Gas-phase pyrolysis of 4-amino-3-allylthio-1,2,4-triazoles: a new route to [1,3]thiazolo[3,2-*b*][1,2,4]triazoles

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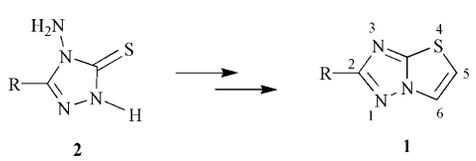
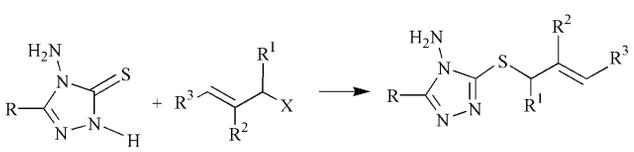
Flash vacuum pyrolysis of the 3-allylthio derivatives of 4-amino-4*H*-1,2,4-triazoles **10**–**13** and **15**–**17** at 750–850 °C (10^{-2}–10^{-3} Torr) gives [1,3]thiazolo[3,2-*b*][1,2,4]triazoles **19** and **24**–**29** in *ca.* 50% yield. The mechanism is thought to involve initial [3,3]sigmatropic shift of the allyl group, followed by cleavage of the N–N bond to generate a thiaza-allyl radical, which then undergoes cyclisation, rearrangement and alkyl group extrusion.

In previous work we have used the flash vacuum pyrolysis (FVP) reactions of aromatic allylthio compounds to generate thiophenoxyl radicals which can take part in rearrangement and cyclisation reactions.[1–3] In attempting to extend this methodology into the heterocyclic series we have discovered in one case an unusual sequence involving a [3,3]sigmatropic shift, thiaza-allyl radical generation, cyclisation, rearrangement and alkyl group extrusion, all of which leads to a convenient synthesis of the [1,3]thiazolo[3,2-*b*][1,2,4]triazole ring system[4] **1** in two steps from readily available *N*-amino-1,2,4-triazoles **2** (Scheme 1).



2 **1**

Scheme 1

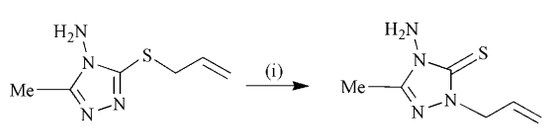


3 R = H **6** $R^1 = R^2 = R^3$ = H, X = Br **10** $R = R^1 = R^2 = R^3$ = H
4 R = Me **7** $R^1 = R^3$ = H, R^2 = Me, X = Cl **11** R = Me, $R^1 = R^2 = R^3$ = H
5 R = Ph **8** $R^1 = R^2$ = H, R^3 = Me, X = Cl **12** R = Me, $R^1 = R^3$ = H, R^2 = Me
9 R^1 = Me, $R^2 = R^3$ = H, X = Cl **13** R = Me, $R^1 = R^2$ = H, R^3 = Me
14 R = Me, $R^2 = R^3$ = H, R^1 = Me
15 R = Ph, $R^1 = R^2 = R^3$ = H
16 R = Ph, $R^1 = R^3$ = H, R^2 = Me
17 R = Ph, $R^1 = R^2$ = H, R^3 = Me

Scheme 2

The triazole precursors **3**–**5** (Scheme 2) were readily obtained by literature methods as described briefly in the Experimental section.[5–7] Allylation of the triazoles **4** and **5** using allyl bromide **6** or methallyl chloride **7**† in *N*,*N*-dimethylformamide containing anhydrous potassium carbonate gave products which were obtained as single isomers in 54–81% yield. The product obtained from the 5-unsubstituted compound **3** decomposed on work-up under these conditions, but a product was obtained in satisfactory yield (79%) when the reaction was carried out using acetonitrile as the solvent. The assignment of the products as the *S*-allyl compounds **10**–**12**, **15** and **16** followed in particular from their ^{13}C NMR spectra. Thus *N*-alkylation (either at the exocyclic amino group or at the ring N2 atom) would give a product which has a thione group. These are known to show signals in the range δ_C 166–167 in triazole-3-thiones,[8] whereas the spectra of **10**–**12**, **15** and **16** show no peaks at δ_C >155 ppm. The corresponding reaction of **4** with either crotyl chloride **8** or 3-chlorobut-1-ene **9** gave a mixture of *S*-allylated isomers in 6:1 and 13:1 ratio respectively. The ^{13}C NMR DEPT spectrum of the mixture confirmed that both isomers had a CH_2 group adjacent to the sulfur atom (δ_C 35.65) and therefore they are likely to be the *E* and *Z* isomers of **13**. Recrystallisation from toluene gave a single compound which is likely to be the *E*-isomer. No trace of the regioisomer **14** was apparent from the crude spectra. Similarly the butenyl compound **17** was obtained by reaction of the phenyl-substituted precursor **5** with crotyl chloride.‡

FVP of the *S*-allyl compound **11** at 650 °C (0.01 Torr) gave a mixture of two products in 9:1 ratio from which the major compound could be isolated by chromatography on silica. This product was clearly isomeric with the starting material and was identified as the *N*-allyl compound **18** by its spectra (Scheme 3).



