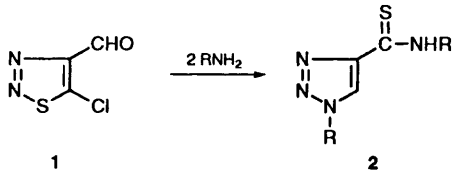
Thermal Rearrangement of 4-Iminomethyl-1,2,3-thiadiazoles

Gerrit L'abbé,* Mikaëla Verbeke, Wim Dehaen and Suzanne Toppet
Department of Chemistry, University of Leuven, Celestijnenlaan 200F, 3001 Leuven (Heverlee), Belgium

Imines derived from 1,2,3-thiadiazole-4-carbaldehyde **4** rearrange thermally into 1,2,3-triazole-4-thiocarbaldehydes **6** which were trapped with anthracene or 2,3-dimethylbutadiene. In two cases, 1,2,3-thiadiazole-4-thiocarbaldehyde **9** was intercepted as the Diels–Alder adduct **11**. 5-Phenyl-1,2,3-thiadiazole-4-carbaldehyde **14** reacts with amines to give 4-benzoyl-1,2,3-triazoles **17** *via* the intermediate 4-thiobenzoyltriazoles **16**, whose existence has been demonstrated by NMR. The reactions of 5-*tert*-butylthio-1,2,3-thiadiazole-4-carbaldehyde **18** with amines yield either 1,2,3-triazole-4-dithio esters **20** or 1,2,3-triazole-4-thioamides **21**. In solution, the dithioesters **20** equilibrate with the imines **19** when the R-substituent is aryl. From the reaction conditions we conclude that the facility of rearrangement of the title compounds depends on the nucleophilicity of the imine nitrogen and on the 5-substituent in the order Bu^{t}S > Ph > H.

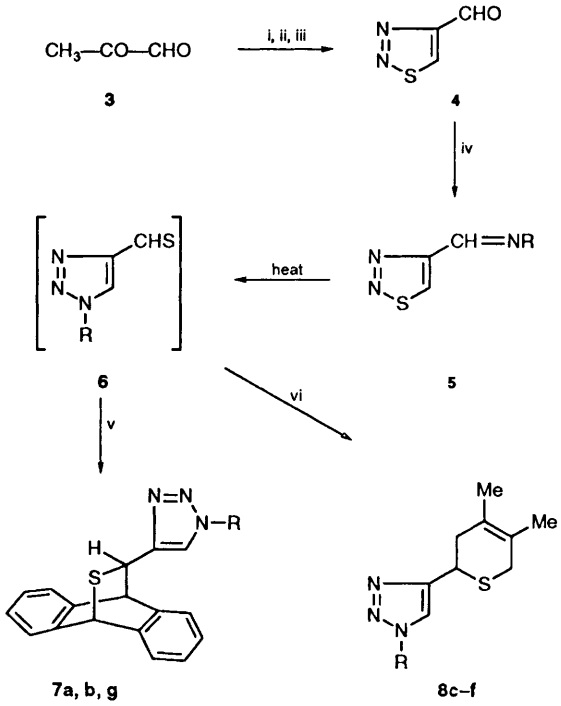
Recently we reported that 5-chloro-1,2,3-thiadiazole-4-carbaldehyde **1** reacts with amines to give 1,2,3-triazole-4-thiocarboxamides **2** *via* α-diazo thioketone intermediates.[1] This reaction is similar to the Cornforth rearrangement of 4-carbonyl substituted oxazoles,[2] and to the ring-degenerate rearrangement of 4-iminomethyl substituted 1*H*-1,2,3-triazoles[3] which all involve the participation of two side-chain atoms during the rearrangement. In contrast, the classical Dimroth rearrangement of 5-amino substituted thiadiazoles and triazoles involve the exchange of the exocyclic N-atom with the adjacent endocyclic S- or N-atom.[4] In continuation of our research in this field, we have now investigated the generality of the title thiadiazole–triazole rearrangement by introducing different substituents at the 5-position; *i.e.* H, Ph and SR. The results are discussed below.



1 **2**

The parent aldehyde **4** was prepared from methylglyoxal **3** by the method of Kobori *et al.*[5] and treated with a series of amines in ethanol at room temperature. The products **5a–h** all had the *E*-configuration about the C=N bond as evidenced by the one-bond $^{13}CH{=}N$ coupling constants of 164–167 Hz which would be larger for the *Z*-isomers (*ca.* 177 Hz).[6] This *cis*-relationship between the thiadiazole ring and the imine-nitrogen lone pair is a necessary condition for observing any rearrangement to a triazole.[7] This was found to be the case for the imines **5a–f** which rearranged readily in tetrahydrofuran or toluene at 65 °C, and for **5g** which required heating in toluene at 110 °C. In contrast, the imine **5h** remained unchanged in dimethyl sulfoxide at 120 °C although it also possessed the *E*-configuration (^1J 164). The thermolyses were carried out in the presence of anthracene or 2,3-dimethylbutadiene as traps[8] for the thioaldehydes **6**, resulting in the formation of the Diels–Alder adducts **7a**, **b**, **g** and **8c–f** (Scheme 1).

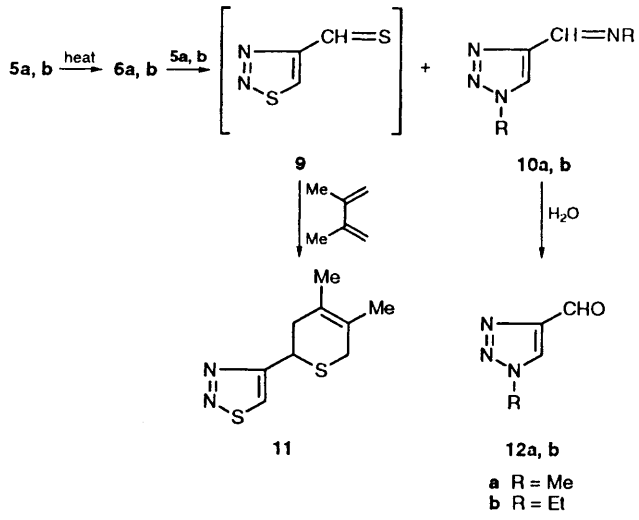
The imines **5a**, **b** furnished the expected products **7a**, **b** with anthracene, but with 2,3-dimethylbutadiene the same thiadiazole derivative **11** was isolated in both cases together with the triazoles **12a**, **b**. This is rationalized in Scheme 2 where the intermediate thioaldehydes **6a**, **b** undergo a (2 + 2)-cycloaddition–cycloreversion process with unchanged **5a**, **b** to give the thioaldehyde **9** and the iminotriazoles **10a**, **b**. Compound **9** is trapped with the diene under the reaction conditions to give the thiadiazole derivative **11**, whereas the imines **10a**, **b** are hydrolysed during the chromatographic work-up procedure.



	R		R
a	Me	e	Ph
b	Et	f	4-MeOC$_6$H$_4$
c	Pr^i	g	4-ClC$_6$H$_4$
d	Bu^t	h	3,4-Cl$_2$C$_6$H$_3$

Scheme 1 *Reagents:* i, EtO_2CNHNH_2; ii, $SOCl_2$; iii, H_2SO_4/CH_2O; iv, RNH_2; v, anthracene; vi, $CH_2{=}C(Me){-}C(Me){=}CH_2$

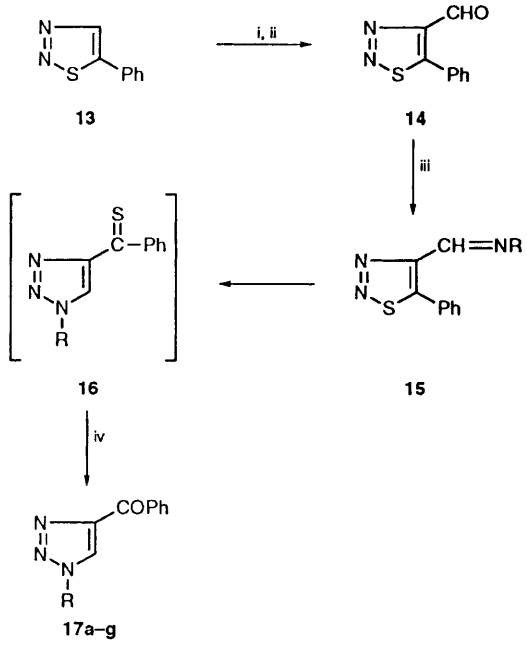
Differentiation between the triazoles and the thiadiazoles is easily made on the basis of their ^{13}C NMR spectra. Indeed, the triazoles **7**, **8** and **12** exhibit characteristic C-4 and C-5 resonances at δ 148–150 and δ 118–124 respectively, whereas those of the thiadiazole **11** occur at lower field (C-4 at δ 164.7, C-5 at δ 132.1), and in the same region as those of the aldehyde **4** (C-4 at δ 161.9, C-5 at δ 140.7) and the imines **5** (C-4 at δ 161–



