Pergamon

Tetrahedron, Vol. 52, No. 13, pp. 4803-4816, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00148-2

Chemistry of Silyl Thioketones Part 9.[1] A New Selective Synthesis of 1-Silyl-1-Enethiols and of 2-Silyl-Thiacycloalk-2-Enes of Common to Large Ring Size.

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Abstract: ω-Haloacylsilanes **1** were selectively transformed *via* thioacylsilanes into Z-silyl-enethiols **4** with solid sodium hydrogen carbonate or into 2-silylthiacycloalk-2-enes**5** of common to large ring size with solid sodium hydroxide. Compounds **5** underwent protiodesilylation.

Among thiones, silylthioketones[2] are versatile compounds due to the high reactivity of the carbon-sulfur double bond in either nucleophilic or electrophilic addition, in cycloaddition reactions and owing to their synthetic equivalence with thioaldehydes.[2,3a,b] In earlier studies we reported the synthesis and reactivity of aryl[4], methyl[5], tert-butyl[5] and cycloalkyl[6] silyl thioketones. More recently we found that aliphatic enethiolizable alkyl thiones, obtained from the corresponding ω-haloacylsilanes, can be used in a convenient one-pot synthesis of silylated unsaturated sulfur heterocycles.[7] Simple cyclic sulfides with three- to seven-membered rings are commercially available, but more functionalized compounds of interest as synthetic intermediates must be prepared, usually from acyclic materials. The cyclic sulfides with eight or more members are usually prepared by ring expansion methods,[8] due to the difficulties in obtaining medium and large ring systems by direct cyclization. In the preliminary work[7] we showed that the thionation of ω-halo acylsilanes followed by treatment with a base provides a novel method applicable not only to the synthesis of common rings but also to medium rings; thus five- to eight-membered rings have been synthesized in very good yields. These interesting and potentially useful results prompted us to undertake more systematic investigations on the synthetic transformations of these sulfur heterocycles which combine both vinylsilane and vinylsulfide functional groups. Herein we report the full details of such a systematic study including the result of our preliminary investigation.

Results and discussion

A number of satisfactory methods are known for the preparation of acylsilanes.[9a,b] For the synthesis of **1a** we employed the same conditions used by Danheiser[10] for the synthesis of 2-bromo-1-tert-butyldimethylsilyl-1-ethanone (method A). The ω-haloacylsilanes **1b-e** were synthesized by novel methods through the reaction of commercially available ω-halo acyl chlorides with bis(dimethylphenylsilyl) copper-zinc cyano cuprates (method B)[11] or with bis(dimethylphenylsilyl) copper lithium[6,12] (method C). When the ω-halo acyl chlorides or the corresponding acids were not commercially available, the acylsilanes **1f-h** were prepared according with Brook[13] and Corey[14] procedure (method D) (Scheme 1). Problems were encountered during the silylation of 3-chloro-propanoyl chloride **1b**, Table 1, entry b, with both methods B and C.

Scheme 1

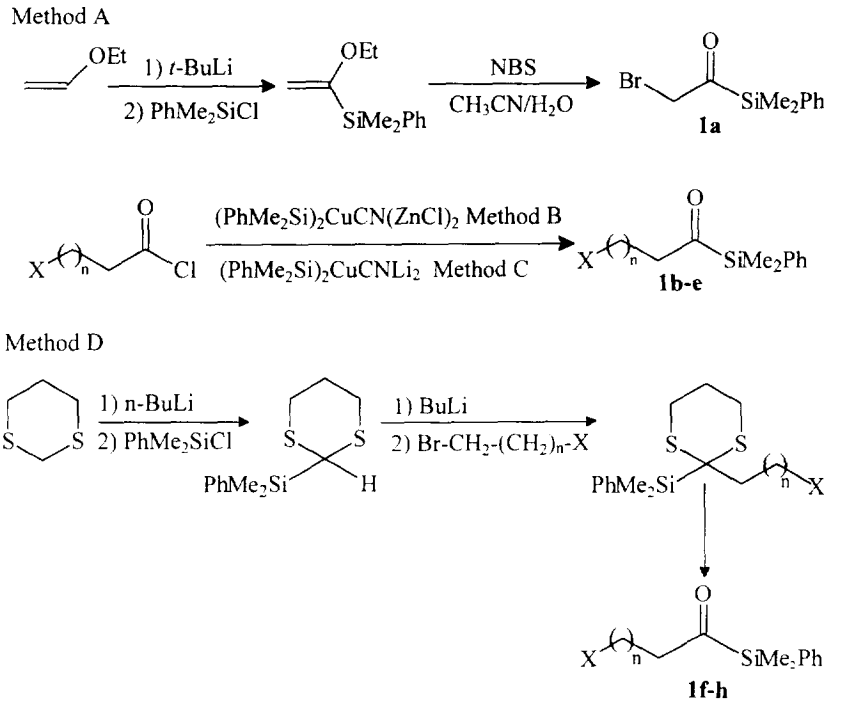


Table 1. Synthesis of acylsilanes **1**.

Entry	n	X	Product	Method	Yield%	Reference
a	0	Br	**1a**	A	91	
b	1	Cl	**1b** *	B,C	30	
c	2	Cl	**1c**	B	70	11
d	3	Cl	**1d**	B	65	11
e	4	Br	**1e**	C	66	12
f	5	Br	**1f**	D	77	
g	9	Br	**1g**	D	50	
h	11	Br	**1h**	D	50	

* contaminated with propenoyldimethylphenylsilane.

^{1}H NMR analysis of the crude mixture showed a 1:1 mixture of the acylsilane **1b** and of the propenoyl dimethylphenylsilane arising from **1b** by loss of hydrogen chloride. Attempts to separate the two products by chromatography on silica failed, and only the partially degraded unsaturated product was obtained. Thionation of **1a-h** was performed with the same procedure as used for aryl[4] and alkyl[5] silylketones, i.e. the acid-catalyzed reaction of acylsilanes dissolved in diethyl ether with hydrogen sulfide. The *gem*-dithiols **3** were obtained, (Scheme 2) from the addition of hydrogen sulphide to the thione **2**. Only in a few cases was there evidence of the presence of the thione as indicated by the blue colour of the solution. *Gem*-dithiols **3c-e** were isolated in quantitative yields by evaporation of the solvent prior to the alkaline treatment and were characterized by ^{1}H NMR. Compounds **3c-e** showed a singlet for the SH resonance at δ 2.15. On standing, by

