Chemistry of Silylated Thioketones. Part 2.[1] Cycloaddition Reactions with 1,3-Dienes

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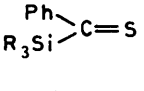
Trimethylsilylphenyl- and triphenylsilylphenyl thioketones easily undergo [4 + 2]-cycloadditions with cyclic and open chain 1,3-dienes at room temperature to give silylated thiabicyclo[2.2.1]heptenes and dihydrothiopyrans in very good yields. With cyclopentadiene the reaction produces exclusively the *endo*-silylated adducts. Sulphur oxidation and desilylation of the adducts were also investigated.

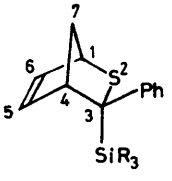
Aryl and alkyl substituted thioketones behave as reactive heterodienophiles in cycloadditions with 1,3-dienes[2-8] and heterodienes[9-11] leading to a variety of six-membered thia-heterocycles. Recently we have succeeded[1] in preparing α-silylated thioketones in good to very good yields. It seemed therefore worthwhile to investigate the Diels–Alder reactivity † and the synthetic usefulness of the products thus obtained. It seemed to us also interesting to test the effect of silicon on the π-system of the C=S double bond in view of its known ability to reduce the electron density within the C=C double bond of aryl vinyl silanes.[12] Moreover, the adducts of silylated thioketones are intrinsically interesting because of the possibility of reactions at both sulphur (oxidation) and/or silicon (C–Si bond cleavage; in the case of substitution with a proton, the silyl thioketone would behave as a masked thioaldehyde).

Results and Discussion

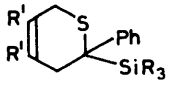
The reactions between the thioketones (**1a—b**) and cyclopentadiene, buta-1,3-diene, 2,3-dimethylbuta-1,3-diene were performed at 0—20 °C in ether or benzene by the addition of the diene to the blue solution of the thione until the colour had completely disappeared. The reaction was complete within a few minutes and afforded the adducts (**2**) and (**3**) in good or very good yields (Table).



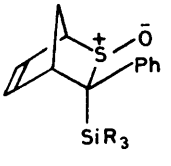
(**1**)
a; R = Me
b; R = Ph



(**2**)



(**3**)



(**4**)

Reactions with Cyclopentadiene.—The reaction of the thiones (**1a,b**) with cyclopentadiene was completely diastereoselective giving only one of the two possible diastereoisomers, namely the *endo*-silyl derivatives (**2**). The adduct configuration was elucidated with n.O.e. experiments in the case of 3-phenyl-3-trimethylsilyl-2-thiabicyclo[2.2.1]hept-5-ene (**2a**).

Saturation of the $SiMe_3$ resonance at −0.07 p.p.m. produced a significant (13%) increase in the intensity of the vinylic proton signal at 6.00 p.p.m. That signal can therefore be assigned to 5-H which is closer to the $SiMe_3$ group. A minor enhancement (5.5%) was found for the signal at 6.35 p.p.m. which was assigned to 6-H. The observation of a significant n.O.e. in both vinylic protons indicates an *endo* position for the $SiMe_3$ group, since an *exo* position would put the trimethylsilyl group too far apart from 5-H to produce a significant n.O.e. for this proton or for 6-H. An *exo* position would have an n.O.e. for only one of the C-7 methylene protons. The *endo* positioning of the trimethylsilyl group and, logically of the triphenylsilyl group of (**2b**), may be related to the preference of the more bulky group to occupy the less congested *endo*-position in 2-thiabicyclo-[2.2.1]hept-5-ene derivatives bearing an alkyl, aryl, or carboxy group in position 3.[13,14]

Homodecoupling experiments also made assignments of the bridgehead hydrogens possible: irradiation at 6.35 p.p.m. (6-H) caused a decoupling of the signal at 4.04 p.p.m. which could therefore be attributed to 1-H; irradiation at 6.00 p.p.m. produced a decoupling of the 3.97 p.p.m. signal which was therefore attributed to 4-H.

