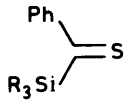
Chemistry of Silyl Thioketones. Part 3.[1] Cycloaddition Reactions with Heterodienes (α-Nitrosostyrene and Ketene Imines)

Patrizia Carisi, Germana Mazzanti,* and Paolo Zani
Istituto di Chimica Organica dell'Università, Viale Risorgimento 4, 40136 Bologna, Italy
Gaetano Barbaro, Arturo Battaglia,* and Patrizia Giorgianni
Istituto dei Composti del Carbonio contenenti Eteroatomi del CNR, 40064 Ozzano Emilia, Italy

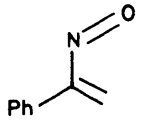
Silylated heterocycles *viz*: 4*H*-1,5,2-oxathiazines (**4a, b**), 4*H*-3,1-benzothiazines (**8**), (**9**), 5,6-dihydro-2*H*-thiopyrans (**11a, b**), were obtained in reactions of silyl thioketones (**1a, b**) with α-nitrosostyrene (**2**), dimethylketene *N*-*p*-tolylimine (**3a**), and methylvinylketene *N*-*p*-tolylimine (**3b**) respectively.

In the reaction of (**1a, b**) with (**3b**), in which a heterodiene and a homodiene system is present, a variation in the periselectivity is found with respect to diaryl thioketones. Desilylation of trimethylsilyl adducts was also investigated. In the case of (**4a**), desilylation affords α-aminostyryl benzoyl sulphide (**5**) whereas the adducts (**9**) and (**11a**) give, in good yield, the corresponding hydrogen-substituted heterocycles (**10**) and (**12**) respectively.

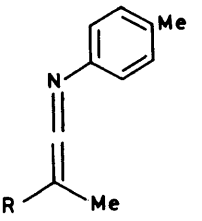
[4 + 2]-Cycloadditions of thiones with dienes[2] and heterodienes[3] serve as an important source of sulphur-containing six-membered heterocycles. The use of phenyl α-silyl thiones can, in principle, provide a simple route to adducts formally derived from the unstable thiobenzaldehyde, because of the possibility of protodesilylation of the silylated adducts. We report here our results concerning the cycloadditions of the silyl thioketones (**1a, b**)[4] with two types of heterodienes,† namely, α-nitrosostyrene (**2**)[5] and the ketene imines (**3a, b**).[6]



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



(**2**)

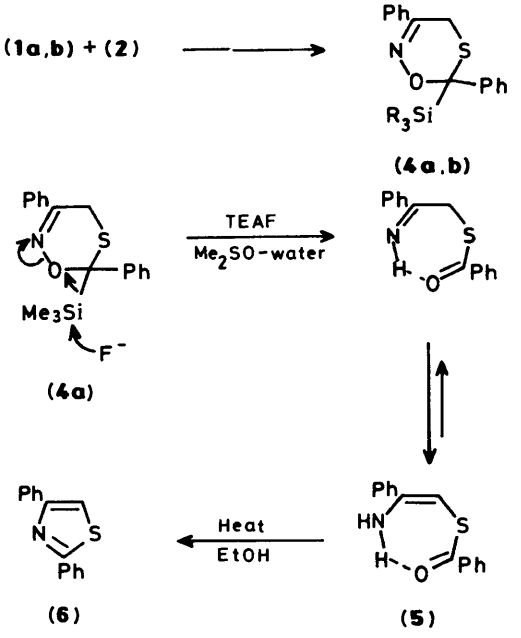


(**3**) **a** ; R = Me
b ; R = CH=CH$_2$

Results and Discussion

We have shown previously[3b] that the thiones (**1a, b**) react with α-nitrosostyrene, generated *in situ via* the dehydrobromination of α-bromoacetophenone oxime, to give, in very high yields, the adducts (**4a, b**) (Scheme 1).