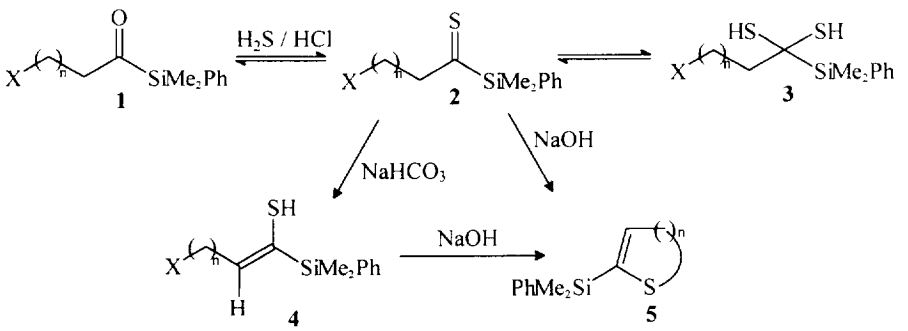
chromatography on silica, or by reaction with base, they were slowly transformed into enethiols **4** or into 2-silyl-thiacycloalk-2-enes **5**, the selectivity of the reaction depending on the base (see below). Generally, the thionation solution was treated directly with a base without isolating the *gem*-dithiols to afford products **4** and/or **5** (Scheme 2). However, upon treatment of the isolated *gem*-dithiols **3** with bases, the blue colour of the thione **2** was observed in several cases. This is in line with the role played by thiones as precursors of enethiols **4**. It is worth noting the different behaviour of the various bases. Solid sodium hydrogen carbonate led selectively to the (Z)-enethiols **4c-h** in good to quantitative yield (Table 2).

Table 2. Synthesis of enethiols and their relevant NMR data ($CDCl_3$, 200MHz).

n	X	Product	Yield%	δ CH= (t)	δ SH (s)
2	Cl	**4c**	87	6.05	2.55
3	Cl	**4d**	100	5.95	2.58
4	Br	**4e**	100	5.95	2.55
5	Br	**4f**	100	5.95	2.55
9	Br	**4g**	100	6.05	2.45
11	Br	**4h**	96	5.95	2.45

Enethiols, usually obtained as mixtures with their isomeric thioketones[15], were only recently prepared in pure form.[16] The quantitative enethiolization of silylthioketones could be due to the presence of the silyl group which enhances the acidity of the hydrogen α to the thiocarbonyl group; this behavior has also been observed for the corresponding carbonyl compounds.[17] The determination of the Z-configuration to the enethiols was performed by n.O.e. experiments.

Scheme 2



On the other hand, treatment of the thionation solution directly with sodium hydroxide led to the formation of 2-silyl-thiacycloalk-2-enes **5c-e** (Scheme 2) in quantitative yields (table 3). The low yield (35%) obtained in the formation of the eight-membered ring **5f** is due to the fact that in this case the reaction is more sluggish and prone to give competing side reactions, especially dimerization. Through the use of the high dilution technique these difficulties could be circumvented and eight-**5f**, twelve-**5g** and fourteen-**5h**-membered rings have been synthesized in 65, 71 and 63% yield respectively, by adding the isolated enethiols **4f**, **4g** and **4h** to a suspension of solid sodium hydroxide in diethyl ether over eight hours (see experimental). The stereochemistry of the cyclization reaction is also interesting. As it might be expected from the well-known relative thermodynamic stability,[18] the eight-membered ring was formed exclusively as the Z-isomer as can be seen from its ^1H NMR spectrum where only one triplet for the olefinic proton was observed. The

twelve- **5f** and fourteen- membered **5g** rings were obtained as mixtures of E and Z isomers in 1:1 and 7:3 ratios, respectively as shown by ^{1}H NMR spectra and n.O.e. experiments (see experimental).

Table 3. Synthesis and relevant NMR data ($CDCl_3$ 200MHz) of 2-silyl-thiacycloalk-2-enes **5**.

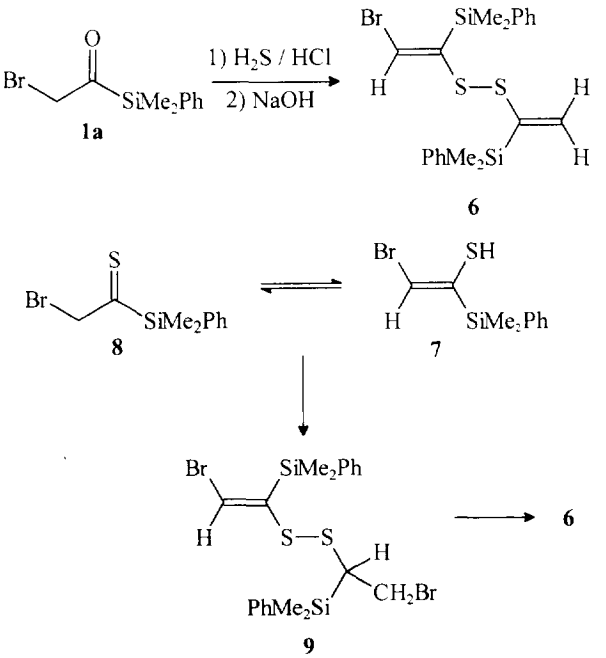
n	Product	Yield%	δ CH= (t)	J (Hz)	E : Z
2	**5c**	100	5.8	2.8	
3	**5d**	100	6.0	4.4	
4	**5e**	100	6.5	6.5	
5	**5f**	65[a]	6.5	7.8	
9	**5g**	71[a]	6.3	7.1	1 : 1
			6.4	6.8	
11	**5h**	63[a]	6.31[b]	6.6	2.4 : 1
			6.32[b]	5.9	

a high dilution technique.

b in C_6D_6.

The cyclization reaction could also be performed in the presence of solid sodium carbonate, although the reaction appeared to be less selective. Complete cyclization (100% yield) occurred only for **5c** whereas mixtures of cyclic compounds **5** and enethiols **4**, whose ratio depended on the reaction time and on ring size, were obtained in all the other cases. Thionation of acylsilane **1a** followed by treatment with solid sodium hydroxide gave the disulfide **6** as the only product in 78% yield. This result can be explained in terms of a thiophilic addition of the enethiol form **7** to another molecule of the thione **8** to give product **9** which loses HBr to give **6** (Scheme 3). This type of reaction has been demonstrated by us in the case of methyltrimethylsilyl thioketones.[5]

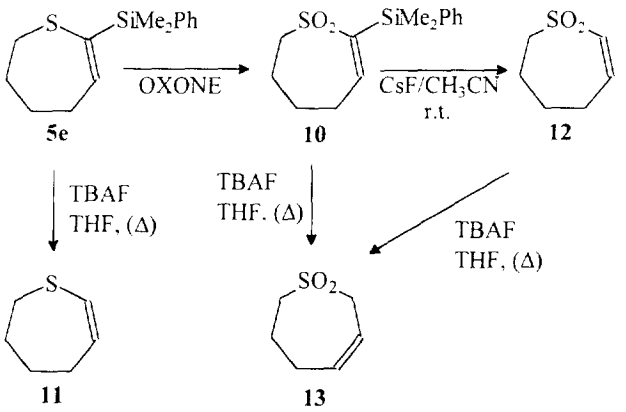
Scheme 3



The thionation reaction of **1b** contaminated with propenoylsilane followed by treatment with solid sodium hydroxide failed to yield the desired four membered ring to any detectable extent. Different thionation methodologies for the thionation of ω-haloacylsilanes **1** were also employed. Compound **1e**, taken as a model compound, was treated with Lawesson Reagent (LR) in boiling toluene[19] to give the enethiol **4e** contaminated with other products (probably disulfides) as demonstrated by ^{1}H NMR of the crude mixture. Addition of solid sodium hydroxide to the crude mixture dissolved in diethyl ether gave, after preparative chromatography on silica, 2-dimethylphenylsilyl-thiacyclohept-2-ene **5e** in 60% yield. The same acylsilane **1e** treated with P_4S_{10} and $NaHCO_3$[20] in THF at room temperature gave the *gem*-dithiol **3e** in 70% yield, while this product treated with sodium hydroxide gave **5e** in 78% yield after chromatography. As far as the mechanism of the cyclization is concerned, we propose that the reaction occurs *via* an intramolecular nucleophilic substitution of the enethiol form on the carbon bearing a good leaving group in the ω-position.

