CHEMISTRY OF SILYL THIOKETONES : STUDIES CONCERNING THE REGIOCHEMISTRY OF THE CYCLOADDITION WITH SUBSTITUTED 1,3-DIENES

B. F. Bonini, G. Mazzanti, P. Zani*
Dipartimento di Chimica Organica "A.Mangini", Università di Bologna.
Viale Risorgimento 4 , I- 40136 Bologna (Italy)

Abstract. The cycloaddition between a series of silyl thioketones and substituted, open-chain 1,3-dienes was investigated: mixtures of regioisomeric 5,6-dihydro (2H) thiopyrans are formed. The structures of the major isomers were assigned on the basis of both spectroscopic analysis and chemical correlations.

Introduction. Silyl thioketones are a class of reactive organic molecules which allow the preparation of a variety of compounds containing the Si-C-S unit: further synthetic transformations of these primary adducts can be accomplished either through desilylation or manipulation at S.

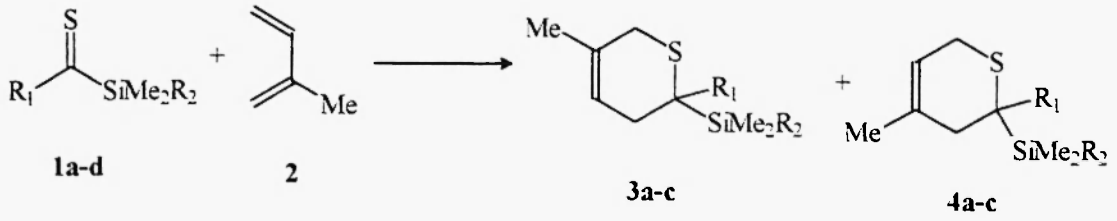
In the recent years some contributions to this subject have been reported (1) showing the preparation of silyl thiones of various structures, their stability and reactivity as well as their synthetic applications, mainly as equivalents of unstable thioaldehydes (2).

Among the reactions investigated, the [4+2] cycloaddition of silyl thiones to 1,3-dienes is very easy to perform, gives high yields and the thiaheterocycles obtained are amenable to many synthetic transformations (3). Through our studies, the reactivity and stereoselectivity of this cycloaddition was investigated in the case of cyclic 1,3-dienes and symmetrical butadienes (4); on the contrary a detailed study concerning the regiochemistry of the cycloaddition was performed in the case of 1,3-heterodienes only (5).

Independently, a paper by Kang et al. (6) discussed the regiochemistry of the cycloaddition between the sole *t*-butyl trimethylsilyl thione and a series of 2- and 1-substituted 1,3 dienes. This prompted us to extend the investigation including the reaction of more silyl thiones with unsymmetrically substituted 1,3 dienes: in fact, the adducts derived from *t*-butyl silyl thione are often desilylate difficultly (7); moreover, it is worth studying a larger number of substrates which may give more useful informations about reactivity, regioselectivity and synthetic usefulness of cycloadducts.

Discussion The regiochemical outcome of the cycloaddition between a series of silyl thiones **1a-d**, carrying substituents of different steric and electronic effects, and isoprene **2** as standard unsymmetrical 1,3-diene are reported in Scheme 1 + Table 1 .The reactions were run in ethereal solution under an inert

atmosphere employing a twofold molar excess of diene **2** and could be followed visually through the disappearance of the colour typical of the thione. After the reaction was completed, the composition of the crude reaction mixture was determined by 1H NMR then the products were isolated by preparative layer chromatography and fully characterized.



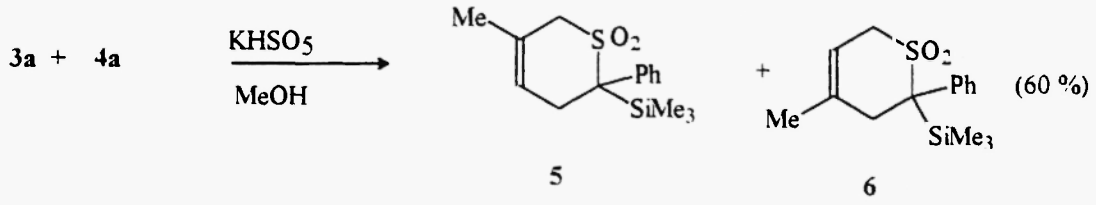
1a-d **2** **3a-c** **4a-c**

Scheme 1

entry	1	R_1	R_2	T (°C)	time	yield (**3+4**)	**3** : **4**
1	1a	Ph	Me	0	10 min	68%	2 : 1
2	"	"	"	- 60	30 h	63%	2.5 : 1
3	1b	t-Bu	Me	4	10 d	63%	5 : 1
4	1c	cyclopropyl	Ph	4	40 h	69%	2.6 : 1
5	1d	2,4,6-$Me_3C_6H_2$	Ph	25	7 d	-	-
6	"	"	"	40	24 h	-	-

Table 1 Cycloaddition of silyl thiones **1a-d** with isoprene **2**.