Scheme 2

162, C-5 at δ 134–137). The incremental substituent effects for triazoles and thiadiazoles have been discussed recently.[9]

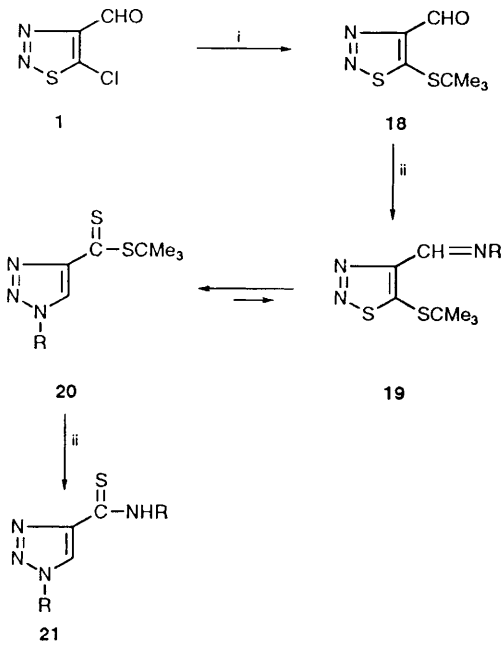
We next investigated the influence of a 5-phenyl substituent on the ease of rearrangement of thiadiazoles. 5-Phenyl-1,2,3-thiadiazole-4-carbaldehyde **14** was readily obtained from the known 5-phenylthiadiazole **13** by treatment of its 4-lithio derivative[10] with *N*-formylmorpholine in tetrahydrofuran at −70 °C (Scheme 3). This method has already been utilized successfully by Olah[11] and Dondoni[12] to prepare different aldehydes.



	R		R
a	Me	e	Ph
b	Et	f	4-$MeOC_6H_4$
c	Pr^i	g	4-ClC_6H_4
d	Bu^t	h	3, 4-$Cl_2C_6H_3$

Scheme 3 *Reagents*: i, MeLi; ii, *N*-formylmorpholine; iii, RNH_2; iv, RNH_2/H_2O

Methylamine and ethylamine reacted with compound **14** at room temperature to give products which were characterized as the 4-benzoyltriazoles **17a**, **b** on the basis of their spectral data. Under similar conditions, isopropylamine, *tert*-butylamine, aniline and *p*-methoxyaniline provided a mixture



	R		R
a	Me	e	Ph
b	Et	f	4-$MeOC_6H_4$
c	Pr^i	g	4-ClC_6H_4
d	Bu^t	h	3, 4-$Cl_2C_6H_3$

Scheme 4 *Reagents:* i, Me_3C–SNa; ii, RNH_2

of the imines **15c–f** and ketones **17c–f**, and complete conversion into **17c–f** was achieved in refluxing ethanol. The imine **15g**, derived from *p*-chloroaniline, did not rearrange at room temperature but gave the ketone **17g** at 120 °C in dimethyl sulfoxide solution. In contrast, 3,4-dichloroaniline yielded the imine **15h** which proved to be stable at 100–120 °C. From these results we conclude that the propensity of the imines **15** to rearrange depends on the nucleophilicity of the imine nitrogen.

That the rearranged products have structure **17** instead of **16** is evident from the C=O stretching absorptions at ~1650 cm^{-1} in their IR spectra and the typical ketone C signals at δ ~185 in their ^{13}C NMR spectra; aromatic thioketones would resonate at δ 210–240.[13] In order to elucidate the mechanism of the conversion **16**→**17**, we have followed the reaction of isopropylamine with a slight excess of the aldehyde **14** in deuteriated chloroform by ^1H and ^{13}C NMR spectroscopy. The imine **15c** was formed first at room temperature, and the thioketone **16c** was obtained after 2 h at 60 °C (C=S at δ_C 222). The blue colour of **16c** remained unchanged when the solution was stored at room temperature, even in the presence of D_2O, but disappeared immediately upon addition of isopropylamine. The NMR spectrum then showed resonances of the ketone **17c**. This experiment indicates that hydrolysis of the thioketones **16** is catalysed by the amine present in excess. Full details of the NMR data are given in the Experimental section, but it is appropriate to note here that the phenyl C-*ipso* resonates at much lower field in the thioketone **16c** (δ 145.5) than in the ketone **17c** (δ 136.7) as expected.[14]

Since the chloro aldehyde **1** is readily substituted by alkanethiolates, we have also prepared the *tert*-butyl derivative **18** and studied its reactions with amines. Methylamine, ethylamine and isopropylamine yielded the triazole-4-thiocarboxamides **21a–c**, apparently as a result of rearrangement of the imines **19a–c**, followed by nucleophilic substitution of the dithioester function of **20a–c** by amine (Scheme 4). The amount of amine used (1 or more equivalents) had no influence on the

Table 1 Equilibrium concentrations (%) of the imines **19d–h** in $CDCl_3$ at room temperature.

19d	19e	19f	19g	19h
0	7	5	18	50

outcome of the reactions, indicating that aminolysis of the dithioesters **20** is a fast process. The products **21a, b** have already been obtained from compound **1** and amines,[1] and were further characterized by the triazole resonances[9] at δ 148 (C-4) and δ 125–129 (C-5), and the thioamide resonances[15] at δ 184 in the ^{13}C NMR spectra.

tert-Butylamine and aromatic amines also reacted with the aldehyde **18** at room temperature, but furnished rose-red coloured products which were identified as the dithioesters **20d–h**. These compounds exhibited C=S carbon resonances at δ 214–215 in their NMR spectra.[16] Furthermore, when freshly prepared chloroform solutions of the aromatic derivatives **20e–h** were analysed, the NMR spectra indicated the presence of minor amounts of the imines **19e–h**, whose concentrations increased with time until equilibria positions were reached. The results are summarized in Table 1 and point out that the shift towards the imine is favoured by electron-withdrawing R substituents. This is most pronounced for the dichlorophenyl derivative **20h** which equilibrates with 50% imine **19h** after 1 day in deuteriated chloroform treated with alumina. The same equilibrium position was reached in untreated chloroform, but only after several days. In other solvents, such as deuteriated benzene, tetrahydrofuran and acetonitrile, the equilibrium concentration of **19h** is much lower, 30, 20 and 27% respectively; hence, no correlation with the solvent polarity was found.

Experimental

M.p.s were determined using a Reichert Thermovar apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1720 FT spectrometer, NMR spectra on a Bruker WM-250 or AMX-400 spectrometer, and mass spectra (EI) on a Hewlett Packard 5989A or Kratos MS50 TC (for high resolution) instrument, both operating at 70 eV. *J* Values are recorded in Hz.

1,2,3-Thiadiazole-4-carbaldehyde **4** was prepared from methylglyoxal in 3 steps by the method of Kobori *et al.*;[5] it had m.p. 87 °C; $\delta_H(CDCl_3)$ 9.37 (1 H, s, 5-H) and 10.6 (1 H, s, CHO); $\delta_C(CDCl_3)$ 140.7 (C-5, ^1J 195, ^3J 4.5), 161.9 (C-4, ^2J 25.5 and 6.5) and 183.2 (CHO, ^1J 187, ^3J 1).

4-[9,10-*Dihydro*-10,9-(*epithiomethano*)*anthracen*-12-*yl*]-1-*methyl*-1,2,3-*triazole* **7a**.—To a solution of the aldehyde **4** (0.5 g, 4.4 mmol) in ethanol (20 cm^3) was added aq. methylamine (40%; 1.7 g, 22 mmol) and the mixture was stirred overnight at room temperature. Evaporation of the solvent left the imine **5a** as an impure oil (0.52 g, 93%); ν_{max}(neat)/cm^{-1} 1667s (C=N); $\delta_H(CDCl_3)$ 3.62 (3 H, d, Me, *J* 1.5), 8.91 (1 H, q, CH=N, *J* 1.5) and 9.04 (1 H, s, 5-H); $\delta_C(CDCl_3)$ 48.4 (Me, ^1J 136, ^3J 12.7), 134.9 (C-5, ^1J 194, ^3J 4), 153.7 (C=N, ^1J 165.6, ^3J 10 and 1) and 161.3 (C-4).