The structures of the oxathiazines (**4a, b**) were assigned on the basis of the following evidence: both gave correct elemental analyses; mass spectra showed their molecular ions at *m/z* 327 and 513 respectively along with prominent peaks at 178 ($PhCOSiMe_3$) and 264 ($PhCOSiPh_3$). Further proof of the regiochemistry of (**4a**) was obtained by its desilylation with tetraethylammonium fluoride (TEAF) in Me_2SO, which led to α-aminostyryl benzoyl sulphide (**5**), instead of the parent 6*H*-derivative. Compound (**5**), derived from a concomitant opening of the oxathiazine ring (see Scheme 1), was rather unstable at room temperature and could not be purified for elemental analysis. Its structure was assigned on the basis of the following evidence: i.r. spectrum in KBr showed a broad band at 3 100—3 400 cm^{-1} and a strong band at 1 640 cm^{-1} attributed respectively to NH_2 and CO groups



Scheme 1.

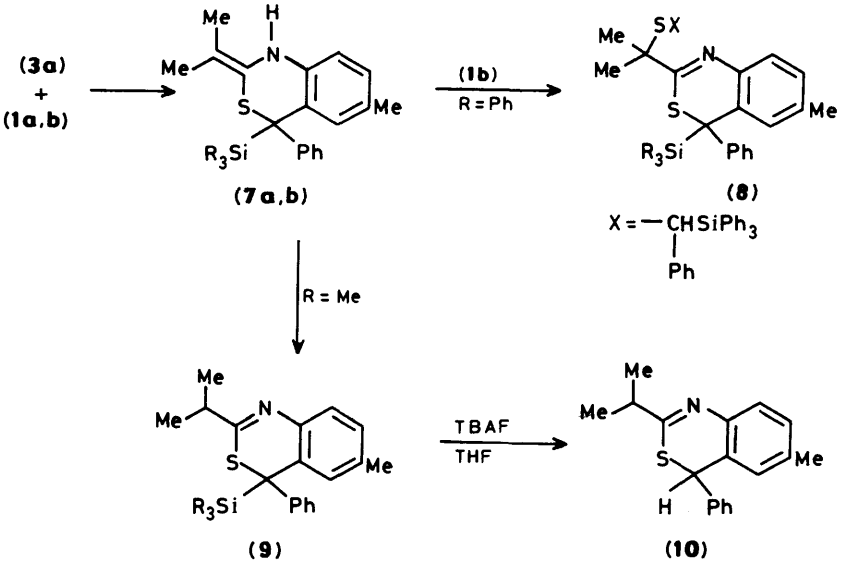
hydrogen-bonded to each other; the mass spectrum showed the molecular ion at *m/z* 255 and prominent peaks at *m/z* 237 ($M^+ - H_2O$), 150 ($M^+ - PhCO$), and 134 (PhCCHS).

Moreover, compound (**5**), in boiling ethanol, gave 2,4-diphenylthiazole (**6**), which was identified by comparison with an authentic sample.[7] Therefore the regiochemistry of the cycloaddition of α-nitrosostyrene with the thiones (**1a, b**) is the same as that obtained from the cycloaddition with diarylthiones.[3b]

The silyl thioketones (**1a, b**) react easily with dimethylketene *N*-*p*-tolylimine (**3a**) and methyl(vinyl)ketene *N*-*p*-tolylimine (**3b**). Reactions of (**1a, b**) with the ketene imine (**3a**) afforded the benzothiazine derivatives (**8**) and (**9**) (Scheme 2).

These heterocycles are derived, in both cases, from an initial [4 + 2]-cycloaddition of the thione on the heterodiene system formed from the cumulative C=N bond and the conjugated C=C bond of the *N*-aryl ring, leading to the intermediates (**7a, b**), the existence of which was previously proved in the reaction of (**3a**) and diphenylthioketone.[3e]

† For the reaction of silyl thioketones with homodienes see Part 2, preceding paper.



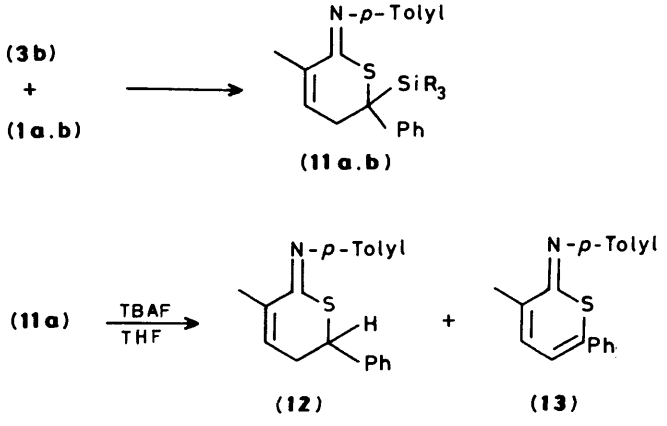
Scheme 2.

