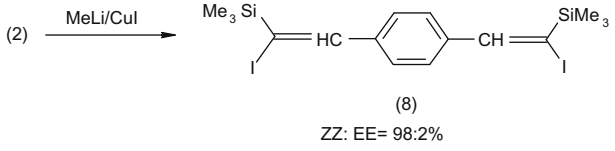
[a] Yields calculated by GC–mass spectrometry.

It has been reported [14] that the reaction of epoxybis(silane) with $LiAlH_4$ gave the β-hydroxybis(silane) without any formation of vinylsilane by Peterson-type reaction. However, in the case of epoxybis(silane) **2**, Peterson-type olefination was found to take place after or concurrently with the addition, to give the corresponding vinylsilane **4** stereoselectively (Scheme 2). The extremely high stereoselectivity of the compound **4** (only trans–trans) is worth mentioning. It has been well documented that acid or base catalyzed elimination from isolated β-hydroxysilanes is highly stereoselective. However, this is not the case for the direct addition/elimination sequences. For example, the condensation of $(Me_3Si)_2CHLi$ with benzaldehyde gave a mixture of stereoisomers (E/Z = 1.4/1) [14].

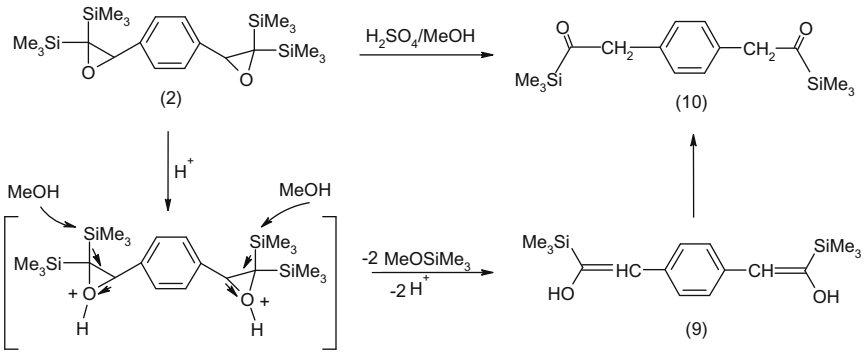
Halovinylsilanes are useful for the synthesis of geometrically defined trisubstituted alkenes, and as synthetic equivalents of carbonyl anions and cations [4,15]. One method for 1-halovinylsilane synthesis could be via reaction of epoxybis(silane) with hydrogen



Scheme 2. Reaction of epoxybis(silane) **2** with $LiAlH_4$.



Scheme 3. Treatment of **2** with methylcopper reagent (MeLi/CuI 2:1).



Scheme 4. The plausible mechanism for the formation of acylsilane **10**.

halides. Reaction of epoxybis(silane) **2** with aqueous HX (X = Cl, Br) in THF at room temperature gave the compounds **5**, **6** and **7** with excellent stereocontrol. It is worth noting that in the case of HCl, we did not detect the halohydrin **7a**. Formation of the *E*-alkene is most likely greatly favored due to pronounced differences in eclipsing intraction between the two possible conformations for *syn* elimination [4,16]. The effect of temperature on the reaction was also examined (Table 2). Heating hydrogen halides with epoxybis(silane) **2** gave only halovinylsilane **5a** for 24 h with excellent control over alkene geometry. However, in the case of hydrogen bromide the both **5b** and **6b** were observed, noting that the compound **5b** was the major product.

Mechanistic studies of halovinylsilane formation from epoxybis(silane), indicate that the preferred site of nucleophilic attack in epoxybis(silanes) is at the disilyl-substituted carbon. The reasons for the preference for α-opening of the α,β-epoxy silanes are not completely obvious. The α-position is frequently more hindered and ring opening at the α-position (under electrophilic conditions) might be expected to produce a highly stabilized β-silyl cation. However, the lack of β-opening, although remarkable, is perhaps less surprising in view of the relative orientation of the C–Si bond. Also the β-C–O bond greatly deviates from the parallel alignment that is favorable for stabilization of a developing positive β-charge by the silicon initial coordination of the nucleophile with both silicon and carbon. Coordination of the nucleophile to silicon followed by 1,2-rearrangement to the α-carbon has also been suggested for the α-opening reactions [17].