All the products **5** reported herein can be used as starting materials for other useful transformations. As model compounds we used the product **5e** and its corresponding sulfone **10** obtained in 97% yield by oxidation with oxone (potassium hydrogen persulfate).

Scheme 4



The protiodesilylation reactions deserve special attention. The reaction of **5e** with TBAF in boiling THF for 12 hours gave product **11**[21] in 55% yield. Protiodesilylation of the silyl sulfone **10** depends on the reaction conditions: reaction with CsF in CH_3CN at room temperature gave the corresponding α,β-unsaturated sulfone **12** in 70% yield, and with TBAF in boiling THF gave the β,γ-unsaturated derivative **13** (60% yield). **12** Could also be converted to **13** by reaction with TBAF in boiling THF. The products **12** and **13** were characterized by analytical and spectral data. In particular, the presence of two double triplets at 6.10 and 6.48 in the ^{1}H NMR spectrum of **12** is typical of two vinylic protons coupled with an allylic CH_2, while on the contrary the presence of two multiplets (six triplet each) at 5.73 and 6.10 in the ^{1}H NMR spectrum of **13** is in agreement with two vinylic protons coupled with two allylic CH_2.

Conclusion

A new cyclization procedure providing an easy one-pot access to unsaturated 2-silyl sulfur heterocycles has been applied to the synthesis of five- to fourteen-membered rings in quantitative to good yields. The use of the dilute solution technique is advantageous in the synthesis of eight-membered and larger rings. It is worth noting the possibility to stop the reaction at the stage of the formation of Z-enethiols which can be fully

characterized. Heterocycles **5,** combining both vinylsilane and vinylsulfide functional groups, provide a handle for useful transformations.

Experimental Section.

B.p.s. and m.p.s. are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded with a Varian Gemini 200 spectrometer as solutions in $CDCl_3$: chemical shifts (δ) are given in ppm relative to tetramethylsilane TMS. J values are given in Hz. ^{13}C NMR spectral assignments were made by DEPT. Mass spectra were obtained using a VG 7070-E (EI, 70 Ev) spectrometer. IR spectra were recorded on a Perkin Elmer model 257 grating spectrometer. Reactions were conducted in oven-dried (120 °C) glassware under a positive argon atmosphere. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes. THF and Et_2O were distilled from sodium benzophenone just prior to use and stored under argon. CH_2Cl_2 was passed though basic alumina and distilled from CaH_2 just prior to use. All chemicals were used as obtained or purified by distillation as needed. Sodium hydrogen carbonate 99% was purchased from Aldrich; sodium hydroxide RPH anhydrous pearls was purchased from Carlo Erba Reagenti. The reactions were monitored by TLC performed on silica gel plates (Baker-flex IB2-F). Column chromatography was performed with Merk silica gel 60 (70-230 mesh) and preparative thick layer chromatography was carried out on glass plates using a 10 mm layer of Merk silica gel 60 Pf_{254} or aluminium oxide F_{254}. Light petroleum refers to the fraction with b.p. 40-60 °C. In the characterization of the new compounds, elementar analysis has been performed for crystalline products. Oily products, because of the small scale used for the preparation, have been characterized by accurate mass measurements.

Synthesis of ω-halo acylsilanes.

Method A

1-Dimethylphenyl-1-ethoxy-vinyl silane

A solution of *t*-Butyllithium (1.7 M in pentane, 25 ml, 42.5 mmol) was added slowly to a solution of ethyl vinyl ether (5 ml, 52.5 mmol) in anhydrous THF (25 ml) under argon atmosphere at -78 °C. The mixture was allowed to warm to 0 °C and was stirred for 30 min. at this temperature. The solution was then cooled to -78 °C and dimethylphenyl chloro silane (5 ml, 29.9 mmol) in THF (5 ml) was then added. The mixture was stirred at room temperature for 12 h. The reaction was quenched with saturated aqueous ammonium chloride, and extracted with diethyl ether. The organic layer was dried and concentrated under reduced pressure giving the title product (6.0 g, 55%) as an oil. ^1H NMR (200 MHz, $CDCl_3$): δ 0.55 (s, 6H, $SiMe_2$), 1.40 (t, J = 6.5 Hz, 3H, CH_3), 3.90 (q, J = 6.5 Hz, 2H, OCH_2), 4.50 (δ, J = 3.0 Hz, 1H, CH=), 4.80 (s, 1H, CH=), 7.50 (m, 3H, ArH), 7.70 (m, 2H, ArH); MS: m/z 206 (M^+), 177 ($M^+ - C_2H_5$), 135 ($PhMe_2Si^+$), 105 ($PhSi^+$); HRMS: m/z for $C_{12}H_{18}OSi$ found M^+, 206.1131; calcd M, 206.117.

Bromoacetyl dimethylphenyl silane 1a

1-Dimethylphenyl-1-ethoxy-vinyl silane (2.5 g, 12.1 mmol) was added slowly to a solution of N-bromosuccinimide (NBS) (2.4 g, 13.5 mmol) in CH_3CN (70 ml) and H_2O (3.5 ml) at -40 °C. After 2 h the temperature was allowed to warm to -10 °C and the reaction was then stirred for 1 h. The mixture was quenched with water and extracted with pentane. The organic layer was dried and concentrated under reduced pressure giving the title product (2.3 g, 91%) as an oil. IR (neat) ν_{max}: 1645 (SiC=O), 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 830 $SiMe_2$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.60 (s, 6H, $SiMe_2$), 4.15 (s, 2H, CH_2C=O), 7.35-7.65 (m, 5H, ArH); MS: m/z 216 ($M^{+81}Br - CH_2CO$), 214 ($M^{+79}Br - CH_2CO$), 201 (216 - CH_3), 199 (214 - CH_3), 177 ($M^{+81}Br$, $M^{+79}Br$ - 79), 163 ($M^{+81}Br$, $M^{+79}Br$ - 95), 135 ($PhMe_2Si^+$).

