Functionalized Heterocumulenes: Synthesis and Applications of Phenylthiomethyl, Methylthiomethyl, Bis[phenylthio]methyl Isocyanates and Phenylthio-acetyl and Methylthio-acetyl Isothiocyanates

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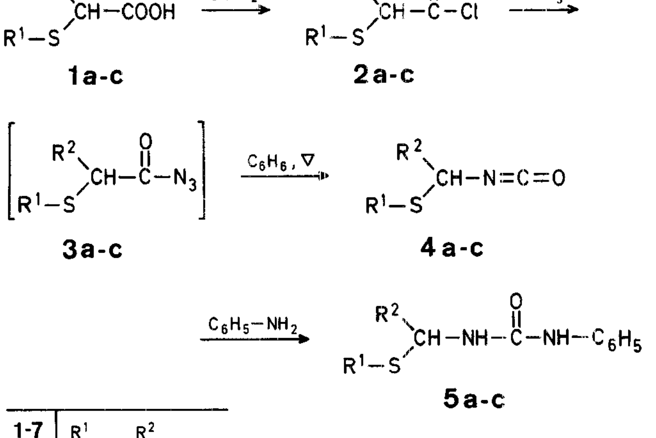
Heterocumulenes are useful reagents for the synthesis of heterocyclic compounds, but they show limitations when applied to the synthesis of heterocycles having functional groups. We previously reported[1] the preparation and synthetic applications of some heterocumulenes. We now describe the synthesis and reactions of isocyanates and isothiocyanates having an alkylthiomethyl or arylthiomethyl substituent. Although a few preparations of such compounds have been reported[2,3,4], their utilisation in heterocyclic synthesis is less well known.

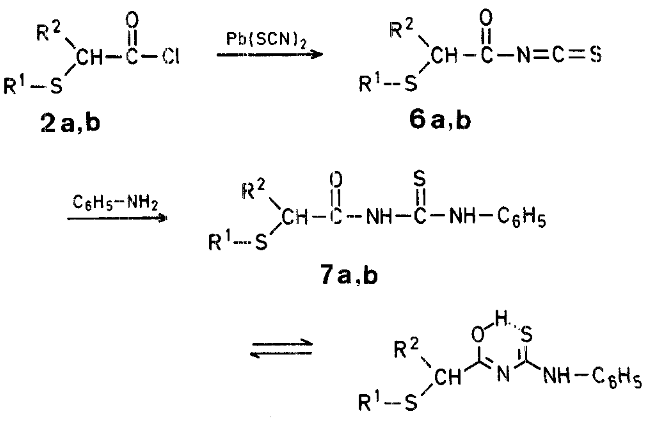
The isocyanates **4** were prepared starting from the corresponding thioacetic acids **1**. The acid chlorides **2**, obtained by reacting **1** with thionyl chloride, were refluxed[2] with sodium azide in benzene to give the azides **3**. Thermolysis of azides **3** furnished the desired isocyanates. The isocyanates **4a** and **4b**[3] could be distilled as colorless liquids (77% and 76% yields respectively based on the acid **1**) and were stable at room temperature under a nitrogen atmosphere. However, the bis[phenylthio]derivative **4c** was not stable enough to be distilled at higher temperature than 150 °C. The isocyanates **4** were characterized by the strong I.R. absorption band at $\nu = 2240-2250\ \mathrm{cm}^{-1}$. Purity of the isocyanates was ascertained by quantitative formation of the ureas **5** upon addition of aniline. The yield of **4c** was 44% starting from the acid **1c** as determined by ^{1}H-N.M.R. (Scheme **A**).