A solution of the imine **5a** (0.5 g, 3.9 mmol) and a threefold excess of anthracene (2.1 g) in dry tetrahydrofuran (60 cm^3) was heated at 65 °C for 2 days and then poured into ice–water (200 cm^3). The resulting precipitate was collected and chromatographed on silica gel with diethyl ether as the eluent to give the triazole **7a** (0.23 g, 21%), m.p. 177 °C (from Et_2O) (Found: C, 70.6; H, 5.1. $C_{18}H_{15}N_3S$ requires C, 70.79; H, 4.95%); $\delta_H(CDCl_3)$ 3.85 (3 H, s, Me), 4.83 and 4.92 (2 H, 2 d, SCH–CH), 5.18 (1 H, s, CH), 6.49 (1 H, s, triazole 5-H) and 6.9–7.5 (8 H, 4 d + t + m, Ar); $\delta_C(CDCl_3)$ 36.5 (Me), 45.6, 45.8 and 51.4 (CH–S–CH–CH), 121.6–126.8, 138.3, 141.4, 142.3 and 143.3 (Ar), 123.9 (triazole C-5) and 149.4 (triazole C-4); *m/z* 305 ($M^{\bullet+}$, 0.07%), 178 ($C_{14}H_{10}^{\bullet+}$, 100), 176 (12), 58 (12) and 42 (23).

1-*Ethyl*-4-[9,10-*dihydro*-10,9-(*epithiomethano*)*anthracen*-12-*yl*]-1,2,3-*triazole* **7b**.—To a solution of the aldehyde **4** (1 g, 8.8 mmol) in ethanol (40 cm^3) was added aq. ethylamine (70%; 2.8 g, 44 mmol) and the mixture was stirred overnight at room temperature. The solvent was replaced by chloroform, and the mixture dried ($MgSO_4$) and evaporated to give the imine **5b** as an impure oil (1.09 g, 87%); ν_{max}(neat)/cm^{-1} 1651s (C=N); $\delta_H(CDCl_3)$ 1.28 (3 H, t, Me), 3.7 (2 H, q, CH_2), 8.87 (1 H, s, CH=N) and 9.0 (1 H, s, 5-H); $\delta_C(CDCl_3)$ 15.7 and 55.8 (Et), 135.0 (C-5, ^1J 193, ^3J 4), 151.6 (C=N, ^1J 165) and 161.4 (C-4, ^2J 11 and 6).

A solution of the imine **5b** (1 g, 7.1 mmol) and a threefold excess of anthracene (3.8 g) in dry toluene (100 cm^3) was heated at 65 °C for 24 h. After cooling, the solution was filtered and the filtrate was evaporated. The residue was chromatographed on silica gel with diethyl ether–hexane (1 : 1) as the eluent to give triazole **7b** (0.39 g, 17%), m.p. 153 °C (from Et_2O) (Found: C, 71.5; H, 5.4. $C_{19}H_{17}N_3S$ requires C, 71.44; H, 5.36%); $\delta_H(CDCl_3)$ 1.33 (3 H, t, Me), 4.17 (2 H, m, CH_2), 4.86 and 4.9 (2 H, 2 d, SCH–CH), 5.19 (1 H, s, CH), 6.48 (1 H, s, triazole 5-H) and 6.9–7.5 (8 H, 4 d + t + m, Ar); $\delta_C(CDCl_3)$ 15.4 and 45.1 (Et), 45.7, 45.8 and 51.6 (CH–S–CH–CH), 121.7–126.8, 138.4, 141.3, 142.4 and 143.2 (Ar), 122.3 (triazole C-5, ^1J 195, ^3J 4) and 149.3 (triazole C-4); *m/z* 319 ($M^{\bullet+}$, 0.2%), 178 ($C_{14}H_{10}^{\bullet+}$, 100) and 176 (16).

1-(4-*Chlorophenyl*)-4-[9,10-*dihydro*-10,9-(*epithiomethano*)-*anthracen*-12-*yl*]-1,2,3-*triazole* **7g**.—To a solution of the aldehyde **4** (1 g, 8.8 mmol) in ethanol (20 cm^3) was added *p*-chloroaniline (1.12 g, 8.8 mmol) and the whole mixture was stirred at room temperature for 12 h. The precipitated imine **5g** was filtered off (1.03 g, 52%), m.p. 121 °C (from Et_2O) (Found: C, 48.2; H, 2.7. $C_9H_6ClN_3S$ requires C, 48.33; H, 2.70%); ν_{max}(KBr)/cm^{-1} 1627s (C=N); $\delta_H(CDCl_3)$ 7.28 and 7.43 (4 H, 2 d, C_6H_4), 9.12 (1 H, s, CH=N) and 9.28 (1 H, s, 5-H); $\delta_C(CDCl_3)$ 122.3, 129.5, 132.9 and 148.9 (Ar), 136.2 (C-5, ^1J 194, ^3J 4), 150.9 (C=N, ^1J 166) and 161.6 (C-4, ^2J 11 and 6.5).

A solution of **5g** (0.5 g, 2.2 mmol) and a fivefold excess of anthracene (2 g) in dry toluene (100 cm^3) was refluxed for 2 days. After cooling, the solution was filtered and the filtrate was evaporated. The residue was chromatographed on silica gel with diethyl ether–light petroleum (1 : 3) as the eluent to give triazole **7g** (0.14 g, 18%), m.p. 161 °C (from Et_2O); $\delta_H(CDCl_3)$ 4.89 and 4.96 (2 H, 2 d, SCH–CH), 5.24 (1 H, s, CH), 6.88 (1 H, s, triazole 5-H) and 6.95–7.5 (12 H, 2 d + td + 4 m, Ar); $\delta_C(CDCl_3)$ 45.5, 45.9 and 51.4 (CH–S–CH–CH), 121.2 (triazole C-5, ^1J 197, ^3J 5), 121.4, 129.8, 134.3 and 135.3 (Ar), 121.9–126.9, 138.2, 141.1, 142.3 and 143.2 (Ar) and 150.3 (triazole C-4); *m/z* 369 ($M^{\bullet+}$, 0%), 178 ($C_{14}H_{10}^{\bullet+}$, 100), 176 (16) and 111 ($C_6H_4Cl^+$, 11).

4-(3,6-*Dihydro*-4,5-*dimethyl*-2H-*thiopyran*-2-*yl*)-1-*isopropyl*-1,2,3-*triazole* **8c**.—To a solution of the aldehyde **4** (0.5 g, 4.4 mmol) in ethanol (20 cm^3) was added isopropylamine (0.26 g, 4.4 mmol) and the mixture was stirred overnight at room temperature. The solvent was replaced by chloroform, dried ($MgSO_4$) and evaporated to give the imine **5c** as an oil (0.55 g, 80%); ν_{max}(neat)/cm^{-1} 1650s (C=N); $\delta_H(CDCl_3)$ 1.3 (6 H, d, 2 Me), 3.7 (1 H, sept, CH), 8.93 (1 H, s, CH=N) and 9.08 (1 H, s, 5-H); $\delta_C(CDCl_3)$ 23.8 and 61.8 (Pr^i), 134.9 (C-5, ^1J 193.7, ^3J 4), 149.7 (C=N, ^1J 164.5, ^3J 9) and 161.6 (C-4).

A solution of imine **5c** (0.5 g, 3.2 mmol) and a tenfold excess of 2,3-dimethylbutadiene (2.6 g) in dry toluene (30 cm^3) was heated at 65 °C for 2 days. After removal of the solvent, the

residue was chromatographed on silica gel with diethyl ether as the eluent to give triazole **8c** as an oil (0.29 g, 37.5%) (Found: $M^{\bullet+}$, 237.1296. $C_{12}H_{19}N_3S$ requires $M^{\bullet+}$, 237.1300); $\delta_H(CDCl_3)$ 1.58 (6 H, d, $CHMe_2$), 1.72 and 1.75 (6 H, 2 br s, MeC=CMe), 2.62 (2 H, br d, CH_2), 2.91 and 3.38 (2 H, 2 br d, SCH_2), 4.22 (1 H, t, SCH), 4.8 (1 H, sept. $CHMe_2$) and 7.45 (1 H, s, triazole 5-H); $\delta_C(CDCl_3)$ 19.3 and 20.15 (Me), 22.9 and 52.9 (Pr^i), 31.8 (SCH_2, ^1J 136), 34.7 (SCH, ^1J 144), 38.3 (CH_2, ^1J 127.8), 118.1 (triazole C-5, ^1J 191), 123.1 and 126.8 (C=C) and 148.9 (triazole C-4).