In order to complete the ^1H n.m.r. spectroscopic assignments for (**2a**), we oxidized the adducts (**2**) with *m*-chloroperbenzoic acid in ether at −50 °C. The sulphoxide (**4a**) thus obtained was thermally stable. LIS ‡ analysis on (**4a**), carried out in order to ascertain the configuration of the sulphoxide group, was unsuccessful owing to insufficient complexation between the lanthanide reagent and substrate, probably due to steric inhibition. Also, n.O.e. experiments gave no useful information because of the limited stability of (**4a**) during the lengthy n.m.r. measurements. Nevertheless, we can assume an *E* configuration for the sulphoxides (**4**) on the basis of the following considerations. The sulphur atom of 2-thiabicyclo[2.2.1]heptane derivatives has a well-documented preference for oxidation by peroxy acids to the *exo*-sulphoxide.[15] As pointed out above, the sulphoxides (**4**) exhibit thermal stability. This would indicate that the silyl and the sulphinyl group have an *E*-stereochemistry (*anti*-periplanar configuration). A *Z*-stereochemistry (*syn*-

† See also the following paper.

‡ Lanthanide induced shift.

Table.

Thione	Diene	Solvent	Adduct	R	R'	Yield (%)	M.p. (°C)
(1a)	Cyclopentadiene	Ether	(2a)	Me		82	78—80
(1b)	Cyclopentadiene	Benzene	(2b)	Ph		79	128—130
(1a)	Buta-1,3-diene	Ether	(3a)	Me	H	77	77—78
(1b)	Buta-1,3-diene	Ether	(3b)	Ph	H	92	142—144
(1a)	2,3-Dimethylbuta-1,3-diene	Ether	(3c)	Me	Me	72	Oil
(1b)	2,3-Dimethylbuta-1,3-diene	Benzene	(3d)	Ph	Me	99	127—129

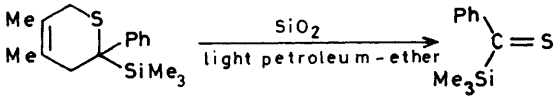
coplanar configuration) would put the sulphinyl oxygen and the silyl group in such close proximity as to render a silyl-Pummerer type rearrangement extremely facile.[16] We have already demonstrated[11,17] that an *anti*-periplanar stereochemistry of the sulphinyl oxygen and the silicon atom prevents such a rearrangement.

On the basis of the proposed *E*-geometry for (4) we could assign the signals of the ^{1}H n.m.r. spectrum, in particular those relative to the C-7 protons. All the protons of the sulphoxide (4a) have ^{1}H n.m.r. spectroscopic multiplicities analogous to those of the sulphide (2a) except for the signal attributed to the C-7 protons which experience the deshielding effect of the *exo* oxygen; the proton *syn* to oxygen being more deshielded at 2.30 p.p.m. and the proton *anti* to oxygen at 2.21 p.p.m. [in the sulphide (2a) these protons resonate at 1.36 and 1.53 p.p.m. respectively].

Attempted desilylation of (2a) gave a mixture of two unstable liquid products whose structure was not elucidated till now.

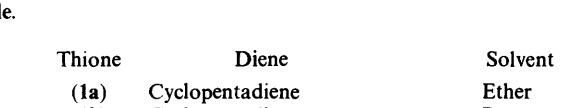
Reactions with Open-chain Dienes.—[4 + 2]-Cycloadditions of the thiones (1a,b) with butadiene or dimethylbutadiene gave the dihydrothiopyrans (3a—d) in high to very high yields (see Table). The adducts (3a,b) suffered chromatographic purification and crystallization, whereas the adducts (3c,d) were more unstable.