11 **18**

Scheme 3 *Reagents and conditions*: (i) 650 °C (0.01 Torr).

For example, the thione function is apparent from the signal at δ_C 165.99 in the ^{13}C NMR spectrum (see above). [3,3]Sigmatropic rearrangements of this type have been previously reported in the triazole series[8] and in the present example may take place to some extent during the sublimation stage of the pyrolysis.

† The IUPAC name for methallyl is 2-methylprop-2-enyl.

‡ The IUPAC name for crotyl is but-2-enyl.

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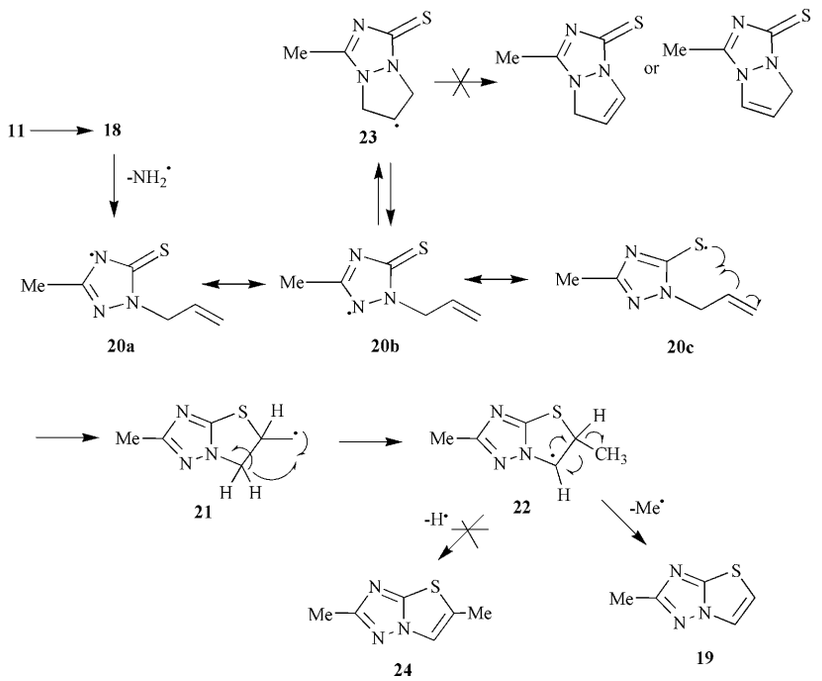
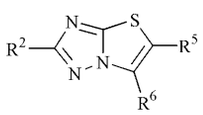


Scheme 4

At higher furnace temperatures, FVP of **11** gave a single major product (identical with the minor product obtained in the 650 °C pyrolysis described above) which was purified by distillation. The mass spectrum of this material showed a molecular ion at *m*/*z* 139 corresponding to loss of 31 Daltons (= CH_5N) from the starting material. The assignment of the structure of the product as the known[9] 2-methyl[1,3]thiazolo-[3,2-*b*][1,2,4]triazole **19** (54%) followed by comparison of its

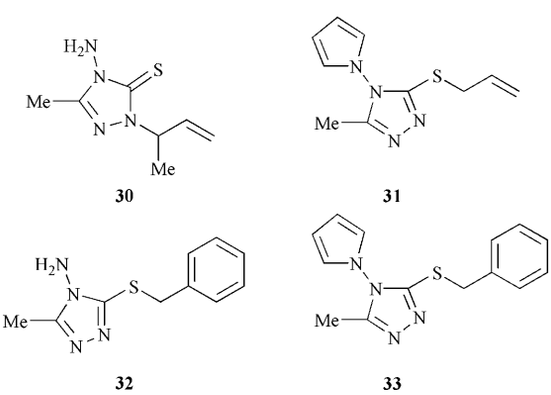


19 R^2 = Me, R^5 = R^6 = H
24 R^2 = R^5 = Me, R^6 = H
25 R^2 = R^5 = R^6 = H
26 R^2 = R^6 = Me, R^5 = H
27 R^2 = Ph, R^5 = R^6 = H
28 R^2 = Ph, R^5 = Me, R^6 = H
29 R^2 = Ph, R^5 = H, R^6 = Me

spectra with those in the literature. For example the ^{1}H NMR spectrum shows three signals in 1 : 1 : 3 ratio [δ_H 7.69 (*J* 4.5 Hz), 6.91 (*J* 4.5 Hz) and 2.50] which correspond closely with the reported data for **19** [δ_H 7.69 (*J* 5 Hz), 6.91 (*J* 5 Hz) and 2.47].[9] In addition the mass spectrum of our product (see Experimental section) shows the same initial breakdown peaks as previously reported.[9]

