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Chemistry of Thioacylsilanes Part 11[1]. Cyclic and Open Chain α-Silyl Vinyl Sulfides as Precursors of Thioannulated Cyclopentenones and Thiofunctionalized Enones

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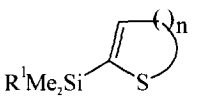
Abstract: Cyclic and open chain α-silyl vinyl sulfides, obtained from thioacylsilanes, react with acid chlorides in the presence of Lewis acid to give thioannulated cyclopentenones and thiofunctionalized enones. The effect of the substituents at silicon on these reactions has been investigated.

Introduction

Previously we demonstrated that enolizable ω-haloacylsilanes can be readily transformed into cyclic α-silyl vinyl sulfides **1** (R^1 = Ph) through thionation and subsequent intramolecular cyclization in the presence of base.[2] In a similar way (Z)-α-silyl vinyl sulfides **2a** and **2b** were synthesized in a stereoselective manner trapping the (Z)-α-silyl enethiols with halides R^2X.[1]



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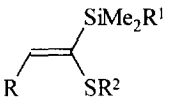


2a R = Ph, R^1 = Me, R^2 = Me
2b R = Et, R^1 = Ph, R^2 = Me

To our knowledge, cyclic α-silyl vinyl sulfides **1**, have not been reported previously. Relatively few synthetic methods for the preparation of open chain α-silyl vinyl sulfides are known;[3a-d] of these, only very few give the products in a stereoselective manner.[4a,b]

α-Silyl vinyl sulfides are interesting compounds as they combine both vinyl silane and vinyl sulfide functional groups with their opposed polarization.[5] The reaction of acid chlorides with these substrates, in the presence of Lewis acids, might in principle give either an ipso substitution of the silyl group due to the β-effect of the silicon[6] or an attack at the β-position directed by the nucleophilicity of the thioether function.

In previous reports only the reactions of 1-arylsulfanyl-1-trimethylsilylethene with cyclic α,β-unsaturated acid chlorides[5] and with open chain acid chlorides[7] were described. In both cases the attack of the electrophile is directed by the sulfur and occurs at the β-position.

Efficient synthesis of annulated cyclopentenone and methods for preparing α,β-unsaturated ketones are a continuous challenge for organic chemists. For this reason we undertook a systematic investigation on the use of trisubstituted olefins **1** and **2** in the reaction with unsaturated and saturated acid chlorides in the presence of Lewis acids. These reactions should lead to thioannulated cyclopentenones and thiofunctionalized α,β-unsaturated ketones. Furthermore, we studied in detail the effect of the substituent R^1 on the silyl moiety.

Results and discussion

The efficient conversion of ω-haloacyldimethylphenylsilanes into five- to fourteen-membered 2-dimethylphenylsilyl thiacycloalk-2-enes **1** (R^1 = Ph) has been reported previously by us.[2] For the synthesis of

the corresponding trimethylsilyl derivatives **1** (R^1 = Me), the ω-haloacyltrimethylsilanes **3a-e** were synthesized *via* alkylation of the commercially available 2-trimethylsilyl-1,3-dithiane with α,ω-dihaloalkanes and subsequent hydrolysis (Scheme 1, Table 1) according to the procedure reported by Tsai and other[8] for the synthesis of **3b**.

Compounds **3** were then converted into products **1** (R^1 = Me) as depicted in Scheme 1, in a one pot reaction of ω-haloacylsilanes with hydrogen sulfide and hydrogen chloride followed by treatment with solid sodium hydroxide. The yields of the cyclization were fairly good for five- to seven-membered rings. The eight-membered ring **1d** (R^1 = Me), however, was obtained in low yield (Table 1).

Scheme 1

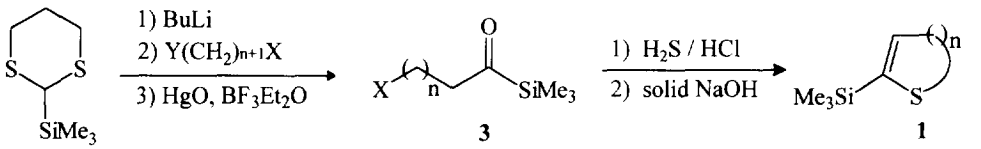


Table1. Synthesis of ω-haloacylsilanes **3** and of 2-trimethylsilyl-thiacycloalk-2-enes **1** (R^1 = Me).

n	X	Y	**3**	Yield of[a] **3** (%)	**1**	Yield[a] of **1** (%)
2	Cl	Br	**a**	36	**a**	67
3	Cl	Br	**b**[8]	76	**b**	82
4	Cl	Br	**c**	65	**c**	92
5	Cl	Br	**d**	75	**d**	8[b]
5	Br	Br	**e**	61	**d**	9[c]

a The yields were determined after chromatography. b The disulfide **6a** was obtained in 55 % yield (vide infra). c The disulfide **6b** was obtained in 20% yield and the dimeric ring product **5** in 25% yield (vide infra).

With the aim of improving the yield of **1d** and studying the byproducts observed, we repeated the procedure already used by us for the synthesis of meso- and macro-cycles.[2] The enethiols **4a** and **4b** were isolated by treatment of the thionation solution of **3d** or **3e** with solid sodium hydrogen carbonate and then these enethiols were added, under high dilution conditions, to a suspension of base (NaOH, Cs_2CO_3) in diethyl ether. (Scheme 2, Table 2).

Scheme 2

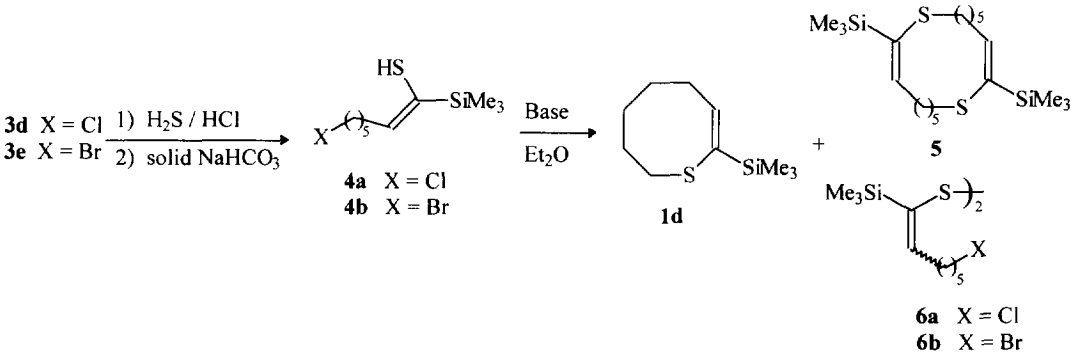


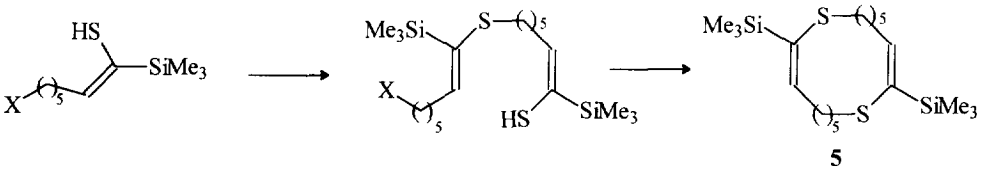
Table 2. Synthesis of 2-trimetilsilyl-thiacyclooct-2-ene **1d** in high dilution conditions.

X	Base	Yield[a] of **1d** (%)	Yield[a] of **5** (%)	Yield[a] of **6** (%)
Cl	NaOH	22	5	45
Br	NaOH	50	13	10
Br	Cs_2CO_3	35	20	10

a The yields were determined after chromatography.