Method B

3-Chloropropanoyl-dimethylphenyl silane 1b

3-Chloropropanoyl chloride (430 mg, 0.32 ml, 3.4 mmol), in anhydrous THF (2 ml), was added slowly to bis(dimethylphenylsilyl)copper-zinc cyano cuprate[11] (4.0 mmol) at -20 °C under argon. After 15 min. the temperature was allowed to warm slowly to room temperature and the reaction was then stirred for 15 h. The mixture was quenched with saturated aqueous ammonium chloride, and extracted with diethyl ether. The organic layer was dried and concentrated under reduced pressure. An NMR analysis of the reaction mixture showed the presence of **1b** and propenoyl dimethylphenyl silane in a 1:1 ratio (60% yield). **1b:** ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.60 (s, 6H, $SiMe_2$), 2.70 (m, 2H, $CH_2C{=}O$), 3.65 (t, 2H, CH_2Cl), 7.30-7.65 (m, 5H, ArH). **Propenoyl dimethylphenyl silane:** ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.55 (s, 6H, $SiMe_2$), 6.00 (dd, J_1 = 17.5 Hz, J_2 = 10 Hz, 2H, CH_2=), 6.55 (dd, J_1 = 17.5 Hz, J_2 = 10 Hz, 1H, CH=). Chromatography on silica gel using 10 : 1 light petroleum-diethyl ether as eluent, gave only the unsaturated product.

Method C

3-Chloropropanoyl choride (504 mg, 0.38 ml, 4.0 mmol), in anhydrous THF (2 ml), was slowly added to bis(dimethylphenylsilyl)copper-cyano cuprate[22] (4 mmol) at -78 °C under argon. The mixture was stirred at -78 °C for 1 h, then was allowed to warm to 0 °C and was stirred for 1 h at 0 °C. The mixture was quenched with saturated aqueous ammonium chloride, and extracted with diethyl ether. The organic layer was dried and concentrated under reduced pressure. An NMR analysis of the reaction mixture showed the presence of both **1b** and propenoyl dimethylphenyl silane in a 1:1 ratio.

Synthesis of ω-haloacylsilanes 1f-h (general procedure) Method D

2-Dimethylphenylsilyl-1,3-dithiane

A solution of *n*-butyllithium (1.6M in hexane, 34.4 ml, 55 mmol) was added at -35 °C under argon atmosphere to a solution of 1,3-dithiane (6.0 g, 50 mmol) in anhydrous THF (200 ml). The reaction was stirred at -15 °C for 2 h, then after warming to 0 °C, dimethylphenylchloro silane (10 ml, 60 mmol) in anhydrous THF (50 ml) was added over 30 min. The resulting mixture was maintained at 15 °C for 12 h. The mixture was quenched with saturated aqueous ammonium chloride, and extracted with diethyl ether. The organic layer was dried and concentrated under reduced pressure. The crude was crystallized from EtOH giving the 2,2-bis(dimethylphenyl silyl)-1,3-dithiane. Chromatography of the mother liquor on silica using 20:1 light petroleum-diethyl ether as eluent gave 2-dimethylphenylsilyl-1,3-dithiane (6.4 g, 50%) as an oil; IR (neat) ν_{max}: 1430 (SiPh), 1240 ($SiMe_2$), 1110 (SiPh), 830 ($SiMe_2$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.45 (s, 6H, $SiMe_2$), 2.10 (m, 2H, CH_2), 2.65 (m, 2H, CH_2), 2.80 (m, 2H, CH_2), 3.85 (s, 1H, S-C(S)-H), 7.35 (m, 3H, ArH), 7.50 (m, 2H, ArH); MS: m/z 254 (M^+), 135 ($PhMe_2Si^+$), 119 (M^+ - $PhMe_2Si$), 105 ($PhSi^+$), 87 (119-S); HRMS: m/z for $C_{12}H_{18}S_2Si$ found M^+, 254.0617; calcd M, 254.0619.

ω-Haloalkanoyl-dimethylphenyl silane

A solution of *n*-butyllithium (1.6M in hexane, 4.1 ml, 6.6 mmol) was added at -35 °C to a solution of 2-dimethylphenylsilyl-1,3-dithiane (1.5 g, 6.0 mmol) in anhydrous THF (30 ml) under argon atmosphere. After 2 h the mixture was cooled to -78 °C and the α,ω-dibromo alkane (13.2 mmol) in anhydrous THF (20 ml) was added. The mixture was slowly warmed to room temperature. After 12 h the reaction was quenched with saturated aqueous ammonium chloride, and extracted with diethyl ether. The organic layer was dried and concentrated under reduced pressure giving the crude 2-dimethylphenylsilyl-2-ω-bromoalkyl-1,3-dithiane. This product (3.6 mmol) was added to 3.2 g (18 mmol) of cadmium carbonate suspended in a solution of 5.0 g (18 mmol) of mercuric chloride dissolved in 73.5 ml of acetone, 17 ml of benzene and 0.7 ml of water. The mixture was stirred under argon atmosphere till the disappearance of the starting 2-dimethylphenylsilyl-2-ω-

bromoalkyl-1,3-dithiane. The mixture was filtered and the organic layer was dried and concentrated under reduced pressure. Chromatography on silica gel using 20:1 light petroleum-diethyl ether as eluent gave the ω-halo acylsilane.

7-Bromoheptanoyl dimethylphenyl silane 1f

Oil. Yield 55%. IR (neat) ν_{max}: 1645 (SiC=O), 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 830 ($SiMe_2$), 730 (C-Br) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.50 (s, 6H, $SiMe_2$), 1.10-1.50 (m, 6H, CH_2), 1.75 (m, 2H, CH_2), 2.50 (t, J = 7.5 Hz, 2H, CH_2C=O), 3.35 (t, J = 6.0 Hz, 2H, CH_2Br), 7.45 (m, 3H, ArH), 7.55 (m, 2H, ArH); MS: m/z 325 (M^+ - 1), 311 (M^+ - CH_3), 259 (M^+ - C_4H_9), 199 (M^+ - $C_8H_{15}O$), 163 ($PhMe_2SiCO$), 135 ($PhMe_2Si$), 105 (PhSi).

11-Bromoundecanoyl dimethylphenyl silane 1g

Oil. Yield 50%. IR (neat) ν_{max}: 1645 (SiC=O), 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 830 ($SiMe_2$), 730 (C-Br) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.50 (s, 6H, $SiMe_2$), 1.15-1.55 (m, 14H, CH_2), 1.80-2.00 (m, 2H, CH_2), 2.55 (t, J = 7.5 Hz, 2H, CH_2C=O), 3.45 (t, J = 6.0 Hz, 2H, CH_2Cl), 7.40 (m, 3H, ArH), 7.55 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -4.82 ($SiMe_2$), 22.00, 28.00, 28.56, 29.02, 29.18, 32.67, 33.81, 48.66 (CH_2), 127.99, 129.68, 133.82 (ArCH), 134.40 (ArC), 246.00 (C=O); MS: m/z 269 (M^+ - C_8H_{17}), 212 (269 - C_4H_9), 199 (269 - C_5H_{10}), 191, 163 ($PhMe_2SiCO$), 135 ($PhMe_2Si$), 105 (PhSi).