1-7	R¹	R²
a	C_6H_5	H
b	CH_3	H
c	C_6H_5	C_6H_5-S-

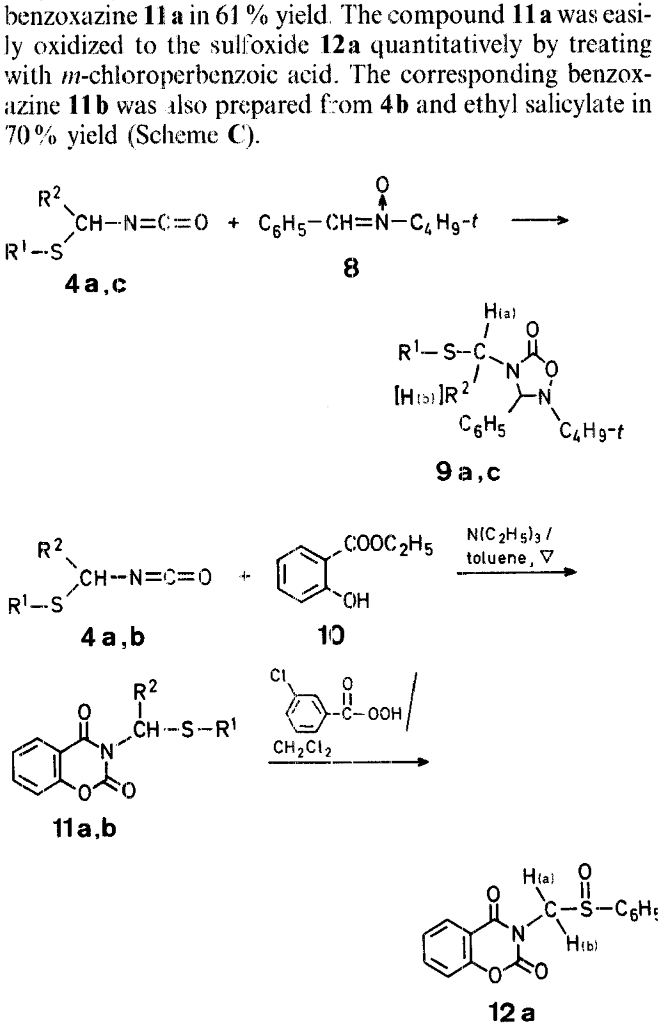
Scheme A

Preparation of isothiocyanates **6** was carried out by the reaction of the acid chlorides **2** with lead thiocyanate in refluxing benzene for 2 h[4]. The acyl isothiocyanates **6** were obtained as colorless liquids in good yields and the structures were confirmed by the strong I.R. absorption at $\nu = 1950-1970\ \mathrm{cm}^{-1}$ and by quantitative formation of the thiourea derivatives **7** (Scheme **B**).



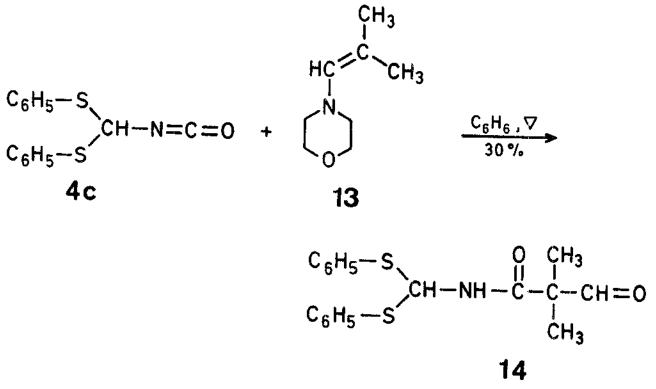
Scheme B

The above heterocumulenes **4** and **6** having a sulfenyl substituent are good building blocks for the preparation of heterocycles having a sulfur-containing functional group. Thus, cycloaddition of the isocyanates **4a** and **4c** (generated *in situ*) with *N*-*t*-butyl-*C*-phenylnitrone (**8**) gave the oxadiazolidinones **9a** and **9c** in high yields. Cyclocondensation of **4a** with ethyl salicylate (**10**) in the presence of triethylamine gave the benzoxazine **11a** in 61% yield. The compound **11a** was easily oxidized to the sulfoxide **12a** quantitatively by treating with *m*-chloroperbenzoic acid. The corresponding benzoxazine **11b** was also prepared from **4b** and ethyl salicylate in 70% yield (Scheme **C**).