1-tert-*Butyl*-4-(3,6-*dihydro*-4,5-*dimethyl*-2H-*thiopyran*-2-*yl*)-1,2,3-*triazole* **8d**.—To a solution of the aldehyde **4** (1 g, 8.8 mmol) in ethanol (40 cm^3) was added *tert*-butylamine (3.2 g, 44 mmol) and the mixture was stirred at room temperature for 5 h. The solvent was replaced by chloroform, dried ($MgSO_4$) and evaporated to give the imine **5d** as an oil (1.34 g, 90%); ν_{max}(neat)/cm^{-1} 1645s (C=N); $\delta_H(CDCl_3)$ 1.34 (9 H, s, Bu^t), 8.9 (1 H, s, CH=N) and 9.1 (1 H, s, 5-H); $\delta_C(CDCl_3)$ 29.4 and 58.5 (Bu^t), 134.5 (C-5), 147.1 (C=N) and 162.6 (C-4).

A solution of imine **5d** (1 g, 5.9 mmol) and a tenfold excess of 2,3-dimethylbutadiene (4.85 g) in dry toluene (60 cm^3) was heated at 65 °C for 2 days. After removal of the solvent, the residue was chromatographed on silica gel with diethyl ether–hexane (4:1) as the eluent to give triazole **8d** (1.04 g, 70%), m.p. 68 °C (from hexane) (Found: C, 62.2; H, 8.4. $C_{13}H_{21}N_3S$ requires C, 62.11; H, 8.42%); $\delta_H(CDCl_3)$ 1.69 (9 H, s, Bu^t), 1.73 and 1.76 (6 H, 2 br s, MeC=CMe), 2.63 (2 H, br d, CH_2), 2.91 and 3.4 (2 H, 2 br d, SCH_2), 4.22 (1 H, t, SCH) and 7.51 (1 H, s, triazole 5-H); $\delta_C(CDCl_3)$ 19.3 and 20.1 (Me), 29.9 and 59.2 (Bu^t), 31.9 (SCH_2), 34.7 (SCH), 38.3 (CH_2), 117.7 (triazole C-5), 123.0 and 126.8 (C=C) and 148.2 (triazole C-4).

4-(3,6-*Dihydro*-4,5-*dimethyl*-2H-*thiopyran*-2-*yl*)-1-*phenyl*-1,2,3-*triazole* **8e**.—To a solution of the aldehyde **4** (0.5 g, 4.4 mmol) in ethanol (20 cm^3) was added aniline (0.41 g, 4.4 mmol) and the mixture was stirred at room temperature for 24 h. After evaporation of the solvent, the residue was crystallized from diethyl ether–hexane to give the imine **5e** (0.59 g, 70%), m.p. 79 °C (from Et_2O) (Found: C, 57.1; H, 3.8. $C_9H_7N_3S$ requires C, 57.12; H, 3.73%); ν_{max}(KBr)/cm^{-1} 1625s (C=N); $\delta_H(CDCl_3)$ 7.3–7.4 (5 H, 2 m, Ph), 9.12 (1 H, s, CH=N) and 9.22 (1 H, s, 5-H); $\delta_C(CDCl_3)$ 121.0, 127.2, 129.4 and 150.5 (Ph), 135.9 (C-5, ^1J 195, ^3J 4.5), 150.6 (C=N, ^1J 167) and 161.8 (C-4, ^2J 11 and 6).

A solution of the imine **5e** (1 g, 5.3 mmol) and a tenfold excess of 2,3-dimethylbutadiene (4.3 g) in dry toluene (50 cm^3) was heated at 65 °C for 2 days. After removal of the solvent, the residue was chromatographed on silica gel with diethyl ether–hexane (5:1) as the eluent to give the triazole **8e** (1.02 g, 70%), m.p. 105 °C (from Et_2O) (Found: C, 66.4; H, 6.3. $C_{15}H_{17}N_3S$ requires C, 66.39; H, 6.31%); $\delta_H(CDCl_3)$ 1.75 (6 H, br s, MeC=CMe), 2.69 (2 H, br d, CH_2), 2.95 and 3.34 (2 H, 2 br d, SCH_2), 4.29 (1 H, t, SCH), 7.4–7.8 (5 H, m + d, Ph) and 7.89 (1 H, s, triazole 5-H); $\delta_C(CDCl_3)$ 19.4 and 20.2 (Me), 31.5 (SCH_2), 34.4 (SCH), 38.0 (CH_2), 119.1 (triazole C-5), 120.5, 128.6, 129.6 and 137.1 (Ph), 123.2 and 126.6 (C=C) and 149.8 (triazole C-4).

4-(3,6-*Dihydro*-4,5-*dimethyl*-2H-*thiopyran*-2-*yl*)-1-(4-*methoxyphenyl*)-1,2,3-*triazole* **8f**.—To a solution of the aldehyde **4** (1 g, 8.8 mmol) in ethanol (20 cm^3) was added *p*-methoxyaniline (1.08 g, 8.8 mmol) and the mixture was allowed to react at room temperature for 12 h. Crystalline needles of the imine **5f** were collected (1.11 g, 58%), m.p. 93 °C (from Et_2O) (Found: C, 54.7; H, 4.3. $C_{10}H_9N_3OS$ requires C, 54.78; H, 4.14%); ν_{max}(KBr)/cm^{-1} 1628s (C=N); $\delta_H(CDCl_3)$ 3.9 (3 H, s, Me), 6.98 and 7.35 (4 H, 2 d, C_6H_4), 9.15 (1 H, s, CH=N) and 9.20 (1 H, s, 5-H); $\delta_C(CDCl_3)$ 55.5 (OMe), 114.6, 122.5, 143.3 and 159.3 (Ar), 135.2 (C-5, ^1J 194.2, ^3J 4.5), 148.2 (C=N, ^1J 165.9) and 162.2 (C-4).

A solution of the imine **5f** (0.5 g, 2.3 mmol) and a tenfold excess of 2,3-dimethylbutadiene (1.9g) in dry toluene (30 cm^3) was heated at 65 °C for 2 days. After removal of the solvent, the residue was chromatographed on silica gel with diethyl ether as the eluent to give the triazole **8f** (0.47 g, 68%), m.p. 109 °C (from Et_2O) (Found: C, 63.9; H, 6.2. $C_{16}H_{19}N_3SO$ requires C, 63.76; H, 6.35%); $\delta_H(CDCl_3)$ 1.73 (6 H, br s, MeC=CMe), 2.66 (2 H, br d, CH_2), 2.95 and 3.35 (2 H, 2 br d, SCH_2), 3.82 (3 H, s, OMe), 4.28 (1 H, t, SCH), 7.0 and 7.6 (4 H, 2 d, C_6H_4) and 7.8 (1 H, s, triazole 5-H); $\delta_C(CDCl_3)$ 19.4 and 20.3 (Me), 31.5 (SCH_2), 34.4 (SCH), 38.1 (CH_2), 55.6 (OMe), 114.7, 122.1, 130.6 and 159.8 (Ar), 119.3 (triazole C-5), 123.1 and 126.7 (C=C) and 149.5 (triazole C-4).

4-(3,4-*Dichlorophenyl*)*iminomethyl*-1,2,3-*thiadiazole* **5h**.—To a solution of the aldehyde **4** (1 g, 8.8 mmol) in ethanol (20 cm^3) was added 3,4-dichloroaniline (1.43 g, 8.8 mmol) and the mixture was allowed to react at room temperature for 12 h. The precipitated imine **5h** was then filtered off (1.32 g, 58%), m.p. 127 °C (from EtOH) (Found: C, 42.0; H, 2.0. $C_9H_5Cl_2N_3S$ requires C, 41.88; H, 1.95%); ν_{max}(KBr)/cm^{-1} 1623s (C=N); $\delta_H(CDCl_3)$ 7.15, 7.41 and 7.50 (3 H, dd + 2 d, C_6H_3), 9.1 (1 H, s, CH=N) and 9.25 (1 H, s, H-5); $\delta_C(CDCl_3)$ 120.5, 123.1, 131.1 (×2), 133.3 and 149.9 (Ar), 136.8 (C-5, ^1J 196), 151.9 (C=N, ^1J 164) and 161.3 (C-5).

Note: This imine remained unchanged when heated in dimethyl sulfoxide at 120 °C for 24 h.