It has also been reported [18] that reaction of α,β-epoxysilanes with organocuprate reagents result in regiospecific opening of the epoxide ring to form β-hydroxyalkylsilanes. Surprisingly, in the reaction of epoxybis(silane) **2** with methylcopper reagent (MeLi/CuI 2:1), the iodovinylsilane **8** was the major product (Scheme 3). This is in contrast to the results of α,β-epoxysilanes with organocuprate reagents [18]. FT-IR, NMR (^{1}H and ^{13}C), and mass spectrometry data has confirmed the formation of the iodovinylsilane **8** [8]. The scope and mechanisms of this reaction are under investigation.

Epoxybis(silane) **2** was treated with H_2SO_4 (Conc.) in MeOH at room temperature and converted to the related acylsilane **10**. This reaction may proceed [19] by the protonation of the oxygen of epoxide, followed by a nucleophilic attack of MeOH on a trimethylsilyl group, inducing the trimethylsilylmethyl ether elimination, and generating the corresponding α-silyl enol **9**. α-Silyl enol **9** then converts to the related acylsilane **10** (Scheme 4).

3. Conclusion

We demonstrated the convenient one-pot preparation of 1,4-bis[2,2-bis(trimethylsilyl)ethenyl]benzene (**1**) via Peterson protocol. Treatment of **1** with MCPBA affords the mixture of mono and disubstituted epoxybis(silane) **2** and **3**. Whenever 3-fold the mole ratio of MCPBA was used, **2** was the sole product formed. We have also investigated the reaction of epoxybis(silane) **2** with a variety of nucleophiles. On treatment with acids, the epoxybis(silane) **2** provides halovinylsilane **5**, hybrid of halovinylsilane and halohydrin **6**, halohydrin **7**, and acylsilane **10**. It is noteworthy that, heating and prolongation of the reaction time play crucial role in the percentage of the compounds **5**, **6** and **7**. Interestingly, reaction of methylcopper reagent with epoxybis(silane) **2** gave iodovinylsilane **8** .This transformation is quite different from those observed in the literature. In these reactions all the evidences are consistent with the bis(silyl)-substituted carbon being the site of nucleophilic attack.

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 substrate for the preparation of 1,4-bis[2,2-bis(trimethyl silyl)ethenyl]benzene, viz. terephthalaldehyde (Merck) and MCPBA (Acros) were used as received.

4.2. Spectra

The ^{1}H NMR and ^{13}C NMR were recorded with a Bruker FT-400 MHz spectrometer at room temperature and $CDCl_3$ as a solvent. The mass spectra were obtained with a GC–mass Agilent, quadrupole mode 5973 N instrument, operating at 70 eV. The 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 *1–10*

4.3.1. Preparation of 1,4-bis[1,1-bis(trimethylsilyl)ethenyl]benzene (*1*)

Tris(trimethylsilyl)methyllithium (50 mmol) and terephtalaldehyde 3.4 g (25 mmol) in ether (30 cm^3) was refluxed for 18 h, and then poured into water and extracted into ether. The organic layer was washed with water and dried ($MgSO_4$). The solvent was evaporated to give a semi-liquid which was crystallized on ethanol to give 69% white crystal **1**. (m.p. 95 °C). FTIR (KBr, cm^{-1}): 3119 (CH vinyl), 3062 (Ar), 2954 (CH), 1640–1403 (*C*=C, Ar), 1249, 921 and 837 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.00 and 0.20 (s, 18H, $SiMe_3$), 7.13 (s, 4H, Ar), 7.73 (s, 2H, vinyl); ^{13}C NMR ($CDCl_3$): δ −0.45 and 1.20 ($SiMe_3$), 126.3–140.3 (Ar), 145.2 and 153.6 (*C*=C); *m*/*z* (EI): 418 (24%, $[M]^+$), 217 (23%), 171 (26%, $[CH{=}C(SiMe_2)]^+$), 73 (100%, $[SiMe_3]^+$). Anal. Calc. for $C_{22}H_{42}Si_4$: C, 63.0; H, 10.0. Found: C, 62.8; H, 9.8%.