The intermediate (**7a**) rearranges by hydrogen migration to the more stable 4*H*-3,1-benzothiazine (**9**), while the intermediate (**7b**) reacts with a second molecule of (**1b**), to afford the 4*H*-3,1-benzothiazine (**8**). This behaviour was also observed in the reaction between diaryl thioketones and (**3a**).[3e] Structures for compounds (**8**) and (**9**) were determined from elemental analyses and spectroscopic evidence. A common feature was a double i.r. band at 1 615—1 580 and 1 620—1 590 respectively (C=N bond of the thiazine ring).[8] Compound (**9**) showed ^{1}H n.m.r. resonances at 2.96 (septet) and 1.18 (d) for the Me_2CH group and the ^{13}C n.m.r. resonance, observed at δ 170.10, assigned to the imino carbon, C=N.[3e] The mass spectrum showed a molecular ion at *m/z* 353. The 2:1 adduct (**8**) showed a n.m.r. signal at δ 4.32 for the tertiary hydrogen, and two signals at 0.63 and 1.45, attributed to the diastereotopic methyl groups of the substituted isopropyl group. The molecular ion of (**8**) was not observed in the mass spectrum, but prominent peaks were present at *m/z* 660 ($M^+ - Ph_3Si$), 538 ($M^+ - Ph_3SiCHSPh$), and 381 ($Ph_3SiCHSPh$). Compound (**9**) was desilylated with TEAF in THF–water leading to the parent 4*H*-derivative (**10**), whose structure was determined from the elemental analysis and spectroscopic data, *i.e.* a singlet at 5.80 p.p.m. in the ^{1}H n.m.r. spectrum, due to 4-H, the molecular ion in the mass spectrum at *m/z* 281, and the presence of the typical benzothiazine bands in the i.r. spectrum at 1 620 and 1 585 cm^{-1} (Scheme 2).

Reaction of the thiones (**1a, b**) with methyl(vinyl) ketene *N*-*p*-tolylimine (**3b**) (Scheme 3) gave, unexpectedly, adducts (**11a, b**) derived from a 1,4-*C* cycloaddition of the C=S bond on the homodiene system formed by the cumulative C=C bond and the C-vinyl group. With the same ketene imine, diaryl thioketones give benzothiazine derivatives[3d] arising from a 1,4-*N* cycloaddition on the heterodiene system of (**3b**) (Figure 1).

The observed change in periselectivity[9] may be related to the electronic character of vinylketene imines, which react as 1,3-dienes with electrophilic dienophiles and as 1,3-heterodienes with electron-rich partners.[10] On this basis, silyl thioketones seem to be more electrophilic than diaryl thioketones. This conclusion has been substantiated by an *ab-initio* STO 3-21 G* MO calculation.[11]

Figure 2 shows an energy correlation diagram of the relevant FMOs † of thioformaldehyde and thioformylsilane. Comparing



Scheme 3.

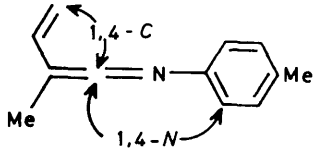


Figure 1.

the FMO energies, we can see that N-HOMO ($\pi_{C=S}$) and HOMO (n_S) are practically unaffected by the introduction of silicon, whereas substantial energy stabilization of LUMO ($\pi^*_{C=S}$, *ca.* 0.58 eV) was found when silicon is present, leading to a more electrophilic dienophile. The relevant FMOs of formaldehyde and formylsilane are also given for comparison in Figure 2. Again, the introduction of silicon causes a strong lowering of the LUMO's energy ($\Delta\pi^*_{C=O}$, *ca.* 1.2 eV); furthermore a pronounced effect is also found on HOMO (n_O) and N-HOMO ($\pi_{C=O}$), whose energies are substantially raised by the presence of silicon.‡

The adduct (**11a**) was desilylated with tetrabutylammonium

† Frontier molecular orbital.