A possible mechanism for this unexpected transformation is shown in Scheme 4. After the initial [3,3]sigmatropic shift to give **18**, cleavage of the N–N bond apparently takes place to generate the resonance-stabilised radical **20**. This species then adds exclusively from its sulfur centre **20c** in 5-*exo*-*trig* fashion to the double bond of the allyl group. The primary radical **21** thus generated can achieve more stability by hydrogen shift from the site adjacent to the bridgehead nitrogen atom to give **22**. Aromatisation by C–C cleavage (and ejection of a methyl radical) gives the product **19**. Two instances of high selectivity in the chemistry of these radicals are apparent in this sequence. First, no products were obtained from an alternative cyclisation route which formally involves the nitrogen-centred canonical form **20b** (to give the secondary radical intermediate **23**). This suggests either that formation of **23** is reversible or that thiyl radicals are more reactive than aminyl radicals in such competitive cyclisation situations. Alternatively, the 5-*exo*-*trig* mode of cyclisation (to give **21**) may be inherently favoured over the 5-*endo*-*trig* to give **23**. Second, no trace of the dimethylthiazolo-[3,2-*b*][1,2,4]triazole **24** (see below) which might have been formed by loss of a hydrogen atom from **22**, was observed in the crude pyrolysate; C–C cleavage is normally observed in preference to C–H cleavage under competitive conditions in the gas-phase.[10]

The synthetic potential of this two step sequence from 4-amino-1,2,4-triazole-3-thiones to [1,3]thiazolo[3,2-*b*][1,2,4]-triazoles was then investigated using the 5-unsubstituted compound **10**, the 5-methyltriazoles **12** and **13**, and the 5-phenyl compounds **15**–**17** as model substrates. In all cases the pyrolysis step was carried out in the range 750–850 °C (10^{-2}–10^{-3} Torr) and the products were purified by Kugelrohr distillation; in general, chromatography was not required. Pyrolysis of **10** (850 °C) gave the unsubstituted [1,3]thiazolo[3,2-*b*][1,2,4]-triazole **25** (45%) and that of the methallyl derivative **12** gave the expected 2,5-dimethyl[1,3]thiazolo[3,2-*b*][1,2,4]triazole **24** in 48% yield. In the case of the butenyl precursor **13**, the initial sigmatropic shift produces **30** and hence leads to the 2,6-



dimethyl[1,3]thiazolo[3,2-*b*][1,2,4]triazole skeleton **26** (54%). Pyrolysis of the phenyl-substituted triazoles **15**–**17** proceeded normally and the [1,3]thiazolo[3,2-*b*][1,2,4]triazoles **27**–**29** were obtained in 23, 48 and 54% yields respectively, though chromatography was required to purify **29**. In general, the

2,6-disubstituted products were obtained in a less pure state than the other derivatives. 2,5-Disubstitution in the [1,3]thiazolo[3,2-*b*][1,2,4]triazole ring system is apparently a rare substituent pattern[4] and both **24** and **28** are new compounds.

In the pyrolyses of the phenyl-substituted substrates **15**–**17**, some benzonitrile was detected in the crude pyrolysate, presumably due to breakdown of the heterocycle at the high temperatures required for the initial N–N bond cleavage. Since pyrolysis of **16** or **17** at 750 °C (rather than 850 °C) did not significantly reduce the level of benzonitrile, an attempt was made to design a substrate in which the co-formed aminyl radical was stabilised. Thus condensation of **4** with 2,5-dimethoxytetrahydrofuran gave the pyrrolyltriazole **31** (87%), which on FVP at 750 °C (10^{-2} Torr) gave a mixture of the [1,3]thiazolo[3,2-*b*][1,2,4]triazole **19** (15%) and pyrrole, which were separated by chromatography. Since the yield of product was much lower than that obtained from the pyrolysis of **11** and a chromatographic separation was required, this strategy was not pursued further.

Finally, in an attempt to induce cyclisation without an initial sigmatropic shift, the benzyl compounds **32** and **33** were synthesised by standard methods and subjected to FVP, but no cyclisation products were obtained (see Experimental section).

Although many spectroscopic studies of the [1,3]thiazolo-[3,2-*b*][1,2,4]triazole system have been carried out, no systematic study of their ^{13}C NMR spectra has been reported.[4] The parent compound of the system **25** apparently shows only three signals in the proton decoupled spectrum, at δ_C 156.34, 119.86 and 113.85. However, a ^{1}H coupled spectrum revealed the bridgehead quaternary signal (C-3a), also at δ_C 156.34, and the following coupling constants: C-2, $^1J_{CH}$ 208.7; C-5, $^1J_{CH}$ 195.2, $^2J_{CH}$ 10.2; C-6 $^1J_{CH}$ 198.2, $^2J_{CH}$ 7.2 Hz. The 2-methyl compound **19** shows 4 signals due to the ring carbon atoms, quaternaries at δ_C 166.52 (C-2) and 156.84 (C-3a) and methine resonances at δ_C 119.66 and 112.14. Because methyl substitution at an adjacent position is likely to cause a high frequency shift of that signal (*cf.* data for thiazoles[11,12]) comparison of the spectra of **19**, **24** and **26** allow the assignment of the resonances of C5 (δ_C 112–114) and C6 (δ_C 119–120) in compounds **19** and **24**. Further assignments are given in the Experimental section.