The data in Table 2 reveal that the best yield of **1d** is obtained using NaOH as the base and bromide as the leaving group. In all the experiments performed, the formation of the eight-membered ring **1d** was accompanied by a significant amount of the dimeric ring product **5** and by the disulfide **6** already observed in the one pot reaction. The structure of product **5** was assigned on the basis of its spectral features: the mass spectrum m/z = 400 was indicative of a dimeric ring product; the ^{1}H NMR spectrum showed a symmetric structure with the vinylic protons as a triplet at 6.5 ppm. The *cis* geometry of the double bond was established by n.O.e. experiments (see experimental). The formation of a dimeric ring product is in agreement with other results[9] obtained under high dilution conditions. The formation of product **5** could be rationalized through an intermolecular reaction of the ω-haloenethiol followed by intramolecular cyclization to the 16-membered ring **5** (Scheme 3).

Scheme 3



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The assignment of the structure of product **6a** was predominantly based on the analysis of its ^{1}H NMR spectrum which is very similar to that of the enethiol **4a**. The chemical shift of one of the methylene groups is particularly relevant as it appears as a triplet at 3.55 ppm, typical for a CH_2 bonded to a halogen atom; the mass spectrum m/z = 470 was in agreement with the proposed structure. The geometry of the double bond of **6** was not established. Product **6** probably arises from an oxidative dimerization of the (Z)-α-silylenethiol **4**.

Cyclic α-silyl vinyl sulfides **1** can be considered as the substrates of choice for the synthesis of thioannulated cyclopentenone *via* the so-called Nazarov cyclization.[10] When products **1** were treated with 3,3-dimethylacryloyl chloride in the presence of silver tetrafluoroborate (1.5 equiv) bicyclic enones **7** were isolated (Scheme 4, Table 3). The reactions proceeded in excellent yields in the case of R^1 = Me irrespective of the size of the starting 2-silylthiacycloalk-2-enes. In contrast, very low yields of products **7** were obtained using substrate **1** with R^1 = Ph. The structure of products **7** was assigned on the basis of analytical and spectral data (see experimental).

Scheme 4

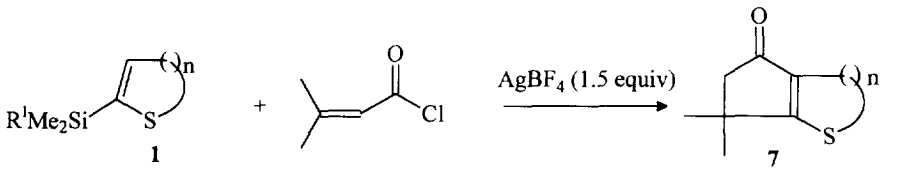


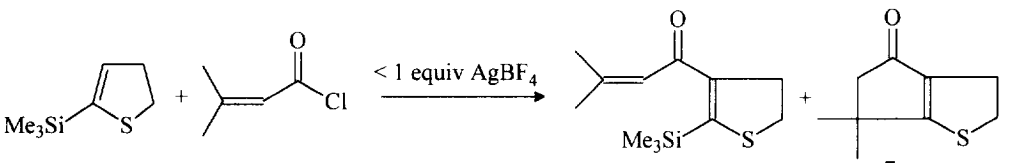
Table 3. Synthesis of thioannulated cyclopentenones **7**.

n	R^1	7	Yield of **7** (%)
2	Me	**a**	83
3	Me	**b**	92
4	Me	**c**	90
5	Me	**d**	91
3	Ph	**a**	12[a]
4	Ph	**b**	17[a]

a beside many unidentified products.

In the reaction of 2-trimethylsilyl-thiacyclopent-2-ene **1a** with 3,3-dimethylacryloyl chloride, in the presence of less than one equivalent of $AgBF_4$, compound **7a** was obtained as a minor product (10% yield) in addition to the cross-conjugated dienone **8** which was the major product (30% yield) (Scheme 5).

Scheme 5

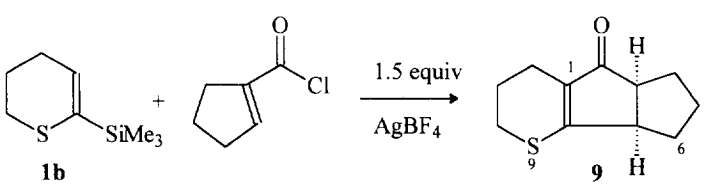


1a **8** **7a**

The isolation of product **8** is in agreement with the mechanistic interpretation of Magnus[5] who assumed, in the reaction between 1-phenylsulfanyl-1-trimethylsilyl ethene and cyclopentenoyl chloride, the intermediacy of a silylated cross-conjugated dienone arising from the attack of the acid chloride directed by the sulfur.

The reaction of 2-trimethylsilyl-thiacyclohex-2-ene **1b** with cyclopentenoyl chloride in the presence of 1.5 equivalents of $AgBF_4$ gave a tricyclic enone **9** in 45% yield (Scheme 6). The structure of product **9** was assigned on the basis of its spectral features (see experimental).

Scheme 6

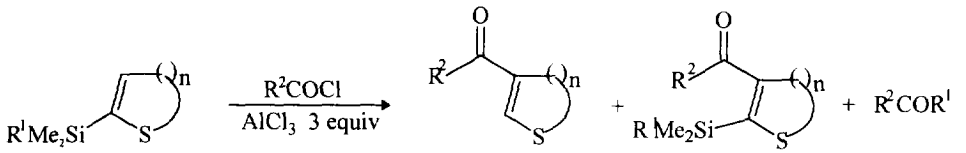


1b **9**

Next the reaction of compounds **1** and **2** with acid chlorides in the presence of aluminium trichloride was studied. As far as compound **1** is concerned the results reported in Scheme 7 and Table 4 show that the attack of the electrophile occurs at the β-position as demonstrated by the ^1H NMR spectrum of **10** in which the vinylic proton signal is a singlet. An ipso substitution of the silicon would have given a product with the vinylic CH as a triplet. When R^1 is a phenyl group (entry 1-3), the final enones did not contain the silyl group (products **10**) but in some cases (entry 1,2) the competitive formation of phenylketones **12** arising from the attack of the electrophile on the phenyl group at the silyl moiety[11] lower the yield. When R^1 is a methyl (entry 4-7), mixtures of products **10** and **11**, the latter still containing the trimethylsilyl group, are obtained.

The mixture could be further protiodesilylated by treatment with tetrabutylammonium fluoride (TBAF) in boiling THF: for instance, protiodesilylation of the mixture in entry 6 gave **10a** in 80% yield.

Scheme 7



1 **10** **11** **12**

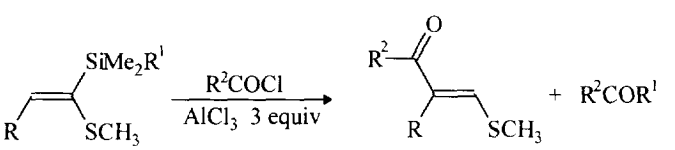
Table 4. Synthesis of cyclic thiofunctionalized enones **10**.

Entry	n	R^1	R^2	**10**	Yield[a] of **10**(%)	**11**	Yield[a] of **11** (%)	**12**	Yield[a] of **12** (%)
1	4	Ph	Me	**a**	35			**a**	60
2	4	Ph		**b**	54			**b**	15
3	4	Ph	Ph	**c**	68				
4	3	Me	Me	**d**	44	**d**	15		
5	3	Me	Ph	**e**	42	**e**	11		
6	4	Me	Me	**a**	47	**a**	46		
7	4	Me	Ph	**b**	20	**c**	15		

a The yields were determined after chromatography.

As model compounds of open chain α-trimethylsilyl and α-dimethylphenylsilyl vinyl sulfides we used **2a** and **2b** prepared according to a procedure previously reported by us.[1] The reaction of these substrates with acid chlorides in the presence of aluminium trichloride is again controlled by the sulfur and occurs at the β-position (Scheme 8).

Scheme 8



2a,b **13** **12**

Table 5. Synthesis of open chain thiofunctionalized enones **13**.