‡ A preliminary experiment showed that benzoyltrimethylsilane does not react with an excess of 2,3-dimethylbuta-1,3-diene in a sealed ampoule at 100 °C for 36 h.

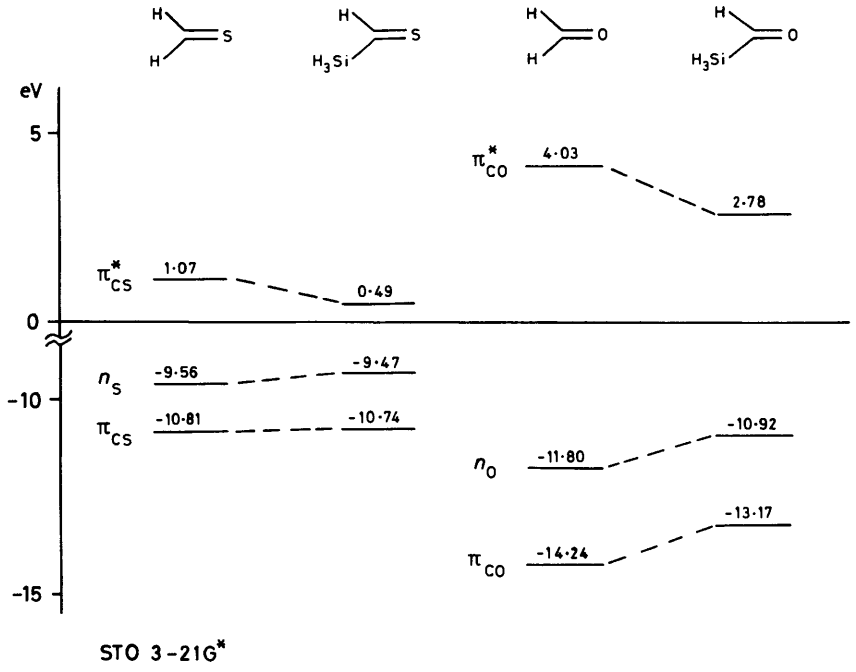


Figure 2. Energy correlation diagram

fluoride (TBAF) in THF–water to give the dihydrothiopyran (**12**), together with a small amount of the thiopyran (**13**), derived from an elimination process (Scheme 3). Compounds (**11a**), (**11b**), (**12**), and (**13**) gave correct elemental analyses and showed a common strong i.r. absorption at 1 580 cm^{-1}, attributed to the exocyclic C=N bond.[3d] Their mass spectra showed the molecular ions at *m/z* 365, 551, 293, and 291 respectively. Compounds (**11a**), (**11b**), and (**12**) showed ^{13}C n.m.r. resonances at 30.8, 32.8, and 33.11, respectively, due to the methylene carbon, and at 157.5 (**11a**), 156.6 (**11b**), 160.2 (**12**), and 158.5 (**13**) for S–C=N. Moreover, compound (**12**) showed, in the ^1H n.m.r. spectrum, a multiplet (1 H) centred at 4.4 p.p.m. attributed to the benzylic hydrogen and compound (**13**) showed a doublet (1 H) at 6.67 p.p.m. (*J* 7.5 Hz) corresponding to the vinylic 5-H. In the n.m.r. spectra of both (**12**) and (**13**) the $SiMe_3$ signal, found at −0.07 p.p.m. in the parent compound (**11a**), was absent.

Other extended conjugated heterocumulenes, as benzoyl isocyanates and thiocyanates[12] failed to react with the silyl thioketones (**1a, b**).

Experimental

^1H N.m.r. and ^{13}C n.m.r. spectra were recorded at 90 MHz on Varian EM 390 and Varian CFT-80 spectrometers; chemical shifts were given on the δ scale referenced to tetramethylsilane. I.r. spectra were obtained on a Perkin–Elmer 257 grating spectrometer. Low-resolution mass spectra were recorded at an ionizing voltage of 70 eV on a Varian MAT-112 S spectrometer. Column chromatography was carried out with Merck gel 60 (70—230 mesh). Melting points are uncorrected. All solvents were purified before use according to standard procedures.