4-(3,6-*Dihydro*-4,5-*dimethyl*-2H-*thiopyran*-2-*yl*)-1,2,3-*thiadiazole* **11**.— A solution of the imine **5a** (0.5 g, 3.9 mmol) and a tenfold excess of 2,3-dimethylbutadiene (3.3 g, 39 mmol) in dry tetrahydrofuran (30 cm^3) was heated at 65 °C for 2 days. The reaction mixture was poured into ice–water (100 cm^3) and extracted with chloroform. The combined extracts were washed with water, dried ($MgSO_4$) and evaporated. The resulting oil was chromatographed on silica gel with diethyl ether and ethyl acetate as the eluents to give triazole[3] **12a** (0.07 g, 16%) and thiadiazole **11** (0.32 g, 39%), m.p. 63 °C (Et_2O) (Found: C, 50.7; H, 5.7. $C_9H_{12}N_2S_2$ requires C, 50.91; H, 5.70%); $\delta_H(CDCl_3)$ 1.75 and 1.78 (6 H, 2 br s, MeC=CMe), 2.75 (2 H, br s, CH_2), 2.98 and 3.38 (2 H, 2 br d, SCH_2), 4.7 (1 H, t, SCH) and 8.39 (1 H, s, thiadiazole 5-H); $\delta_C(CDCl_3)$ 19.4 and 20.2 (Me), 31.2 (SCH_2, ^1J 138) 36.3 (SCH, ^1J 142), 38.3 (CH_2, ^1J 128), 123.4 and 126.4 (C=C), 132.1 (thiadiazole C-5) and 164.7 (thiadiazole C-4).

Note: When the imine **5b** was heated with 2,3-dimethylbutadiene under similar conditions in toluene at 65 °C, the known[3] triazole **12b** (20%) and thiadiazole **11** (36%) were obtained.

5-*Phenyl*-1,2,3-*thiadiazole*-4-*carbaldehyde* **14**.—To a stirred solution of 5-phenyl-1,2,3-thiadiazole[17] (5.0 g, 30.9 mmol) in tetrahydrofuran (75 cm^3), cooled at −70 °C under nitrogen was added slowly a 1.6 mol dm^{-3} solution of methyllithium in diethyl ether (19.4 cm^3, 31 mmol). This was followed after 1 h by *N*-formylmorpholine (3.55 g, 30.9 mmol) dissolved in dry tetrahydrofuran (10 cm^3), and the solution was stirred at −70 °C for 1 h; it was then kept at room temperature for a further 12 h. The reaction mixture was poured into aq. hydrochloric acid (4 mol dm^{-3}; 50 cm^3) and the aqueous layer extracted with diethyl ether. The combined organic portions were washed with water, dried ($MgSO_4$) and evaporated to give the crude product **14**. This was purified by column chromatography on silica gel with ethyl acetate–hexane (1:1) as the eluent, and then crystallized from diethyl ether (4.1 g, 70%), m.p. 54 °C (Found: C, 56.8; H, 3.2. $C_9H_6N_2OS$ requires C, 56.83; H, 3.18%); ν_{max}(KBr)/cm^{-1} 1705s and 1680s (C=O); $\delta_H(CDCl_3)$ 7.45–7.6 (5 H, 2 m, Ph) and 10.5 (1 H, s, CHO); $\delta_C(CDCl_3)$ 125.2, 129.1, 130.0 and 131.5 (Ph), 154.2 (C-4, ^2J 26), 162.9 (C-5), 183.2 (CHO, ^1J 187); *m/z* 190 ($M^{\bullet+}$, 5%), 162 (23) and 134 ($M^{\bullet+}$ − N_2 − CO, 100).

4-*Benzoyl*-1-*methyl*-1,2,3-*triazole* **17a**.—To a solution of the aldehyde **14** (0.5 g, 2.6 mmol) in ethanol (20 cm^3) was added aq. methylamine (40%; 1.02 g, 13.2 mmol) and the mixture was stirred at room temperature for 24 h. After removal of the solvent, the residue was chromatographed on silica gel with dichloromethane–ethyl acetate (9:1) as the eluent to give triazole **17a** (0.2 g, 42%), m.p. 111.5 °C (Et_2O) (Found: C, 64.1; H, 4.75. $C_{10}H_9N_3O$ requires C, 64.16; H, 4.85%); ν_{max}(KBr)/cm^{-1} 3138m and 1653s (C=O); δ_H($CDCl_3$) 4.2 (3 H, s, Me), 7.49, 7.59 and 8.38 (5 H, 2 t + d, Ph) and 8.24 (1 H, s, 5-H); δ_C($CDCl_3$) 36.9 (Me), 129.3 (C-5, ^1J 197, ^3J 3), 128.4, 130.5, 133.3 and 136.6 (Ph), 148.2 (C-4, ^2J 9) and 185.7 (CO); *m/z* 187 ($M^{\cdot+}$, 40%), 159 ($M^{\cdot+}$ − N_2 or CO, 25), 158 ($M^{\cdot+}$ − MeN, 41), 131 ($M^{\cdot+}$ − N_2 − CO, 33), 130 ($PhCOC{\equiv}CH^{\cdot+}$, 31), 118 (54), 116 (32), 105 ($PhCO^+$, 42), 90 (26), 89 (36), 82 ($M^{\cdot+}$ − PhCO, 21) and 77 (Ph^+, 100).

4-*Benzoyl*-1-*ethyl*-1,2,3-*triazole* **17b**.—To a solution of the aldehyde **14** (0.5 g, 2.6 mmol) in ethanol (20 cm^3) was added aq. ethylamine (70%; 0.85 g, 13.2 mmol) and the mixture was stirred at room temperature for 24 h. After removal of the solvent, the residue was chromatographed on silica gel with dichloromethane–ethyl acetate (9:1) as the eluent to give unchanged starting material **14** (0.25 g) and the triazole **17b** (0.23 g, 42%), m.p. 56 °C (from Et_2O) (Found: C, 65.6; H, 5.6. $C_{11}H_{11}N_3O$ requires C, 65.66; H, 5.51%); ν_{max}(KBr)/cm^{-1} 3137m and 1644s (C=O); δ_H($CDCl_3$) 1.65 (3 H, t, Me), 4.5 (2 H, q, CH_2), 7.5, 7.65 and 8.48 (5 H, 2 t + d, Ph) and 8.3 (1 H, s, H-5); δ_C($CDCl_3$) 15.4 and 45.6 (Et), 127.7 (C-5, ^1J 196, ^3J 2.5), 128.4, 130.6, 133.25 and 136.6 (Ph), 148.1 (C-4) and 185.8 (CO); *m/z* 201 ($M^{\cdot+}$, 25%), 173 ($M^{\cdot+}$ − N_2 or CO, 20), 172 ($M^{\cdot+}$ − Et, 23), 158 ($M^{\cdot+}$ − EtN, 23), 145 (20), 130 ($PhCOC{\equiv}CH^{\cdot+}$, 21), 116 (40), 105 ($PhCO^+$, 76), 104 (48), 96 ($M^{\cdot+}$ − PhCO, 13), 90 (29), 89 (31) and 77 (Ph^+, 100).

4-*Benzoyl*-1-*isopropyl*-1,2,3-*triazole* **17c**.—A solution of the aldehyde **14** (0.5 g, 2.6 mmol) and a fivefold excess of isopropylamine (0.78 g, 13.2 mmol) in ethanol (20 cm^3) was refluxed for 16 h. After removal of the solvent, the residue was chromatographed on silica gel with dichloromethane–ethyl acetate (20:1) as the eluent to give the triazole **17c** (0.34 g, 62%), m.p. 65 °C (from Et_3O) (Found: C, 67.1; H, 6.1. $C_{12}H_{13}N_3O$ requires C, 66.96; H, 6.09%); ν_{max}(KBr)/cm^{-1} 3159m, 1656s, (C=O); δ_H($CDCl_3$) 1.65 (6 H, d, 2 Me), 4.9 (1 H, sept, CH), 7.5, 7.6 and 8.45 (5 H, 2t + d, Ph) and 8.3 (1 H, s, 5-H); δ_C($CDCl_3$) 23.0 and 53.5 (Pr^i), 126.0 (C-5), 128.4, 130.6, 133.2 and 136.6 (Ph), 147.9 (C-4) and 185.9 (CO); *m/z* 215 ($M^{\cdot+}$, 100%), 187 ($M^{\cdot+}$ − N_2 or CO, 14), 186 (13), 145 (63), 144 (*m/z* 187 − C_3H_7, 27), 117 (19), 116 ($M^{\cdot+}$ − N_2 − CO − C_3H_7, 43) and 105 ($PhCO^+$, 86).