In conclusion we have shown that an unusual pyrolysis sequence has provided a short route to the [1,3]thiazolo[3,2-*b*]-[1,2,4]triazole ring system in moderate overall yield. The carbon atoms in the fused triazole and thiazole rings are derived initially from a 4-aminotriazole-3-thione unit and an allyl group respectively. The sequence is compatible with substituents at all three possible positions on the rings and complements traditional condensation routes from triazoles to the [1,3]thiazolo[3,2-*b*][1,2,4]triazole system.[4]

Experimental

Unless otherwise stated ^{1}H and ^{13}C NMR spectra were recorded in [^{2}H]chloroform at 250 (or 200) and 63 (or 50) MHz respectively and mass spectra were recorded under electron impact (EI) conditions. Coupling constants are quoted in Hz. Dry-flash chromatography was carried out on silica gel (GF_{254}) using a hexane–ethyl acetate gradient as eluent.

4-Amino-2,4-dihydro-3*H*-1,2,4-triazole-3-thione 3

Treatment of thiocarbohydrazide (5.3 g, 0.05 mol) with refluxing formic acid (10 cm^3)[5] gave the parent triazole **3** (3.2 g, 55%) mp 166–167 °C (lit.,[5] 166–167 °C); δ_H ([^{2}H]$_6$DMSO) 13.51 (1H, s), 8.41 (1H, s) and 5.62 (2H, s).

4-Amino-5-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione 4

Prepared from thiocarbohydrazide (5.3 g, 0.05 mol) and acetic acid (15 cm^3) by the standard method[6] the product **4** was obtained as white crystals (6.31 g, 97%) mp 203–204 °C (lit.,[6] 205–206 °C); δ_H ([^{2}H]$_6$DMSO) 13.40 (1H, s), 5.50 (2H, s) and 2.22 (3H, s).

4-Amino-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione 5

This compound was made by treatment of benzoic acid hydrazide (1.0 g, 7.4 mmol) with carbon disulfide (0.84 g, 0.011 mol) under basic conditions in ethanol followed by reaction with aqueous hydrazine hydrate (0.38 g, 0.012 mol).[7] The triazole **5** so obtained (0.49 g, 35%) had mp 204–206 °C (lit.,[6] 204–206 °C); δ_H ([^{2}H]$_6$DMSO) 7.60 (5H, m) and 5.83 (2H, s); *m*/*z* 192 (M$^+$, 100%) and 104 (45).

Allylation of 4-amino-3*H*-1,2,4-triazole-3-thione derivatives

The appropriate 1,2,4-triazole **3**–**5** (8 mmol) was added to *N*,*N*-dimethylformamide (50 cm^3) containing potassium carbonate (1.0 g, 8 mmol). The appropriate allyl halide **6**–**9** (8 mmol) was added dropwise with stirring, then the mixture was stirred at room temperature for 21–48 hours. The inorganic salts were removed by filtration, the filtrate was concentrated *in vacuo*, dichloromethane (20 cm^3) was added and the mixture was filtered once more. The product was obtained on removal of the solvent. The following preparations were carried out by this method:

4-Amino-5-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione **4** (1.04 g, 8 mmol) and allyl bromide **6** (0.96 g, 8 mmol) gave, after 48 h, *4-amino-3-allylthio-5-methyl-4H-1,2,4-triazole* **11** as a pale pink solid (1.1 g, 81%), mp 77–80 °C (from toluene) [Found, MH$^+$ (FAB) 171.0710. $C_6H_{11}N_4S$ requires *MH* 171.0704]; δ_H 5.91 (1H, m), 5.15 (2H, m), 4.83 (2H, s), 3.68 (2H, m) and 2.37 (3H, s); δ_C 153.48 (quat), 150.31 (quat), 132.62 (CH), 118.80 (CH_2), 36.04 (CH_2) and 10.23 (CH_3); *m*/*z* (FAB) 171 (MH$^+$, 100%).

4-Amino-5-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione **4** (1.04 g, 8 mmol) and 2-methylprop-2-enyl chloride **7** (0.72 g, 8 mmol) gave, after 21 h, *4-amino-3-(2-methylprop-2-enyl)thio-5-methyl-4H-1,2,4-triazole* **12** as a white solid, (0.6 g, 81%), mp 102–103 °C (from toluene) (Found, M$^+$ 184.0782. $C_7H_{12}N_4S$ requires *M* 184.0783); δ_H 4.86 (1H, m), 4.82 (1H, m), 4.64 (2H, s), 3.71 (2H, s), 2.39 (3H, s) and 1.86 (3H, m); δ_C 153.42 (quat), 150.62 (quat), 140.36 (quat), 115.03 (CH_2), 40.77 (CH_2), 20.99 (CH_3) and 10.24 (CH_3); *m*/*z* 184 (M$^+$, 55%), 169 (68), 130 (31), 102 (66) and 70 (100).