The silyl thioketones (**1a, b**)[5] and the ketene imines (**3a, b**)[3d,e] were prepared as previously described; α-nitrososstyrene was generated *in situ* according to the literature.[6] Phenyl trimethylsilyl thioketone (**1a**) was prepared immediately prior to use in diethyl ether; its concentration was calculated through the absorbance at λ = 678 nm (ε 37) in the u.v. spectrum.[5]

Typical Procedure for the Preparation of the Oxathiazines (**4a, b**).—α-Chloroacetophenone oxime (3.2 mmol) and anhydrous sodium carbonate (16 mmol) were added to a solution of the silyl thioketone (3.2 mmol) in diethyl ether (30 ml). The resulting suspension was stirred under nitrogen at room temperature until the blue colour of the thione had disappeared (*ca.* 24 h). The solid residue was filtered off and the solution was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography followed by washing with pentane.

3,6-*Diphenyl*-6-*trimethylsilyl*-4H-1,5,2-*oxathiazine* (**4a**). Elution with methylene chloride–light petroleum (1 : 1, v/v) gave (**4a**) (0.96 g, 91.5%), m.p. 95—96 °C; $\nu_{max.}$(KBr) 1 590 (C=N), 1 240, 840, and 745 cm^{-1} ($SiMe_3$); $\delta_H(CDCl_3)$ 0.17 (9 H, s), 2.9 and 3.3 (2 H, dd, *J* 18 Hz), and 7.1—7.8 (10 H, m); *m/z* 327 (M^+), 312 (M^+ − Me), 295 (M^+ − S), 238 (M^+ − Me_3SiO), 178 ($PhCOSiMe_3$), 149 (M^+ − $PhCOSiMe_3$), 135 ($PhCSCH_2$), 121 (PhCS), 103 (PhCN), 77 (Ph), and 73 ($SiMe_3$) (Found: C, 65.8; H, 6.4; N, 4.2; S, 9.6. $C_{18}H_{21}NOSSi$ requires C, 66.01; H, 6.46; N, 4.28; S, 9.79%).

3,6-*Diphenyl*-6-*triphenylsiliyl*-4H-1,5,2-*oxathiazine* (**4b**). Elution with methylene chloride gave (**4b**) (1.46 g, 89%), m.p. 166—167 °C; $\nu_{max.}$(KBr) 1 590 (C=N), and 1 430 and 1 100 cm^{-1} (SiPh); $\delta_H(CDCl_3)$ 2.78 and 3.26 (2 H, dd, *J* 18 Hz) and 6.8—8.2 (25 H, m); *m/z* 513 (M^+), 364 ($PhCOSiPh_3$), 276 (Ph_3SiOH), 259 ($SiPh_3$), 237 (M^+ − Ph_3SiOH), 149 (M^+ − $PhCOSiPh_3$), 121 (PhCS), 105 (PhCO), and 103 (PhCN) (Found: C, 77.05; H, 5.2; N, 2.6; S, 6.3. $C_{33}H_{27}NOSSi$ requires C, 77.15; H, 5.30; N, 2.73; S, 6.24%).

Desilylation of (**4a**).—Tetraethylammonium fluoride dihydrate (0.34 g, 1.8 mmol) was added, at room temperature under nitrogen, to a stirred solution of (**4a**) (0.4 g, 1.2 mmol) in Me_2SO (8 ml). After 30 min saturated aqueous ammonium chloride was added and the mixture was extracted with diethyl ether. The ethereal layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified on a silica gel column. Elution with light petroleum–ethyl acetate (3:7, v/v) gave α-aminostyryl benzoyl sulphide (**5**) (0.20 g, 64.5%), m.p. 120—130 °C; $\nu_{max.}$(KBr) 3 100—3 400 (NH_2 hydrogen bonded to CO) and 1 640 (CO hydrogen bonded to NH_2) cm^{-1}; $\delta_H(CDCl_3)$ 6.8—8.3 (aromatic-

and vinylic-H); *m/z* 255 (M^+), 253 ($M^+ - 2$ H), 237 ($M^+ - H_2O$), 222 (PhCCSCPh), 150 ($M^+ -$ PhCO), 134 (PhCCHS), 121 (PhCS), and 105 (PhCO).