The very reactive phenyl trimethylsilyl thione **1a** affords in high yield the two isomeric cycloadducts **3a** and **4a** with an isomer ratio of 2:1 at 0 °C (table 1 ,entry 1); on lowering the temperature down to - 60 °C the regioselectivity was little influenced (isomer ratio 2.5 : 1, entry 2). The attribution of the correct structures to **3a** and **4a** required both chemical transformations and application of NMR spectroscopy; in fact, signals of the protons at C-2 and C-5 of both isomers overlap in the spectrum of the mixture as well as of the pure isomer, hampering an unequivocal attribution through decoupling experiments. Separation of the regioisomers could not be accomplished by chromatography, whereas repeated crystallisations led to the major isomer **3a** as a pure crystalline product: again, 1H NMR experiments with homonuclear decoupling in different solvents proved to be inconclusive for the structural attribution due to signal overlapping. Finally, the mixture of regioisomeric dihydrothiopyrans **3a** and **4a** was oxidized to the corresponding α-silyl sulfones **5** and **6** using oxone in methanol (8) (Scheme 2). The major isomeric sulfone was obtained pure after crystallisation: in this case, the resonance of the protons at C-2 (δ 3.30) and C-5 (δ 3.15) are separated enough to perform homonuclear decoupling. By irradiating the signal at δ 5.7 (vinylic proton) only the signals at δ 3.15 (CH_2 -5) are affected, thus demonstrating the presence of the CH_3 at the position 3 of the dihydrothiopyrane ring in the major isomer **5** (*para*-like position with respect to the Ph and $SiMe_3$ groups). This orientation is the same found previously (6) in the main adduct from *t*-butyl silyl thione **1b** and the diene **2**.

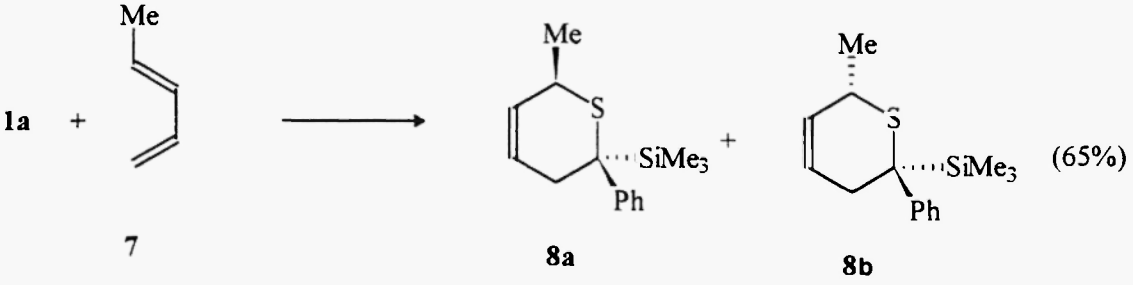


Scheme 2

When compared to **1a** in the same reaction conditions. **1b** is by far less reactive with isoprene: ten days were required at 4 °C in ethereal solution to afford the cycloadducts **3b** and **4b** (entry 3) in an isomeric ratio 5:1 which matches perfectly that reported in the previous investigation, where different conditions were employed (large excess of the diene, 80°C for 6 hours).

Comparing the results from **1a** and **1b**, the regioselectivity appears to be influenced by steric effects: this is confirmed by the reaction of cyclopropyl silyl thione **1c** where the steric bulk of the cycloalkylic substituent can be similar to that of the phenyl ring; the reactivity instead is much lower compared to **1a**, probably due to the absence of electronic activation. However, the regiochemical outcome in the reaction with **2** (isomer ratio 2.5 : 1) is much similar to **1a** (table 1, entry 4). To test further the hypothesis of sterically controlled regioselectivity the very hindered mesityl (dimethylphenyl)silyl thione **1d** was prepared, but it proved to be unreactive with isoprene, both at room temperature and on heating (table 1, entries 5,6). The correct isomeric structures could be attributed to the products **3b,c** and **4b,c** simply by inspection of the NMR spectrum of the mixtures, because in these cases the signals of the protons at C-2 and C-5 were separated enough to recognize the vicinal coupling between the vinylic proton at C-4 and the CH_2 at C-5 in the major isomer.

The reaction of phenyl trimethylsilyl thione **1a** with *trans*-1,3-pentadiene (piperylene) **7** was subsequently investigated (Scheme 3) : **7** was chosen as a typical 1,3 diene substituted at the terminal position. The reaction was carried out at 0 °C in ethereal solution employing an almost equimolar ratio diene/thione.