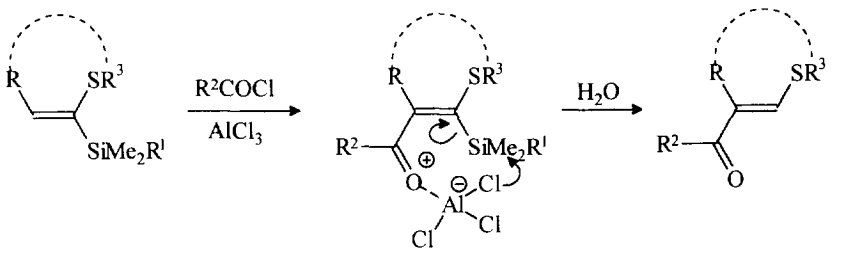
Entry	R	R^1	R^2	**13**	Yield[a] of **13**(%)	**12**	Yield[a] of **12** (%)
1	Ph	Me	Me	**a**[b]	78		
2	Ph	Me	Ph	**b**	100		
3	Et	Ph	Me	**c**	-	**a**	62
4	Et	Ph		**d**	20	**b**	21
5	Et	Ph	Ph	**e**	97		

a The yields were determined after chromatography. b The regiochemistry and stereochemistry of **13a** was assigned on the basis of n.O.e. and Lis. experiments (see experimental).

The results collected in Table 5 show that the yield of enones is good for substrates containing the trimethylsilyl moiety (Table 5, entry 1,2). The dimethylphenylsilyl derivatives, on the contrary, only gave a good yield with benzoyl chloride (entry 5); with other acid chlorides (entry 3 and 4) the competitive formation of phenylketones **12** lowered the yield of enones.

Ager[7] found that the reaction of 1-phenylsulfanyl-1-trimethylsilylethene with acid chloride in the presence of Lewis acid catalyst, gave, after a basic work-up, enones still containing the silyl group. With our substrates the enones obtained had lost the silyl group irrespective of the work-up procedure (see experimental). A possible explanation of this result is depicted in Scheme 9. The carbonyl group *cis* to the silicon can coordinate a molecule of aluminium trichloride giving intermediate **14** in which the chlorine is in a suitable position for the desilylation.

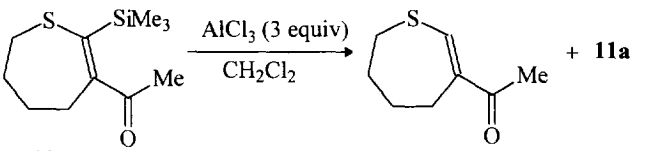
Scheme 9



14

In order to prove this hypothesis the silylated enone **11a** was treated with 3 equivalents of aluminium trichloride in dichloromethane: the final mixture contained the desilylated product **10a** (70%) and some starting material (30%) (Scheme 10).

Scheme 10



11a **10a**

Conclusion

This paper describes a detailed study on the reactivity of cyclic and open chain α-silyl vinyl sulfides with acid chlorides in the presence of Lewis acids. The results clearly show that substrates containing the phenyl group on the silyl moiety are generally incompatible with the reaction conditions unless the less electrophilic benzoyl chloride is used. The enones ultimately obtained are completely (in the case of the open chain α-silyl vinyl sulfides) or partially desilylated.

Cyclic α-silyl vinyl sulfides of different ring size can be used as substrates for the Nazarov cyclization with both open chain and cyclic α,β-unsaturated acid chlorides to give various sulfur-annulated cyclopentenones.

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 and with a Varian Gemini 300 spectrometers 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 through 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; hydrogen chloride was purchased from Praxair (Belgium). 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. The characterization of the new compounds has been performed by accurate mass measurements.

General method for the Synthesis of ω-haloacylsilanes 3a, 3c-e. A solution of the 2-trimethylsilyl-1,3-dithiane in dry THF (0.85M), under argon atmosphere, was cooled to 0 °C and a solution of butyllithium in hexane (1.6M, 1.15 equiv) was added dropwise over a period of 10 min The resulting solution was stirred at 0 °C for 30 min then transferred *via* syringe to another solution of the dihalide (2 equiv) in dry THF cooled to -20 °C under argon atmosphere. After stirring at -20 °C for 1h, the reaction mixture was quenched with water and extracted with diethyl ether. The organic phase was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The resulting mixture was dissolved in 15%aq THF (0.35M) and red mercury oxide (2 equiv) and Celite (equal weight as red mercury oxide) were added. Boron trifluoride etherate (2 equiv) was added and the resulting mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with diethyl ether and filtered. The filtrate was washed with water and brine, was dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography on silica of the residue (light petroleum as eluent) gave, as the higher R_f fraction the dihalide, and, as the second R_f fraction (light petroleum: diethyl ether 10:1 as eluent), the title product.

4-Chlorobutanoyl trimethyl silane 3a. Starting from 2.0 g (10.42 mmol) of 2-trimethylsilyl-1,3-dithiane and 2.06 ml (20.84 mmol 3.28 g) of 1-bromo-3-chloro propane the title product was obtained as a yellow oil (0.67 g 3.75 mmol yield 36%). IR (neat) ν_{max}: 1638 (CO), 1248 ($SiMe_3$), 839 ($SiMe_3$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.22 (s, 9H, $SiMe_3$), 2.00 (m, 2H, CH_2), 2.78 (t, 2H, J = 6.0 Hz , CH_2CO), 3.5 (t, 2H, J = 5.0 Hz , CH_2Cl); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -3.39 ($SiMe_3$), 24.77, 44.62, 44.72 (CH_2), 245.52 (CO); MS: m/z 178 (M^+), 150 (M^+-CO), 142 (M^+-HCl), 93 (C_3H_6ClO), 73 ($SiMe_3$); HRMS: m/z for $C_7H_{15}ClOSi$ found M^+, 178.0586 calcd M, 178.0581.

6-Chlorohexanoyl trimethyl silane 3c. Starting from 2.0 g (10.42 mmol) of 2-trimethylsilyl-1,3-dithiane and 2.75 ml (20.84 mmol, 3.8 g) of 1-bromo-5-chloro pentane the title product was obtained as a yellow oil (1.3 g 6.31 mmol, yield 61%) IR (neat) ν_{max}: 1640 (CO), 1250 ($SiMe_3$), 839 ($SiMe_3$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.22 (s, 9H, $SiMe_3$), 1.43 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 2.65 (t, 2H, J = 6.8 Hz, CH_2CO), 3.75 (t, 2H, J = 6.5 Hz, CH_2Cl); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -3.06 ($SiMe_3$), 21.43, 26.70, 32.68, 44.88, 48.19 (CH_2), 247.09 (CO); MS: m/z 206 (M^+), 191 (M^+-CH_3), 73 ($SiMe_3$); HRMS: m/z for $C_9H_{19}ClOSi$ found M^+, 206.0898; calcd M, 206.0894.

7-Chloroheptanoyl trimethyl silane 3d. Starting from 2.0 g (10.42 mmol) of 2-trimethylsilyl-1,3-dithiane and 2.57 ml. (20.84 mmol, 4.12 g) 1-bromo-6-chloro hexane, the title product was obtained as a yellow oil (1.7 g 7.72 mmol, yield 75%) IR (neat) ν_{max}: 1640 (CO), 1248, 845 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 9H, $SiMe_3$), 1.23 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.71 (m, 2H, CH_2), 2.55 (t, 2H, J = 7.2 Hz, CH_2CO), 3.47 (t, 2H, J = 6.7 Hz, CH_2Cl); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ -3.44

$SiMe_3$, 21.61, 26.46, 28.27, 32.15, 44.66, 47.90 (CH_2), 247.26 (CO); MS: m/z 220 (M^+), 73 ($SiMe_3$); HRMS: m/z for $C_{10}H_{21}ClOSi$ found M^+, 220.1056; calcd M, 220.1050.