Compound (**5**) could not be further purified, as it was easily decomposed by chromatography or crystallization. A solution of (**5**) (0.08 g) in ethanol (5 ml) was refluxed for 30 h, to afford 2,4-diphenylthiazole (**6**) (0.06 g, 80%), m.p. 92—93 °C, which was identified by comparison with an authentic sample.[7]

*2-Isopropyl-6-methyl-4-phenyl-4-trimethylsilyl-*4H-3,1-*benzothiazine* (**9**).—The blue solution of the thioketone (**1a**) (1.85 mmol) in diethyl ether (35 ml) was treated with the ketene imine (**3a**) (0.26 g, 1.63 mmol) for 14 h at room temperature under N_2. When the blue colour of the thioketone had completely disappeared, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (eluant: benzene) to afford the benzothiazine (**9**) (0.31 g, 54%), m.p. 84—85 °C (methanol); $\nu_{max.}$(CCl_4–C_2Cl_4–CS_2) 1 620, 1 590 (C=N) and 1 252, 823, and 728 cm^{-1} ($SiMe_3$); δ_H($CDCl_3$) 0.27 (9 H, s, $SiMe_3$), 1.18 (6 H, d, *J* 7 Hz), 2.45 (3 H, s, ArMe), 2.96 (1 H, septet, *J* 7 Hz), and 7.0—7.4 (8 H, m, ArH); δ_C($CDCl_3$) −1.00 (q), 20.38 (q), 21.85 (q), 22.61 (q), 41.36 (d), 43.95 (s), 126.80 (d), 129.91 (d), 136.96 (s), 143.21 (s), 144.16 (s), and 170.10 (s); *m/z* 353 (M^+), 338 ($M^+ -$ Me), 310 ($M^+ - Me_2CH$), and 280 ($M^+ - SiMe_3$) (Found: C, 71.15; H, 7.75; N, 3.9; S, 9.1. $C_{21}H_{27}NSSi$ requires C, 71.33; H, 7.69; N, 3.96; S, 9.07%).

*6-Methyl-4-phenyl-4-triphenylsilyl-2-(α-triphenylsilylbenzylthio)propan-2-yl-*4H-3,1-*benzothiazine* (**8**).—Phenyl triphenylsilyl thioketone (**1b**) (0.60 g, 1.58 mmol) was treated with the ketene imine (**3a**) (0.29 g, 1.82 mmol) in carbon tetrachloride (80 ml) at room temperature for 15 h under N_2. The reaction mixture was chromatographed on silica gel [eluant: methylene chloride–pentane (2:1, v/v)] to give the benzothiazine derivative (**8**) as a 2:1 adduct (0.41 g, 56%), m.p. 203—205 °C (benzene–pentane); $\nu_{max.}$(CCl_4–C_2Cl_4–CS_2) 1 615, 1 580 (C=N), 1 430 (SiPh), and 1 100 cm^{-1} (SiPh); δ_H($CDCl_3$) 0.63 (3 H, s), 1.45 (3 H, s), 2.0 (3 H, s), 4.32 (1 H, s), 6.50—7.57 (43 H, m, ArH); δ_C 20.92 (q), 25.43 (q), 30.22 (q), 36.20 (d), 43.54 (s), 54.73 (s), 125.25 (d), 126.02 (d), 126.59 (d), 126.93 (s), 127.15 (d), 127.32 (d), 127.48 (d), 127.71 (d), 127.98 (d), 129.50 (d), 129.57 (d), 129.76 (d), 130.34 (d), 132.95 (s), 133.41 (s), 135.56 (s), 136.62 (d), 137.71 (d), 139.25 (s), 142.15 (s), 142.22 (s), and 166.55 (s); *m/z* (M^+ absent), 660 ($M^+ - Ph_3Si$), 538 ($M^+ - Ph_3SiCHSPh$), and 381 ($Ph_3SiCHSPh$) (Found: C, 79.5; H, 5.9; N, 1.55; S, 7.0. $C_{61}H_{53}NS_2Si_2$ requires C, 79.60; H, 5.80; N, 1.52; S, 6.97%).