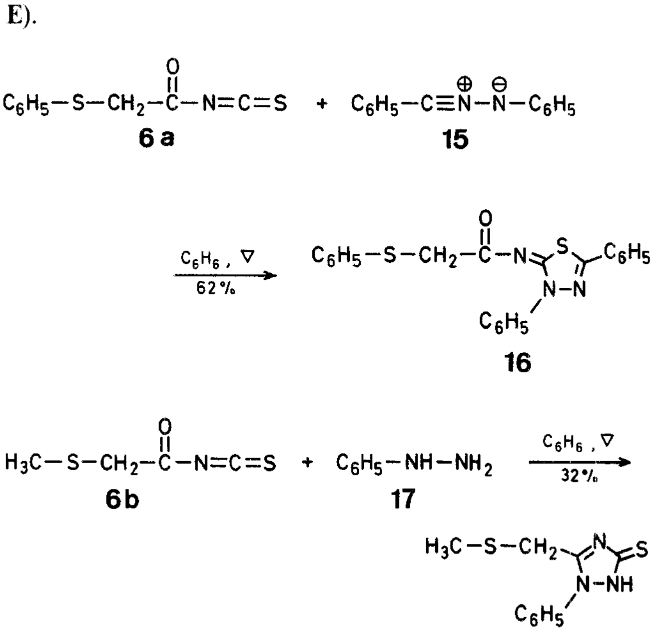
Scheme C

Although enamines having no *β*-hydrogens often form cycloadducts with heterocumulenes, the reaction of the isocyanate **4c** with 4-isobuten-1-ylmorpholine (**13**) gave *N*-bis[phenylthio]methyl-2-formylisobutyramide (**14**, 30% yield based on the starting acid **1c**), which was probably formed by hydrolysis of the expected 1:1 cycloadduct during chromatography on silica gel (Scheme **D**).



Scheme D

The acyl isothiocyanates **6** are also found to be good reagents for heterocyclic synthesis. The reaction of **6a** with benzonitrile *N*-phenylimine (**15**) caused the addition across the C=S bond of **6a** to afford the thiadiazoline **16** in 62% yield. Cyclocondensation of the isothiocyanate **6b** with phenylhydrazine (**17**) gave the triazolinethione **18** in 32% yield (Scheme E).



Scheme E

The heterocycles herein prepared are of interest because of the well-known convertibility of sulfur-containing functional groups. For example, the sulfenylmethyl group can be converted into a formyl group via the Pummerer reaction[5] and dithioacetals are also hydrolyzed to aldehydes[6]. Thus, these heterocumulenes could be versatile synthetic reagents for functionalized heterocycles.

Phenylthiomethyl Isocyanate (4a):

Phenylthioacetyl Chloride (**2a**): This is prepared by the conventional method from phenylthiomethylacetic acid (**1a**; 180 g, 1.07 mol) and thionyl chloride (92 ml, 1.26 mol) at 70 °C for 1 h; yield: 185.7 g (93%); b.p. 87–93 °C/2 torr (Lit.[7], b.p. 117–119 °C/6 torr).

Conversion of **2a** *to* **4a**: To a solution of sodium azide (40 g, 214 mmol) in water (50 ml) maintained at 0 °C is added a solution of **2a** (40 g, 214 mmol) in benzene (30 ml) and stirred for 0.5 h. The benzene layer is separated and dried with magnesium sulfate. The dried organic layer is then added dropwise into refluxing benzene (500 ml) under a nitrogen atmosphere. The solution is heated under reflux for 3 h until the nitrogen evolution ceased. Distillation of the residue obtained after removal of benzene gives **4a** as a colorless liquid; yield: 29 g (77% based on **1a**); b.p. 80–82 °C/2 torr (Lit.[3], b.p. 117 °C/13 torr).

I.R. (Film): $\nu = 2240\ \mathrm{cm}^{-1}$ (N=C=O; Lit.[3], $\nu = 2252\ \mathrm{cm}^{-1}$).

Methylthiomethyl Isocyanate (4b):

Methylthioacetyl Chloride (**2b**): Methylthioacetic acid (**1b**; 18 g, 170 mmol) and thionyl chloride (14.7 ml, 202 mmol) are reacted to give **2b**; yield: 20.3 g (96%); b.p. 57–63 °C/15 torr (Lit.[7], b.p. 49–50 °C/14 torr).