7-Bromoheptanoyl trimethyl silane 3e. Starting from 2.0 g (10.42 mmol) of 2-trimethylsilyl-1,3-dithiane and 3.36 ml. (20.84 mmol, 5.0 g) 1,6-dibromo hexane, the title product was obtained as a yellow oil (1.68 g 6.35 mmol, yield 61%) IR (neat) ν_{max}: 1640 (CO), 1248, 845 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.15 (s, 9H, $SiMe_3$), 1.1-1.6 (m, 6H, $3CH_2$), 1.8 (m, 2H, $3CH_2$), 2.55 (t, 2H, J = 7.5 Hz, CH_2CO), 3.35 (t, 2H, J = 6.5 Hz, CH_2Br); ^{13}C NMR (75.4..45 MHz, $CDCl_3$): δ -3.19 $SiMe_3$, 21.80, 27.95, 28.36, 32.51, 33.80, 48.16 (CH_2), 248.70 (CO); MS: m/z 264 (M^+), 185 (M^+-Br), 73 ($SiMe_3$); HRMS: m/z for $C_{10}H_{21}BrOSi$ found M^+, 264.0542; calcd M, 264.0545.

General method for the Synthesis of 2-Silyl-thiacycloalk-2-enes 1 (one-pot synthesis from acylsilanes). Hydrogen chloride and hydrogen sulfide were bubbled into a solution of the ω-halo acyl silane (1.0 mmol) in anhydrous diethyl ether (50 ml) at -15 °C, until the starting ketone had disappeared (TLC with 10:1 light petroleum-diethyl ether as eluent). In some cases 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 solid sodium hydroxide was added until neutralization, checked by universal indicator paper (pH 1-11), then left overnight. The mixture was filtered and concentrated under reduced pressure. The residue gave **1** as the only product. Purification was performed by chromatography on silica (9:1 light petroleum: diethyl ether as eluent).

2-Trimethylsilyl-thiacyclo pent-2-ene 1a. Starting from 4-chlorobutanoyl trimethyl silane **3a** the title compound was obtained as an oil in 67% yield. IR (CCl_4) ν_{max}: 1564, 1425, 1248 ($SiMe_3$), 839 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 9H, $SiMe_3$), 2.80 (dt 2H, CH_2), 3.20 (t, 2H, J = 7.5 Hz, CH_2S), 5.80 (t, 1H, J = 2.5 Hz, vinylic H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ -1.32 ($SiMe_3$), 32.86, 37.92 (CH_2), 112.31 (vinylic C), 130.76 (vinylic CH); MS: m/z 158 (M^+), 143 (M^+-CH_3), 73 ($SiMe_3$); HRMS: m/z for $C_7H_{14}SSi$ found M^+, 158.0589; calcd M, 158.05855.

2-Trimethylsilyl-thiacyclo hex-2-ene 1b. Starting from 5-chloropentanoyl trimethyl silane **3b**[7a] the title compound was obtained as an oil in 82% yield. IR (CCl_4) ν_{max}: 1247, 838 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.15 (s, 9H, $SiMe_3$), 2.0 (m, 2H, CH_2), 2.2 (m, 2H, CH_2), 2.85 (m, 2H, CH_2), 5.98 (t, 1H, J = 4.3 Hz, vinylic H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ –1.88 ($SiMe_3$), 21.88, 25.00, 26.55 (CH_2), 127.72 (vinylic CH), 132.42 (vinylic C); MS: m/z 172(M^+), 157(M^+-CH_3), 73 ($SiMe_3$); HRMS: m/z for $C_8H_{16}SSi$ found M^+, 172.0746; calcd M, 172.0742.

2-Trimethylsilyl-thiacyclo hept-2-ene 1c. Starting from 6-chlorohexanoyl trimethyl silane **3c** the title compound was obtained as an oil in 92% yield. IR (neat) ν_{max}: 1584, 1437, 1245 ($SiMe_3$), 840 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 9H, $SiMe_3$), 1.53 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 2.40 (m, 2H, CH_2), 2.60 (m, 2H, CH_2), 6.40 (t, 1H, J = 6.4 Hz, vinylic H)); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ -1.46 ($SiMe_3$), 25.16, 31.52, 33.00, 34.98 (CH_2), 141.00 (vinylic C), 144.35 (vinylic CH); MS: m/z 186 (M^+), 171 (M^+- CH_3), 73 (Me_3Si); HRMS: m/z for $C_9H_{18}SSi$ found M^+, 186.0892; calcd M, 186.08985.

2-Trimethylsilyl-thiacyclo oct-2-ene 1d. Starting from 7-Chloro heptanoyl trimethyl silane **3d** a mixture of two products was obtained as shown by the ^1H NMR of the crude reaction mixture. Preparative thick layer chromatography on silica of the mixture (light petroleum as eluent) gave, as the higher R_f fraction **1d** (8%), oil, IR (film) ν_{max}: 1244 ($SiMe_3$), 837 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$); δ 0.12 (s, 9H, $SiMe_3$), 1.53 (m, 4H, 2(CH_2)), 1.81 (m, 2H, CH_2), 2.63 (m, 4H, $2CH_2$), 6.50 (t, 1H, J = 8.00 Hz, vinylic H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ -1.73 ($SiMe_3$), 25.40, 28.45, 28.58, 29.86, 36.78 (CH_2), 137.09 (vinylic C), 149.52 (vinylic CH); MS: m/z 200 (M^+), 185 (M^+-CH_3), 73 ($SiMe_3$); HRMS: m/z for $C_{10}H_{20}SSi$ found M^+, 200.1052; calcd M, 200.1055, and as the second R_f fraction the disulfide **6a** (55%), oil, IR (film) ν_{max}: 1250 ($SiMe_3$), 840 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 9H, $SiMe_3$), 1.4 (m, 4H, 2(CH_2)), 1.78 (m, 2H, CH_2), 2.40 (m, 2H, CH_2), 3.55 (t, 2H, J = 6.6 Hz, CH_2Cl), 6.18 (t, 1H, J = 6.8 Hz, vinylic H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ -0.59 ($SiMe_3$), 26.59, 28.40, 30.74, 32.40 (CH_2), 44.95 (CH_2Cl), 139.16 (vinylic C), 148.65 (vinylic CH); MS: m/z 470 (M^+), 455 (M^+-CH_3), 365 (M^+-$Cl(CH_2)_5$), 235

($Cl(CH_2)_5CH{=}CSSiMe_3$), 73 ($SiMe_3$); HRMS: m/z for $C_{20}H_{40}Cl_2S_2Si_2$ found M^+, 470.1483; calcd M, 470.1487.

2-Trimethylsilyl-thiacyclo oct-2-ene 1d. Starting from 7-Bromo heptanoyl trimethyl silane **3e** a mixture of three products (three different vinylic triplets) was obtained as shown by ^1H NMR of the crude reaction mixture: **1d** (δ = 6.5), product **5** (δ = 6.32) and the disulfide **6b** (δ = 6.22). Preparative thick layer chromatography on silica of the mixture (light petroleum as eluent) gave, as the higher R_f fraction **1d** (9%) as second R_f fraction product **5** (25%) pf 102-104 (from methanol); IR (film) ν_{max}: 1247 ($SiMe_3$), 837 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, 9H, $SiMe_3$), 1.49 (m, 6H, 3(CH_2)), 2.50 (m, 4H, 2(CH_2)), 6.32 (t, 1H, J = 7.1 Hz, vinylic H).^{13}C NMR (75.4 MHz, $CDCl_3$): δ 0.63 ($SiMe_3$), 28.13, 29.00, 29.14, 30.66, 34.76, (CH_2), 134.59 (vinylic C), 151.563 (vinylic CH); MS: m/z 400 (M^+), 385 (M^+-CH_3), 295 (M^+-$SSiMe_3$), 199 (M^+-$C_7H_{10}SSiMe_3$), 73 ($SiMe_3$); HRMS: m/z for $C_{20}H_{40}S_2Si_2$ found M^+, 400.2216; calcd M, 400.2210. (The (Z) configuration of the double bond of the dimeric product was elucidated by noe experiments. Saturation of the $SiMe_3$ resonance at 0.10 ppm produced a significant increase (16 %) in the intensity of the vinylic proton signal.)and as the lower R_f fraction **6b** (20%) oil, IR (film) ν_{max}: 1247 ($SiMe_3$), 837 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 9H, $SiMe_3$), 1.4 (m, 4H, 2(CH_2)), 1.78 (m, 2H, CH_2), 2.50 (m, 2H, CH_2), 3.35 (t, 2H, J = 6.5 Hz, CH_2Cl), 6.18 (t, 1H, J = 6.4 Hz, vinylic H); MS: m/z 400 (M^+-Br_2), 385 (400-CH_3), 281 ($Br(CH_2)_5CH{=}CSSiMe_3$), 73 ($SiMe_3$).