Elution of (3c) through silica caused a ready retrocycloaddition and the blue fraction gave the pure phenyl trimethylsilyl thioketone (1a). On this basis the adduct (3c) can be regarded as a handy source of the unstable (1a).[1] Compound (3c) can be safely stored over long periods in the refrigerator



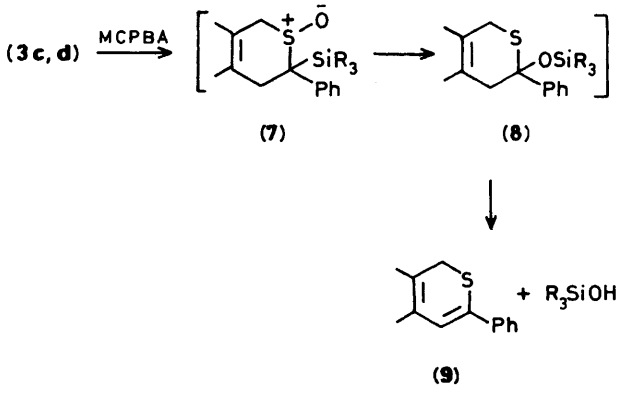
(3c) (1a) 100%

and chromatographed, as necessary, to produce quantitatively the pure silylthioketone (1a). The adducts (3a—d) were protodesilylated with tetrabutylammonium fluoride in THF–water at room temperature for 12 h to give the thiopyrans (5a,b). From the two adducts (3c,d),3,4-dimethyl-6-phenyl-5,6-dihydro-2*H*-thiopyran (5b) was obtained, identical in all respects to the product obtained by Baldwin[18] who trapped the highly unstable thiobenzaldehyde with 2,3-dimethylbuta-1,3-diene. Dihydrothiopyrans (5) could also be characterized as the corresponding sulphoxides[19] and sulphones (6) after oxidation with *m*-chloroperbenzoic acid (MCPBA). However, attempted oxidation of (3c,d) with the same peracid did not afford the expected *S*-oxides but the thiacyclohexadiene (9) in which the silyl group was lost. Silyl group elimination can be explained by an initial formation of the sulphoxide (7) in which the distance between the sulphinyl and silyl groups (presumably *trans* to each other in the more stable conformation) becomes short enough to allow a thermal sila-Pummerer-type rearrangement:[16] the *O*-silyl monothioacetal (8) thus formed eliminates silanol to give the isolated diene (9) (see Scheme). In no cases could we isolate the intermediates (7) and (8). The cyclic diene (9) was rather unstable at room temperature but was fully characterized on the basis of its analytical and spectral data.



(5) (6)

a; R = H
b; R = Me



Scheme.

The dienophilic reactivity of silylated thioketones deserves a short, though at present only qualitative, comment. With the 1,3-dienes employed, the reaction was almost instantaneous even at 0 °C. This indicates that the already known[2–8] high reactivity of thioketones towards dienes is not diminished at all, and is probably enhanced by the presence of the silyl group.[20]

Experimental

All m.p.s are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer. Routine n.m.r. spectra (60 MHz) were obtained with a Varian 360 L instrument. High field ^{1}H and ^{13}C n.m.r. spectra were obtained at 300 and 75.46 MHz respectively with the Bruker CXP 300 spectrometer of the High Field N.m.r. Spectroscopy Service of CNR in Bologna. Mass spectra were recorded with a JEOL JMS D 100 spectrometer.

Phenyl trimethylsilyl thioketone (1a) was obtained from the corresponding ketone as previously described[1] and used, after evaporation of the solvent, as the crude material. *Phenyl*

triphenylsilyl thioketone (**1b**) was obtained using the same procedure as described for (**1a**), as a crystalline material m.p. 98—100 °C.[1]

All reactions involving silylated thioketones were carried out under nitrogen or argon. Diethyl ether was distilled from P_2O_5 and benzene from CaH_2 immediately before use. Light petroleum refers to the fraction b.p. 40—70 °C.