Conversion of **2b** *to* **4b**: Methylthioacetyl chloride (**2b**; 16 g, 128 mmol) dissolved in benzene (30 ml) is first reacted with sodium azide (10 g, 154 mmol) in water (40 ml) at 0 °C to form the azide **3b**, which is then thermolyzed in an analogous manner described above to give **4b**; yield: 10.5 g (76% based on **1b**); b.p. 134–136 °C/760 torr (Lit.[3], b.p. 34 °C/15 torr).

I.R. (Film): $\nu = 2250\ \mathrm{cm}^{-1}$ (N=C=O; Lit.[3], $\nu = 2237\ \mathrm{cm}^{-1}$).

Bis[phenylthio]methyl Isocyanate (4c):

Bis[phenylthio]acetic Acid (**1c**): To a solution of sodium ethoxide in ethanol, prepared from metallic sodium (21 g, 913 mmol) in ethanol (500 ml), is added dropwise thiophenol (66 g, 599 mmol) at 0 °C. After stirring for 10 min, dichloroacetic acid (39 g, 302 mmol) is added dropwise and the mixture is heated at 60 °C for 3 h to give **1c**; yield: 56 g (67%).

Bis[phenylthio]acetyl Chloride (**2c**): The acid **1c** (11.4 g, 41 mmol) is treated with thionyl chloride (5.7 g, 48 mmol) at 60–70 °C for 2 h in hexane/tetrahydrofuran (45 ml, 8:1) in the usual manner to give **2c**; crude yield: 11.8 g (97%).

I.R. (Film): $\nu = 1780\ \mathrm{cm}^{-1}$ (C=O).

Bis[phenylthio]acetyl Azide (**3c**): An ethereal solution of the chloride **2c** (11.8 g, 40 mmol) is added dropwise to a solution of sodium azide (3.12 g, 48 mmol) in water (30 ml) at 0 °C and the mixture is stirred for 1 h to give the azide **3c**.

I.R. (Film): $\nu = 2140$ (N=N=N), $1700\ \mathrm{cm}^{-1}$ (C=O).

Conversion of **3c** *to* **4c**: A dried ethereal solution of the azide **3c** thus obtained is added to refluxing benzene (200 ml) containing copper powder (3 g). The reflux is maintained for 1 h until nitrogen evolution ceased. Copper is filtered off under nitrogen and the filtrate is concentrated. The residual oil shows strong I.R. absorption at $\nu = 2240\ \mathrm{cm}^{-1}$, indicating the formation of **4c**. The yield determined by ^{1}H-N.M.R. is 44% based on the acid **1c**.

Phenylthio-acetyl Isothiocyanate (6a):

A mixture of **2a** (57 g, 305 mmol) and lead thiocyanate (50 g, 155 mmol) in benzene (50 ml) is refluxed for 2 h with stirring. Filtration of lead chloride and distillation of the residue obtained by evaporating the filtrate gives **6a**; yield: 53.1 g (83%); 120–125 °C/2 torr.

I.R. (Film): $\nu = 1970$ (N=C=S), $1720\ \mathrm{cm}^{-1}$ (C=O).

Methylthio-acetyl Isothiocyanate (6b):

Similar treatment of **2b** (17 g, 136 mmol) with lead thiocyanate (25 g, 77 mmol) as described above affords **6b**; yield: 16.6 g (82%); b.p. 85–87 °C/5 torr.

I.R. (Film): $\nu = 1950$ (N=C=S), $1700\ \mathrm{cm}^{-1}$ (C=O).

Thiomethylureas 5; General Procedure:

To a solution of the isocyanate **4** (20 mmol) in benzene (20 ml) is added dropwise aniline (1.86 g, 20 mmol) at 0 °C and the mixture is stirred for 0.5 h. The solvent is removed and the product recrystallized.

N-*Phenyl*-N′-*(phenylthiomethyl)-urea* (**5a**); yield: 5.16 g (100%); m.p. 107–108 °C (colorless powder from ethanol/benzene); (Lit.[3], m.p. 110–111 °C).

I.R. (Nujol): $\nu = 3340, 3300$ (NH); $1630\ \mathrm{cm}^{-1}$ (C=O).