4-Amino-5-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione **4** (1.04 g, 8 mmol) and but-2-enyl chloride **8** (0.72 g, 8 mmol) gave, after 21 h, a 6:1 mixture of *E* and *Z* isomers, from which *4-amino-3-(but-2-enylthio)-5-methyl-4H-1,2,4-triazole* **13** was obtained as a white solid after recrystallisation from toluene, (0.26 g, 50%) mp 105–107 °C (from toluene) (Found, C, 43.6; H, 6.3; N, 28.75. $C_7H_{12}N_4S{\cdot}0.5H_2O$ requires C, 43.5; H, 6.2; N, 29.0%. Found, M$^+$,184.0790. $C_7H_{12}N_4S$ requires *M* 184.0783); δ_H 5.55 (1H, m), 5.50 (1H, m), 4.82 (2H, s), 3.60 (2H, m), 2.33 (3H, s) and 1.58 (3H, d, *J* 4.8); δ_C 153.28 (quat), 150.57 (quat), 130.50 (CH), 125.13 (CH), 35.65 (CH_2), 17.56 (CH_3) and 10.15 (CH_3); *m*/*z* 184 (M$^+$, 19%), 169 (74), 143 (49), 130 (71) and 55 (100).

The corresponding reaction of 4-amino-5-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione **4** (1.04 g, 8 mmol) and 3-chlorobut-1-ene **9** (0.72 g, 8 mmol) gave, after 21 h, a 13:1 mixture of the *E* and *Z* isomers of **13**, whose spectra were identical with those reported above.

4-Amino-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione **5** (1.54 g, 8 mmol) and allyl bromide **6** (0.96 g, 8 mmol) gave, after 48 h, *4-amino-3-allylthio-5-phenyl-4H-1,2,4-triazole* **15** as a white solid, (0.74 g, 64%), mp 132–134 °C (from toluene) (Found, C, 55.75; H, 5.2; N, 23.3. $C_{11}H_{12}N_4S{\cdot}0.25H_2O$ requires C, 55.8; H, 5.3; N, 23.7%); δ_H 8.00 (2H, m), 7.44 (3H, m), 5.99 (1H, m), 5.19 (2H, m), 4.82 (2H, s) and 3.81 (2H, m); δ_C 154.04 (quat), 152.06 (quat), 132.61 (CH) 129.93 (CH), 128.44

(CH), 127.99 (CH), 126.32 (quat), 119.12 (CH_2) and 36.10 (CH_2); *m/z* 232 (M^+, 39%), 217 (36), 129 (47), 103 (80) and 41 (100).

4-Amino-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione **5** (1.54 g, 8 mmol) and 2-methylprop-2-enyl chloride **7** (0.72 g, 8 mmol) gave, after 48 h, *4-amino-3-(2-methylprop-2-enyl)thio-5-phenyl-4H-1,2,4-triazole* **16** as a white solid, (0.66 g, 54%), mp 130–132 °C (from toluene) (Found, C, 58.3; H, 5.85; N, 22.5. $C_{12}H_{14}N_4S$ requires C, 58.5; H, 5.7; N, 22.8%); δ_H 8.00 (2H, m), 7.40 (3H, m), 4.92 (2H, m), 4.84 (2H, m), 3.78 (2H, s) and 1.87 (3H, s); δ_C 153.97 (quat), 152.44 (quat), 140.23 (quat), 129.94 (CH), 128.41 (CH), 128.00 (CH), 126.23 (quat), 115.23 (CH_2), 40.62 (CH_2) and 21.03 (CH_3); *m/z* 246 (M^+, 88%), 201 (52), 143 (30), 103 (56) and 70 (100).

4-Amino-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione **5** (1.54 g, 8 mmol) and but-2-enyl chloride **8** (0.72 g, 8 mmol) gave, after 48 h, *4-amino-3-(but-2-enylthio)-5-phenyl-4H-1,2,4-triazole* **17** as a gummy yellow solid, which was recrystallised from toluene to give the product as pale yellow crystals (0.64 g, 33%), mp 145–147 °C (from toluene) [Found, MH^+ (FAB) 247.1016. $C_{12}H_{15}N_4S$ requires MH^+ 247.1017]; δ_H 7.99 (2H, m), 7.44 (3H, m), 5.66 (1H, m), 5.63 (1H, m), 4.78 (2H, s), 3.76 (2H, m) and 1.65 (3H, d, *J* 4.8); δ_C 153.94 (quat), 152.29 (quat), 130.89 (CH), 129.91 (CH), 128.43 (CH), 127.98 (CH), 126.36 (quat), 125.08 (CH), 35.78 (CH_2) and 17.67 (CH_3); *m/z* (FAB) 247 (MH^+, 100%).

