CHEMISTRY OF SILYL THIOKETONES. Part 6.[#] SYNTHESIS OF 5-MEMBERED SILYL-HETEROCYCLES VIA 1,3-DIPOLAR CYCLOADDITION TO ARYL SILYL THIOKETONES

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Abstract - Aryl silyl thioketones react with 1,3-dipoles (nitriloxides, nitrilimine and nitrile ylide) to give regiospecifically silyl thiaheterocycles. These cycloadducts undergo desilylation leading either to ring fragmentation products or to the H-substituted heterocycles.

INTRODUCTION

1,3-Dipolar cycloadditions between thiocarbonyl compounds as heterodipolarophiles and a broad series of 1,3-dipoles constitute an easy entry to 5-membered thiaheterocycles.[1]
Among thiocarbonyls, thioaldehydes may represent an attractive class of reagents, suitable to obtain H-substituted thiaheterocycles by cycloaddition reactions. This approach was hampered by the extreme instability of thioaldehydes in the isolation conditions. Only hindered thioaldehydes could be isolated, but their reactivity is very low.[2] In contrast, many thioaldehydes have been generated and trapped "in situ" with 1,3-dienes or stable 1,3-dipoles.[3-5] A problem may arise in the reaction with 1,3-dipoles also generated "in situ". To circumvent the problem, silyl thioketones[6] can be used as synthetic equivalents of thioaldehydes because they are good dienophiles and dipolarophiles

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≠ for part 5 see ref. 6e

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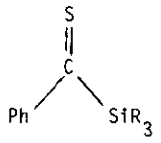
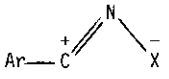
and their silyl adducts can be protodesilylated leading to the adducts formally deriving from thioaldehydes. As reported elsewhere, we found that protodesilylation occurred easily on the adducts between aryl silyl thiones and 1,3-dienes[6c] whereas it was more difficult and complicated by side reactions when performed upon the adducts arising from alkyl silyl thiones.[6e] Since removal of silicon from the primary adduct is an essential step in order to exploit the synthetic equivalence between silyl thioketones and thioaldehydes, we had to restrict our investigation to aryl derivatives. We reported previously[6a,b] about the cycloaddition of some 1,3-dipoles to phenyl trimethylsilyl thione; we wish to report here our complete results concerning the cycloaddition of representative 1,3-dipoles - nitrile oxides **2a,b**, nitrile imine **2c** and nitrile ylide **2d** to aryl silyl thioketones **1a,b** and the desilylation of the silyl heterocycles obtained.



1

a R = Me
b R = Ph

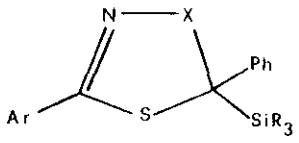


2

a Ar = Ph X = O
b Ar = p-Cl-Ph X = O
c Ar = Ph X = NPh
d Ar = Ph X = p-NO_2-C_6H_4CH

RESULTS AND DISCUSSION

Phenyl trimethylsilyl thioketone **1a** was reacted with 1,3-dipoles **2a,c,d** generated in situ by dehydrochlorination of a suitable precursor with triethylamine. Only the stable p-chlorobenzonitriloxide **2b** was reacted directly with phenyl triphenylsilyl thioketone **1b**. After the disappearance of the starting thione (generally few hours) filtration of triethylamine hydrochloride and chromatography of the reaction mixture afforded the silylated cycloadducts **3**, whose yields and physical data are reported in **Table 1**. Only the adduct **3b** could be isolated simply by crystallization from the reaction mixture. The differences between reaction yields can derive from the different reactivity of the 1,3-dipoles **2a-d**. In fact, when the 1,3-dipole presents low reactivity, as for **2c** and **2d**, an higher reaction temperature is required, favouring the competitive trimerisation[6d] of the thione. This was in fact the major pathway in the reaction between **1a** and the nitrile ylide **2d**. The elucidation of the structure of the adducts **3a-e** was based on spectroscopic evidence as well as on chemical correlations obtained during the subsequent desilylation step. The yields and physical data of desilylated adducts **4** are reported in **Table 2**.