13-Bromotridecanoyl dimethylphenyl silane 1h

Oil. Yield 40%. IR (C_2Cl_4) ν_{max}: 1640 (SiC=O), 1430 (SiPh), 1240 ($SiMe_2$), 1110 (SiPh), 830 ($SiMe_2$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.50 (s, 6H, $SiMe_2$), 1.10-1.50 (m, 18H, $(CH_2)_9$), 1.85 (m, 2H, CH_2), 2.65 (t, J = 7.2 Hz, 2H, CH_2C=O), 3.45 (t, J = 6.7 Hz, 2H, CH_2Br), 7.40 (m, 2H, ArH), 7.60 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -4.25 ($SiMe_2$), 22.64, 23.07, 28.65, 29.24, 29.70, 29.88, 29.92, 29.98, 30.10, 33.34, 34.36 (CH_2), 49.32 (CH_2Br), 128.59, 130.29, 134.44 (ArCH), 135.07 (ArC), 247.00 (C=O); MS: m/z 410(M^+), 395 (M^+ - CH_3), 381 (M^+ - C_2H_5), 367 (M^+ - C_3H_7), 353 (M^+ - C_4H_9), 332 (M^+ - C_6H_6), 269 ($PhMe_2SiC_4H_7$), 163 ($PhMe_2SiCO$), 135 ($SiMe_2Ph$); HRMS: m/z for $C_{21}H_{35}BrOSi$ found M^+ 410.1642; calcd M, 410.1641.

Synthesis of *gem*-dithiols 3

Hydrogen chloride and hydrogen sulfide were bubbled into a solution of the acyl silane (1.0 mmol) in anhydrous diethyl ether (50 ml) at -30 °C, until the starting ketone had disappeared (TLC with 10:1 light petroleum-diethyl ether as eluent). In some case, it was possible to see the blue colour characteristic of the thioketone that quickly faded. The mixture was allowed to warm to room temperature and concentrated under reduced pressure. The *gem*-dithiols were characterized, without further purification, by ^1H NMR.

4-Chloro-1-dimethylphenylsilyl-1,1-butane dithiol 3c

^1H NMR (200 MHz, $CDCl_3$): δ 0.55 (s, 6H, $SiMe_2$), 1.85-2.00 (m, 2H, CH_2), 2.05-2.25 (m, 2H, CH_2), 2.15 (s, 2H, SH), 3.55 (t, J = 8.5 Hz, 2H, CH_2Cl), 7.20-7.80 (5H, m, ArH); MS: m/z 290 (M^+), 221 (M^+ - HCl - HS), 178 (221 - C_3H_7), 135 ($PhMe_2Si^+$).

5-Chloro-1-dimethylphenylsilyl-1,1-pentane dithiol 3d

^1H NMR (200 MHz, $CDCl_3$): δ 0.55 (s, 6H, $SiMe_2$), 1.8 (m, 6H, CH_2), 2.15 (s, 2H, SH), 3.5 (m, 2H, CH_2Cl), 7.30-7.50 (m, 3H, ArH), 7.60-7.80 (m, 2H, ArH).

6-Bromo-1-dimethylphenylsilyl-1,1-hexane dithiol 3e

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.55 (s, 6H, $SiMe_2$), 1.25-1.48 (m, 2H, CH_2), 1.55-1.75 (m, 2H, CH_2), 1.72-1.95 (m, 4H, CH_2), 2.12 (s, 2H, SH), 3.38 (t, J = 9.5 Hz, CH_2Br), 7.20-7.80 (5H, m, ArH).

General method for the Synthesis of Z-ω-halo-1-dimethylphenylsilyl-alk-1-enethiols 4

Solid sodium hydrogen carbonate was added to the thionation solution until the evolution of carbon dioxide ceased, then the reaction was left overnight. The crude, filtered and concentrated under reduced pressure, gave the Z-enethiol. If the reaction time, after the neutralization, was shorter (few hours), the NMR spectrum showed the presence of the enethiol and of the corresponding *gem*-dithiol in different ratio depending on the reaction time.

(Z)-4-Chloro-1-dimethylphenylsilyl-but-1-enethiol 4c

Starting from 4-chlorobutanoyl dimethylphenyl silane[11] the title compound[6] was obtained as an oil in 87% yield. IR (CCl_4) ν_{max}: 2560 (SH), 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 850 ($SiMe_2$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.45 (s, 6H, $SiMe_2$), 2.55 (s, 1H, SH), 2.70 (dd, $J_1 = J_2 = 7.0$ Hz, 2H, allylic-H), 3.60 (t, J = 7.0 Hz, 2H, CH_2Cl), 5.95 (t, J = 6.4 Hz, 1H, CH=), 7.35 (m, 3H, ArH), 7.60 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -3.56 ($SiMe_2$), 33.33, 42.89 (CH_2), 128.14, 129.78, 134.31 (ArCH), 132.05 (ArC), 134.98 (CH=); MS: m/z 255 (M^+ - 1), 220 (M^+ - HCl), 178 (M^+ - C_6H_6), 135 ($PhMe_2Si^+$), 105 ($PhSi^+$). Irradiation of the dimethylsilyl signal at 0.45 ppm produced a significant increase (19%) of the intensity of the signal of the vinylic proton at 5.95 ppm and of the signal at 2.55 (SH 12%). An attempt of purification of **4c** by preparative thick layer chromatography, using light petroleum as eluent, caused cyclization to **5c** and the formation of a product having a signal at δ 6.25 that probably was a disulfide. For this reason the other enethiols were characterized without purification.

(Z)-5-Chloro-1-dimethylphenylsilyl-pent-1-enethiol 4d

Starting from 5-Choropentanoyl dimethylphenyl silane[11], the title compound[7] was obtained as an oil in 100% yield. IR (neat) ν_{max}: 2560 (SH), 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 830 ($SiMe_2$) cm^{-1}.

(Z)-6-Bromo-1-dimethylphenylsilyl-hex-1-enethiol 4e

Starting from 6-bromohexanoyl dimethylphenyl silane[12], the title compound was obtained as an oil in 100% yield. IR (neat) ν_{max}: 2560 (SH), 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 850 ($SiMe_2$), 730 (C-Br) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.50 (s, 6H, $SiMe_2$), 1.65 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), 2.25 (m, 2H, allylic-H), 2.55 (s, 1H, SH), 3.45 (t, J = 6.5 Hz, 2H, CH_2Br), 5.95 (t, J = 6.6 Hz, 1H, CH=), 7.40 (m, 3H, ArH), 7.60 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -3.52 ($SiMe_2$), 26.76, 29.33, 32.10, 33.42 (CH_2), 128.03, 129.58, 134.22 (ArCH), 129.20 (ArC), 136.35 (C=), 139.33(CH=); MS: m/z 250 (M^+- C_6H_6), 135 ($PhMe_2Si^+$), 105 (PhSi).