^{1}H-N.M.R. (DMSO-d_6): $\delta = 4.77$ (d, 2H, CH_2); 6.6–7.6 (m, $10\,H_{\mathrm{arom}}$ + NH); 8.60 ppm (s, 1H, NH).

M.S.: $m/e = 149$ ($M^+ - C_6H_5S$).

N-Phenyl-N'-(methylthiomethyl)-urea (**5b**); yield: 3.92 g (100%); m.p. 124–126 °C (colorless powder from ethanol/benzene); (Lit.[3], m.p. 131 °C).

I.R. (Nujol): ν = 3280 (NH); 1640 cm^{-1} (C=O).

^{1}H-N.M.R. (DMSO-d_6): δ = 2.17 (s, 3H, CH_3); 4.33 (d, 2H, CH_2); 6.4–7.6 (m, 5H_{arom} + NH); 8.53 ppm (s, 1H, NH).

M.S.: m/e = 196 (M$^+$).

N-Phenyl-N'-(bis[phenylthio]methyl)-urea (**5c**); m.p. 160–161 °C (colorless needles from benzene/chloroform).

$C_{20}H_{18}N_2OS_2$	calc.	C 65.56	H 4.95	N 7.65	S 17.47
(366.5)	found	65.65	4.87	7.79	17.38

I.R. (Nujol): ν = 3320, 3260 (NH); 1640 cm^{-1} (C=O).

^{1}H-N.M.R. (DMSO-d_6): δ = 6.62 (s, 1H, CH); 6.80 (s, 1H, NH); 6.9–8.0 (m, 15H_{arom}); 8.70 ppm (s, 1H, NH).

M.S.: m/e = 257 (M$^+$ − C_6H_5S).

N-Phenyl-N'-phenylthioacetylthiourea (7a):

To a solution of **6a** (3.0 g, 14 mmol) in benzene (10 ml) is added aniline (1.33 g, 14 mmol) in benzene (10 ml) at room temperature. The mixture is stirred for 5 h and the solvent is removed; yield: 4.33 g (~ 100%); m.p. 97–98 °C (colorless needles from benzene/hexane).

$C_{15}H_{14}N_2OS_2$	calc.	C 59.60	H 4,67	N 9.27	S 21.17
(302.4)	found	59.59	4.48	9.22	21.00

I.R. (Nujol): ν = 3180 (NH); 1680 cm^{-1} (C=O).

^{1}H-N.M.R. (DMSO-d_6): δ = 4.00 (s, 2H, CH_2); 6.9–7.8 (m, 10H_{arom}); 11.60 (s, 1H, NH); 12.20 ppm (s, 1H, NH).

M.S. m/e = 302 (M$^+$).

N-Phenyl-N'-methylthioacetylthiourea (7b):

To a solution of **6b** (1.47 g, 10 mmol) in benzene (10 ml) is added aniline (0.93 g, 10 mmol) in benzene (10 ml) at room temperature. The mixture is stirred for 1 h and the solvent is removed; yield: 2.4 g (~ 100%); m.p. 106–107 °C (colorless needles from ethanol/benzene).

$C_{10}H_{12}N_2OS_2$	calc.	C 50.00	H 5.04	N 11.66	S 26.64
(240.3)	found	50.00	5.00	11.70	26.54

I.R. (Nujol): ν = 3200 (NH); 1680 cm^{-1} (C=O).

^{1}H-N.M.R. (DMSO-d_6): δ = 2.23 (s, 3H, CH_3); 3.40 (s, 2H, CH_2); 7.0–8.0 (m, 5H_{arom}); 11.43 (s, 1H, NH); 12.47 ppm (s, 1H, NH).

M.S.: m/e = 240 (M$^+$).

2-t-Butyl-3-phenyl-4-phenylthiomethyl-1,2,4-oxadiazolidin-5-one (9a):

A mixture of N-t-butyl-C-phenylnitrone (**8**; 1.6 g, 9.0 mmol) and **4a** (1.5 g, 9.1 mmol) in benzene (20 ml) is stirred under reflux for 14 h. The solvent is removed and the residue is recrystallized from hexane; yield: 2.88 g (94%); m.p. 70–71 °C.