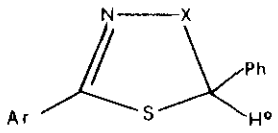


3

Table I

entry	Ar	R	X	Yield≠ (%)	mp (°C)	$\delta_H(SiMe_3)$
3a	Ph	Me	O	81	91-92	0.18
3b	p-Cl-C_6H_4	Ph	O	95	144-146	-
3c	Ph	Me	NPh	65	146-148	0.30
3d+3e*	Ph	Me	p-NO_2-C_6H_4-CH	20	174-176	0.10 (E) -0.30 (Z)

≠ based on the thioketone
* diastereomeric mixture



4

Table 2

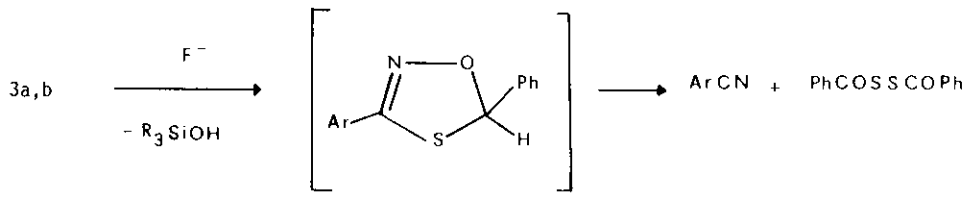
entry	Ar	X	Yield (%)	mp (°C)	δ_H(°H)
4a	Ph	O	-*	-	-
4b	p-Cl-C_6H_4	O	-*	-	-
4c	Ph	NPh	50	82-84	6.80 (s)
4d	Ph	p-NO_2-C_6H_4-CH	12	106-107	4.83 (d) J 7.5 Hz

* not isolated

Cycloadditions of aryl silyl thiones with nitrile oxides. The reaction between phenyl trimethylsilyl thione 1a and benzonitriloxide 2a gave 2,5-diphenyl-5-trimethylsilyl-5H-1,4,2-oxathiazole 3a. This cycloaddition proved to be regiospecific as others already described[7] between thiocarbonyl compounds and nitrile oxides. The regiochemistry was confirmed by correct spectral data and chemical evidence. In fact protodesilylation of the adduct 3a, performed either with tetraethylammonium fluoride (TEAF) in wet dimethyl sulphoxide or with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran did not afford 3,5-diphenyl-5H-1,4,2-oxathiazole 4a but benzonitrile and dibenzoyl disulphide in nearly quantitative yield. Both isolated products arise from the fragmentation of the unknown heterocycle 4a. It is not clear whether 4a is an intrinsecally labile product or the basic conditions employed during desilylation favour a base-catalyzed ring fragmentation (see scheme 1). Nevertheless, this result confirms the regiochemistry proposed for 3a.

The reaction of phenyl triphenylsilyl thione 1b with p-chlorobenzonitriloxide 2b led regiospecifically and in nearly quantitative yield to the cycloadduct 3b. Desilylation of 3b gave the same results as for 3a (see experimental).