3-exo-*Phenyl*-3-endo-*trimethylsilyl*-2-*thiabicyclo*[2.2.1]*hept*-5-*ene* (**2a**).—To an ethereal solution (20 ml) of phenyl trimethylsilyl thioketone (**1a**)[1] [obtained from the corresponding ketone] (1.0 g, 5.6 mmol) was added freshly distilled cyclopentadiene (10 mmol) at 0 °C. The blue colour of the thioketone disappeared almost instantaneously. The solvent was removed under reduced pressure and chromatography of the residue on Florisil [light petroleum–diethyl ether (8:2) as the eluant] afforded the adduct (**2a**) (1.2 g, 82% based on the starting ketone), m.p. 78—80 °C (from methanol) (Found: C, 69.7; H, 7.5; S, 12.4. $C_{15}H_{20}SSi$ requires C, 69.2; H, 7.7; S, 12.3%); $\nu_{max.}$(KBr) 3 060, 2 940, 1 475, 1 435, 1 325, 1 240s, 1 070, 1 015, 940, 830s, 725s, and 685s cm^{-1}; $\delta_H(CDCl_3)$ 0.07 (9 H, s, $SiMe_3$), 1.36 (1 H, dm, 7-H, *syn* to sulphur), 1.53 (1 H, dt, 7-H, *anti* to sulphur), 3.97 (1 H, m, 4-H), 4.04 (1 H, m, 1-H), 6.00 (1 H, m, 5-H), 6.35 (1 H, m, 6-H), and 7.13—7.28, and 7.52 (5 H, m, ArH); $\delta_C(CDCl_3)$ −0.5 ($SiMe_3$), 50.0 (C-7), 52.12 (C-4 or C-1), 54.72 (C-1 or C-4), 55.8 (C-3), 125.2, 127.6, 129.0, 132.1, 138.6, and 146.4 (C-5, C-6, and ArC); *m/z* 260 (M^+), 194 ($M^+ - C_5H_6$), 187 ($M^+ - SiMe_3$), 155 ($M^+ - PhCO$), and 121 (PhCS).

3-exo-*Phenyl*-3-endo-*triphenylsilyl*-2-*thiabicyclo*[2.2.1]*hept*-5-*ene* (**2b**).—To a solution of phenyl triphenylsilyl thioketone (**1b**)[1] (0.15 g, 0.4 mmol) in anhydrous benzene (4 ml) was added cyclopentadiene (0.8 mmol) at 5 °C. The blue colour of the thioketone had disappeared, the solvent was removed under reduced pressure and the adduct (**2b**) was crystallized from methanol, m.p. 128—130 °C (0.14 g, 78%) (Found: C, 81.0; H, 5.6; S, 7.1. $C_{30}H_{26}SSi$ requires C, 80.7; H, 5.9; S, 7.2%); $\nu_{max.}$(KBr) 1 425, 1 095, 740, and 695 cm^{-1}; $\delta_H(CDCl_3)$ 1.31 (1 H, d, 7-H *syn* to sulphur), 1.43 (1 H, dt, 7-H *anti* to sulphur), 4.05 (1 H, m, 1-H or 4-H), 4.11 (1 H, m, 4-H or 1-H), 5.72 (1 H, m, 5-H or 6-H), 5.88 (1 H, m, 6-H or 5-H), and 6.5—7.7 (20 H, m, ArH); *m/z* 446 (M^+), 380 ($M^+ - C_5H_6$), 303 (Ph_3SiCS), and 259 (Ph_3Si).

6-*Phenyl*-6-*trimethylsilyl*-5,6-*dihydro*-2H-*thiopyran* (**3a**).—Buta-1,3-diene was bubbled through a solution (20 ml) of (**1a**) [prepared from phenyl trimethylsilyl ketone (1 g, 5.6 mmol)] until the blue colour of the thioketone disappeared. After the usual work-up, the adduct (**3a**) (79% based on the starting ketone) was obtained, m.p. 77—78 °C (from methanol) (Found: C, 67.5; H, 8.0; S, 12.7. $C_{14}H_{20}SSi$ requires C, 67.7; H, 8.1; S, 12.9%); $\nu_{max.}$(KBr) 1 410, 1 235, and 830 cm^{-1}; $\delta_H(CDCl_3)$ 0.0 (9 H, s, $SiMe_3$), 2.86 (4 H, m, CH_2), 5.73 (2 H, m, vinylic-H), and 6.93—7.73 (5 H, m, ArH); *m/z* 248 (M^+), 233 (M^+ − Me), 129 ($M^+ - C_4H_6$), 175 ($M^+ - SiMe_3$), and 121 (PhCS).