$C_{19}H_{22}N_2O_2S$	calc.	C 66.65	H 6.48	N 8.18	S 9.35
(342.5)	found	66.75	6.45	8.13	9.18

I.R. (Nujol): ν = 1740 cm^{-1} (C=O).

^{1}H-N.M.R. (CDCl$_3$): δ = 1.00 (s, 9H, t-C_4H_9); 3.77 (d, 1H, J = 21 Hz, H_a); 5.20 (d, 1H, J = 21 Hz, H_b); 5.57 (s, 1H, C$\underline{H}$—C_6H_5); 7.00–7.60 ppm (m, 10H_{arom}).

M.S.: m/e = 342 (M$^+$).

4-Bis[phenylthiomethyl]-2-t-butyl-3-phenyl-1,2,4-oxadiazolidin-5-one (9c):

A mixture of **4c** (5.46 g, 20 mmol) and the nitrone **8** (3.54 g, 20 mmol) in benzene (40 ml) is refluxed for 16 h. The reaction mixture is chromatographed on silica gel using benzene/hexane (1 : 4) as eluent; yield: 6.66 g (74%); m.p. 133–134 °C (colorless needles from benzene/hexane).

$C_{25}H_{26}N_2O_2S_2$	calc.	C 66.65	H 5.82	N 6.22	S 14.21
(450.6)	found	66.69	5.72	6.32	14.33

I.R. (Nujol): ν = 1740 cm^{-1} (C=O).

^{1}H-N.M.R. (CDCl$_3$): δ = 0.87 (s, 9H, t-C_4H_9); 5.67 (s, 1H, C$\underline{H}$—C_6H_5); 6.53 (s, 1H, CH); 7.00–7.80 ppm (m, 15H_{arom}).

M.S.: m/e = 341 (M$^+$ − C_6H_5S).

3-Phenylthiomethyl-3,4-dihydro-1,3,2-benzoxazine-2,4-dione (11a):

A mixture of triethylamine (9.2 ml, 66 mmol), ethyl salicylate (**10**; 10.97 g, 66 mmol), and **4a** (10.9 g, 66 mmol) in toluene (20 ml) is refluxed for 35 h. After removal of the solvent, the residue is chromatographed on silica gel using 1/4 benzene/hexane as eluent; yield: 11.47 g (61%); m.p. 154–155 °C (colorless needles form hexane/chloroform).

$C_{15}H_{11}NO_3S$	calc.	C 63.16	H 3.89	N 4.91
(285.3)	found	63.07	3.65	4.88

I.R. (Nujol): ν = 1760, 1680 cm^{-1} (C=O).

^{1}H-N.M.R. (CDCl$_3$): δ = 5.33 (s, 2H, CH_2); 7.00–8.10 ppm (m, 9H_{arom}).

M.S.: m/e = 285(M$^+$).

3-Methylthiomethyl-3,4-dihydro-1,3,2-benzoxazine-2,4-dione (11b):

A mixture of triethylamine (4.2 ml, 30 mmol), ethyl salicylate (**10**; 4.99 g, 30 mmol) and **4b** (3.09 g, 30 mmol) in toluene (20 ml) is refluxed for 45 h and concentrated to give **11b**; yield: 4.68 g (70%); m.p. 128–130 °C.

I.R. (Nujol): ν = 1750 and 1680 cm^{-1} (C=O).

^{1}H-N.M.R. (CDCl$_3$): δ = 2.33 (s, 3H, CH_3); 5.10 (s, 2H, CH_2); 7.10–8.30 ppm (m, 4H_{arom}).

M.S.: m/e = 223 (M$^+$).

3-Phenylsulfinylmethyl-3,4-dihydro-1,3,2-benzoxazine-2,4-dione (12a):

To a solution of **11a** (550 mg, 1.9 mmol) in dichloromethane (10 ml) is added m-chloroperbenzoic acid (410 mg, 2.0 mmol) dissolved in dichloromethane (10 ml) at 0 °C and the mixture is stirred for 5 h at room temperature. The organic phase is then washed with 20% aqueous sodium bisulfite (2 × 5 ml), 10% aqueous sodium hydrogen carbonate (3 × 10 ml), dried with magnesium sulfate and concentrated to give **12a**; yield: 0.57 g (~ 100%); m.p. 185–186 °C (colorless needles from hexane/chloroform).