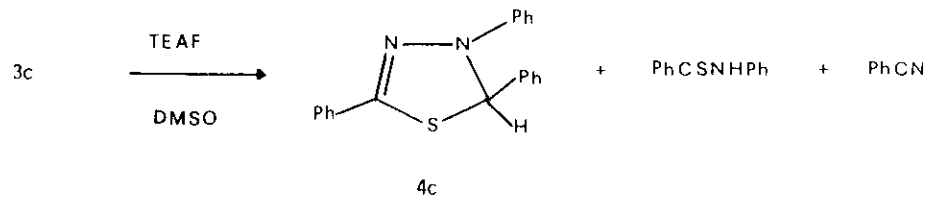
Scheme 1



4a,b

Cycloaddition of phenyl trimethylsilyl thione 1a with diphenylnitrilimine 2c. The reaction between the silyl thione 1a and the nitrilimine 2c gave 2,3,5-triphenyl-2-trimethylsilyl-2,3-dihydro-1,3,4-thiadiazole 3c, whose structure was assigned on the basis of correct spectral data as well as chemical evidence obtained through its desilylation. As reported previously,[6a] compound 3c could be protodesilylated upon treatment with TEAF in dimethyl sulphoxide at room temperature to the corresponding 2,3-dihydro-2,3,5-triphenyl-1,3,4-thiadiazole 4c[8] (50%); in addition, N-phenyl-thiobenzamide and benzonitrile were found: these two products arise from a partial decomposition of 4c. In fact, the 5-H substituted thiadiazoline 4c is transformed into benzonitrile and N-phenyl-thiobenzamide on standing for some days at room temperature or by heating at 80°C for some minutes (see Scheme 2). In this case again, the products arising from the fragmentation of the H-substituted heterocycle confirm the regiochemistry of the primary adduct.

Scheme 2



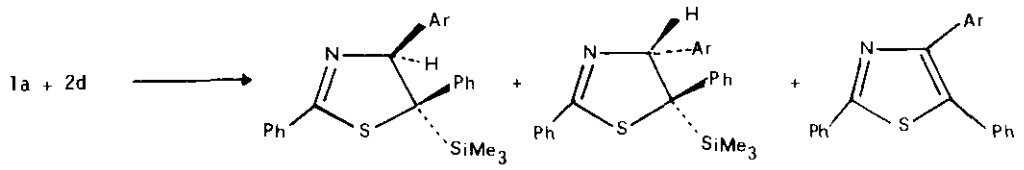
4c

Cycloaddition of phenyl trimethylsilyl thione **1a** with benzonitrile 4-nitrobenzylide **2d**. The reaction between **1a** and **2d** gave in 20% yield the primary adduct 2,5-diphenyl-4-(p-nitrophenyl)-5-trimethylsilyl-4,5-dihydrothiazole **3d,e** as a mixture of two diastereomers, together with a comparable yield of 2,5-diphenyl-4-(p-nitrophenyl)thiazole **5** arising from the aromatization of the primary adduct **3d,e**: the thiazole **5** was formed even during the chromatography of pure **3d,e**. We were not able to detect either the alternative regioisomer 4,5-diphenyl-2(p-nitrophenyl)-5-trimethylsilyl-2,5-dihydrothiazole or its aromatization product 4,5-diphenyl-2(p-nitrophenyl)thiazole in the reaction mixture: the reaction is therefore regiospecific with the same regiochemistry previously found by Huisgen in the cycloaddition of **2d** with methyl dithiobenzoate and methyl thionobenzoate.[9] It is worth of note that Huisgen's thiazolines **6a,b** carrying a leaving group like methoxy or methylthio also underwent a very easy aromatisation to the thiazole **5** upon heating or during work-up (see Scheme 3).[9]

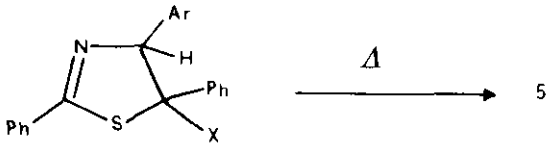
The cycloaddition is not stereospecific: the two isomers **3d,e** were obtained in a ratio 65:35. An attempt of separation led only to the pure **3d**, beside the aromatised product **5**. The relative stereochemistry was attributed to the primary adducts **3d,e** on the basis of nOe experiments. Saturation of the $SiMe_3$ signal of the major isomer **3d** at 0.10 ppm caused an increase (up to 16%) of the signal of the corresponding C-4 hydrogen at 6.15 ppm. A control experiment was run on the mixture of **3d,e**: saturation of the $SiMe_3$ signal of the minor isomer **3e** at -0.3 ppm caused no significant increase in the intensity of the corresponding C-4 hydrogen signal at 6.45 ppm. On this basis we were able to assign the E relative configuration to **3d** and the Z configuration to the isomeric adduct **3e**. Inspection of molecular models shows that in the E-isomer a cis arrangement of the C-4 p-nitrophenyl and C-5 phenyl groups corresponds to an average distance of 0.35 nm between the C-4 hydrogen and the hydrogens of the $SiMe_3$ group.