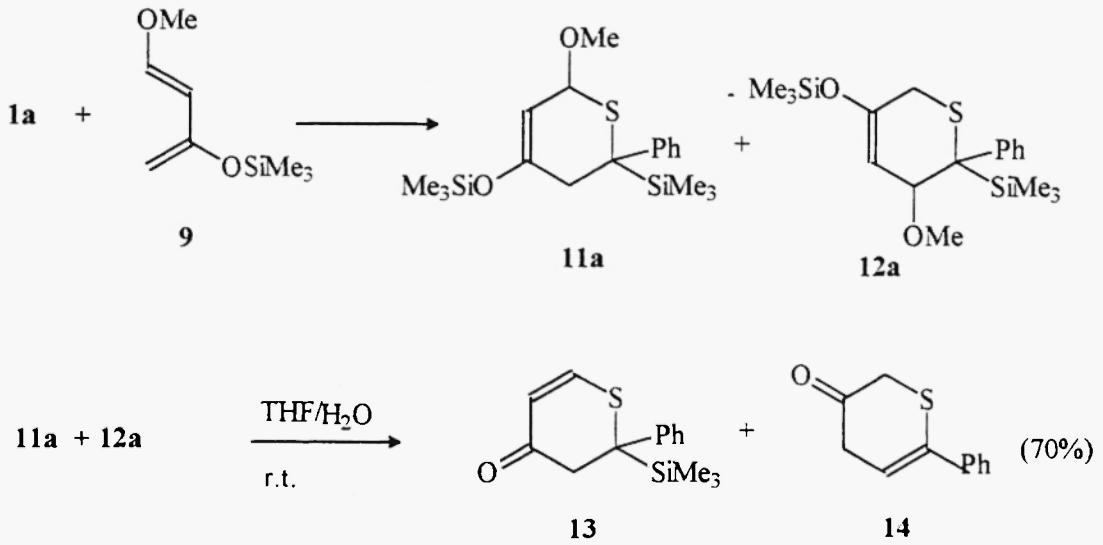


Scheme 3

Inspection of the crude by NMR revealed the presence of two isomeric adducts **8a** and **8b** in a ratio 75/25 characterised by the signals of their methyl groups (doublets) at δ 1.20 and 1.45 respectively. Purification by

chromatography followed by crystallisation of the mixture of cycloadducts afforded the pure 2-methyl 6-phenyl 6-trimethylsilyl 5,6-dihydro (2H) thiopyran **8a** as a single isomer, whose configuration was elucidated by means of NOe experiments. Saturation of the $SiMe_3$ resonance at δ 0.25 (C_6D_6) caused a significant increase in the intensity of both ortho aromatic hydrogens at δ 8.85 (+ 2.8%) and one of the methylene hydrogens at C-5 (δ 2.95, + 2.2%), whereas the signals of both substituents at C-2 were unaffected (tertiary H at δ 3.35 and methyl at δ 1.30). Saturation of the ortho aromatic hydrogens at δ 8.85 caused variations on the intensity of the signals for the other methylene hydrogen at C-5 (δ 2.85, +2.5%), for the tertiary H at C-2 (δ 3.35, + 1.7%), and for $SiMe_3$. Finally, saturation of the methyl resonance at δ 1.30 caused variations on the intensity of the signals at δ 3.3 (vicinal, tertiary H at C-2), and δ 5.6 (vinylic H at C-3).These findings are in agreement with a structure where the bulkier substituent at C-6, i.e. the trimethylsilyl group, occupies an endo position in the half-chair dihydrothiopyrane ring; the observed NOe effects are explained only by an exo position of the Me at C-2, which leads to a shorter separation in space between the tertiary H at C-2 and the ortho H of the phenyl ring in an exo-like position. The preferred stereoisomer **8a** should then be described as (2S,6R)/(2R,6S) (or E by application of sequence rules).

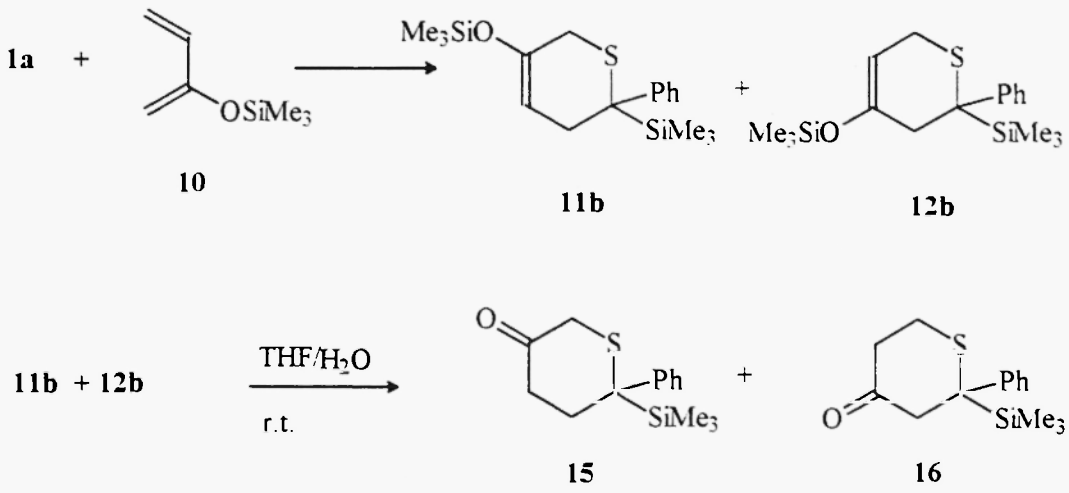
The cycloadditions between **1a** and the silyloxy-substituted dienes **9** and **10** were then examined . The very reactive Danishefsky diene **9** afforded in good yield a mixture of regioisomeric primary adducts **11a** and **12a** (ratio 2 : 1) which displayed a limited stability (Scheme 4).