A modified procedure was adopted for the preparation of the 5-unsubstituted derivative **10**. A solution of 4-amino-2,4-dihydro-3*H*-1,2,4-triazole-3-thione **3** (0.25 g, 2.1 mmol) and allyl bromide **6** (0.23 g, 2.1 mmol) in acetonitrile (10 cm^3) containing anhydrous potassium carbonate (0.40 g, 2.5 mmol) was stirred at room temperature for 21 h. The inorganic salts were removed by filtration, the filtrate was concentrated *in vacuo* at room temperature or below, ethanol (10 cm^3) was added and the mixture was filtered once more. On removal of the solvent *4-amino-3-allylthio-4H-1,2,4-triazole* **10** (0.26 g, 79%), was obtained mp 83–85 °C (from ethanol) (Found, C, 37.9; H, 4.65; N, 34.8. $C_5H_8N_4S{\cdot}0.2\ H_2O$ requires C, 37.6; H, 5.3; N, 35.1%. Found, M^+,156.0469. $C_5H_8N_4S$ requires *M* 156.0470); δ_H ($[^2H]_6$DMSO) 8.46 (1H, s), 6.08 (2H, s), 5.95 (1H, m), 5.24 (1H, m), 5.07 (1H, m) and 3.77 (2H, m); δ_C 150.40 (quat), 146.39 (CH), 133.72 (CH), 118.44 (CH_2) and 34.15 (CH_2); *m/z* 156 (M^+, 37%), 141 (25), 129 (20) 56 (80) and 41 (100).

Flash vacuum pyrolysis of 4-amino-3-allylthio-4*H*-1,2,4-triazoles 10–13 and 15–17

The aminotriazoles **10**–**13** and **15**–**17** were distilled at a pressure of *ca.* 1×10^{-2} Torr into an empty silica furnace tube which was maintained at the stated temperature by an electrically heated furnace. The products were trapped in a U-tube cooled with liquid nitrogen, and were washed from the trap with solvent at the end of the pyrolysis.

When 4-amino-3-allylthio-5-methyl-4*H*-1,2,4-triazole **11** (0.30 g, 1.8 mmol) was sublimed at 120 °C over a period of 1.5 h into the furnace tube at a temperature of 650 °C a mixture of products was obtained, which was separated by dry flash chromatography (silica), hexane–ethyl acetate (6:1), to give *2-allyl-4-amino-5-methyl-2,4-dihydro-3H-1,2,4-triazole-3-thione* **18** as a pale yellow liquid, (0.10 g, 33%) (Found, M^+ 170.0623. $C_6H_{10}N_4S$ requires *M* 170.0626); δ_H 5.85 (1H, m), 5.28 (2H, m), 4.72 (2H, m), 4.65 (2H, s) and 2.37 (3H, s); δ_C 165.99 (quat), 148.66 (quat), 130.53 (CH), 119.23 (CH_2), 51.55 (CH_2) and 10.37 (CH_3); *m/z* 170 (M^+, 80%), 155 (64), 102 (45), 74 (42) and 56 (100).

The triazole **11** (0.30 g, 1.8 mmol) was pyrolysed using the same conditions as above, but at a furnace temperature of 850 °C. The pyrolysate was distilled to give 2-methyl[1,3]-thiazolo[3,2-*b*][1,2,4]triazole[9] **19** as a golden liquid (0.14 g, 54%), bp 120 °C (2.5 Torr) (mp lit.,[9] 49.5–51 °C); δ_H 7.69 (1H, d, ^3J 4.5), 6.91 (1H, d, ^3J 4.5) and 2.50 (3H, s); δ_C 166.52 (quat), 156.84 (quat), 119.66 (CH), 112.14 (CH) and 14.79 (CH_3); *m/z* 139 (M^+, 100%), 98 (73), 71 (51) and 58 (57).

The triazole **10** (0.14 g, 1.0 mmol) was pyrolysed at 850 °C (0.01 Torr) (inlet temperature 120 °C). The pyrolysate was distilled to give [1,3]thiazolo[3,2-*b*][1,2,4]triazole[13] **25** as a pale yellow solid, (0.055 g, 55%), bp 50–55 °C (4 Torr) mp 96–98 °C (lit.,[13] 98–100 °C); δ_H 8.15 (1H, d, ^6J 1.4), 7.81 (1H, d, ^3J 4.4) and 6.91 (1H, dd, ^3J 4.4 and ^6J 1.4); δ_C 156.34 (CH and quat), 119.86 (CH) and 113.85 (CH); *m/z* 125 (M^+, 100%), 98 (49), 71 (53) and 45 (65).