Desilylation of the isomeric mixture of the silylthiazolines **3d,e** was attempted under different conditions. When TEAF in DMSO was used as desilylating agent, the only recovered product was thiazole **5**. Instead, when TBAF was used in THF, the expected protodesilylated 2,5-diphenyl-4-(p-nitrophenyl)-4,5-dihydrothiazole **4d** was formed in 12% yield together with the thiazole **5** (40%) (Scheme 4). Compound **4d** is a single diastereomer and its stereochemistry is easily

Scheme 3



3d 3e 5



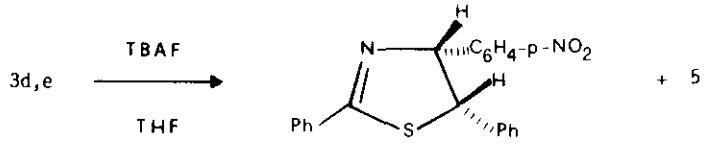
6a X = SMe

6b X = OMe

Ar = p-NO_2-C_6H_4

assigned on the basis of its ^1H nmr spectrum, where the two hydrogens at C-4 and C-5 display an AX system with a coupling constant of 7.5 Hz: this indicates a syn coplanar arrangement of these two hydrogens and a Z-stereochemistry about the C-4 - C-5 bond. Unfortunately, the stereochemistry of the desilylation cannot be discussed because the silylated educt was a mixture of two isomers and the aromatized product 5 is far largely formed.

Scheme 4



4d

CONCLUSIONS

The aim of the present investigation was turned towards two distinct points: studying the cycloaddition between silyl thioketones and 1,3-dipoles and probing the synthetic equivalence between silyl thioketones and thioaldehydes through protodesilylation of the silylated cycloadducts. As far as the first point is concerned, our results show that silyl thiones behave similarly to not-silylated thiones with respect to reactivity towards the chosen 1,3-dipoles. The cycloadducts are formed regiospecifically and the regiochemistry is the same as discussed by Huisgen[10] or Houk.[11] The proposed synthetic equivalence can be exploited if the hydrogen substituted heterocycle has some stability. Our results show that the stability of compounds **4a-d** depends on the type of heteroatoms there present being poor for the thiadiazoline **4c** which easily decomposes into thioamide and nitrile. Chemical stability seems higher for thiazoline **4d**, which in turn arises from a quite unstable silyl heterocycle, with a very strong tendency to aromatise. Finally the oxathiazine **4a** is totally unstable in the desilylation conditions and only the products arising from its fragmentation were found.

EXPERIMENTAL

^{1}H Nmr spectra were recorded routinely at 60 MHz on a Varian EM-360-L spectrometer; nOe experiments were run at 200 MHz on a Varian Gemini 200 spectrometer; ^{13}C nmr spectra were recorded on a Varian FT-80-A spectrometer; chemical shifts are reported on the δ scale (reference tetramethylsilane). Ir spectra were obtained on a Perkin Elmer 177 spectrophotometer. Mass spectra were recorded with a VG 7070-E spectrometer at an ionizing voltage of 70 eV. Routine uv-vis spectra were obtained from a Jasco Uvidec-650 spectrophotometer. Glc analyses were performed on a Varian 3700 gaschromagraph, equipped with a flame ionization detector and fitted to a Varian 4270 electronic integrator. Melting points and ppm are uncorrected. Ether refers to diethyl ether.

Materials: the silyl thioketones **1a,b** were prepared as previously described.[6b] Phenyl trimethylsilyl thioketone **1a** was prepared immediately prior to use in diethyl ether; its concentration was determined through the adsorbance at λ = 678 nm (ε 37) in the uv-vis spectrum.