Scheme 4

It was possible to purify by crystallisation the major adduct **11a** 2-methoxy 6-phenyl 6-trimethylsilyl 4-trimethylsilyloxy 5,6-dihydro (2H) thiopyran whose structure was assigned on the basis of 1H and 13C NMR spectra. Subsequently, the mixture of **11a** + **12a** was subjected to hydrolysis in aqueous THF: two products were isolated, the α,β unsaturated ketone **13**, which is the expected product from the hydrolysis of cycloadduct **11a**, and the desilylated β,γ unsaturated ketone **14**. Product **14** can arise from the hydrolysis of

the silyl enol ether function in the adduct **12a** followed by the removal of MeO-$SiMe_3$ (instead of MeO-H) across the positions 5 and 6 of the heterocyclic ring. The ratio between products **13** and **14** (2 : 1) matches perfectly that between the regioisomers **11a** and **12a** and this is an independent proof of the structural assignments.



Scheme 5

The reaction of silyl thione **1a** with 2-trimethylsilyloxy 1.3-butadiene **10** led again to a mixture of isomers **11b + 12b** in a 2:1 ratio. In this case, separation of isomers and attribution of the structures was not possible at the stage of primary adducts: therefore, they were subjected to hydrolysis in THF-water, affording the two saturated ketones **15** and **16** (Scheme 5) whose structure could be attributed on the basis of 13C NMR spectra (see Experimental). Again the transformation of the primary adducts **11b** and **12b** into **15** and **16** (2:1 ratio) supported the regiochemical attribution.

Conclusions. The cycloaddition between 1,3-dienes and thiocarbonyl compounds acting as heterodienophiles is one of the most efficient methods for the synthesis of dihydro (2H)thiopyrans (9) which, in turn, may be useful synthetic intermediates (10). For this reason, it should be important to control, or at least to predict, the regiochemistry of those cycloadducts derived from unsymmetrically substituted dienes. During recent years, many results have been reported and partly reviewed (11), leading to some tentative generalizations: -**with acceptor substituted thiocarbonyls** the thione substituent prefers the *ortho* or *para* like position related to diene donor group; regioselectivity is high to medium and 2-substituted dienes (like isoprene and 2-silyloxybutadienes) afford *para*-dihydrothiopyrans, whereas 1-alkyl or alkoxy dienes afford *ortho* dihydrothiopyrans; - **with donor-substituted thiocarbonyls** the regiochemistry is usually reversed; with the exception of thioaldehydes, selectivity is limited and *meta* adducts are formed in slight excess from 2-substituted dienes and simple thiones (12).

As far as the present investigation is concerned, our results from silyl thiones could be compared to those obtained with the corresponding thioaldehydes (whose silyl thiones are proposed as synthetic equivalents),

besides a closer comparison to *t*-butyl silyl thione **1b** (whose reactivity has been already investigated). Our results show that regioselectivity is low in the reaction between 2-substituted dienes **2** and **10** and silyl thiones. The preferred regioisomers in the reaction with **2** show the 1,4 relationship in the ring between silicon and methyl (*para*-like adduct) , which is opposite to the structural relation found in the adducts of diaryl or alkyl aryl thiones with the same diene (12a,c).

The reaction between oxygenated dienes and aryl silyl thiones showed a somewhat different picture : in fact, both dienes **9** and **10** gave a modest regioselectivity (isomer ratio 2 : 1) where exclusive formation of a *meta* regioisomer was previously found by Kang (6) when Danishefsky diene **9** reacted with silyl thione **1b**, whereas diene **10** led to an about 1 : 1 mixture. The subsequent transformations of the primary adducts **11** and **12** follow the expected course. Finally, the cycloaddition of aryl silyl thiones with 1-substituted dienes like **7** is highly regioselective as found previously for the *t*-butyl derivative (6), with a slightly better selectivity in favour of an E isomer.

Experimental. Melting points were obtained with a Buchi SMP 20 apparatus and are uncorrected. 1H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or Gemini 300 (300 MHz) spectrometer as solutions in $CDCl_3$ if not otherwise stated; 13C NMR spectra were recorded on the same spectrometers at 50.3 and 75.46 MHz respectively, using $CDCl_3$ as internal standard; multiplicities were assigned by DEPT experiments. Low resolution mass spectra were obtained with a VG 7070E spectrometer (ionisation potential 70 eV): these spectra are collected in Table 2. Infrared spectra were recorded with a Perkin Elmer 177 spectrometer. Chromatography was performed with E.Merck silica gel 60 (70-230 mesh) for column separation and with E.Merck silica gel 60 PF_{254} for preparative 20*20 plates. Petroleum ether refers to the fraction b.p. 40 - 70 °C.