(Z)-7-Bromo-1-dimethylphenylsilyl-hept-1-enethiol 4f

Starting from 7-bromoheptanoyl dimethylphenyl silane **1f** the title compound was obtained as an oil in 100% yield. IR (CCl_4) ν_{max}: 2560 (SH), 1590, 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 840 ($SiMe_2$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.45 (s, 6H, $SiMe_2$), 1.50 (m, 4H, CH_2), 1.90 (m, 2H, CH_2), 2.25 (m, 2H, CH_2), 2.55 (s, 1H, SH), 3.45 (t, J = 7.5 Hz, 2H, CH_2Br), 5.95 (t, J = 6.6 Hz, 1H, CH=), 7.45 (m, 3H, ArH), 7.55 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ -3.42 ($SiMe_2$), 27.45, 27.62, 29.55, 30.11, 32.40, 33.67 (CH_2), 128.10, 129.64, 134.32 (ArCH), 128.75 (ArC), 136.56 (C=), 139.99 (CH=); MS: m/z 264 (M^+ - C_6H_6), 135 ($PhMe_2Si$), 105 (PhSi).

(Z)-11-Bromo-1-dimethylphenylsilyl-undec-1-enethiol 4g

Starting from 11-bromoundecanoyl dimethylphenyl silane **1g** the title compound was obtained as an oil in 100% yield. IR (CCl_4) ν_{max}: 2560 (SH), 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 850 ($SiMe_2$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.55 (s, 6H, $SiMe_2$), 1.30-1.60 (bs, 12H, CH_2), 1.85-2.00 (m, 2H, CH_2), 2.20-2.40 (m, 2H, CH_2), 2.45 (s, 1H, SH), 3.45 (t, J = 7.5 Hz, 2H, CH_2Br), 6.05 (t, 1H, J = 6.60 Hz, CH=), 7.45 (m, 3H, ArH), 7.60 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, C_6D_6): δ -2.60 ($SiMe_2$), 28.79, 29.30, 29.40, 30.06, 31.37, 33.47, 34.15 (CH_2), 127.95, 130.18, 134.96 (ArCH), 129.42 (ArC), 137.11 (C=), 140.86 (CH=); MS: m/z 320 ($M^+ - C_6H_6$), 318 (M^+ - HBr), 263 (M^+- $SiMe_2Ph$), 135 ($PhMe_2Si$), 105 (PhSi).

(Z)-13-Bromo-1-dimethylphenylsilyl-tridec-1-enethiol 4h

Starting from 13-bromotridecanoyl dimethylphenyl silane **1h** the title compound was obtained as an oil in 96% yield. IR (neat) ν_{max}: 2550 (SH), 1430 (PhSi), 1250 ($SiMe_2$), 1110 (SiPh), 850 ($SiMe_2$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$); δ 0.40 (s, 6H, $SiPhMe_2$), 1.20-1.35 (M, 16H, $(CH_2)_8$), 1.82 (m, 2H, CH_2), 2.18 (q, J = 7.5 Hz, 2H, CH_2), 2.45 (s, 1H, SH), 3.38 (t, J = 6.0 Hz, 2H, CH_2Br), 5.95 (t, J = 6.5 Hz, 1H, CH=), 7.35 (m, 2H, ArH), 7.55 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -3.22 ($SiMe_2$), 28.12, 28.48, 28.71, 29.37, 29.38, 30.53,32.78, 33.96 (CH_2), 127.87, 129.38, 134.11 (ArCH), 129.71 (ArC), 136.31 (C=), 140.55 (CH=); MS: m/z 348 ($M^+ - C_6H_6$), 268 (M^+- C_6H_6 - HBr), 135 ($SiMe_2Ph$).

General method for the Synthesis of 2-Silyl-thiacyclo alk-2-enes 5 (one-pot synthesis from acylsilanes)

Solid sodium hydroxide was added to the thionation solution untill neutralization, checked by universal indicator paper (pH 1-11), then left overnight. The mixture was filtered and concentrated under reduced pressure. The residue gave **5** as the only products. Purification can be performed by chromatography on silica (9:1 light petroleum:diethyl ether as eluent) or by crystallization.

2-Dimethylphenylsilyl-thiacyclo pent-2-ene 5c

5c[6]: oil, 100% yield.

2-Dimethylphenylsilyl-thiacyclo hex-2-ene 5d

5d[7]: oil, 100% yield; IR (neat) ν_{max}: 1560, 1430 (SiPh), 1250 ($SiMe_2$), 1120 (SiPh), 830 ($SiMe_2$) cm^{-1}; HRMS: m/z for $C_{13}H_{18}SSi$ found M^+, 234.0887; calcd M, 234.0898.

2-Dimethylphenylsilyl-thiacyclo hept-2-ene 5e

5e[7]: oil, 100% yield; IR (neat) ν_{max}: 1740, 1590, 1430 (SiPh), 1250 ($SiMe_2$), 1120 (SiPh), 830 ($SiMe_2$) cm^{-1} HRMS: m/z for $C_{14}H_{20}SSi$ found M^+, 248.1047; calcd M, 248.1055.

General method for the synthesis of 2-Silyl-thiacyclo alk-2-enes 5 under high dilution conditions

A solution of (Z)-enethiol (1 mmol) in anhydrous diethyl ether (150 ml) was added over 12 h to a stirred suspension of solid sodium hydroxide (0.1 mol) in anhydrous diethyl ether (100 ml) at room temperature. After the disappearance of the starting product, the solution was filtered and concentrated under reduced pressure and the residue gave the 2-silyl-thiacyclo alk-2-ene.

2-Dimethylpheny silyl-thiacyclo oct-2-ene 5f

5f[7]: solid under 25 °C, 65% yield; IR (neat) ν_{max}: 1430 (SiPh), 1250 ($SiMe_2$), 1120 (SiPh), 830 ($SiMe_2$) cm^{-1}; HRMS: m/z for $C_{15}H_{22}SSi$ found M^+, 262.1212; calcd M, 262.1211.

2-Dimethylphenylsilyl-thiacyclo dodec-2-ene 5g

Yield 70%. The ^{1}H NMR of the crude revealed a mixture of Z and E isomers in a 1: 1 ratio (two triplets at 6.30 and 6.40 for the vinylic proton). Chromatography on silica (20:1 light petroleum:diethyl ether as eluent) gave as the higher R_f fraction a mixture of the two isomers enriched of E isomer and as the lower R_f fraction the pure Z isomer as a waxy product: further purification of the E isomer was performed by preparative thick layer chromatography (20:1 light petroleum:diethyl ether as eluent). The configuration of the isomers was elucidated by n.O.e. experiments on the two separated isomers. Saturation of the $SiMe_2$ resonance produced a significant increase (13%) in the intensity of the vinylic proton signal for the isomer with the vinylic H at 6.4 ppm. A minor enhancement (7%) was found for the signal at 6.3 ppm of the other isomer. For these reasons we assign the Z configuration at the isomer with vinylic H at 6.4 ppm.