4.3.2. Typical procedure for the preparation of epoxybis(silanes) (2)

A mixture of vinylbis(silane) **1** (4 g, 9.6 mmol), MCPBA (75% w/w pure) and CH_2Cl_2 (150 cm^3) was stirred at room temperature for 18 h. The reaction was washed with aq. $NaHCO_3$ (5 × 80 cm^3), water (80 cm^3), brine (80 cm^3) and dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography (2:3 *n*-hexane:CH_2Cl_2) to give a white solid, epoxybis(silane) **2** (R_f = 0.57, m.p. 99–100 °C). FTIR (KBr, cm^{-1}): 2957 (CH), 1516–1408 (Ar), 1254 (C–Si), 1177 (C–O), 934 and 844 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ *−0.19* and 0.14 (s, 18 H, $SiMe_3$), 4.10 (s, 2H, HC–O), 7.28 (d, 4H, *J* = 1.59 Hz, Ar); ^{13}C NMR ($CDCl_3$): δ −3.1 and −1.3 ($SiMe_3$), 54.4 and 6o.4 (C–O), 125.2, 136.4 and 139.4 (Ar); Anal. Calc. for $C_{22}H_{42}Si_4O_2$: C, 58.6; H, 9.0. Found: C, 58.5; H, 8.6%.

4.3.3. Analytical data for previously described mono-substituted epoxybis(silane) ***3***

Purification by column chromatography (2:3 *n*-hexane:CH_2Cl_2) gave a white solid epoxybis(silane) **3** (R_f = 0.83, m.p.78–79 °C). FTIR (KBr, cm^{-1}): 3032 (CH vinyl), 2959 (C–H), 1617–1402 (*C*=C, Ar), 1253 (C–Si), 1096 (C–O), 938 and 838 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ *−0.17,* −0.01, 0.15 and 0.18(s, 9H, $SiMe_3$), 4.16 (s, 1H, HC–O), 7.10 (d, 2H, *J* = 7.98 Hz, Ar), 7.20 (d, 2H, *J* = 8.09 Hz, Ar), 7.71(s, 1H, vinyl); ^{13}C NMR ($CDCl_3$): δ −3.0, −1.2, −0.4 and 1.2 ($SiMe_3$), 54.4 and 60.5 (C–O), 125.1–142.2 (Ar), 145.2 and 153.5 (*C*=C); Anal. Calc. for $C_{22}H_{24}Si_4O$: C, 58.7; H, 9.4. Found: C, 58.3; H, 9.0%.

4.3.4. Reaction of epoxybis(silane) ***2*** *with $LiAlH_4$*

To 305 mg (8.04 mmol) of $LiAlH_4$ in 50 cm^3 of anhydrous ether cooled in an ice bath was added 400 mg (0.96 mmol) of epoxybis(silane) **2**, and the reaction mixture was allowed to warm to room temperature with stirring for 150 min. The mixture was cooled in N_2/ethyl acetate bath (−78 °C), and cold aqueous $NaHCO_3$ was added dropwise, and was allowed to warm to room temperature. Ether was added, the layers were separated, and the aqueous layer was extracted with ether (2 × 30 cm^3). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated and the residue separated by preparative TLC on silica gel (4:1 *n*-hexane:Et_2O) to give 67.5% white solid **4** (R_f = 0.43, m.p. 52–54 °C). FTIR (KBr, cm^{-1}): 3070 (CH vinyl), 3038 (Ar), 2925 (CH), 1647 (*C*=C), 1601–1405 (Ar), 1246, 987 and 845 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ *−0.15* (s, 18H, $SiMe_3$), 6.47 (d, 2H, *J* = 19.13 Hz, vinyl), 6.85 (d, 2H, *J* = 19.13 Hz, vinyl), 7.39 (s, 4H, Ar); ^{13}C NMR ($CDCl_3$): δ −2.2 ($SiMe_3$), 125.5–142.1 (*C*=C, Ar); *m*/*z* (EI): 274 (30%, $[M]^+$), 259 (23%, $[M–Me]^+$), 201 (10%, $[M–SiMe_3]^+$), 187(70%), 147(30%), 99 (8%, $[HC{=}CHSiMe_3]^+$), 73 (100%, $[SiMe_3]^+$). Anal. Calc. for $C_{16}H_{26}Si_2$: C, 70.0; H, 9.0. Found: C, 69.7; H, 8.7%.

4.3.5. General procedure for the preparation of ***5****, 6 and* ***7***

A mixture of epoxybis(silane) **2** (500 mg, 1.1 mmol), HX (2 mol dm^{-3}; 5 cm^3) and THF (20 cm^3) was stirred at 70 °C. After 14 h the reaction mixture was cooled, Et_2O (30 cm^3) was then added and the mixture was washed with saturated aq. Na_2CO_3 (2 × 30 cm^3), aq. $Na_2S_2O_3$ (1 mol dm^{-3}; 30 cm^3), water (30 cm^3) and brine (30 cm^3). The organic layer was dried ($MgSO_4$) and evaporated to give a residue which was purified by TLC (silica gel) (2:3 *n*-hexane:CH_2Cl_2) to give white solids **5** and **6**.