Cycloaddition of **1a** *with isoprene* **2.** An ethereal solution of phenyl trimethylsilyl thione **1a** (freshly prepared from 0.60 g., 3.37 mmol, of benzoyl trimethylsilane as previously reported (4)) was treated at 0 °C with isoprene **2** (0.7 mL, 6.74 mmol). After stirring at 0 °C for 10 min under argon the blue colour of the solution had disappeared; the solvent was removed at reduced pressure and the residue chromatographed on a silica gel column (eluent : petroleum ether/benzene 2/1) affording 0.6 g of 3-Methyl-6-phenyl-6-trimethylsilyl-5,6-dihydro-(2H) thiopyran **3a** and 4-Methyl-6-phenyl-6-trimethylsilyl-5,6-dihydro-(2H) thiopyran **4a** (68% yield based on the starting acyl silane) as a low melting solid: δ_H 0.00 and 0.02 (9H, s, $SiMe_3$), 1.57 and 1.89 (3H, b.s., CH_3), 2.47-3.05, (4H, m, 2 CH_2), 5.44 and 5. 62 (1H, m, vinyl H), 7.10-7.77 (5H, m, ArH).The 2 : 1 ratio between the isomers **3a** and **4a** was determined by integration of the signals at δ 1.57 vs,1.79, 5.62 vs. 5.44 and 0.00 vs. 0.02 respectively. When the cycloaddition was performed at -60 °C for 30 h this ratio increased to 2.5 : 1. Chromatography of the isomeric mixture on preparative plates with n-pentane did not afford separation, whereas crystallisation from methanol gave **3a** containing less than 10% of **4a**.

Oxidation of the dihydrothiopyrans **3a + 4a** *to the corresponding* α*-silyl sulfones* **5** *and* **6**. A mixture of the cycloadducts **3a + 4a** in a 2 : 1 ratio (0.134 g, 0.55 mmol) was dissolved in methanol (5 mL) and cooled at 0

Table 2 Spectroscopic data of compounds **3a-c**, **4a-c**, **5**, **8a**, **11a**, **13-16**.