Note: When the reaction of isopropylamine with a slight excess of the aldehyde **14** in $CDCl_3$, treated with basic alumina, was followed by NMR spectroscopy, the imine **15c** was observed as major product after 2 h at room temperature. The mixture when heated at 60 °C for 2 h furnished a blue solution composed essentially of the imine **15c** and thioketone **16c** in a ratio of 1:3. This solution decolorized upon addition of ispropylamine and provided NMR signals characteristic of the triazole **17c**.

Imine **15c**: δ_H 1.31 (6 H, d, 2 Me), 3.6 (1 H, sept, CH), 7.51 (5 H, s, Ph) and 8.57 (1 H, s, CH=N); δ_C 23.8 and 62.4 (Pr^i), 126.6, 129.0, 129.7 and 130.3 (Ph), 148.5 (C=N, ^1J 163.8, ^3J 9), 153.9 (C-4, ^2J 14) and 156.3 (C-5).

Thioketone **16c**: δ_H 1.64 (6 H, d, 2 Me), 4.85 (1H, sept, CH), 7.4–7.5 and 8.0 (5 H, m + d, Ph) and 8.26 (1 H, s, 5-H); δ_C 22.8 and 53.4 (Pr^i), 126.5 (C-5, ^1J 197), 128.0, 129.8, 132.3 and 145.5 (Ph), 155.0 (C-4) and 222.4 (C=S).

4-*Benzoyl*-1-(tert-*butyl*)-1,2,3-*triazole* **17d**.—A solution of the aldehyde **14** (0.5 g, 2.6 mmol) and a fivefold excess of *tert*-butylamine (0.95 g, 13.2 mmol) in ethanol (20 cm^3) was refluxed for 4 h. After removal of the solvent, the residue was chromatographed on silica gel with dichloromethane–ethyl acetate (9:1) as the eluent to give triazole **17d** (0.35 g, 58%), m.p. 104 °C (from Et_2O) (Found: C, 68.2; H, 6.45. $C_{13}H_{15}N_3O$ requires C, 68.10; H, 6.59%); ν_{max}(KBr)/cm^{-1} 3159m, 2994m, and 1653s (C=O); δ_H($CDCl_3$) 1.75 (9 H, s, Bu^t), 7.5, 7.6 and 8.47 (5 H, 2 t + d, Ph) and 8.36 (1 H, s, 5-H); δ_C($CDCl_3$) 29.9 and 60.2 (Bu^t), 125.8 (C-5), 128.3, 130.7, 133.2 and 136.7 (Ph), 147.5 (C-4) and 186.0 (CO); *m/z* 229 ($M^{\cdot+}$, 23%), 201 ($M^{\cdot+}$ − N_2 or CO, 11), 200 (10), 145 (53), 144 (*m/z* 201 − C_4H_9, 13), 117 (15), 116 ($M^{\cdot+}$ − N_2 − CO − C_4H_9, 13), 105 ($PhCO^+$, 61), 77 (Ph^+, 30) and 57 ($C_4H_9^+$, 100).

4-*Benzoyl*-1-*phenyl*-1,2,3-*triazole* **17e**.—A solution of the aldehyde **14** (0.5 g, 2.6 mmol) and aniline (0.28 g, 3.1 mmol) in diethyl ether (30 cm^3) was refluxed for 24 h. After removal of the solvent, the residue was chromatographed on silica gel with dichloromethane–ethyl acetate (9:1) as the eluent to give the triazole **17e** (0.41 g, 62%), m.p. 131 °C (from Et_2O, lit.,[18] 125 °C) (Found: C, 72.3; H, 4.5. $C_{15}H_{11}N_3O$ requires C, 72.28: H, 4.45%); ν_{max}(KBr)/cm^{-1} 3134m and 1641s (C=O); δ_H($CDCl_3$) 7.49–7.67, 7.82 and 8.5 (10 H, m + 2 d, 2 Ph) and 8.71 (1 H, s, 5-H); δ_C($CDCl_3$) 120.8, 128.5, 129.6, 130.0, 130.7, 133.5, 136.4 and 136.5 (Ph), 126.4 (C-5, ^1J 198.3), 148.6 (C-4, ^2J 8.5) and 185.6 (CO); *m/z* 249 ($M^{\cdot+}$, 2%), 221 ($M^{\cdot+}$ − N_2 or CO, 9), 220 (10), 193 ($M^{\cdot+}$ − N_2 − CO, 14), 180 (18), 105 ($PhCO^+$, 61) and 77 (Ph^+, 100).

4-*Benzoyl*-1-(4-*methoxyphenyl*)-1,2,3-*triazole* **17f**.—A solution of the aldehyde **14** (0.5 g, 2.6 mmol) and *p*-methoxyaniline (0.32 g, 2.6 mmol) in ethanol (20 cm^3) was refluxed for 24 h. After removal of the solvent, the residue was chromatographed on silica gel with dichloromethane–ethyl acetate (20:1) as the eluent to give **17f** (0.43 g, 58%), m.p. 153 °C (from CH_2Cl_2) (Found: C, 68.7; H, 4.8. $C_{16}H_{13}N_3O_2$ requires C, 68.81; H, 4.69%); ν_{max}(KBr)/cm^{-1} 3140m and 1636s (C=O); δ_H($CDCl_3$) 3.9 (3 H, s, OMe), 7.06 and 7.71 (4 H, 2 d, C_6H_4), 7.55, 7.64 and 8.49 (5 H, 2 t + d, Ph) and 8.63 (1 H, s, 5-H); δ_C($CDCl_3$) 115.0, 122.4, 129.7 and 160.4 (Ar), 126.4 (C-5), 128.5, 130.7, 133.4 and 136.5 (Ph), 148.4 (C-4) and 185.6 (CO); *m/z* 279 ($M^{\cdot+}$, 5%), 251 ($M^{\cdot+}$ − N_2 or CO, 26), 236 (*m/z* 251 − Me, 11), 208 ($M^{\cdot+}$ − N_2 − CO, 12), 174, (14) and 105 ($PhCO^+$, 100).

4-*Benzoyl*-1-(4-*chlorophenyl*)-1,2,3-*triazole* **17g**.—A solution of the aldehyde **14** (0.5 g, 2.6 mmol) and *p*-chloroaniline (0.33 g, 2.6 mmol) in ethanol (20 cm^3) was stirred at room temperature for 24 h. The solvent was then evaporated and the residue crystallized from diethyl ether to give **15g** (0.6 g, 77%), m.p. 105 °C; ν_{max}(KBr)/cm^{-1} 1615s (C=N); δ_H($CDCl_3$) 7.2 and 7.35 (4 H, 2 d, C_6H_4), 7.5–7.6 (5 H, m, Ph) and 8.74 (1 H, s, CH=N); δ_C($CDCl_3$) 122.4, 126.4, 129.2, 129.3, 129.9, 130.7, 132.6 and 149.4 (Ar), 150.1 (C=N, ^1J 165), 153.8 (C-4, ^2J 13) and 158.3 (C-5).

A solution of **15g** (0.6 g, 2 mmol) in dimethyl sulfoxide (20 cm^3) was heated at 120 °C for 48 h. The reaction mixture was poured into ice–water (100 cm^3) and extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$) and evaporated. The resulting crude product was crystallized from dichloromethane–diethyl ether to give the triazole **17g** (0.1 g, 20%), m.p. 221 °C (Found: C, 63.35; H, 3.65. $C_{15}H_{10}ClN_3O$ requires C, 63.50; H, 3.55%); ν_{max}(KBr)/cm^{-1} 3130m and 1642s (C=O); δ_H[$(CD_3)_2SO$] 7.62, 7.73 and 8.27 (5 H, 2 t + d, Ph), 7.72 and 8.08 (4 H, 2 d, C_6H_4) and 9.61 (1 H, s, 5-H); δ_C[$(CD_3)_2SO$] 122.5, 128.6, 129.9, 130.0, 133.5, 133.8, 134.9 and 136.5 (Ar), 128.2 (C-5), 147.2 (C-4) and 185.1 (CO); *m/z* 283

($M^{\bullet+}$, 9%), 255 ($M^{\bullet+}$ − N_2 or CO, 24), 227 ($M^{\bullet+}$ − N_2 − CO, 19), 214 (28) and 105 ($PhCO^+$, 100).