6-*Phenyl*-6-*triphenylsilyl*-5,6-*dihydro*-2H-*thiopyran* (**3b**).—Compound (**3b**) was prepared from the thioketone (**1b**) (0.28 g, 0.74 mmol) as described above. The product (0.29 g, 91%) was chromatographed on silica [pentane–ethyl acetate (19:1) as the eluant], m.p. 142—144 °C (from benzene–light petroleum) (Found: C, 79.9; H, 6.2; S, 7.5. $C_{29}H_{26}SSi$ requires C, 80.1; H, 6.0; S, 7.4%); $\nu_{max.}$(KBr) 1 420, 1 095, and 690 cm^{-1}; $\delta_H(CDCl_3)$ 2.5—3.66 (4 H, m, CH_2), 5.66 (2 H, m, vinylic-H), and 7.1—8.16 (20 H, m, ArH); *m/z* 434 (M^+), 259 ($SiPh_3$), and 121 (PhCS).

3,4-*Dimethyl*-6-*phenyl*-6-*trimethylsilyl*-5,6-*dihydro*-2H-*thiopyran* (**3c**).—The reaction was carried out as described for (**2a**). Starting from (**1a**) [obtained from phenyl trimethylsilyl-ketone] (1 g, 5.6 mmol) and using 2,3-dimethylbuta-1,3-diene (10 mmol), the cycloadduct (1.08 g, 70% based on the starting ketone) was obtained as an oily product. Chromatography on silica [light petroleum–ether (8:2) as the eluant] gave complete retrocycloaddition and the pure thioketone was obtained as the first fraction. To this solution of the thioketone, an excess of 2,3-dimethyl-buta-1,3-diene was added at room temperature. After the solvent had been evaporated, the oily adduct (**3c**) (0.92 g, 59%) pure by t.l.c., was obtained, $\nu_{max.}$(neat) 2 960, 2 900, 1 440, 1 245 ($SiMe_3$), 870, 840 ($SiMe_3$), 735, and 695 cm^{-1}; $\delta_H(CDCl_3)$ 0.0 (9 H, s, $SiMe_3$), 1.43 (3 H, s, Me), 1.72 (3 H, s, Me), 2.13—3.13 (4 H, m, CH_2), and 6.83—7.66 (5 H, m, ArH); *m/z* 276 (M^+), 261 (M^+ − Me), 203 ($M^+ - SiMe_3$), 171 ($M^+ - SiMe_3$ − S), and 121 (PhCS).

3,4-*Dimethyl*-6-*phenyl*-6-*triphenylsilyl*-5,6-*dihydro*-2H-*thiopyran* (**3d**).—Under the conditions used for (**3c**), starting from phenyl triphenylsilyl thioketone (0.15 g, 0.40 mmol) and 2,3-dimethylbuta-1,3-diene (0.055 ml) was obtained compound (**3d**) (0.18 g, 99%), m.p. 127—129 °C (from ethanol), $\nu_{max.}$ (KBr) 3 040, 2 900, 1 480, 1 425, 1 100, 740, and 695 cm^{-1}; $\delta_H(CDCl_3)$ 1.48 (3 H, s, Me), 1.60 (3 H, s, Me), 2.9—3.7 (4 H, m, CH_2), and 6.8—7.8 (20 H, m, ArH); *m/z* 462 (M^+), 380 ($M^+ - C_6H_{10}$), 259, ($SiPh_3$), 182 ($SiPh_2$), and 121 (PhCS). During crystallization some retrocycloaddition was observed.