Desilylation of (**9**).—Tetraethylammonium fluoride dihydrate (0.11 g, 0.62 mmol) was added to a solution of (**9**) (0.22 g, 0.62 mmol) in THF (10 ml) containing a drop of water: the solution was stirred under N_2 at room temperature for 15 h, then poured into ice–water (40 g) and extracted with diethyl ether (4 × 10 ml). The ethereal layer was dried (Na_2SO_4) and evaporated under reduced pressure. Chromatography of the residue on silica gel (eluant: benzene) afforded *2-isopropyl-6-methyl-4-phenyl-*4H-3,1-*benzothiazine* (**10**) (0.15 g, 85%) as an oil: $\nu_{max.}$(CCl_4–C_2Cl_4–CS_2) 1 620 and 1 585 cm^{-1} (C=N); δ_H($CDCl_3$) 1.11 (3 H, d, *J* 6.2 Hz), 1.13 (3 H, d, *J* 6.2 Hz), 2.27 (3 H, s), 2.73 (1 H, septet, *J* 6.2 Hz), 5.80 (1 H, s), 6.73—6.83 (1 H, br, ArH), and 7.0—7.5 (7 H, m, ArH); *m/z* 281 (M^+), 266 ($M^+ -$ Me), 238 ($M^+ - Me_2CH$), and 204 ($M^+ -$ Ph) (Found: C, 77.05; H, 6.7; N, 5.0; S, 11.25. $C_{18}H_{18}NS$ requires C, 76.82; H, 6.80; N, 4.98; S, 11.39%).

*3-Methyl-6-phenyl-2-(*p-*tolyl)imino-6-trimethylsilyl-*5,6-*dihydro-*2H-*thiopyran* (**11a**).—The blue solution of thioketone (**1a**) (3.3 mmol) in diethyl ether was treated with the ketene imine (**3b**) (0.50 g, 2.9 mmol) in CH_2Cl_2 at 20 °C for 6 h, under N_2. Chromatography of the residue on silica gel [eluant: methylene chloride–pentane (1:1 v/v)] afforded (**11a**) (0.90 g, 85%) as an oil which crystallized from pentane at −20 °C and had m.p. 93—94 °C; $\nu_{max.}$(Nujol) 1 580 (C=N) and 1 255, 842, and 735 cm^{-1} ($SiMe_3$); δ_H($CDCl_3$) −0.07 (9 H, s, $SiMe_3$), 1.85 (3 H, m, Me), 2.37 (3 H, s, Me), 3.0—3.2 (2 H, m, CH_2), 6.2—6.4 (1 H, m, vinylic-H), and 6.67—7.43 (9 H, m, ArH); δ_C($CDCl_3$) −3.50 (q), 20.35 (q), 20.99 (q), 30.81 (t), 43.21 (s), 119.61 (d), 125.14 (d), 127.61 (d), 127.68 (d), 129.42 (d), 132.99 (s), 133.27 (d), 134.81 (s), 142.19 (s), 148.21 (s), and 157.53 (s); *m/z* 365 (M^+), 292 ($M^+ - SiMe_3$), and 260 ($M^+ - C_7H_7N$) (Found: C, 72.35; H, 7.4; N, 3.9; S, 8.7. $C_{22}H_{27}NSSi$ requires C, 72.27; H, 7.44; N, 3.83; S, 8.77%).