$C_{15}H_{11}NO_4S$	calc.	C 59.80	H 3.68	N 4.65	S 10.62
(301.3)	found	59.55	3.50	4.59	10.68

I.R. (Nujol): ν = 1750 and 1690 cm^{-1} (C=O).

^{1}H-N.M.R. (CDCl$_3$): δ = 4.97 (d, 1H, J = 18 Hz, H_a); 5.40 (d, 1H, J = 18 Hz, H_b); 7.10–8.30 ppm (m, 9H_{arom}).

M.S.: m/e = 301 (M$^+$).

N-Bis(phenylthio)methyl-2-formylisobutyramide (14):

To a solution of **4c** (4.37 g, 16 mmol) in benzene (20 ml) is added 4-isobuten-1-ylmorpholine (**13**; 2.22 g, 16 mmol) in benzene (20 ml) at 0 °C. The mixture is refluxed for 10 h and the residue obtained after removal of the solvent is chromatographed on silica gel using benzene/hexane as eluent; yield: 1.65 g (30%); m.p. 91–92 °C (colorless needles from benzene/hexane).

$C_{18}H_{19}NO_2S_2$	calc.	C 62.60	H 5.55	N 4.06	S 18.53
(345.5)	found	62.36	5.45	4.10	18.43

I.R. (Nujol): ν = 3270 (NH); 1730 (CH=O); 1630 cm^{-1} (C=O).

^{1}H-N.M.R. (DMSO-d_6): δ = 1.03 (s, 6H, 2CH_3); 6.60 (s, 1H, CH); 6.73 (s, 1H, NH); 7.2–7.8 (m, 10H_{arom}); 9.43 ppm (s, 1H, CHO).

M.S.: m/e = 236 (M$^+$ − C_6H_5S).

3,5-Diphenyl-2-phenylthioacetylimino-1,3,4-thiadiazoline (16):

To a solution of N-phenylbenzhydrazidoyl chloride (2.31 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in benzene (20 ml) is added **6a** (2.09 g, 10 mmol) in benzene (10 ml) and the mixture is refluxed for 1 h. The reaction mixture is washed with water (3 × 10 ml), dried with sodium sulfate and the solvent evaporated. The residue is chromatographed on silica gel using benzene/hexane (1 : 4) as eluent to give **16**; yield: 2.5 g (62%); m.p. 110–111 °C (colorless needles from benzene/hexane).

$C_{22}H_{17}N_3OS_2$	calc.	C 65.48	H 4.25	N 10.41
(403.5)	found	65.52	4.31	10.46

I.R. (Nujol): ν = 1620 cm^{-1} (C=O).

^{1}H-N.M.R. (CDCl$_3$): δ = 3.93 (s, 2H, CH_2); 7.00–8.10 ppm (m, 15H_{arom}).

M.S.: m/e = 403 (M$^+$).

5-Methylthiomethyl-1-phenyl-1,2,4-triazoline-3-thione (18):

To a solution of **6b** (2.94 g, 20 mmol) in benzene (10 ml) is added dropwise phenylhydrazine (**17**; 2.16 g, 20 mmol) in benzene (10 ml) at room temperature. The reaction mixture is refluxed for 5 h. Upon standing, the product **18** crystallizes out; yield: 1.5 g (32%); m.p. 191–192 °C (colorless plates from chloroform).

$C_{10}H_{11}N_3S_2$	calc.	C 50.61	H 4.67	N 17.70	S 27.02
(237.3)	found	50.34	4.53	17.63	27.16

I.R. (Nujol): $\nu = 2400-2800$ (NH or SH); 1590 cm^{-1} (conjugated C=N).

^{1}H-N.M.R. (DMSO-d_6): $\delta = 2.17$ (s, 3H, CH_3); 3.73 (s, 2H, CH_2); 7.1–8.2 (m, 5H_{arom}); 13.73 ppm (s, 1H, NH).

M.S.: $m/e = 237$ (M^+).

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