N°	NMR δ_H (ppm)	δ_C (ppm)	Mass : (m/e)
3a	0.00 (9H, s, SiMe$_3$), 1.54 (3H, b.s., CH$_3$), 2.52 (1H, d, J 17.5 Hz, H-CH), 2.7-2.9 (3H, m, CH$_2$ + CH), 5.62 (1H, b.s. vinyl H), 7.1-7.6 (5H, m, ArH).	-3.91 (3 CH$_3$), 24.36 (CH$_3$), 26.49 (CH$_2$), 30.52 (CH$_2$), 37.41 (Cq), 120.66 (CH), 124.72 (CH), 127.38 (CH), 127.66 (2 CH), 127.78 (2 CH), 130.97 (Cq), 141.80 (Cq)	262 (M+), 247 (M+ - Me), 189 (M+ - SiMe$_3$), 157 (M+ - S-SiMe$_3$), 121(PhCS), 73 (SiMe$_3$)
3b and **4b**	0.10 and 0.12 (9H, s, SiMe$_3$), 0.99 and 1.05 (9H, s, *t*-Bu), 1.75 and 1.77 (3H, b.s., Me), 2.25 and 2.35 (2H, m, CH$_2$-5), 2.65-2.95 (2H, q$_{AB}$ J 15 Hz, CH$_2$ 2), 5.50 and 5.65 (1H, m vinyl H).	(major isomer **3b**) 1.29 (3 CH$_3$, SiMe$_3$), 23.42 (CH$_3$), 28.12 (CH$_2$), 28.45 (3CH$_3$, *t*-Bu), 29.67 (CH$_2$), 40.35 (Cq), 43.35 (Cq), 124.29 (CH), 133.58 (Cq)	242 (M+), 227 (M+ - Me), 185 (M+ - *t*-Bu), 169, 137,121, 73 (SiMe$_3$), 57 (*t*-Bu).
3c and **4c**	0.0 and -0.6 (4H, m, 2 CH$_2$ cyclopropyl), 0.405 and 0.414, 0.421 and 0.428 (6H, s, Me$_2$Si), 0.85 - 1.05 (1H, m CH cyclopropyl), 1.65 and 1.72 (3H, b.s., CH$_3$), 2.15 - 2.45 (2H, m, CH$_2$), 2.65 and 2.80 (1H, d, J 17.5 Hz, H-CHS), 3.20 and 3.30 (1H, d, J 17.5 Hz, H-CHS), 5.40 and 5.60 (1H, b.s., vinyl H), 7.25 - 7.70 (5H, m, HAr)	-5.03, -4.85, -4.44 (2 CH$_3$, SiMe$_2$), 1.10, 0.38, 1.64, 2.50 (2 CH$_2$, CH$_2$ cyclopropyl), 4.75, 6.29 (CH, CH cyclopropyl), 23.95, 25.12, 26.41, 28.05 (CH$_2$, 2 CH$_2$ heterocycle), 24.24, 24.90 (CH$_3$), 121.63, 121.73 (CH), 127.26, 127.52 (CH, 2 CHAr), 128.99, 129.19 (CH), 129.30 (Cq), 129.51 (CH), 134.61, 134.81 (CH, 2 CHAr).	288(M+), 271 (M+ -Me 2H), 259 (M+ - Me- CH$_2$), 245 (M+ - Me-2CH$_2$), 220 (C$_3$H$_3$CSSiMe$_2$Ph), 181 (M+ - PhSi - 2H), 152 (M+ - PhMe$_2$Si - H), 135 (PhMe$_2$Si), 120 (PhMeS).
5	0.20 (9H, s, SiMe$_3$), 1.69 (3H, b.s. CH$_3$), 2.95 - 3.15 (3H, m CH$_2$ + CH), 3.30 (1H, dm, J 17.5 Hz, CH-SO$_2$), 5.70 (1H, m vinyl H), 7.2 - 7.4 and 7.6 - 7.75 (5H, m, HAr)	-1.81 (3 CH$_3$), 23.31 (CH$_3$), 31.28 (CH$_2$), 51.65 (CH$_2$), 58.60 (Cq), 119.72 (CH), 127.25 (CH), 127.93 (Cq), 128.37(4 CH), 134.4 (Cq).	294 (M+), 215 (M+ - SO$_2$ - Me), 157 (M+ - SO$_2$ - SiMe$_3$), 142 (M+ - SO$_2$ - SiMe$_3$ - Me), 129, 115, 91, 73 (SiMe$_3$)
8a	0.01 (9H, s, SiMe$_3$), 1.19 (3H, d, J 7.2 Hz, CH$_3$), 2.66-2.94 (2H, qm, J_{gem} 18.1 Hz, CH$_2$), 2.95 - 3.10 (1H, m, CH), 5.49 (1H, b.d., J_{cis} 10.6 Hz, CH), 5.75-5.9 (1H, dm, J_{cis} 10.6 Hz, CH), 7.1 -7.6 (5H, m, HAr). δ_H (C$_6$D$_6$) 0.0 (9H, s, SiMe$_3$), 1.09 (3H, d, J 7.2 Hz, CH$_3$), 2.5-2.8 (2H, qm, CH$_2$), 3.1 (1H, m, CH), 5.32 (1H, dq, J_{cis} 12 Hz), 5.6 - 5.75 (1H, m, CH), 6.95 - 7.25 (3H, m, HAr), 7.60 (2H, d, HAr).	-3.99 (3CH$_3$, Me$_3$Si), 19.93 (CH$_3$), 29.68 (CH$_2$), 30.50 (CH), 40.47 (Cq), 124.73 (CH), 125.81(CH), 127.61(2 CH), 127.78 (2 CH), 131.42 (CH), 142.3 (Cq). δ_C (C$_6$D$_6$) -3.49 (3 CH$_3$, Me$_3$Si), 20.50 (CH$_3$), 30.29 (CH$_2$), 31.33 (CH), 41.23 (Cq), 125.6 (CH), 126.37 (CH), 132.04 (CH), 143.21 (Cq).	262 (M+), 247 (M+ - Me), 189 (M+ - SiMe$_3$), 173, 157 (M+ -SiMe$_3$ - S), 142, 129, 121 (PhCS), 91 (C$_7$H$_7$), 73 (SiMe$_3$)
11a	-0.08 (9H, s, SiMe$_3$), -0.06 (9H,s, OSiMe$_3$), 2.6 and 2.9 (2H, q$_{AB}$ J 16 Hz, CH$_2$-5), 3.5 (3H, s, CH$_3$O), 4.55 (1H, d, J 6 Hz, CH-OMe), 5.23 (1H, d, J 6 Hz, vinyl H), 7.05 - 7.60 (5H, m, HAr)	-2.48 (3 CH$_3$, SiMe$_3$), -0.37 (3 CH$_3$, SiMe$_3$), 26.07 (CH$_2$), 55.66 (CH$_3$, OMe), 77.98 (CH, S-CH-O), 104.80 (CH), 125.42 (CH), 127.30 (2 CH), 128.19 (2 CH), 139.71 (Cq), 151.88 (Cq, =C-OSi)	366 (M+), 351(M+ -Me), 335 (M+ - MeO), 293 (M+ - SiMe$_3$), 262 (M+ - Me$_3$SiO), 230 (M+ - Me$_3$SiO - MeO), 173, 157, 89 (Me$_3$SiO).
13	0.05 (9H, s, SiMe$_3$), 3.05 and 3.35 (2H, q$_{AB}$, J 15 Hz, CH$_2$-5), 5.96 (1H, d, J 10 Hz, vinyl H), 7.10 - 7.40 (6H, m, ArH + vinyl H)	(in presence of **14**) -4.3 (3 CH$_3$, SiMe$_3$), 37.5 (CH$_2$), 40.9 (CH$_2$), 43.4 (CH$_2$), 124.4 (CH), 126.3 (CH), 126.8 (CH), 127.3 (CH), 128.0 (CH), 128.6 (CH), 128.8 (Cq), 132 (Cq), 139.8 (Cq), 143.9 (CH), 193.6 (CO), 204 (CO).	262 (M+), 261 (M+ - H), 247 (M+ - Me), 229 (M+ - H - Si), 121 (PhCS), 77 (Ph), 73 (SiMe$_3$).
14	3.20 (2H, d, J 4.2 Hz, CH$_2$- 4), 3.40 (2H, b.s. CH$_2$ -2), 6.19 (1H, t, J 4.2 Hz, vinyl H-5), 7.1-7.6 (5H, m, HAr)		190 (M+), 173 (M+ - OH), 148 (M+ -CO - CH$_2$), 77 (Ph).
15 and **16**	-0.005 and 0.013 (9H, s, SiMe$_3$), 2.30 - 3.40 (6H, m, 3 CH$_2$), 7.10 - 7.80 (5H, m, HAr).	major isomer (attributed as **15**) -3.78 (3 Me, SiMe$_3$), 36.03 (CH$_2$), 38.48 (CH$_2$), 38.88 (CH$_2$), 42.67(Cq), 127.54 (2 CH Ar), 128.0 (CH Ar), 128.70 (2 CH Ar), 139.06 (Cq), 204.87(C=O); minor isomer (attributed as **16**) -4.11(3 Me, SiMe$_3$), 27.33 (CH$_2$), 43.23 (CH$_2$), 48.59(CH$_2$), 45.80(Cq), 125.45(CH Ar), 125.64 (2 CH Ar), 128.29 (2 CH Ar), 140.3 (Cq), 208.76 (C=O)	264 (M+), 249 (M+ - Me), 236 (M+ - CO), 231 (M+ - SH), 191 (M+ - SiMe$_3$), 159 (M+ - CO -Ph), 143, 117, 77 (Ph), 73 (SiMe$_3$).