*3-Methyl-6-phenyl-2-(*p-*tolyl)imino-6-triphenylsilyl-*5,6-*dihydro-*2H-*thiopyran* (**11b**).—The thioketone (**1b**) (0.25 g, 0.66 mmol) was treated with the ketene imine (**3b**) (0.12 g, 0.70 mmol) in CH_2Cl_2 (15 ml), at 20 °C, for 15 h, under N_2. Chromatography on silica gel [eluant: methylene chloride–pentane (1:1, v/v)] afforded (**11b**) (0.23 g, 63%); m.p. 157—158 °C (benzene–pentane); $\nu_{max.}$(CCl_4–C_2Cl_4–CS_2) 1 580 (C=N) and 1 432 and 1 100 cm^{-1} ($SiPh_3$); δ_H($CDCl_3$) 1.8—1.97 (3 H, m, Me), 2.33 (1 H, s), 3.03—3.77 (2 H, m, CH_2), 6.07—6.27 (1 H, m, C*H*CH_2), and 6.50—7.8 (24 H, ArH); δ_C($CDCl_3$) 20.5 (q), 20.99 (q), 32.34 (t), 43.76 (s), 119.74 (d), 125.63 (d), 127.16 (d), 127.52 (d), 129.26 (d), 129.35 (d), 129.76 (d), 132.01 (s), 132.75 (d), 133.19 (s), 134.94 (s), 137.32 (d), 140.8 (s), 147.66 (s), and 156.60 (s); *m/z* 551 (M^+), 474 ($M^+ -$ Ph), 292 ($M^+ - SiPh_3$), and 259 ($SiPh_3$) (Found: C, 80.15; H, 6.15; N, 2.6; S, 5.95. $C_{37}H_{33}NSSi$ requires C, 80.53; H, 6.03; N, 2.54; S, 5.81%).

Desilylation of (**11a**).—A solution of tetrabutylammonium fluoride in THF (1M; 1.4 ml) was added to a solution of (**11a**) (0.51 g, 1.4 mmol) in THF (10 ml) containing a drop of water. The reaction mixture was stirred under N_2 at 0 °C for 15 min, then poured into ice–water (40 g) and extracted with diethyl ether (4 × 15 ml). The ethereal layer was dried (Na_2SO_4), evaporated under reduced pressure, and the residue was chromatographed on silica gel (eluant: benzene) to afford the following two products:

*3-Methyl-6-phenyl-2-(*p-*tolyl)imino-*5,6-*dihydro-*2H-*thiopyran* (**12**): (0.32 g, 78%), m.p. 102—103 °C (methanol); $\nu_{max.}$(CCl_4–C_2Cl_4–CS_2) 1 580 cm^{-1} (C=N); δ_H($CDCl_3$) 2.10—2.20 (3 H, m, Me), 2.27 (3 H, s), 2.63—2.93 (2 H, m, CH_2), 4.27—4.50 (1 H, m, PhC*H*S), 6.37—6.57 (1 H, m, C*H*CH_2), and 7.03—7.40 (9 H, m, ArH); δ_C($CDCl_3$) 20.55 (q), 20.92 (q), 33.11 (t), 46.29 (d), 119.75 (d), 127.77 (d), 127.99 (s), 128.35 (d), 128.67 (d), 129.45 (d), 133.45 (s), 134.23 (d), 139.73 (s), 148.07 (s), and 160.18 (s); *m/z* 293 (M^+), 171 ($M^+ -$ PhCHS), and 91 (C_7H_7) (Found: C, 77.9; H, 6.55; N, 4.65; S, 11.05. $C_{19}H_{19}NS$ requires C, 77.77; H, 6.53; N, 4.77; S, 10.93%).

*3-Methyl-6-phenyl-2-(*p-*tolyl)imino-*2H-*thiopyran* (**13**): (0.02 g, 5%), m.p. 113—114 °C (methanol); $\nu_{max.}$(CCl_4–C_2Cl_4–CS_2) 1 580 cm^{-1} (C=N); δ_H($CDCl_3$) 2.20—2.30 (3 H, m, Me), 2.33 (3 H, s), 6.67 (1 H, d, *J* 7.5 Hz), 6.77—6.97 (1 H, m of C*H*=CMe and 2 H, ArH), and 7.13 (7 H, m, ArH); δ_C($CDCl_3$) 20.24 (q), 21.02 (q), 115.66 (d), 119.60 (d), 126.37 (d), 128.78 (d), 129.08 (d), 130.46 (d), 132.47 (s), 132.57 (d), 133.36 (s), 137.38 (s), 141.90 (s), 148.46 (s), and 158.34 (s); *m/z* 291 (M^+) and 117 (C_7H_7NC) (Found: C, 78.5; H, 5.9; N, 4.75; S, 11.05. $C_{19}H_{17}NS$ requires C, 78.31; H, 5.88; N, 4.81; S, 11.00%).

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