4-Amino-3-(2-methylprop-2-enyl)thio-5-methyl-4*H*-1,2,4-triazole **12** (0.20 g, 1.1 mmol) was pyrolysed at an inlet temperature of 130 °C and furnace temperature of 850 °C over a period of 1 h. The pyrolysate was collected in DCM, and distilled to give *2,5-dimethyl[1,3]thiazolo[3,2-b][1,2,4]triazole* **24** as a pale yellow liquid (0.08 g, 48%), bp 85 °C (2 Torr) (Found, M^+ 153.0363. $C_6H_7N_3S$ requires *M* 153.0361); δ_H 7.41 (1H, q, ^4J 1.4), 2.48 (3H, s) and 2.45 (3H, d, ^4J 1.4); δ_C 165.13 (quat), 156.00 (quat), 126.40 (quat), 116.34 (CH), 14.68 (CH_3) and 13.94 (CH_3); *m/z* 153 (M^+, 100%), 112 (58) and 59 (95).

4-Amino-3-(but-2-enylthio)-5-methyl-4*H*-1,2,4-triazole **13** (0.20 g, 1.1 mmol) was pyrolysed at an inlet temperature of 135 °C and a furnace temperature of 850 °C over a period of 0.5 h. The pyrolysate was collected in DCM, and distilled to give 2,6-dimethyl[1,3]thiazolo[3,2-*b*][1,2,4]triazole[14,15] **26** as a pale yellow liquid (0.09 g, 54%), bp 90 °C (2 Torr) [lit.,[14] 112–114 °C (5 Torr); mp[14] 62–64 °C] (Found, M^+ 153.0355. $C_6H_7N_3S$ requires *M* 153.0361); δ_H 6.50 (1H, q, ^4J 1.3), 2.53 (3H, s) and 2.50 (3H, d, ^4J 1.3); δ_C (quaternaries not reported) 106.11 (CH), 14.77 (CH_3) and 12.32 (CH_3); *m/z* 153 (M^+, 100%), 112 (48), 67 (98) and 42 (69).

4-Amino-3-allylthio-5-phenyl-4*H*-1,2,4-triazole **15** (0.10 g, 0.4 mmol) was pyrolysed at an inlet temperature of 135 °C and a furnace temperature of 850 °C over a period of 1 h. The pyrolysate was collected in DCM, and distilled to give 2-phenyl[1,3]thiazolo[3,2-*b*][1,2,4]triazole[9] **27** as a pale yellow liquid (0.02 g, 23%), bp 75 °C (0.7 Torr) which crystallised, mp 114–116 °C (lit.,[9] 118–119 °C) (Found M^+ 201.0360. $C_{10}H_7N_3S$ requires *M* 201.0361); δ_H 8.15 (2H, m), 7.81 (1H, d, *J* 4.5), 7.44 (3H, m) and 6.99 (1H, d, *J* 4.5); δ_C 167.35 (quat), 157.40 (quat), 130.92 (quat), 129.66 (CH), 128.60 (CH), 126.53 (CH), 119.92 (CH) and 112.95 (CH); *m/z* 201 (M^+, 100%), 116 (26), 103 (41) and 76 (33).

4-Amino-3-(2-methylprop-2-enyl)thio-5-phenyl-4*H*-1,2,4-triazole **16** (0.20 g, 0.8 mmol) was pyrolysed at a furnace temperature of 750 °C with an inlet temperature of 130 °C over a period of 1 h. The pyrolysate was collected in DCM, and distilled to give *5-methyl-2-phenyl[1,3]thiazolo[3,2-b][1,2,4]triazole* **28** as a pale yellow liquid (0.08 g, 48%), bp 85 °C (2 Torr) mp 126–128 °C (Found, M^+ 215.0512. $C_{11}H_9N_3S$ requires *M* 215.0517); δ_H 8.37 (2H, m), 7.77 (1H, q, ^4J 1.4), 7.75 (3H, m) and 2.74 (3H, d, ^4J 1.4); δ_C (quaternary signals not quoted) 129.43 (CH), 128.55 (CH), 126.39 (CH), 116.56 (CH) and 14.10 (CH_3); *m/z* 215 (M^+, 31%), 169 (46), 128 (43), 104 (58), 77 (47) and 55 (100).

4-Amino-3-(but-2-enylthio)-5-phenyl-4*H*-1,2,4-triazole **17** (0.20 g, 0.8 mmol) was pyrolysed at an inlet temperature of 135 °C and a furnace temperature of 750 °C over a period of 0.5 h. The pyrolysate was collected in DCM, and distilled to give 6-methyl-2-phenyl[1,3]thiazolo[3,2-*b*][1,2,4]triazole[9,13] **29** as a pale yellow liquid which was contaminated with benzonitrile. Dry-flash chromatography on silica gave **29** (0.09 g, 54%), bp 90 °C (2 Torr) (mp lit.,[9] 125–126 °C) (Found, M^+ 215.0513. $C_{11}H_9N_3S$ requires *M* 215.0517); δ_H 8.16 (2H, m), 7.46 (3H, m), 6.57 (1H, q, ^4J 1.4) and 2.58 (3H, d, ^4J 1.4); δ_C (quaternary signals not reported) 129.56 (CH), 128.56 (CH), 126.56 (CH), 106.98 (CH) and 12.52 (CH_3); *m/z* 215 (M^+, 100%), 144 (25), 103 (50) and 72 (52).