(E)-5g: waxy product; IR (CCl_4) ν_{max}: 1560, 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 830 ($SiMe_2$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.45 (s, 6H, $SiMe_2$), 1.10-1.30 (m, 10H, CH_2), 1.40-1.60 (m, 4H, CH_2), 2.40 (m, 2H, CH_2), 2.55 (dd, J_1 = 5.0 Hz, J_2 = 6.5 Hz, 2H, CH_2), 6.30 (t, 1H, J = 7.1 Hz, CH=), 7.35 (m, 3H, ArH), 7.55 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -2.27 ($SiMe_2$), 28.54, 28.89, 29.43, 29.70 , 29.95, 30.73, 34.56 (CH_2), 127.70, 129.01, 133.94 (ArCH), 133.14 (ArC), 138.53 (C=), 152.67 (CH=); MS: m/z 318 (M^+), 303 (M^+ - CH_3), 240 (M^+ - C_6H_6), 183 (M^+ - $SiMe_2Ph$), 153, 135, ($PhMe_2Si^+$), 105 ($PhSi^+$); HRMS: m/z for $C_{19}H_{30}SSi$ found M^+, 318.1829; calcd M, 318.1837.

(Z)-5g: waxy product; IR (neat) ν_{max} : 1560, 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 830 ($SiMe_2$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.50 (s, 6H, $SiMe_2$), 1.40 (bs, 14H, CH_2), 2.30-2.60 (m, 4H, CH_2), 6.40 (t, 1H, J = 6.8 Hz, CH=), 7.35 (m, 3H, ArH), 7.55 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -1.77 ($SiMe_2$), 22.19, 22.30, 24.69, 25.54, 25.75, 26.44, 27.54, 33.96 (CH_2), 127.65, 128.94, 133.85 (ArCH), 138.542 (C=), 152.43 (CH=); MS: m/z 318 (M^+), 303 (M^+ - CH_3), 240 (M^+ - C_6H_6), 183 (M^+ - $SiMe_2Ph$), 153, 135, ($PhMe_2Si^+$), 105 ($PhSi^+$); HRMS: m/z for $C_{19}H_{30}SSi$ found M^+, 318.1841; calcd M, 318.1837.

2-Dimethylphenylsilyl-thiacyclo tetradec-2-ene 5h

Oil. Yield 63%. The ^{1}H NMR (300MHz) of the crude recorded in C_6D_6 showed the presence of two isomers in a 2.4:1 ratio (two triplets at 6.31, J = 6.6 Hz and at 6.32, J = 5.9 Hz for the vinylic proton). The configuration of the two isomers was elucidated from n.O.e. experiments performed on the mixture of the two products: saturation of the methyl resonance at δ 0.45 of the dimethylsilyl group produced a significant increase in the intensity of the vinylic proton signal at δ 6.32 of the Z isomer. The two product were not separated and the ^{1}H NMR, ^{13}C NMR, IR, MS, HRMS spectra were recorded on the mixture of the two isomers. IR (CCl_4) ν_{max}: 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 830 ($SiMe_2$) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.45 (s, 6H, $SiMe_2$), 1.30 (m, 18H, CH_2), 2.42 (t, J = 9.0 Hz, 2H, CH_2). 2.42 (m, 2H, CH_2), 6.30 (t, J = 6.75 Hz, 1H, CH=), 7.35 (m, 2H, ArH), 7.55 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -4.45 ($SiMe_2$ *cis*), -2.25 ($SiMe_2$ *trans*), 24.37, 24.71, 25.19, 25.44, 25.56, 26.64, 27.05, 28.20, 28.56, 28.87, 29.23, 29.42, 29.76, 29.97, 30.75, 31.20, 34.10, 34.54, (CH_2), 127.72, 129.02, 133.96 (ArCH), 133.14 (ArC), 138.52 (C=), 152.20 (CH= *cis*), 152.36 (CH= *trans*); MS: m/z 346 (M^+), 331 (M^+ - CH_3), 135 ($SiMe_2Ph^+$); HRMS: m/z for $C_{21}H_{34}SSi$ found M^+, 346.214; calcd M, 346.2150.

2-Bromo-1-dimethylphenylsilyl-1'-dimethylphenylsilyl-divinyldisulfide 6

Thionation of **1a** followed by treatment with solid sodium hydroxide gave product **6** as an oil in 78% yield, IR (neat) ν_{max}: 1515, 1430 (SiPh), 1250 ($SiMe_2$), 1110 (SiPh), 830 ($SiMe_2$), 730 (C-Br) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.40 (s, 6H, $SiMe_2$), 0.48 (s, 6H, $SiMe_2$), 5.60 (s, 1H, CH=), 6.00 (s, 1H, CH=), 6.35 (s, 1H, CH=) 7.30-7.55 (m, 10H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -2.82 ($SiMe_2$), -1.51 ($SiMe_2$), 116.05 (BrCH=), 121.08 (CH_2=), 127.85, 127.94, 129.48, 129.61, 134.00 (ArCH), 135.78, 138.38, 143.61, 144.66 (C); MS: m/z 464 (M^+), 385 (M^+ - Br), 384 (M^+ - HBr), 250 (385 - $SiMe_2Ph$), 235, 199 ($BrSiMe_2Ph$), 135 ($SiMe_2Ph$), 105 (SiPh); HRMS: m/z for $C_{20}H_{25}BrS_2Si_2$ found M^+, 464.0118; calcd M, 464.0120.

Synthesis of 2-dimethylphenylsilyl-thiacyclo hept-2-ene 5e using Lawesson reagent

A solution of 6-bromohexanoyl dimethylphenyl silane **1e** (624 mg, 2.0 mmol) and Lawesson reagent (960 mg, 2.4 mmol) in anhydrous toluene were heated at reflux until the starting acylsilane disappeared on TLC (30 min.) (30:1 light petroleum-diethyl ether as eluent). The reaction mixture was then cooled to room temperature and filtered. The organic layer was concentrated under reduced pressure. An NMR spectrum of the crude showed the presence of the enethiol **4e** and of other products that probably are disulfides (Z,Z and E,Z) arising from the enethiol ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.40 (s), 0.45 (s), 1.50 (m), 1.8 (m), 2.10 (m), 2.30 (m), 3.12 (t, 2H, CH_2),3.32 (t, 2H, CH_2), 3.40 (t, 2H, CH_2), 5.45 (t, 1H, CH=), 6.08 (t, 1H, CH=), 6.62 (t, 1H, CH=), 7.30-7.60 (m, 15H ArH). The residue was then dissolved in anhydrous diethyl ether (10 ml) and was added to a stirred suspension of solid sodium hydroxide (0.20 mol) in anhydrous diethyl ether (40 ml) at room temperature. After the disappearance of the enethiol, the solution was filtered and concentrated under reduced pressure. Preparative thick layer chromatography (light petroleum as eluent) gave as the higher R_f fraction **5e** (300 mg, 60%) and as the lower R_f fraction fraction a mixture of disulfides (200 mg, 35%) arising from enethiols.