General method for the Synthesis of (Z)-7-Halo-1-trimethylsilyl-hept-1-enethiol 4. Hydrogen chloride and hydrogen sulfide were bubbled into a solution of 7-halo-eptanoyl trimethyl silane (1.0 mmol) in anhydrous diethyl ether (50 ml) at -15 °C, until the starting ketone had disappeared (TLC with 10:1 light petroleum-diethyl ether as eluent). The mixture was allowed to warm to room temperature and solid sodium hydrogen carbonate was added until neutralization, checked by universal indicator paper (pH 1-11), then left overnight. The mixture was filtered and concentrated under reduced pressure. The residue gave the title compound as the only product. The enethiol was characterized without further purification.

(Z)-7-Chloro-1-trimethylsilyl-hept-1-enethiol 4a. Oil, 98% yield, IR (neat) ν_{max}: 2560 (SH), 1250 ($SiMe_3$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.12 (s, 9H, $SiMe_3$), 1.43 (m, 4H, 2CH_2), 1.78 (m, 2H, CH_2), 2.17 (m, 2H, CH_2), 2.5 (s, 1H, SH), 3.51 (t, 2H, J = 6.0 Hz, CH_2Cl), 5.81 (t, 1H, J = 5.5 Hz, vinylic H); MS: m/z 236 (M^+), 220 (M^+-CH_4), 205 (M^+-C_2H_7), 73 ($SiMe_3$); HRMS: m/z for $C_{10}H_{21}ClSSi$ found M^+, 236.0828; calcd M, 236.0822.

(Z)-7-Bromo-1-trimethylsilyl-hept-1-enethiol 4b. Oil, 98% yield, IR (neat) ν_{max}: 1250 ($SiMe_3$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.12 (s, 9H, $SiMe_3$), 1.45 (m, 4H, 2CH_2), 1.85 (m, 2H, CH_2), 2.15 (m, 2H, CH_2), 2.52 (s, 1H, SH), 3.38 (t, 2H, J = 6.85 Hz, CH_2Br), 5.80 (t, 1H, J = 6.55 Hz, vinylic H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ -1.94 ($SiMe_3$), 27.65, 27.81, 30.06, 32.58, 33.75 (CH_2), 137.70 (vinylic CH), MS: m/z 280 (M^+), 201 (M^+-Br), 73 ($SiMe_3$); HRMS: m/z for $C_{10}H_{21}BrSSi$ found M^+, 280.0313; calcd M, 280.0317.

Synthesis of 2-trimethylsilyl-thiacyclo oct-2-ene 1d (high dilution condition). 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.

a) Starting from 4a. The ^1H NMR of the crude reaction mixture showed the presence of three products (three different vinylic triplets): product **1d** (δ = 6.5), product **5** (δ = 6.32) and the disulfide **6a** (δ = 6.22). Preparative thick layer chromatography (light petroleum as eluent) gave as the higher R_f fraction (22%) **1d** as second R_f fraction product **5** (5%) and as the lower R_f fraction the disulfide **6a** (45%).

b) Starting from 4b. Preparative thick layer chromatography (light petroleum as eluent) gave as the higher R_f fraction compound **1d** (50 %) as second R_f fraction product **5** (13%) and as the lower R_f fraction the disulfide **6b** (10%).

c) Starting from 4b using Cs_2CO_3 as base. Preparative thick layer chromatography (light petroleum as eluent) gave as the higher R_f fraction compound **1d** (35%) as second R_f fraction product **5** (20%) and as the lower R_f fraction the disulfide **6b** (10%).

General metod for the synthesis of products 7. To a solution of $AgBF_4$ (1.5 mmol) in dry 1,2-dichloroethane (3 ml) and dry dichloromethane (2 ml), cooled to -50 °C, under argon atmosphere, was added the 2-silyl thiacycloalkene (1 mmol), followed by 3,3-dimethylacryloyl chloride (1.3 mmol). A precipitate was formed and the mixture turned red-brown. After 20 h at room temperature the reaction mixture was filtered and quenched with 10% aqueous $NaHCO_3$. The mixture was extracted with dichloromethane and the organic layer was washed with water, dried and concentrated under reduced pressure. The residue was purified by chromatography on silica plates (7:3 light petroleum: ethyl acetate).

8,8-Dimethyl-2-thiabicyclo[3.3.0]oct-1(5)-en-6-one 7a. Starting from 2-trimethylsilyl thiacyclo pent-2-ene **1a** (R^1 = Me) the title compound was obtained in 83 % yield. pf 55-57 °C (from methanol); IR (film) ν_{max}: 1680 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.21 (s, 6H, $2CH_3$), 2.53 (s, 2H, CH_2), 2.82 (t, 2H, J = 8.7 Hz, CH_2), 3.75 (t, 2H, J = 8.8 Hz, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 26.64 (CH_2), 27.80 ($2CH_3$), 39.03 ($C(CH_3)_2$), 40.25, 56.30 (CH_2), 140.52 (vinylic C), 194.38 (vinylic C), 196.21 (CO); MS: m/z 168 (M^+), 153 (M^+-CH_3), 125 (M^+-$COCH_3$); HRMS: m/z for $C_9H_{12}OS$ found M^+, 168.0605; calcd M, 168.0609.

9,9-Dimethyl-2-thiabicyclo[4.3.0]non-1(6)-en-7-one 7b. Starting from 2-trimethylsilyl thiacyclo hex-2-ene **1b** (R^1 = Me) the title compound was obtained in 92 % yield. pf 63-65 °C (from methanol); IR (film) ν_{max}:1691 (CO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 6H, $2CH_3$), 1.91 (m, 2H, CH_2), 2.27 (m, 2H, CH_2), 2.28 (s, 2H, CH_2), 2.95 (m, 2H, CH_2).^{13}C NMR (75.4 MHz, $CDCl_3$): δ 19.52, 20.86, 27.76 (CH_2), 28.29 ($2CH_3$), 42.31 ($C(CH_3)_2$), 50.83 (CH_2), 130.40 (vinylic C), 178.91 (vinylic C), 202.15 (CO); MS: m/z 182 (M^+), 167 (M^+-CH_3), 139 (M^+-CH_3CO), 125 (M^+-C_2H_5CO); HRMS: m/z for $C_{10}H_{14}OS$ found M^+, 182.0768; calcd M, 182.0765. Starting from 2-dimethylphenylsilyl thiacyclo hex-2-ene **1b** (R^1 = Ph) the title compound was obtained in 12 % yield.

10,10-Dimethyl-2-thiabicyclo[5.3.0]dec-1(7)-en-8-one 7c. Starting from 2-trimethylsilyl thiacyclo hept-2-ene **1c** (R^1 = Me) the title compound was obtained in 92 % yield. pf 70-72 °C (from methanol); IR (film) ν_{max}: 1688 (CO), 1582, 1449, 1269 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.22 (s, 6H, $2CH_3$), 1.86 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 2.35 (s, 2H, CH_2CO), 2.42 (m, 2H, CH_2), 3.07 (m, 2H, CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.02, 24.66 (CH_2), 28.18 (CH_3), 30.44, 31.97 (CH_2), 42.18 ($C(CH_3)_2$), 50.94 (CH_2), 138.30 (vinylic C), 167.40 (vinylic C), 203.07 (CO); MS: m/z 196 (M^+), 181 (M^+-CH_3); HRMS: m/z for $C_{11}H_{16}OS$ found M^+, 196.0928; calcd M, 196.0922. Starting from 2-dimethylphenylsilyl thiacyclo hept-2-ene **1c** (R^1 = Ph) the title compound was obtained in 17 % yield.