5-Methyl-4-(pyrrol-1-yl)-3-allylthio-4*H*-1,2,4-triazole 31

The aminotriazole **11** (2.55 g, 0.015 mol), 2,5-dimethoxytetrahydrofuran (1.9 cm^3, 0.015 mol) and acetic acid (50 cm^3) were heated under reflux for 30 min. The solvent was removed *in vacuo* to give a dark brown liquid, which solidified overnight to give *5-methyl-4-(pyrrol-1-yl)-3-allylthio-4H-1,2,4-triazole* **31** as a brown solid (2.91 g, 87%), mp 61–62 °C (from hexane) (Found, C, 54.3; H, 5.4; N, 25.25. $C_{10}H_{12}N_4S$ requires C, 54.55; H, 5.45; N, 25.25%); δ_H 6.70 (2H, t, *J* 4.5), 6.33 (2H, t, *J* 4.5), 5.91 (1H, m), 5.14 (2H, m), 3.76 (2H, m) and 2.24 (3H, s); δ_C 152.38 (quat), 151.02 (quat), 132.04 (CH), 120.72 (CH), 119.16 (CH_2), 109.77 (CH), 34.99 (CH) and 9.31 (CH_3); *m*/*z* 220 (M^+, 56%), 173 (97) and 124 (100).

4-Amino-3-benzylthio-5-methyl-4*H*-1,2,4-triazole 32

4-Amino-5-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione **4** (1.95 g, 0.015 mol) was added to DMF (50 cm^3) containing potassium carbonate (1.88 g, 0.015 mol). Benzyl chloride (1.89 g, 0.015 mol) was added dropwise with stirring then the mixture was stirred at room temperature for 21 h. The insoluble potassium carbonate was removed by filtration, then the filtrate concentrated *in vacuo* to give a pink solid. The solid was treated with dichloromethane (20 cm^3), the mixture filtered once more and the solvent was removed *in vacuo* to give *4-amino-3-benzylthio-5-methyl-4H-1,2,4-triazole* **32** as an orange–brown solid (0.65 g, 20%), mp 149–150 °C (from toluene) (Found, M^+ 220.0785. $C_{10}H_{12}N_4S$ requires *M* 220.0783); δ_H 7.25 (5H, m), 4.20 (2H, s), 3.93 (2H, s) and 2.33 (3H, s); δ_C 153.58 (quat), 149.48 (quat), 137.27 (quat), 128.71 (CH), 128.67 (CH), 127.89 (CH), 38.97 (CH_2) and 10.32 (CH_3); *m*/*z* 220 (M^+, 21%), 106 (45) and 91 (100).

3-Benzylthio-5-methyl-4-(pyrrol-1-yl)-4*H*-1,2,4-triazole 33

4-Amino-3-benzylthio-5-methyl-4*H*-1,2,4-triazole **32** (0.16 g, 0.7 mmol), 2,5-dimethoxytetrahydrofuran (0.09 g, 0.7 mmol) and acetic acid (30 cm^3) were heated under reflux for 30 minutes. The solvent was removed *in vacuo* to give a brown oil, which was treated with water, then extracted with DCM (3 × 30 cm^3). The combined organic extracts were dried ($MgSO_4$), and concentrated to give a brown oil. The oil was distilled to give pure *3-benzylthio-5-methyl-4-(pyrrol-1-yl)-4H-1,2,4-triazole* **33** as a pale yellow oil (0.14 g, 75%), bp 160 °C (0.5 Torr) (Found, M^+ 270.0933. $C_{14}H_{14}N_4S$ requires *M* 270.0939); δ_H 7.25 (5H, m), 6.47 (2H, t, *J* 4.5), 6.57 (2H, t, *J* 4.5), 4.33 (2H, s) and 2.20 (3H, s); δ_C 152.31 (quat), 151.09 (quat), 135.86 (quat), 128.88 (CH), 128.43 (CH), 127.63 (CH), 120.56 (CH), 109.57 (CH), 36.92 (CH_2) and 9.13 (CH_3); *m*/*z* 270 (M^+, 11%), 156 (33) and 91 (100).

Flash vacuum pyrolysis of the 1,2,4-triazoles 31–33

The triazole **31** (0.20 g, 1 mmol) was sublimed at 160 °C (0.05 Torr) into the furnace tube which was maintained at a temperature of of 750 °C. The pyrolysate was dissolved in dichloromethane and subjected to dry-flash chromatography on silica (3 : 1 hexane–ethyl acetate) to give 2-methyl[1,3]thiazolo[3,2-*b*]-[1,2,4]triazole[9] **19** (0.02 g, 15%) whose spectra were compatible with those reported above.

Pyrolysis of **32** or **33** (inlet temperatures 180 °C) at 650–750 °C (0.004–0.008 Torr) gave complex pyrolysates from which the presence of bibenzyl could be inferred from their ^1H NMR spectra (δ_H 2.85). No cyclisation products could be detected.

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