2,5-Diphenyl-5-trimethylsilyl-5H-1,4,2-oxathiazole **3a**: A solution of triethylamine (1.1 ml, 7.86 mmol) in ether (15 ml) and a solution of benzhydroxamoyl chloride[12] (1.22 g, 7.86 mmol) in ether (30 ml) were added at the same time to a stirred ethereal solution (30 ml) of the thione **1a** (7.86 mmol) at room temperature: the reaction mixture was stirred overnight under nitrogen at room temperature, then the precipitated triethylammonium hydrochloride was filtered off and the filtrate was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (eluant benzene) affording **3a** (2.00 g, 81%) as a white solid: mp 91-92°C (methanol); ν_{max} (CS_2) 1250, 840 and 755 cm^{-1} ($SiMe_3$); δ_H ($CDCl_3$) 0.18 (s, 9H), 7.2-7.7 (m, 10H, HAr); m/z 313 (M^+), 298 (M^+ - Me). 240 (M^+ - $SiMe_3$), 210 (M^+ - PhCN), 135 (PhCNS), 121 (PhCS), 105, 103 (PhCN); (Found: C, 64.85; H, 6.11; N,

4.42; S, 10.33. $C_{17}H_{19}NOSSi$ requires C, 65.13; H, 6.11; N, 4.47; S, 10.23).

2-(p-Chlorophenyl)-5-phenyl-5-triphenylsilyl-5H-1,4,2-oxathiazole **3b**: A solution of p-chlorobenzonitriloxide[13] (0.169 g, 1.1 mmol) in ether (15 ml) was added at -20°C to a solution of phenyl triphenylsilyl thioketone **1b** (0.42 g, 1.1 mmol) in ether (35 ml). The resulting solution was stirred under N_2 at room temperature until the blue colour of the thione had disappeared (30 min). The white precipitate was filtered off; chrystallization gave pure **3b** (0.56 g, 95%) as a greenish-white solid: mp 144-146°C (methanol); ν_{max} (CS_2) 1210 and 595 cm^{-1} ($SiPh_3$); δ_H ($CDCl_3$) 6.8-8.1 (m, 24 H, HAr); δ_C($CDCl_3$) 154.5 (s), 142.9 (s), 137.0 (s), 136.8 (d), 131.1 (d), 130.3 (d), 129.8 (d), 128.8 (d), 127.8 (d), 127.4 (s), 127.2 (d), 126.4 (s), 125.6 (d), 98.6 (s); m/z 396 (M^+ -ClC_6H_4CN), 319 (M^+ -ClC_6H_4CN - C_6H_5), 291 (M^+ - ClC_6H_4CN - C_6H_5Si), 259 (($C_6H_5)_3Si$), 137 - 139 (ClC_6H_4CN), 105 (C_6H_5Si), 102 (C_6H_4CN), 77 (C_6H_5); (Found: C, 71.83; H, 4.61; N, 2.65; S, 6.08. $C_{32}H_{24}ClNOSSi$ requires C, 71.95; H, 4.53; N, 2.62; S, 6.00).

2,3,5-Triphenyl-2-trimethylsilyl-2,3-dihydro-1,3,4-thiadiazole **3c**: A solution of triethylamine (0.38 ml, 2.73 mmol) in benzene (30 ml) and a solution of N-(α-chlorobenzylidene)-N'-phenylhydrazine[14] (0.63 g, 2.73 mmol) in benzene (30 ml) were dropped at the same time to a concentrated ethereal solution (5 ml) of the thione **1a** (2.73 mmol) diluted with benzene (10 ml). The resulting solution was then refluxed for 1 h under N_2. After cooling, the precipitated triethylammonium hydrochloride was filtered off and the filtrate was concentrated *in vacuo*: the residue was chromatographed on a silica gel column (eluant petroleum ether: benzene 8:2) affording **3c** (0.695 g, 65%): mp 146-148°C (ethanol); ν_{max} (CS_2) 1250, 840 and 755 cm^{-1} ($SiMe_3$); δ_H ($CDCl_3$), 0.30(s, 9 H, $SiMe_3$), 6.6 - 7.6 (m, 15 H, HAr); m/z 388 (M^+), 373 (M^+ - Me), 315 (M^+ - $SiMe_3$), 222 (PhCSCNPh), 180 (PhCNPh), 121 (PhCS). (Found C, 71.19; H, 6.36; N, 7.27; S, 8.34. $C_{23}H_{24}N_2SSi$ requires C, 71.08; H, 6.22; N, 7.21; S, 8.25).