4-(3,4-*Dichlorophenyl*)*iminomethyl*-5-*phenyl*-1,2,3-*thiadiazole* **15h**.—A solution of the aldehyde **14** (0.5 g, 2.6 mmol) and 3,4-dichloroaniline (0.42 g, 2.6 mmol) in ethanol (20 cm^3) was allowed to react at room temperature for 24 h. After evaporation of the solvent, the crude product was crystallized from chloroform–diethyl ether to give **15h** (0.45 g, 50%), m.p. 98 °C (Found: C, 53.8; H, 2.8. $C_{15}H_9Cl_2N_3S$ requires C, 53.91; H, 2.71%); ν_{max}(KBr)/cm^{-1} 1627m (C=N); δ_H($CDCl_3$) 7.1–7.5 (3 H, 2 d + s, C_6H_3), 7.5–7.65 (5 H, br s, Ph) and 8.75 (1 H, s, CH=N); δ_C($CDCl_3$) 120.8, 122.8, 126.3, 129.3, 130.0, 130.7, 130.9, 133.1 and 150.4 (Ar), 151.2 (C=N), 153.5 (C-4) and 158.9 (C-5).

Note: This compound remained unchanged when heated in toluene for 2 days.

5-tert-*Butylthio*-1,2,3-*thiadiazole*-4-*carbaldehyde* **18**.—To a solution of the aldehyde **1** (0.5 g, 3.4 mmol) in ethanol (20 cm^3) was added sodium 1,1-dimethylethanethiolate (0.42 g, 3.7 mmol) and the mixture was refluxed under a nitrogen atmosphere for 1 h. The reaction mixture was then poured into water and extracted with chloroform. The extracts were dried ($MgSO_4$) and evaporated and the residue chromatographed on silica gel with diethyl ether–light petroleum (1:3) as the eluent to give compound **18** (0.32 g, 47%), m.p. 59 °C (from hexane) (Found: C, 41.5; H, 4.9. $C_7H_{10}N_2OS_2$ requires C, 41.56; H, 4.98%); ν_{max}(KBr)/cm^{-1} 1685s (C=O); δ_H($CDCl_3$) 1.6 (9 H, s, Bu^t) and 10.58 (1 H, s, CHO); δ_C($CDCl_3$) 29.6 and 49.4 (Bu^t), 155.9 (C-4), 160.6 (C-5) and 183.7 (C=O); *m/z* 202 ($M^{\bullet+}$, 1%) and 57 ($C_4H_9^+$, 100).

tert-*Butyl* 1-tert-*Butyl*-1,2,3-*triazole*-4-*carbodithioate* **20d**.—A solution of the aldehyde **18** (0.5 g, 2.5 mmol) and *tert*-butylamine (0.9 g, 12.5 mmol) in ethanol (20 cm^3) was stirred at room temperature for 12 h. After removal of the solvent, the residue was chromatographed on silica gel with diethyl ether–hexane (1:3) as the eluent to give the triazole **20d** as rose-red crystals (0.45 g, 72%), m.p. 147 °C (from Et_2O) (Found: C, 51.5; H, 7.4. $C_{11}H_{19}N_3S_2$ requires C, 51.33; H, 7.44%); δ_H($CDCl_3$) 1.69 and 1.71 (18 H, 2 s, 2 Bu^t) and 8.18 (1 H, s, 5-H); δ_C($CDCl_3$) 28.6, 29.8, 51.5 and 60.1 (2 Bu^t), 122.1 (C-5), 154.1 (C-4) and 215.5 (C=S); *m/z* 257 ($M^{\bullet+}$, 3%), 201 ($M^{\bullet+}$ − CH_2=CMe_2, 25), 145 ($M^{\bullet+}$ − 2 CH_2=CMe_2, 64), 117 ($M^{\bullet+}$ − 2 CH_2=CMe_2 − N_2, 11), 90 (11) and 57 ($C_4H_9^+$, 100).

tert-*Butyl* 1-*Phenyl*-1,2,3-*triazole*-4-*carbodithioate* **20e**.—A solution of aldehyde **18** (0.5 g, 2.5 mmol) and aniline (0.26 g, 2.8 mmol) in ethanol (20 cm^3) was stirred at room temperature for 12 h. Chromatographic purification on silica gel with diethyl ether–hexane (1:3) as the eluent gave the triazole **20e** as rose-red crystals (0.3 g, 43%), m.p. 101 °C (from Et_2O) (Found: C, 56.6; H, 5.5. $C_{13}H_{15}N_3S_2$ requires C, 56.29; H, 5.45%); δ_H($CDCl_3$) 1.73 (9 H, s, Bu^t), 7.4–7.6 and 7.77 (5 H, m + d, Ph) and 8.54 (1 H, s, 5-H); δ_C($CDCl_3$) 28.5 and 51.9 (Bu^t), 120.7, 129.3, 129.8 and 136.4 (Ph), 122.5 (C-5, ^1J 200), 155.0 (C-4, ^2J 8) and 214.4 (C=S); *m/z* 277 ($M^{\bullet+}$, 3%), 221 ($M^{\bullet+}$ − CH_2=CMe_2, 34), 220 ($M^{\bullet+}$ − Bu^t, 12), 193 ($M^{\bullet+}$ − CH_2=CMe_2 − N_2, 26), 192 ($M^{\bullet+}$ − Bu^t − N_2, 20), 160 (*m/z* 192 − S, 15), 129 (15), 104 (55), 77 (Ph^+, 77) and 57 ($C_4H_9^+$, 100).

Note: In $CDCl_3$ solution, the triazole **20e** equilibrates with 7% thiadiazole **19e**; δ_H 1.59 (s, Bu^t) and 9.08 (s, CH=N).

tert-*Butyl* 1-(4-*Methoxyphenyl*)-1,2,3-*triazole*-4-*carbodithioate* **20f**.—A solution of the aldehyde **18** (0.5 g, 2.5 mmol) and *p*-methoxyaniline (0.34 g, 2.8 mmol) in ethanol (20 cm^3) was stirred at room temperature for 12 h. Chromatographic purification on silica gel with diethyl ether–hexane (1:3) as the eluent gave the triazole **20f** as rose-red crystals (0.32 g, 40%), m.p. 114 °C (from Et_2O) (Found: C, 54.7; H, 5.5. $C_{14}H_{17}N_3OS_2$ requires C, 54.70; H, 5.57%); δ_H($CDCl_3$) 1.73 (9 H, s, Bu^t), 3.87 (3 H, s, OMe), 7.02 and 7.65 (4 H, 2 d, C_6H_4) and 8.45 (1 H, s, 5-H); δ_C($CDCl_3$) 28.6 and 51.8 (Bu^t), 55.6 (OMe), 114.8, 122.3, 129.7 and 160.2 (Ar), 122.6 (C-5), 154.9 (C-4) and 214.5 (C=S); *m/z* 307 ($M^{\bullet+}$, 8%), 251 ($M^{\bullet+}$ − CH_2=CMe_2, 7), 223 ($M^{\bullet+}$ − CH_2=CMe_2 − N_2, 78), 222 ($M^{\bullet+}$ − Bu^t − N_2, 30), 208 (12), 190 (*m/z* 222 − S, 15), 159 (*m/z* 190 − OMe, 23), 134 (72), 107 (22), 92 (22), 77 (36) and 57 ($C_4H_9^+$, 100).

Note: In $CDCl_3$ solution, the triazole **20f** equilibrates with 5% thiadiazole **19f**; δ_H 1.57 (s, Bu^t), 6.95 and 7.35 (2 d, C_6H_4) and 9.08 (s, CH=N).

tert-*Butyl* 1-(4-*Chlorophenyl*)-1,2,3-*triazole*-4-*carbodithioate* **20g**.—A solution of the aldehyde **18** (0.5 g, 2.5 mmol) and *p*-chloroaniline (0.36 g, 2.8 mmol) in ethanol (20 cm^3) was stirred at room temperature for 12 h. Chromatographic purification on silica gel with diethyl ether–hexane (1:3) as the eluent gave the triazole **20g** as rose-red crystals (0.42 g, 56%), m.p. 134 °C (from Et_2O) (Found: C, 49.8; H, 4.4. $C_{13}H_{14}ClN_3S_2$ requires C, 50.07; H, 4.53%); δ_H($CDCl_3$) 1.72 (9 H, s, Bu^t), 7.5 and 7.7 (4 H, 2 d, C_6H_4) and 8.51 (1 H, s, 5-H); δ_C($CDCl_3$) 28.5 and 52.0 (Bu^t), 121.8, 130.0, 134.8 and 135.2 (Ar), 122.3 (C-5), 155.1 (C-4) and 214.1 (C=S); *m/z* 311 ($M^{\bullet+}$, 1%), 255 ($M^{\bullet+}$ − CH_2=CMe_2, 7), 227 ($M^{\bullet+}$ − CH_2=CMe_2 − N_2, 13), 138 (18), 111 (23), 75 (21) and 57 ($C_4H_9^+$, 100).