Synthesis of 2-dimethylphenylsilyl-thiacyclo hept-2-ene 5e using P_4S_{10}

A solution of 6-bromohexanoyl dimethylphenyl silane **1e** (624 mg, 2.0 mmol) in anhydrous THF (2 ml) was added to a stirred suspension of P_4S_{10} (1.14 g, 3.0 mmol) and $NaHCO_3$ (1.0 g, 12 mmol) in anhydrous THF (5 ml). The mixture was stirred until the disappearance of the acylsilane (30 min.) (TLC 10:1 light petroleum:diethyl ether as solvent). The reaction mixture was diluted with water and extracted with diethyl ether. The organic layer was dried and concentrated under reduced pressure. The crude was then analysed by NMR and showed the presence of the pure *gem*-dithiol **3e** (507 mg, 1.4 mmol 70%). A solution of **3e** (507 mg) in anhydrous diethyl ether (10 ml) was added to a stirred suspension of solid sodium hydroxide (0.20 mol) in anhydrous diethyl ether (40 ml) at room temperature. After the disappearance of the starting product (the reaction was left overnight), the solution was filtered and concentrated under reduced pressure. Preparative thick layer chromatography (light petroleum as eluent) gave as the higher R_f fraction the 2-dimethylphenylsilyl-thiacyclo hept-2-ene **5e** (270 mg, 78%).

2-Dimethylphenylsilyl-thiacyclo hept-2-ene S,S-dioxide 10

The 2-dimethylphenylsilyl-thiacyclo hept-2-ene **5e** (150 mg, 0.6 mmol) was dissolved in methanol (5 ml) and cooled at 0 °C. Then a solution of oxone ($KHSO_5$, 1.1 g, 1.8 mmol) in water (4 ml) was added. The mixture was allowed to warm to room temperature. After 5 h the reaction was diluted with water and extracted with chloroform. The organic layer was dried and concentrated under reduced pressure. Preparative thick layer chromatography of the crude (7:3 light petroleum-ethyl acetate as eluent), gave **10** (164 mg, 97%) as an oil; IR (CCl_4) ν_{max}: 1430 (SiPh), 1330 (SO_2), 1250 ($SiMe_2$), 1140 (SO_2), 1110 (SiPh), 830 ($SiMe_2$) cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57 (s, 6H, Me_2Si), 1.63 (m, 2H, CH_2), 2.10 (m, 2H, CH_2), 2.58 (m, 2H, CH_2), 3.02 (m, 2H, CH_2), 6.62 (t, J = 7.3 Hz, 1H, CH=), 7.35(m, 2H, ArH), 7.55 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ -1.72 ($SiMe_2$), 24.97, 25.21, 29.97 (CH_2), 56.89 (CH_2SO_2), 128.49, 130.11, 134.74 (ArCH), 136.52 (ArC), 150.91 (C=), 156.01 (CH=); MS: m/z = 265 (M^+ - CH_3), 203 (M^+ - C_6H_5), 145 (M^+ - $SiMe_2Ph$), 135 ($PhMe_2Si^+$).

Thiacyclo hept-2-ene 11[21]

A solution of tetrabutylammonium fluoride (TBAF) in THF (1.0 M, 1.8 ml, 1.8 mmol) was added to a solution of **5e** (150 mg, 0.6 mmol) in THF (6 ml) and a drop of water. The reaction was stirred at reflux temperature for 12 h then was quenched with saturated aqueous ammonium chloride, and extracted with diethyl ether. The organic layer was washed several times with water then dried and concentrated under

reduced pressure, giving the title product (50 mg, 55%). The reaction was also performed using CsF-CH_3CN, but the starting material was recovered unchanged.

Thiacyclo hept-2-ene S,S-dioxide 12

CsF (84 mg, 0.55 mmol) was added to a solution of **10** (150 mg, 0.5 mmol) in CH_3CN (3 ml) and a drop of water. The reaction was stirred at room temperature for 4 h then was quenched with water and extracted with chloroform. The organic layer was dried and concentrated under reduced pressure. Preparative thick layer chromatography of the concentrate (1:1 light petroleum-ethyl acetate as eluent), gave **12** as an oil (52 mg, 67%); IR (neat) ν_{max}: 1620, 1320, 1120 (SO_2) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.78 (m, 2H, CH_2), 2.15 (m, 2H, CH_2), 2.57 (m, 2H, allylic-CH_2), 3.15 (m, 2H, SO_2CH_2), 6.48 (dt., J_1 = 11.2 Hz, J_2 = 0.8 Hz, 1H, SO_2CH=), 6.10 (dt, J_1 = 11.2 Hz, J_2 = 6.9 Hz, 1H, CH_2CH=); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 24.74, 25.11, 28.03, 55.47 (CH_2), 136.595, 144.48 (CH); MS: m/z 146 (M^+), 129 (M^+ - OH), 117 (M^+ - C_2H_5), 101 (117 - O), 81 (M^+ - HSO_2), 67 (81 - CH_2), 53 (C_4H_5), 41 (C_3H_5); HRMS: m/z for $C_6H_{10}O_2S$ found M^+, 146.0399; calcd M, 146.0401.

Thiacyclo hept-3-ene S,S-dioxide 13

A solution of tetrabutylammonium fluoride (TBAF) in THF (1.0 M, 1.5 ml, 1.5 mmol) was added to a solution of **10** (150 mg, 0.5 mmol) in THF (6 ml) and a drop of water. The reaction was stirred at reflux temperature for 12 h then was quenched with saturated aqueous ammonium chloride, and extracted with chloroform. The organic layer was washed several times with water then dried and concentrated under reduced pressure. Preparative thick layer chromatography of the concentrate, (3:7 light petroleum-ethyl acetate as eluent), gave **13** (55 mg, 60%) as a white crystalline product, mp 175-176 °C. IR (CCl_4) ν_{max}: 1330, 1120 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.10 (m, 2H, CH_2), 2.42 (m, 2H, allylic-CH_2), 3.36 (m, 2H, CH_2), 3.85 (d, J = Hz, 2H, $SO_2C\underline{H}_2CH$=), 5.73 (6t, J_1 = 10.7 Hz, J_2 = 7.1 Hz, J_3 = 1.1 Hz, 1H, SO_2CH=), 6.10 (6t, J_1 = 10.7 Hz, J_2 = 6.4 Hz, J_3 = 0.92 Hz, 1H, CH=); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 23.43, 27.10, 52.89, 58.71 (CH_2), 118.74, 137.83 (CH); MS: m/z 146 (M^+), 81 (M^+ - HSO_2), 67 (81 - CH_2), 54 (C_4H_6). Found: C, 63.12; H, 8.83; Calcd C, 63.14; H, 8.83.

A solution of tetrabutylammonium fluoride (TBAF) in THF (1.0 M, 0.33 ml, 0.33 mmol) was added to a solution of **12** (30 mg, 0.11 mmol) in THF (3 ml) and a drop of water. The reaction was stirred at reflux temperature for 12 h then was quenched with saturated aqueous ammonium chloride, and extracted with chloroform. The organic layer was washed several times with water then dried and concentrated under reduced pressure. An ^1H NMR analysis of the crude showed the presence of a mixture of **12** and **13** in a ratio of 2:1.

Financial support of this work by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), Italy, is gratefully acknowledged.

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(*Received in UK* 31 *December* 1995; *revised* 29 *January* 1996; *accepted* 1 *February* 1996)