2,5-Diphenyl-4-(p-nitrophenyl)-5-trimethylsilyl-4,5-dihydrothiazole **3d-e**: The reaction was performed on **1a** (3.9 mmol) in a concentrated ethereal solution (5 ml) with the same procedure as described for **3c**; N-(p-nitrobenzyl)benzimidoyl chloride[9] was used as the precursor of the 1,3-dipole **2d**. The reaction mixture was refluxed 30 min under N_2, then cooled and the precipitated triethylammonium hydrochloride was filtered off (0.27 g, Yield 50%). The filtrate was concentrated *in vacuo*, then chromatographed on a silica gel column (eluant petroleum ether : ethyl ether 8 : 2) affording as the first fraction 0.38 g (50%) of a mixture of α- and ß-2,4,6-trimethylsilyl-2,4,6-triphenyl-1,3,5-trithiane[6d] and as the second fraction 0.60 g of a mixture of the cycloadducts **3d-e** and the thiazole **5**. This mixture was separated by chromatography on silica gel plates (eluant petroleum ether : ethyl acetate 5 : 1) giving, as the higher R_f fraction the thiazole **5** (0.20 g, 14%), mp 130-132°C (methanol)[9] , ν_{max} (CS_2) 1345, 1220 cm^{-1} (NO_2), and as the lower R_f fraction the thiazolines **3d-e** as a yellow solid: (0.34 g, 20%), mp 174-176°C (n-hexane : ether); ν_{max} (CS_2) 1340 (NO_2), 1250 and 835 cm^{-1} ($SiMe_3$);δ_H ($CDCl_3$) - 0.27 and 0.11 (2s, 9H, $SiMe_3$), 6.20 and 6.43 (2 s, 1H, C-4 H), 6.7-8.2 (m, 14 H, HAr); m/z 432 (M^+), 358 (M^+ - Me_3SiH), 329 (M^+ -PhCN), 238 (M^+ - $PhCSSiMe_3$), 165, 121 (PhCS), 77 (Ph), 73 ($SiMe_3$). (Found: C, 66.70; H, 5.61; N, 6.47; S, 7.43. $C_{24}H_{24}N_2O_2SSi$ requires C, 66.63; H, 5.59; N, 6.48; S, 7.41). The ratio between the isomers **3d** and

3e was determined by integration of the signals of the $SiMe_3$ (0.11 and -0.27 ppm) and C-4 H (6.20 and 6.43 ppm) respectively for the two products **3d** : **3e** ≈ 2 : 1. This mixture was chromatographed six times on silica gel plates (eluant petroleum ether : ethyl acetate 10 : 1) giving almost pure **3d** as the lowest part of the second fraction beside the thiazole **5** as the highest R_f fraction. δ_H (at 200 MHz) 0.11 (s, 9H, $SiMe_3$), 6.13 (s, 1 H, C-4 H), 6.8-6.9 (m, 2 H, HAr), 6.9-7.1 (m, 3 H, HAr), 7.35-7.60 (m, 5 H, HAr), 7.85-8.00 (m, 4 H, HAr).

Desilylation of **3a**: A suspension of 2,5-diphenyl-5-trimethylsilyl- 1,4,2-oxathiazole **3a** (0.156 g, 0.5 mmol) in dimethyl sulphoxide (DMSO) (1 ml) was treated with TEAF (0.14 g, 0.75 mmol). After few minutes at room temperature the reaction mixture was diluted with water, extracted with ether and the ethereal extracts were dried (Na_2SO_4). A glc analysis of the crude reaction mixture revealed the presence of benzonitrile (0.031 g, 61%) which was determined employing the internal standard method. The analyses were performed on a 3% SP-2100 on Supelcoport (100-120 mesh) packed column (m. 2) using a temperature program from 50 to 200 °C, program rate 10°C min^{-1}. At a flow rate of carrier gas (nitrogen) equal to 30 ml min^{-1} retention times were t_R (benzonitrile) 3.8 min.; t_R(biphenyl used as internal standard) 9.9 min. The crude reaction mixture was then evaporated and crystallized from methanol, giving dibenzoyl disulphide (0.038 g, 56%), mp 128-130°C which was compared with a model product.[15]

When the same reaction was repeated using TBAF as desilylating agent in tetrahydrofuran at -30°C determination of products as above reported gave: benzonitrile 85%, dibenzoyl disulphide 92%.