Note: In $CDCl_3$ solution, the triazole **20g** equilibrates with 18% thiadiazole **19g** after 24 h; δ_H 1.59 (s, Bu^t), 7.25 and 7.4 (2 d, C_6H_4) and 9.06 (s, CH=N); δ_C 30 and 49.2 (Bu^t), 122.4, 129.3, 132.4 and 149.4 (Ar), 151.4 (C=N), 153.7 and 155.4 (C-4 and C-5).

tert-*Butyl* 1-(3,4-*Dichlorophenyl*)-1,2,3-*triazole*-4-*carbodithioate* **20h**.—A solution of the aldehyde **18** (0.5 g, 2.5 mmol) and 3,4-dichloroaniline (0.45 g, 2.8 mmol) in ethanol (20 cm^3) was stirred at room temperature for 12 h. Chromatographic purification on silica gel with diethyl ether–hexane (1:3) as the eluent gave the triazole **20h** as rose-red crystals (0.46 g, 52%), m.p. 148 °C (from Et_2O) (Found: C, 45.0; H, 3.9. $C_{13}H_{13}Cl_2N_3S_2$ requires C, 45.09; H, 3.78%); δ_H 1.72 (9 H, s, Bu^t), 7.63, 7.64 and 7.94 (3 H, 2 d + dd, Ar) and 8.52 (1 H, s, H-5); δ_C 28.5 and 52.1 (Bu^t), 119.5, 122.4, 131.6, 133.6, 134.2 and 135.3 (Ar), 122.2 (C-5, ^1J 195), 155.2 (C-4) and 213.8 (C=S); *m/z* 345 ($M^{\bullet+}$, 1%), 289 ($M^{\bullet+}$ − CH_2=CMe_2, 9), 261 ($M^{\bullet+}$ − CH_2=CMe_2 − N_2, 12), 172 (12), 145 ($C_6H_3Cl_2^+$, 13), 109 (11) and 57 ($C_4H_9^+$, 100).

Note: In $CDCl_3$ solution, the triazole **20h** equilibrates with 50% thiadiazole **19h** after 24 h; δ_H 1.6 (s, Bu^t), 7.16, 7.41 and 7.48 (3 d, Ar) and 9.05 (s, CH=N); δ_C 30.1 and 49.4 (Bu^t), 120.5, 123.1, 130.4, 130.9, 133.1 and 150.5 (Ar), 152.5 (C=N, ^1J 165), 154.6 and 155.0 (C-4 and C-5).

N,1-*Dimethyl*-1,2,3-*triazole*-4-*thiocarboxamide* **21a**.—To a solution of the aldehyde **18** (0.5 g, 2.5 mmol) in ethanol (20 cm^3) was added aq. methylamine (40%; 0.97 g, 12.5 mmol) and the mixture was stirred at room temperature. After 1 day, the precipitated triazole **21a** was filtered off and crystallized from ethanol (0.2 g, 52%), m.p. 213 °C (lit.,[1] 210 °C) (for spectral data, see ref. 1).

N,1-*Diethyl*-1,2,3-*triazole*-4-*thiocarboxamide* **21b**.—To a solution of the aldehyde **18** (0.5 g, 2.5 mmol) in ethanol (20 cm^3) was added aq. ethylamine (70%; 0.8 g, 12.5 mmol) and the mixture was stirred at room temperature for 24 h. After

removal of the solvent, the residue was chromatographed on silica gel with diethyl ether–hexane (1 : 1) as the eluent to give the triazole **21b** (0.25 g, 56%), m.p. 96 °C (lit.,[1] 97 °C) (for spectral data, see ref. 1).

N,1-*Diisopropyl*-1,2,3-*triazole*-4-*thiocarboxamide* **21c**.—A solution of the aldehyde **18** (0.5 g, 2.5 mmol) and isopropylamine (0.74 g, 12.5 mmol) was stirred overnight at room temperature. After removal of the solvent, the residue was chromatographed on silica gel with diethyl ether–hexane (1 : 1) as the eluent to give triazole **21c** (0.43 g, 80%), m.p. 77 °C (from hexane) (Found: C, 51.15; H, 7.5. $C_9H_{16}N_4S$ requires C, 50.92; H, 7.60%); $\delta_H(CDCl_3)$ 1.37 and 1.6 (12 H, 2 d, 4 Me), 4.83 and 4.84 (2 H, sept + octet, 2 CH), 8.24 (1 H, s, 5-H) and 8.8 (1 H, br s, NH); $\delta_C(CDCl_3)$ 21.5, 22.9, 46.4 and 53.6 (2 Pr^i), 125.2 (C-5), 148.1 (C-4) and 183.1 (C=S); *m/z* 212 ($M^{\bullet+}$, 16%) and 58 ($C_3H_7NH^+$, 100).

Acknowledgements

This work was carried out with fellowships from the IWONL (M. Verbeke) and NFWO (W. Dehaen). Financial support from the FKFO (Belgium) and the 'Ministerie voor Wetenschapsbeleid' is gratefully acknowledged.

References

1 G. L'abbé, E. Vanderstede, W. Dehaen, P. Delbeke and S. Toppet, *J. Chem. Soc., Perkin Trans. 1*, 1991, 607.
2 J. W. Cornforth in *The Chemistry of Penicillin*, Princeton University Press, Princeton N.J., 1949, pp. 688–730.
3 P. H. Olesen, F. E. Nielsen, E. B. Pedersen and J. Becher, *J. Heterocycl. Chem.*, 1984, **21**, 1603; G. L'abbé and A. Vandendriessche, *J. Heterocycl. Chem.*, 1989, **26**, 701; G. L'abbé, G. Van Essche, P. Delbeke and S. Toppet, *Bull. Soc. Chim. Belg.*, 1990, **99**, 833; G. L'abbé and M. Bruynseels, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1492; G. L'abbé, M. Bruynseels, P. Delbeke and S. Toppet, *J. Heterocycl. Chem.*, 1990, **27**, 2021; G. L'abbé and G. Van Essche, *Bull. Soc. Chim. Belg.*, 1991, **100**, 289.
4 Reviews: G. L'abbé, *J. Heterocycl. Chem.*, 1984, **21**, 627; G. L'abbé, *Bull. Soc. Chim. Belg.*, 1990, **99**, 281.
5 T. Kobori, M. Fujita, T. Hiyama and K. Kondo, *Synthesis*, 1992, 95.
6 J. Bjørgo, D. R. Boyd, C. G. Watson, W. B. Jennings and D. M. Jerina, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1081; V. M. S. Gil and W. von Philipsborn, *Magn. Reson. Chem.*, 1989, **27**, 409.
7 L. A. Burke, J. Elguero, G. Leroy and M. Sana, *J. Am. Chem. Soc.*, 1976, **98**, 1685.
8 J. E. Baldwin and R. C. G. Lopez, *Tetrahedron*, 1983, **39**, 1487.
9 G. L'abbé, P. Delbeke, G. Van Essche, I. Luyten, K. Vercauteren and S. Toppet, *Bull. Soc. Chim. Belg.*, 1990, **99**, 1007; G. L'abbé, P. Delbeke, W. Dehaen, L. Bastin and S. Toppet, *Bull. Soc. Chim. Belg.*, 1991, **100**, 623.
10 E. W. Thomas and D. C. Zimmermann, *Synthesis*, 1985, 945.
11 G. A. Olah, L. Ohannesian and M. Arvanaghi, *J. Org. Chem.*, 1984, **49**, 3856.
12 A. Dondoni, G. Fantin, M. Fogagnolo, A. Medici and P. Pedrini, *Synthesis*, 1987, 998.
13 B. S. Pedersen, S. Scheibye, N. H. Nilsson and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 223.
14 D. F. Ewing, *Org. Magn. Reson.*, 1979, **12**, 449.
15 S. Scheibye, B. S. Pedersen and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 229; A. R. Katritzky, S. Sobiak, and C. M. Marson, *Magn. Reson. Chem.*, 1988, **26**, 665.
16 B. S. Pedersen, S. Scheibye, K. Clausen and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 293.
17 H. Meier, G. Trickes, E. Laping and U. Merkle, *Chem. Ber.*, 1980, **113**, 183.
18 W. Borsche, H. Hahn and M. Wagner-Roemmich, *Liebigs Ann. Chem.*, 1943, **554**, 15.

Paper 3/02495D
Received 30*th April* 1993
Accepted 7*th May* 1993