°C, then a solution of oxone ($KHSO_5$) (0.94 g, 1.53 mmol) in methanol (5 mL) was added . The mixture was stirred at 0 °C for 15 min, then at room temperature for 4h; after dilution with water, it was extracted three times with chloroform. The organic phase was washed with water and concentrated under reduced pressure. The residue was purified by plate chromatography (petroleum ether/ethyl acetate 10/1 as eluant) affording 0.09 g (60%) of of 3-Methyl- and 4- methyl-6-phenyl-6-trimethylsilyl-5,6-dihydro-(2H) thiopyran S,S-dioxides **5** and **6** : ν_{max} (CCl_4) 1305, 1150 and 1120 cm^{-1} (SO_2); δ_H 0.20 (9H, b.s.,$SiMe_3$), 1.69 and 1.90(3H, b.s. CH_3) , 2.8 - 3.4 (4H, m, 2 CH_2), 5.15 and 5.70 (1H, m, vinyl H), 7.2-7.4 and 7.5-7.7 (5H, m, HAr). The ratio between the two isomeric sulfones (about 2:1) was determined through the integrals of the signals at δ 1.69 vs. 1.90 and 5.70 vs. 5.15. The major isomer **5** was obtained pure after crystallisation from methanol :m.p. 125-28 °C.

Cycloaddition of **1b** *with* **2**. The reaction is performed as described previously employing 0.15 g (0.86 mmol) of *t*-butyl trimethylsilyl thione **1b** (7) and 0.18 mL (1.72 mmol) of isoprene **2** in 10 mL of diethyl ether under inert gas. After 10 days in the refrigerator (4 °C) the solvents are removed under vacuum and the residue purified through plate chromatography (petroleum ether/methylene chloride 10/1 as eluent) affording 0.12 g (63 % yield) of 3-Methyl-6-*t*-butyl-6-trimethylsilyl-5,6-dihydro-(2H) thiopyran **3b** and 4-Methyl-6-*t*-butyl-6-trimethylsilyl-5,6-dihydro-(2H) thiopyran **4b** : The 5 : 1 ratio between the isomers **3b** and **4b** was determined by integration of the signals at δ 0.99. vs.1.05, 5.55 vs. 5.70 and 0.10 vs. 0.12 respectively).

Cycloaddition of **1c** *with* **2**. The reaction is performed as described previously employing Cyclopropyl dimethylphenyl silyl thione **1c** (8) (prepared from 0.25 g , 1.22 mmol of the corresponding acyl silane) and 0.25 mL (2.5 mmol) of isoprene **2** in 10 mL of diethyl ether under inert gas. After 40 hours in the refrigerator (4 °C) the solvents are removed under vacuum leaving the pure cycloadducts **3c** and **4c** (0.242 g, 69%).

Attempted cycloaddition of **1d** *with* **2** .In a vial Mesityl dimethylphenyl silyl thione **1d** (0.073 g, 0.245 mmol) is placed and dissolved in 1 mL of methylene chloride; isoprene **2** (0.05 ml, 0.49 mmol) is added and the vial is saturated with argon and sealed. After 1 week at room temperature no reaction had occurred. The vial is then heated at 40 °C for 1 day but no reaction happened again, as confirmed by 1H NMR of the crude.