Desilylation of **3b**: A TBAF in THF 1 M solution (0.23 ml, 0.23 mmol) was added at 0°C to a solution of 2-(p-chlorophenyl)-5-phenyl-5-triphenylsilyl-1,4,2-oxathiazole **3b** (0.119 g, 0.22 mmol)in wet THF (5.0 ml). The reaction mixture was stirred at 0°C under nitrogen for 2 h, then hydrolyzed with saturated acqueous ammonium chloride, extracted with ether and concentrated *in vacuo*. The residue was chromatographed on silica gel plates (eluant petroleum ether : benzene 1 : 1) giving five fractions, *viz (from the top) sulfur (3.5 mg, 50%), p-chlorobenzonitrile (29 mg, 95%),* dibenzoyl disulphide (5 mg, 16%), triphenylsilanol (36.5 mg, 60%), and benzoic acid (21.5 mg, 80%).

Desilylation of **3c**: A suspension of 2,3,5-triphenyl-2-trimethylsilyl-2,3-dihydro-1,3,4-thiadiazole **3c** (0.10 g, 0.25 mmol) in DMSO (1 ml) was treated with TEAF (0.068 g, 0.37 mmol). After few minutes at room temperature the reaction mixture was diluted with water and extracted with ether; the ether extracts were dried (Na_2SO_4) and concentrated *in vacuo*. *The solid residue was chromatographed on* silica gel plates (eluant petroleum ether: ethyl acetate 10 : 1), giving as the higher R_f fraction 2,3-dihydro-2,3,5-triphenyl-1,3,4-thiadiazole[8] **4c** (0.04 g, 50%): mp 82-84°C (n-pentane); δ_H ($CDCl_3$) 6.80(s, 1 H, C-2 H), 7.0 - 8.3 (m, 15 H, HAr); m/z 316 (M^+), 239 (M^+ - Ph), 207 (M^+ -Ph - S), 194 (M^+ - PhCHS), 122 (PhCHS), 105, 91, 77, and as the lower R_f fraction N-phenylthiobenzamide (0.018 g, 34%),[16] mp 93-95°C. In a separate experiment benzonitrile (30%) was determined directly on the reaction mixture by glc as already described for the desilylation of **3a**.

On standing at room temperature, thiadiazoline **4c** was slowly transformed into N-phenylthiobenzamide and benzonitrile; the decomposition was about 30% after 12 h.

Desilylation of **3d-e**: A TBAF in THF 1 M solution (0.75 ml, 0.75 mmol) was added at 0°C to a

solution of the silyl thiazoline **3d-e** (0.31 g, 0.72 mmol) in wet THF (3 ml). The reaction mixture was stirred overnight at room temperature, then diluted with water, extracted with ether and concentrated in vacuo. The residue was chromatographed on silica gel plates (eluant benzene) giving as the higher R_f fraction the thiazole **5** (0.103 g, 40%), and as the lower R_f fraction 2,5-diphenyl-4-(p-nitrophenyl)-4,5-dihydrothiazole (0.031 g, 12%) **4d** as a white solid: mp 106-107°C (ether : n-hexane); ν_{max} (CS_2) 1345 cm^{-1} (NO_2); δ_H 4.83 (d, 1 H, J 7.5 Hz, C-5 H), 5.87 (d, 1 H, J 7.5 Hz, C-4 H), 7.2 - 8.3 (m, 14 H, HAr); m/z 360 (M^+), 257 (M^+ - PhCN), 239 (M^+ -PhCS), 221, 192, 165, 121 (PhCS), 89, 77 (Ph). (Found : C, 70.01; H, 4.49; N, 7.74; S, 8.91. $C_{21}H_{16}N_2O_2S$ requires C, 69.98; H, 4.47; N, 7.77; S, 8.89).

When the same reaction was performed employing TEAF in DMSO as desilylating agent, the only isolated product was the thiazole **5** (47%).

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