3-exo-*Phenyl*-3-endo-*trimethylsilyl*-2-*thiabicyclo*[2.2.1]*hept*-5-*ene* 2-exo-*Oxide* (**4a**).—A solution containing equimolecular amounts of *m*-chloroperbenzoic acid in ether was added at −50 °C under nitrogen to an ethereal solution (8 ml) of (**2a**) (0.25 g, 0.96 mmol). After a few minutes the sulphoxide (**4a**) crystallized as a white precipitate (0.1 g, 38.5%), m.p. 80—81 °C, which was too unstable to be further purified. After work-up, only a complex mixture of decomposition products was obtained from the mother liquor. The crude product (**4a**) showed $\nu_{max.}$(KBr) 1 040 (SO), 1 250, and 840 cm^{-1} ($SiMe_3$); $\delta_H(CDCl_3)$ −0.03 (9 H, s, $SiMe_3$), 2.21 (1 H, dt, 7-H, *anti* to sulphur), 2.30 (1 H, br d, 7-H *syn* to sulphur), 4.07 (1 H, br s, 1-H or 4-H), 4.15 (1 H, br s, 4-H or 1-H), 6.04 (1 H, m, 5-H or 6-H), 6.49 (1 H, m, 6-H or 5-H), and 7.10—8.56 (5 H, m, ArH); *m/z* 276 (M^+), 210 ($M^+ - C_5H_6$), and 121 (PhCS).

3-exo-*Phenyl*-3-endo-*triphenylsilyl*-2-*thiabicyclo*[2.2.1]*hept*-5-*ene* 2-exo-*Oxide* (**4b**).—The reaction was performed using the same conditions described for (**4a**). Starting from (**2b**) (0.25 g) the sulphoxide (**4b**) (0.18 g, 70%) was obtained which was too unstable for complete purification, m.p. 81—82 °C, $\nu_{max.}$(KBr) 3 060, 1 430, 1 100, 1 055 (SO), 740, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 2.12 (1 H, dt, 7-H *anti* to sulphur), 2.35 (1 H, dt, 7-H, *syn* to sulphur), 4.05 (1 H, m, 1-H or 4-H), 4.20 (1 H, m, 4-H or 1-H), 5.77 (1 H, m, 5-H or 6-H), 5.92 (1 H, m, 6-H or 5-H), and 6.75—7.78 (20 H, m, ArH); *m/z* 462 (M^+) 396 ($M^+ - C_5H_6$), 319 (Ph_3SiCSO), 276 (Ph_3SiOH), and 259 ($SiPh_3$).

An attempt to obtain the same product by direct cycloaddition of phenyl triphenylsilyl thioketone oxide to cyclopentadiene in boiling benzene for 20 h was unsuccessful.

6-*Phenyl*-5,6-*dihydro*-2H-*thiopyran* (**5a**).—To a solution of (**3a**) (0.6 g, 2.4 mmol) in THF (15 ml) and water (1.5 ml), was added dropwise a solution of tetrabutylammonium fluoride (TBAF) in THF (1M; 2.4 ml, 2.4 mmol) at room temperature under nitrogen. After having been stirred for 12 h, the mixture was quenched with water and extracted with ether, then dried (Na_2SO_4) and concentrated under reduced pressure to give (**5a**) (0.41 g, 97%), m.p. 40 °C (from methanol) (Found: C, 75.0; H, 6.9; S, 18.3. $C_{11}H_{12}S$ requires C, 74.9; H, 6.9; S, 18.2%); $\delta_H(CDCl_3)$ 2.3—3.7 (4 H, m, CH_2), 3.9 (1 H, t, *J* 7 Hz, CH), 5.8 (2

H, s, vinylic-H), and 7.2 (5 H, s, ArH); *m/z* 176 (M^+), 122 (PhCHS), and 121 (PhCS).

3,4-*Dimethyl*-6-*Phenyl*-5,6-*dihydro*-2H-*thiopyran* (**5b**).—The reaction was performed in the same condition used for (**5a**). Starting from (**3c**) (0.18 g, 0.6 mmol), (**5b**) (0.12 g, 90%) was obtained as a liquid product after being chromatographed on silica [light petroleum–benzene (7:3) as the eluant]. This product was identical in all respect with that obtained by Baldwin.[18]

The same product was obtained by the desylylation of (**3d**) using the same procedure described above. From (**3d**) (0.1 g, 0.22 mmol) after 30 h, (**5b**) (0.022 g, 50.5%) and triphenylsilanol (0.025 g, 42%) were obtained.