(As explained in the text, at room temperature **5, 6** and **7b** were obtained).

4.3.6. Analytical data for ***5a*** *and* ***6a***

5a: (R_f = 0.93 2:3 *n*-hexane:CH_2Cl_2, m.p.78–80 °C), FTIR (KBr, cm^{-1}): 3130 (CH vinyl), 3087 (Ar), 2956 (CH), 1635–1406 (*C*=C, Ar), 1246, 921 and 837 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.27 (s, 18H, $SiMe_3$), 6.84 (s, 2H, vinyl), 7.73 (s, 4H, Ar); ^{13}C NMR ($CDCl_3$): δ −3.2 ($SiMe_3$), 66.9 (C–Cl), 128.3–137.4 (*C*=C, Ar); *m*/*z* (EI): 347 (6%, $[M+4]^+$), 345 (18%, $[M+2]^+$), 343 (24%, $[M]^+$), 342 (84%, $[M-1]^+$), 183 (11%), 95 (76%), 73 (100%, $[SiMe_3]^+$). Anal. Calc. for $C_{16}H_{24}Si_2Cl_2$: C, 55.9; H, 6.9. Found: C, 55.9; H, 6.5%.

6a: (R_f = 0.68 2:3 *n*-hexane:CH_2Cl_2, m.p. 116–118 °C), FTIR (KBr, cm^{-1}): 3512 (OH), 3102 (CH vinyl), 3047 (Ar), 2957 (CH), 1645 (*C*=C), 1609–1411 (Ar), 1250 (C–Si), 1033 (C–O), 927 and 837 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02, 0.14 and 0.26 (s, 9H, $SiMe_3$), 2.24 (s, 1H, OH), 5.07 (s, 1H, HC–OH), 6.84 (s, 1H, vinyl), 7.53 (d, 2H, *J* = 8.37 Hz, Ar), 7.69 (d, 2H, *J* = 8.36 Hz, Ar); ^{13}C NMR ($CDCl_3$): δ −3.2, −1.0 and −0.8 ($SiMe_3$), 55.8 (C–Cl), 77.8 (C–OH), 126.6–141.0 (*C*=C, Ar). Anal. Calc. for $C_{19}H_{34}Si_3Cl_2O$: C, 52.6; H, 7.2. Found: C, 52.7; H, 6.9%.

4.3.7. Analytical data for ***5b****, 6b and* ***7b***

5b: (R_f = 0.93 2:3 *n*-hexane:CH_2Cl_2, m.p. 75–77 °C), FTIR (KBr, cm^{-1}): 3084 (CH vinyl), 3025 (Ar), 2957 (CH), 1636–1406 (*C*=C, Ar), 1247, 901 and 840 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.28 (s, 18H, $SiMe_3$), 7.20 (s, 2H, vinyl), 7.72 (s, 4H, Ar); ^{13}C NMR ($CDCl_3$): δ −2.8 ($SiMe_3$), 53.8 (C–Br), 127.9–136.7 (*C*=C, Ar); *m*/*z* (EI): 436 (9%, $[M+4]^+$), 434 (36%, $[M+2]^+$), 433 (9%, $[M-1]^+$), 432 (64%, $[M]^+$), 183 (11%), 139 (45%), 73 (100%, $[SiMe_3]^+$). Anal. Calc. for $C_{16}H_{24}Si_2Br_2$: C, 44.4; H, 5.5. Found: C, 44.5; H, 5.5%.

6b: (R_f = 0.59 2:3 *n*-hexane:CH_2Cl_2, m.p. 94–96 °C), FTIR (KBr, cm^{-1}): 3472 (OH), 3045 (CH vinyl), 3024 (Ar), 2955 (CH), 1628–1411 (*C*=C, Ar), 1249 (C–Si), 1032 (C–O), 955 and 837 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.13, 0.19 and 0.31 (s, 9H, $SiMe_3$), 2.33 (d, 1H, *J* = 4.77 Hz, OH), 5.15 (d, 1H, *J* = 4.66 Hz, HC–OH), 7.25–7.69 (m, 5H, vinyl and Ar); ^{13}C NMR ($CDCl_3$): δ −2.8, −0.1 and 0.1 ($SiMe_3$), 53.8 (C–Br), 77.4 (C–OH), 126.7–141.1 (*C*=C, Ar). Anal. Calc. for $C_{19}H_{34}Si_3Br_2O$: C, 45.0; H, 5.7. Found: C, 44.7; H, 5.4%.