11,11-Dimethyl-2-thiabicyclo[6.3.0]undec-1(8)-en-9-one 7d. Starting from 2-trimethylsilyl thiacyclo oct-2-ene **1d** (R^1 = Me) the title compound was obtained in 92 % yield. pf 78-80 °C (from methanol); IR (film) ν_{max}: 1689 (CO), 1575, 1266, 1096 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.28 (s, 6H, $C(CH_3)$), 1.67 (m, 4H, $2(CH_2)$), 1.94 (m, 2H, CH_2), 2.30 (s, 2H, CH_2), 2.60 (m, 2H, CH_2), 3.36 (t, 2H, J = 6.57 Hz, CH_2);^{13}C NMR (50.3 MHz, $CDCl_3$): δ 19.94, 22.00, 28.14 (CH_2), 28.98 ($2CH_3$), 29.95, 31.20 (CH_2),42.98 ($C(CH_3)_2$), 50.88 (CH_2), 134.40 (vinylic C), 182.89 (vinylic C), 202.87 (CO); MS: m/z 210 (M^+), 195 (M^+-CH_3),177 (M^+-SH), 126 (M^+-$(CH_3)_2C(CH_2)CO$); HRMS: m/z for $C_{12}H_{18}OS$ found M^+, 210.1073; calcd M, 210.1078.

9-Thiatricyclo[6.4.0.0^{3,7}]dodec-1(8)-en-2-one 9. Starting from 1 mmol, 172 mg of 2-trimethylsilyl thiacyclo hex-2-ene **1b** (R^1 = Me) and 1.3 mmol, 170 mg of 1-cyclopentenoyl chloride[5] using the same procedure as for **7**, after chromatography on silica (8:1 light petroleum: ethyl acetate) the title compound was obtained as an oil in 45% yield (88 mg); IR (film) ν_{max}: 1681 (CO), 1591, 1366, 1274 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.2 (m, 1H, H_A-C(5)), 1.5-2.0 (m, 7H, 2H-C(4), 2H-C(6), H_B-C(5), 2H-C(11)), 2.25 (ddd, 2H, J_1 = 1.8 Hz, J_2 = 6.3 Hz, 2H-C(12)), 2.75 (m, 1H, H-C(7)), 2.94 (m, 2H, 2H-C(10)), 3.22 (m, 1H, H-C(3)); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 19.68 (C-12), 21.09 (C-11), 23.87 (C-5), 28.05 (C-10), 28.90 (C-4), 30.14 (C-6), 47.61 (C-7), 50.21 (C-3), 132.81 (C-8), 172.65 (C-1), 206.17 (C-2); MS: m/z 194 (M^+), 179 (M^+-CH_3), 166 (M^+-CO);

HRMS: m/z for $C_{11}H_{14}OS$ found M^+, 194.0761; calcd M, 194.0765. The *cis* junction of the two cyclopentane has been proved by n.O.e. experiments: in fact the irradiation of the CH signal at 3.22 ppm (H-C(3)) produced a significant increase (19%) in the intensity of the CH signal at 2.75 ppm (H-C(7)) and the irradiation of the CH signal at 2.75 ppm produced a significant increase (13.5%) in the intensity of the CH signal at 3.22 ppm. Attribution of the proton and carbon signals has been carried out by fitting together the information obtained by Hetcor, Cosy and n.O.e. experiments.

Synthesis of 7a using less then one equivalents of $AgBF_4$. Starting from 2-trimethylsilyl thiacyclo pent-2-ene **1a** (0.76 mmol, 120 mg), 3,3-dimethylacryloyl chloride (0.94 mmol, 112 mg) and $AgBF_4$ (0.60 mmol, 120 mg), using the same procedure as for **7**, chromatography on silica of the crude reaction mixture (7:3 light petroleum: ethyl acetate) gave as higher R_f fraction **7a** (0.076 mmol, 12 mg, 10%) and as the lower R_f fraction the silylated cross-conjugated dienone **8** (0.228 mmol, 54 mg, 30%) as an oil, IR (film) ν_{max}: 1650 (CO), 1248 ($SiMe_3$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.22 (s, 9H, $SiMe_3$), 1.86 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 3.60 (m, 4H, $2CH_2$), 6.08 (s, 1H, vinylic H); MS: m/z 240 (M^+), 225 (M^+-CH_3), 73 ($SiMe_3$); HRMS: m/z for $C_{12}H_{20}OSSi$ found M^+, 240.1008; calcd M, 240.1004.

General procedure for the reactions of product 1 or 2 with open chain acid chlorides. To a solution of $AlCl_3$ (3 mmol) in dry dichloromethane (3 ml), cooled to 0 °C, under argon atmosphere, the acyl chloride (1.5 mmol) and product **1** or **2** (1 mmol) were added in sequence. After 12 h at room temperature the reaction mixture was quenched with saturated acqueous ammonium chloride and extracted with dichloromethane and the organic layer was washed with 10% acqueous $NaHCO_3$ and with water, dried and concentrated under reduced pressure. The residue was purified by chromatography on silica (3:1 light petroleum : diethyl ether).

3-Acetyl-thiacyclo hept-2-ene 10a. Starting from 2-dimethylphenylsilyl-thiacyclo hept-2-ene and acetyl chloride, chromatography on silica of the crude (3:1 light petroleum: diethyl ether) gave as the higher R_f fraction acetophenone **12a** (60%) and as the lower R_f fraction 3-acetyl-thiacyclo hept-2-ene **10a** (35%) as an oil IR (film) ν_{max}: 1660 (CO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.78 (m, 2H, CH_2), 1.98 (m, 2H, CH_2), 2.24 (s, 3H, CH_3CO), 2.59 (m, 2H, CH_2), 2.94 (m, 2H, CH_2), 7.33 (s, 1H, vinylic H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 24.06, 24.57 (CH_2), 25.46 (CH_3), 29.36, 32.10 (CH_2), 140.94 (vinylic CH), 141.94 (vinylic C), 195.78 (CO); MS: m/z 156 (M^+), 141 (M^+-CH_3), 128 (M^+-CO), 113 (M^+-CH_3CO), 43 (CH_3CO); HRMS: m/z for $C_8H_{12}OS$ found M^+, 156.0611; calcd M, 156.0609. Starting from 2-trimethylsilyl-thiacyclo hept-2-ene **1e** and acetyl chloride, chromatography on silica of the resulting mixture (3:1 light petroleum: diethyl ether as solvent) gave as the higher R_f fraction 3-acetyl-thiacyclo hept-2-ene **10a** (47 %) and as the lower R_f fraction 2-trimethylsilyl-3-(acetyl)-thiacyclo hept-2-ene **11a** (46 %) ^1H NMR (200 MHz, $CDCl_3$): δ 0.18 (s, 9H, $SiMe_3$), 1.67 (m, 2H, CH_2), 2.1 (m, 2H, CH_2), 2.3 (s, 3H, CH_3CO), 2.8 (m, 4H, 2 CH_2); MS: m/z 228 (M^+), 213 (M^+-CH_3), 185 (M^+-CH_3CO), 73 ($SiMe_3$), 43 (CH_3CO); HRMS: m/z for $C_{11}H_{20}OSSi$ found M^+, 228.1012; calcd M, 228.1004. The final mixture of **10a** and **11a** could also be protiodesilylated using tetrabutylammonium fluoride (TBAF) in moist THF at reflux temperature. Product **10a** was obtained in 80% yield after chromatography (3:1 light petroleum: diethyl ether as solvent).

3-(3,3-Dimethyl)-acryloyl-thiacyclo hept-2-ene 10b. Starting from 2-dimethylphenylsilyl-thiacyclo hept-2-ene and 3,3-dimethyl acryloyl chloride, chromatography on silica of the crude (3:1 light petroleum: diethyl ether) gave as the higher R_f fraction 3-methyl-1-phenylbut-2-ene-1-one **12b**[12] (15%) and as the lower R_f fraction 3-(3,3-Dimethyl acryloyl)-thiacyclo hept-2-ene **10b** (54 %); IR (neat) ν_{max}: 1640 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.85 (m, 2H, CH_2), 1.90 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.05 (m, 2H, CH_2), 2.15 (m, 2H, CH_2), 2.96 (m, 2H, CH_2), 6.28 (m, 1H, vinylic CH), 7.35 (s, 1H, vinylic CHS); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 21.18 (CH_3), 25.32 (CH_2), 27.72(CH_3), 30.21,32.83 (CH_2), 122.11, 140.09 (vinylic CH), 143.96, 152.25 (vinylic C),191.81 (CO); MS: m/z 196 (M^+), 181 (M^+-CH_3), 83 (C_5H_7O), 55 (($CH_3)_2C$=CH); HRMS: m/z for $C_{11}H_{16}OS$ found M^+, 196.0925; calcd M, 196.0922.