Cycloaddition of 1a *with piperylene* **7**. Phenyl trimethylsilyl thione **1a** (1.82 mmol as determined spectrophotometrically at 678 nm) in diethyl ether (16mL) was treated at 0 °C with *trans*-1,3 pentadiene **7** for 2 hours under inert gas. After the disappearance of the blue colour of the thione the solution was concentrated under vacuum and the residue chromatographed on a silica gel column (eluent petroleum ether) affording 0.31 g, (65 % from **1a**) of 2-Methyl-6-phenyl-6-trimethylsilyl-5,6-dihydro-(2H) thiopyran **8a,b** as a mixture of isomers . δ_H 0.0 and 0.1 (9H,s, $SiMe_3$), 1.20 and 1.43 (3H,d, j 7.2 Hz, CH_3), 2.60 - 2.95 (2H, m, CH_2 -5), 3.0 and 3.2 (1H, m, CH-2), 5.40 and 5.49 (1H, dm, vinyl H), 5.68 and 5.80 (1H, dm, vinyl H), 7.2 - 7.6 (5H, m, HAr), The ratio between the isomers (about 2.6:1) was determined through the integrals

of the signals at δ 1.20 vs. 1.43 and 3.0 vs. 3.2 respectively. Homonuclear decoupling experiments performed irradiating the signals of the methyl groups at δ 1.20 and 1.43 showed variations only in the pattern of the signals of the tertiary protons at δ 3.0 and 3.2 respectively, thus confirming the presence of the methyl substituent at the position 2 of the heterocycle. A couple of signals at δ 0.98 and 1.05 (doublets) were present in the spectrum of the crude (less than 10% with respect to **8b**), which could be tentatively attributed to the opposite regioisomer 5-Methyl-6-phenyl-6-trimethylsilyl-5,6-dihydro-(2H) thiopyran (mixture of stereoisomers), but no other signal could be unambigously recognized in the spectrum for this structure. The major isomer **8a** was obtained pure through crystallisation from methanol: m.p. 48-49° C. NOE experiments were run at 300 MHz and 24 °C in deaerated C_6D_6 where a better separation of the signals was found.

Cycloaddition between thione **1a** *and diene* **9**. The reaction is performed as described previously employing phenyl trimethylsilyl thione **1a** (prepared from 0.30 g , 1.68 mmol of the corresponding acyl silane) and 0.33 mL (1.68 mmol) of 1-methoxy 3-trimethylsilyloxy-1,3-butadiene **9** in 15 mL of diethyl ether at 0 °C.The reaction is instantaneous; after addition of n-pentane and cooling at - 60°C the major isomer **11a** is separated by crystallisation: in the 1H NMR spectrum of the crude, some signals could be attributed to the minor isomer **12a** but the elimination of Me_3SiOMe should have occurred already : δ_H 0.03 (9H, s, $SiMe_3$), 3.05 and 3.33 (2H, q_{AB}, *J* 16 Hz, CH_2-2), 5.56 (1H, d, *J* 12 Hz,), 6.0(1H, d, *J* 12 Hz), 7.1 - 7.6 (5H, m, HAr). The crystallised adduct and the mother liquor are put together back , dissolved in 5mL of THF / water (10 : 1) and stirred under Ar at room temperature for 2 days. The reaction mixture is concentrated under vacuum and the residue is purified by preparative plate chromatography (eluent petroleum ether/ ethyl ether 7/3) affording the products 4-oxo-6-phenyl 6-trimethylsilyl (4H) 5,6-dihydrothiopyran **13** and 5-oxo-2-phenyl (4H) 5,6-dihydrothiopyran **14** in a 2 : 1 ratio. Overall yield 70%. **13** ν_{max} (CCl_4) 1655 cm^{-1} (C=C-C=O); **14** ν_{max} (CCl_4) 1710 cm^{-1} (C=C-C=O).

Cycloaddition between thione **1a** *and diene* **10** The reaction is performed as described previously employing phenyl trimethylsilyl thione **1a** (prepared from 0.40 g , 2.24 mmol of the corresponding acyl silane) and 0.30 mL (1.71 mmol) of 2-trimethylsilyloxy-1,3-butadiene **10** in 15 mL of diethyl ether at 0 °C. After 1 hour decoloration is complete: the solvent is removed under vacuum and the solid residue is characterised by NMR and M.S. as the mixture of the regioisomeric 6-phenyl-6-trimethylsilyl -3-trimethylsilyloxy (2H)-5,6-dihydrothiopyran **11b** and 6-phenyl-6-trimethylsilyl -4-trimethylsilyloxy (2H)-5,6-dihydrothiopyran **12b** δ_H -0.10 (s, 9H, $SiMe_3$), -0.05 - -0.01 (9H + 9H, b.s., $OSiMe_3$ + $SiMe_3$), 0.18 (9H, s, $OSiMe_3$), 2.5 - 3.0 (2H + 2H, m, 2 CH_2), 4.8 (1H, m, vinyl H), 5.05 (1H, m, vinyl H), 7.0 - 7.6 (5H, m, HAr). The crude reaction mixture is dissolved in THF (25 mL) containing 2% of water and stirred at room temperature for 3.5 h; the solvent is then removed under vacuum and the residue is purified by chromatography on a silica gel column, eluent petroleum ether / benzene 1/1 then petroleum ether / ethyl ether 8 / 2, affording the products 3-oxo-6-phenyl-6-trimethylsilyl tetrahydrothiopyrane **15** and 4-oxo-2-phenyl-2-trimethylsilyl tetrahydrothiopyrane **16** as a 2 : 1 mixture (0.23 g, 60%); ν_{max} ($CHCl_3$) 1700 cm^{-1}

(C=O). The two alternative structures **15** and **16** were attributed on the basis of the ^{13}C shifts, comparing the experimental values and those calculated for the two isomers using the program ACD /CNMR Predictor (13).

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