7b: (R_f = 0.17 2:3 *n*-hexane:CH_2Cl_2), m.p. 69–70 °C), FTIR (KBr, cm^{-1}): 3524 (OH), 3031 (Ar), 2954 (CH), 1635–1409 (Ar), 1249 (C–Si), 1038 (C–O), 964 and 839 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.10 and 0.16 (s, 18H, $SiMe_3$), 1.86 (s, 2H, OH), 5.20 (d, 2H, *J* = 1.06 Hz, HC–OH), 7.54 (s, 4H, Ar); ^{13}C NMR ($CDCl_3$): δ 0.0 and 0.3 ($SiMe_3$), 53.9 (C–Br), 77.4 (C–OH), 126.7–141.2 (Ar). Anal. Calc. for $C_{22}H_{44}Si_4Br_2O_2$: C, 43.2; H, 7.2. Found: C, 43.6; H, 7.2%.

4.3.8. Reaction of eppoxybis(silane) ***2*** *with MeLi/CuI*

To a mixture of 1.7 g (17.95 mmol) of CuI in 15 cm^3 of anhydrous ether at -45 °C was added 17.95 mmol of methyllithium [1.12 cm^3 (17.95 mmol) MeI in 5 cm^3 anhydrous ether was added dropwise into 250 mg (35.9 mmol) Li in 15 cm^3 anhydrous ether] dropwise. The resulting reaction mixture was stirred for 1 h at −45 °C. Then a solution of 500 mg (1.1 mmol) of epoxybis(silane) **2** in 10 cm^3 of anhydrous ether was added dropwise and the resulting mixture was stirred [2 h at −45 °C, 23 h (−45 °C → r.t.)]. Then 50 cm^3 of saturated $NaHCO_3$ was poured into the reaction mixture, the layers were separated, the aqueous layer was extracted three times with ether, and then the combined organic layers were washed with saturated $NaHCO_3$ followed by water, dried ($MgSO_4$), and concentrated. The residue was separated by TLC on silica gel (*n*-hexane) to give 69.36% white solid **8** (R_f = 0.39, m.p. 118–120 °C). FTIR (KBr, cm^{-1}): 3065 (CH vinyl), 3021 (Ar), 2954 (CH), 1664 (*C*=C), 1626–1399 (Ar), 1244, 906 and 837 (C–Si); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.27 (s, 18H, $SiMe_3$), 7.27 (s, 2H, vinyl), 7.62 (s, 4H, Ar); ^{13}C NMR ($CDCl_3$): δ −2.3 ($SiMe_3$), 110.9 (C–I), 127.2–142.7 (*C*=C, Ar); *m*/*z* (EI): 526 (67%, $[M]^+$), 185 (30%), 73 (100%, $[SiMe_3]^+$). Anal. Calc. for $C_{16}H_{24}Si_2I_2$: C, 38.5; H, 6.6. Found: C, 38.1; H, 6.6%.

4.3.9. Preparation of acylsilane ***10***

Concentrated H_2SO_4 (18 mol dm^{-3}; 0.19 cm^3, 3.4 mmol) was added dropwise to a stirred solution of epoxybis(silane) **2** (400 mg, 0.96 mmol) in MeOH (6 cm^3) at 25 °C. After 90 min at re-

flux condition, the mixture of the reaction was cooled and saturated aq. $NaHCO_3$ (30 cm^3) was added to the reaction mixture and the residue was extracted with Et_2O (3 × 30 cm^3). The combined organic layers were washed successively with water (30 cm^3) and brine (30 cm^3), dried ($MgSO_4$) and evaporated. Purification of the residue by TLC on silica gel (1:1 *n*-hexane:ether) gave a yellow oil, 40% yield, the acylsilane **10** (R_f = 0.43). FTIR (KBr, cm^{-1}): 3032 (Ar), 2957 (CH), 1705 (CO), 1607–1418 (Ar), 1254 and 844 (C–Si); ^1H NMR (400 MHz, $CDCl_3$): δ 0.10 (s, 18H, $SiMe_3$), 3.80 (s, 4H, CH_2), 7.20 (m, 4H, Ar); *m*/*z* (EI): 307 (100%, $[M+1]^+$), 233 (3%, $[M-SiMe_3]^+$), 207 (6%), 73 (15%, $[SiMe_3]^+$).

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