3-Benzoyl-thiacyclo hept-2-ene 10c. Starting from 2-dimethylphenylsilyl-thiacyclo hept-2-ene and benzoyl chloride, the title compound was obtained, after chromatography, as an oil in 68% yield. IR (neat) ν_{max}: 1640

(CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ :2.00 (m, 2H, CH_2), 2.10 (m, 2H, CH_2), 2.80 (2H, t CH_2), 3.10(2H, t CH_2S), 7.1 (s, 1H, Vinylic CH), 7.35-7.65 (m, 5H, Ar-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 25.58, 26.28, 30.21, 32.87 (CH_2), 128.60, 129.50, 131.75.4 (Ar-CH), 133.91 (Ar-C)141.20 (vinylic C), 144.86 (vinylic CH), 211.98 (CO); MS: m/z 218 (M^+), 203 (M^+-CH_3), 115 (M^+-PhCO), 105 (PhCO), 77 (Ph); HRMS: m/z for $C_{13}H_{14}OS$ found M^+, 218.0761; calcd M, 218.0765. Starting from 2-trimethylsilyl-thiacyclo hept-2-ene and benzoyl chloride, preparative thick layer chromatography on silica of the resulting mixture (3:1 light petroleum: diethyl ether as solvent) gave as the higher R_f fraction 3-benzoyl-thiacyclo hept-2-ene **10c** (20 %) and as the lower R_f fraction 2-trimethylsilyl-3-(benzoyl)-thiacyclo hept-2-ene **11c** (15 %) ^1H NMR (200 MHz, $CDCl_3$): δ 0.40 (s, 9H, $SiMe_3$), 1.73 (m, 2H, CH_2), 2.40 (t, 2H, CH_2), 3.10 (t, 2H, CH_2), 7.00-8.00 (m, 5H, ArH).

3-Acetyl-thiacyclo hex-2-ene 10d. Starting from 2-trimethylsilyl-thiacyclo hex-2-ene and acetyl chloride, preparative thick layer chromatography on silica of the resulting mixture (3:1 light petroleum: diethyl ether as solvent) gave as the higher R_f fraction 3-(acetyl)-thiacyclo hex-2-ene **10d** (44 %) IR (film) ν_{max}: 1643 (CO), 1572 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.99 (m, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.38 (t, 2H, J = 6.0 Hz, CH_2), 2.85 (m, 2H, CH_2), 7.45 (s, 1H, vinylic H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 21.33 ($2CH_2$), 24.65 (CH_3), 26.54 (CH_2), 132.74 (vinylic C), 137.71 (vinylic CH), 194.52 (CO); MS: m/z 142(M^+), 127 (M^+-CH_3), 99 (M^+-$COCH_3$); HRMS: m/z for $C_7H_{10}OS$ found M^+, 142.0458; calcd M, 142.0452 and as the lower R_f fraction 2-trimethylsilyl-3-(acetyl)-thiacyclo hex-2-ene **11d** (15 %) IR (film) ν_{max}: 1660 (CO), 1505, 1240 ($SiMe_3$), 840 ($SiMe_3$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.19 (s, 9H, $SiMe_3$), 2.02 (m, 2H, CH_2), 2.18 (s, 3H, CH_3), 2.48 (t, 2H, J = 5.0 Hz, CH_2), 2.76 (m, 2H, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 0.49 ($SiMe_3$), 21.37, 26.65 (CH_2), 27.23 (CH_3), 27.56 (CH_2), 127.90 (vinylic C), 134.43 (vinylic C), 195.54 (CO); MS: m/z 214 (M^+), 199 (M^+-CH_3), 171 (M^+-CH_3CO), 73 ($SiMe_3$), 43 (CH_3CO); HRMS: m/z for $C_{10}H_{18}OSSi$ found M^+, 214.0843; calcd M, 214.0848.

3-Benzoyl-thiacyclo hex-2-ene 10e. Starting from 2-trimethylsilyl-thiacyclo hex-2-ene and benzoyl chloride, preparative thick layer chromatography on silica of the resulting mixture (3:1 light petroleum: diethyl ether as solvent) gave as the higher R_f fraction 3-(benzoyl)-thiacyclo hex-2-ene **10e** (42 %) IR (film) ν_{max}: 1629 (CO), 1566 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.05 (m, 2H, CH_2), 2.58 (t, 2H, J = 5,55 Hz, CH_2), 2.90 (m, 2H, CH_2), 7.2 (s, 1H, vinylic H), 7.30-7.55 (m, 5H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.37, 22.22, 26.96 (CH_2), 128.16, 128.81, 130.92 (ArCH), 138.85 (ArC), 142.06 (vinylic CH), 194.13 (CO); MS: m/z 204 (M^+), 127(M^+-Ph), 105 (PhCO), 77 (Ph); HRMS: m/z for $C_{12}H_{12}OS$ found M^+, 204.0602; calcd M, 204.0609 and as the lower R_f fraction 2-trimethylsilyl-3-(benzoyl)-thiacyclo hex-2-ene **11e** (11 %) IR (film) ν_{max}: 1661(CO), 1249 ($SiMe_3$), 838 ($SiMe_3$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.42 ($SiMe_3$), 2.86 (m, 2H, CH_2), 2.54 (m, 2H, CH_2), 3.15 (t, 2H, J = 7.23 Hz, CH_2), 7.1-7.6 (m, 3H, ArH), 8.0 (m, 2H, ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 0.081 ($SiMe_3$), 24.40, 28.87, 30.19 (CH_2), 127.15, 127.38, 128.51 (ArCH), 137.14 (ArC), 147.29 (vinylic C), 148.96 (vinylic C), 191.70 (CO); MS: m/z 275 (M^+-1), 105 (PhCO), 73 ($SiMe_3$).

(E)-4-Methylsulfanyl-3-phenyl-but-3-en-2-one 13a. Starting from (Z)-1-methylsulfanyl-1-trimethylsilyl-2-phenyl ethylene **2a** and acetyl chloride, the title compound was obtained, after chromatography, in 78% yield, mp = 80-82 °C(methanol); IR (CS_2) ν_{max}: 1680 (CO), 1312, 1218, 697 cm^{-1}; ^1H NMR (200 MHz, C_6D_6): δ 1.55 (s, 3H, SCH_3), 1.90 (s, 3H, $COCH_3$), 7.16-7.18 (m, 5H, ArH), 7.54 (s, 1H, vinylic H);^{13}C NMR (50.3 MHz, C_6D_6): δ 17.35, 27.80 (CH_3), 129.24, 130.19, (ArCH), 137.57 (C), 137.87 (C), 147.18 (vinylic CH), 193.33 (CO); MS: m/z 192 (M^+), 177 (M^+-CH_3), 149 (M^+-$COCH_3$), 134 (149-CH_3), 115 (M^+-Ph), 102 (149-SCH_3); HRMS: m/z for $C_{11}H_{12}OS$ found M^+, 192.0611; calcd M, 192.0609. The regiochemistry of the reaction was elucidated by n.O.e. experiments. Saturation of the vinylic resonance at 7.54 ppm produced a significant increase (13%) in the intensity of the SMe signal and in the intensity of the COMe signal proving that they are both close to the vinylic proton. The stereochemistry of the reaction was elucidated by Lis experiments. The addition of a shift reagent ($Eu(fod)_3$ was used) produced a downfield shift of the vinylic and of the COMe signals proving that they lie at the same part of the double bond.