6-*Phenyl*-5,6-*dihydro*-2H-*thiopyran* S,S-*Dioxide* (**6a**).—A solution of *m*-chloroperbenzoic acid (3.4 mmol) in chloroform (5 ml) was added at room temperature under nitrogen and with stirring to a solution of (**5a**) (0.3 g, 1.7 mmol) in chloroform (5 ml). The reaction was followed by t.l.c. and after 2 h the oxidation was complete. The solution was washed with aqueous sodium hydrogen carbonate and dried (Na_2SO_4). Evaporation of the solvent gave (**6a**) (0.34 g, 97%), m.p. 155—157 °C (from ethanol) (Found: C, 63.3; H, 5.9; S, 15.3. $C_{11}H_{12}O_2S$ requires C, 63.4; H, 5.8; S, 15.4%); $\nu_{max.}(CS_2)$ 1 125 and 1 325 cm^{-1} (SO_2); $\delta_H(CDCl_3)$ 2.9—3.4 (2 H, m, CH_2), 3.6—4.0 (2 H, m, CH_2), 4.24 and 4.42 (1 H, dd, *J* 6 Hz, CH), 5.3—6.4 (2 H, m, vinylic-H), and 7.6 (5 H, s, ArH); *m/z* 208 (M^+) and 144 ($M^+ - SO_2$).

3,4-*Dimethyl*-6-*phenyl*-5,6-*dihydro*-2H-*thiopyran* S,S-*Dioxide* (**6b**).—Using the same reaction conditions described for (**6a**), and starting from (**5b**), (0.3 g, 1.5 mmol), compound (**6b**) (0.25 g, 71%) was obtained, m.p. 64—67 °C (from methanol) (Found: C, 66.0; H, 6.8; S, 13.4. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.8; S, 13.6%); $\nu_{max.}(CS_2)$ 1 120 and 1 320 cm^{-1} (SO_2); $\delta_H(CDCl_3)$ 1.76 (6 H, s, Me), 2.65—3.77 (4 H, m, CH_2), 4.06 and 4.25 (1 H, dd, *J* 6 Hz, CH), and 7.4 (5 H, m, ArH); *m/z* 236 (M^+), 172 ($M^+ - SO_2$), 157 ($M^+ - SO_2 - Me$).

Oxidation of 3,4-*Dimethyl*-6-*phenyl*-6-*trimethylsilyl*-5,6-*dihydro*-2H-*thiopyran* (**3c**).—To a solution of (**3c**) (0.5 g, 1.8 (mmol) in ether (10 ml), was added *m*-chloroperbenzoic acid (3 mmol) in ether (2 ml) at −50 °C. Consumption of the peracid was almost instantaneous. The ethereal solution was washed with aqueous $NaHCO_3$ and water, then dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue on silica [light petroleum–ethyl acetate (10:1) as the eluant] afforded 6-phenyl-2H-thiopyran (**9**) (0.36 g, 100%) as a liquid which was unstable at room temperature but which could be kept at −20 °C for a few days: $\nu_{max.}$(neat) 3 060, 2 910, 2 860, 1 485, 1 440, 1 250, 840, 760, and 690 cm^{-1}; $\delta_H(CDCl_3)$ 1.93 (6 H, s, Me), 3.36 (2 H, s, CH_2), 6.54 (1 H, s, CH), and 7.16—8.0 (5 H, m, ArH); $\delta_C(CDCl_3)$ 18.07 (q), 19.21 (q), 32.28 (t), 119.22 (s), 123.9 (d), 126.9 (d), 127.87 (s), 128.0 (d), 128.2 (d), 132.88 (s), and 138.05 (s); *m/z* 202 (M^+), 201 ($M^+ - H$), and 187 ($M^+ - Me$).

The same product (**9**) was obtained by the oxidation of (**3d**) under the same reaction conditions as described above. Starting from (**3d**) (0.163 g, 0.35 mmol) and *m*-chloroperbenzoic acid (0.35 mmol) compound (**9**) (0.015 g, 21%) was obtained in addition to some starting material (0.052 g, 32%) and triphenylsilanol (0.038 g, 39%).

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20. For a quantitative comparison of the relevant FMOs of thioformaldehyde and thioformylsilane see Part 3, following paper.

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