The same reaction quenched with NH_3/NH_4Cl buffer (pH 10, basic work up) gave, after chromatography on silica (10:1 light petroleum:ethyl acetate) as the higher R_f fraction the silylated enone (0.05 mmol, 14 mg,

8%) as an oil, IR (CS_2) ν_{max}: 1680 (CO), 1250 ($SiMe_3$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ -0.05 (s, 9H, $SiMe_3$), 2.25 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 7.20-7.40 (m, 5H, ArH); MS: m/z 264 (M^+), 249 (M^+-CH_3), 217 (M^+-SCH_3), 159 (M^+-PhCO), 105 (PhCO), 73($SiMe_3$); HRMS: m/z for $C_{14}H_{20}OSSi$ found M^+, 264.1015; calcd M, 264.1004; and as second Rf fraction **13a** (0.40 mmol, 77 mg, 58%).

3-methylsulfanyl-1,2-diphenyl-prop-2-en-1-one 13b. Starting from (Z)-1-methylsulfanyl-1-trimethylsilyl-2-phenyl ethylene **2a** and benzoyl chloride, preparative thick layer chromatography of the crude reaction mixture (5:1 light petroleum: diethyl ether as solvent) gave **13b** in 100% yield as a mixture of the (E) and (Z) isomers in a 2.5:1 ratio. IR, ^1H NMR, ^{13}C NMR, MS, HRMS spectra were recorded on the mixture of the two isomers. IR (CS_2)ν_{max}: 1680 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.23 (s, 3H, SCH_3, (Z) isomer), 2.45 (s, 3H, SCH_3, (E) isomer), 7.34-7.69, 7.91-8.14 (m, 11H (E) isomer, 11H (Z) isomer ArH and (E) isomer, (Z) isomer vinylic H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 12.33 (SCH_3 (Z) isomer), 18.61 (SCH_3 (E) isomer), 128.60, 128.90, 129.00, 129.10, 129.82, 129.90, 135.00, 137.00, 139.70, 132.10, 134.10 (ArCH (E) and (Z) isomers), 136.40 (vinylic C), 137.20 (vinylic C), 150.00 (vinylic CH E isomer), 192.00 (CO (E) isomer), 197.00 (CO (Z) isomer); MS: m/z 254 (M^+); 239 (M^+-CH_3); 207 (M^+-SCH_3); 134 (PhCH=CHS); 105 (PhCO); 77 (Ph). The spectral properties of (E)-**13b** were in good agreement with those previously reported.[13]

Attempted Synthesis of 3-ethyl-4-methylsulfanyl-but-3-en-2-one 13c. Starting from (Z)-1-dimethylphenylsilyl-1-methylsulfanylbut-1-ene **2b** and acetyl chloride, preparative thick layer chromatography of the crude reaction mixture (4:1 light petroleum: diethyl ether as solvent) gave, as the higher R_f fraction a dimeric product arising from the α-dimethylsilylvinyl sulfide moiety IR (CS_2) ν_{max}: 1250 ($SiMe_2$), 1030, 780 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.35 (s, 3H), 0.50 (s, 3H), 0.98 (t, 3H, J = 8.45 Hz), 1.10 (t, 3H, J = 8.48 Hz), 1.95 (t, 2H, J = 7.04 Hz), 2.22 (s, 3H), 2.38 (s, 3H), 2.48 (qd, 2H), 2.75 (qt, 2H), 3.75 (m, 1H), 4.88 (m, 1H), 4.98 (m, 1H); MS: m/z 326 (M^+), 311 (M^+-CH_3), 297 (M^+-Et), 279 (M^+-C_2H_7O), 111 (C_5H_3OS), 75 (C_2H_7SiO); and as the lower R_f fraction acetophenone **12a** (62%).

(E)-2-Ethyl-5-methyl-1-methylsulfanyl-hexa-1,4-dien-3-one 13d. Starting from (Z)-1-dimethylphenylsilyl-1-methylsulfanylbut-1-ene **2b** and 3,3-dimethylacryloyl chloride, preparative thick layer chromatography of the crude reaction mixture (10:1 light petroleum: diethyl ether as solvent) gave, as the higher R_f fraction 3-methyl-1-phenylbut-2-ene-1-one **12b**[12] (21%) and as the lower R_f fraction (E)-**13d** (20%); IR (CS_2) ν_{max}: 1652 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.00 (t, 3H, J = 9 Hz CH_3), 1.90 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.38 (q, 2H, J = 9 Hz, CH_2), 2.45 (s, 3H, SCH_3), 6.30 (bs, 1H, vinylic H), 7.20 (s, 1H, vinylic H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 12.00, 17.80, 20.50 (CH_3), 21.00 (CH_2), 27.50 (SCH_3), 121.50 (vinylic CH), 140.50 (vinylic C), 144.00 (vinylic CH), 152.00 (vinylic C), 189.50 (CO); MS: m/z 184 (M^+), 169 (M^+-CH_3), 155 (M^+-Et), 137 (M^+-SCH_3), 83 ((CH_3)$_2$C=CHC=O), 55 ((CH_3)$_2$C=CH); HRMS: m/z for $C_{10}H_{16}OS$ found M^+, 184.0918; calcd M, 184.0922.

(E)-2-Ethyl-3-methylsulfanyl-1-phenyl-prop-2-en-1-one 13e. Starting from (Z)-1-dimethylphenylsilyl-1-methylsulfanylbut-1-ene **2b** and benzoyl chloride, the title product was obtained, after preparative thick layer chromatography (5:1 light petroleum: diethyl ether as solvent), in 93% yield, as an oil; IR (CS_2) ν_{max}: 1650 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.10 (t, 3H, J = 8 Hz, CH_3), 2.35 (s, 3H, SCH_3), 2.50 (q, 2H, J = 8 Hz, CH_2), 7.40-7.70 (m, 5H, ArH), 7.00 (s, 1H, vinylic H); ^1H NMR (300 MHz, C_6D_6); 1.5 (t, 3H, J = 7.8 Hz, CH_3), 1.73 (s, 3H, SCH_3), 3.0 (q, 2H, J = 7.8 Hz, CH_2), 7.40-7.70 (m, 5H, ArH), 7.00 (s, 1H, vinylic H);^{13}C NMR (75.4 MHz, C_6D_6): δ 12.20, 16.62 (CH_3), 22.59 (CH_2), 128.31, 129.18, 131.02 (ArCH), 147.59 (vinylic CH), 139.56, 140.05(C), 193.30 (CO); MS: m/z 206 (M^+), 191 (M^+-CH_3), 159 (M^+-SCH_3), 105 (PhCO), 77(Ph); HRMS: m/z for $C_{12}H_{14}OS$ found M^+, 206.0769; calcd M, 206.0765. The stereochemistry of the reaction was elucidated by n.O.e. and Lis experiments. Saturation of the CH_2 resonance at 3.0 ppm did not produce a significant increase in the intensity of the vinylic proton signal at 7.0 ppm and produce an increase in the intensity of the SMe signal at 1.7 ppm proving that the CH_2 and the SMe lie at the same part of the double bond. The addition of a shift reagent ($Eu(fod)_3$ was used) produced a downfield shift of the vinylic and of the *orto*-proton signal proving that they lie at the same part of the double bond. The spectral properties

of (E)-**13e** were compared with those previously reported[14] and we found that the previous assignment was wrong.

Desilylation of 11a with $AlCl_3$. To a solution of $AlCl_3$ (1.44 mmol, 200 mg) in dry dichloromethane (2 ml), cooled to 0 °C, under argon atmosphere, was added **11a** (0.48 mmol, 110 mg). After 12 h at room temperature the reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with dichloromethane and the organic layer was washed with 10% aqueous $NaHCO_3$ and with water, dried and concentrated under reduced pressure. The residue was purified by chromatography on silica (3:1 light petroleum : diethyl ether) and gave as the higher R_f fraction **10a** (1.0 mmol, 156 mg, 70%) and as the lower R_f fraction **11a** (0.4 mmol, 90 mg, 30%).

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