Conversion of imino-1,2,3-dithiazoles into 2-cyanobenzothiazoles, cyanoimidoyl chlorides and diatomic sulfur

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Primary aromatic amines condense with 4,5-dichloro-1,2,3-dithiazolium chloride 1 to give high yields of the *N*-aryl imines 2 which on heating give 2-cyanobenzothiazoles 3, thus providing a simple two-step route to these heterocycles from the appropriate aniline. This thermolysis is favoured by electron donating substituents in the aniline ring, and retarded by electron withdrawing groups in favour of a second pathway in which both dithiazole sulfur atoms are lost to form cyanoimidoyl chlorides 4. This is the sole pathway when both aniline *ortho* positions are substituted. Analogous *N*-alkyl imines 5, prepared from the salt 1 and the bis(trimethylsilyl) derivatives of the amine, also decompose with loss of both sulfur atoms as singlet diatomic sulfur, S_2. 4-Chloro-5-methylimino-5*H*-1,2,3-diathiazole 5a does this at 140–150 °C and the S_2 generated is intercepted with 2,3-diphenylbutadiene, 2,3-dimethylbutadiene and norbornene to give 16a, 16b and 17 respectively.

Appel *et al*. reported the ready preparation of 4,5-dichloro-1,2,3-dithiazolium chloride **1** in 85% yield from chloroacetonitrile and disulfur dichloride and showed that the 5-Cl was very susceptible to nucleophilic displacement, for example by primary aromatic amines.[1] We have described the chemistry of some of the amines **2** prepared in this way.[2–5] We now report an extension to the range of aniline derivatives which gives imines **2** and the thermolysis of the latter to give 2-cyanobenzothiazoles **3**, cyanoimidoyl chlorides **4**, and singlet diatomic sulfur, S_2. We also report the preparation of some *N*-alkyl imines **5** and show that the *N*-methyl derivative is the best source of S_2 amongst these compounds. We found that in the preparation of the dithiazolium chloride **1** by Appel's method,[1] the addition of a catalytic amount of the phase transfer catalyst Adogen 464 (a tetraalkylammonium chloride) to the reaction mixture gave a cleaner product, in the same high yield.

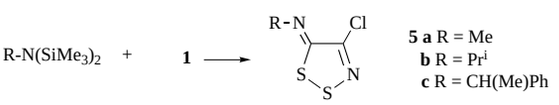
The imines **2** formed from primary aromatic amines are shown in Table 1. Electron withdrawing groups in the benzene ring reduced the reaction rate, and 2,6-dinitroaniline did not react with the salt **1** under our standard conditions (in dichloromethane at room temperature followed by the addition of pyridine). The imines **2** are yellow to orange crystalline compounds which are completely stable on storage in the atmosphere at room temperature, showing no apparent hydrolysis even after many months. They show an imine absorption in the IR at about 1600–1610 cm^{-1}. Their mass spectral fragmentation showed little consistent pattern, though most of the molecular ions lose S_2Cl, often as the base peak representing the cyanonitrilium ion, $Ar-\overset{+}{N}\equiv C-C\equiv N$, a species which is probably involved in formation of the cyanoimidoyl chlorides **4** (see below). Many molecular ions also show the loss of $ClCNS_n$ (n = 0, 1 or 2) by fragmentation of the dithiazole ring.

Table 1 Conversion of anilines into *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)anilines **2** by dithiazolium chloride **1**

Ar in $ArNH_2$	*t*/h	Yield of **2** (%)	Mp/°C	Lit. mp/°C
C_6H_5	0.5	90	66–67	63–65[a]
4-MeC_6H_4	0.5	95	69–70	66–67[a]
2,4-$Me_2C_6H_3$	1	83	85–87	—
2,4,6-$Me_3C_6H_2$	1	86	95–97	—
2,4,6-$Et_3C_6H_2$	1	75	50–51	—
2-BrC_6H_4	1	91	79–80	—
2,6-$Cl_2C_6H_3$	3	46	162–163	—
2,4,6-$Cl_3C_6H_2$	7	62	96–98	—
2-HOC_6H_4	0.3	95	95–96	—
3-$MeOC_6H_4$	1	60	oil	—
4-$MeOC_6H_4$	0.25	80	85–87	89[b]
2-$O_2NC_6H_4$	1	95	104–105	—
3-$O_2NC_6H_4$	2	84	124–125	123–124[a]
4-$O_2NC_6H_4$	2	95	166–168	160[b]
4-$Et_2NC_6H_4$	1	34	138–139	—
2-Pyridyl	4	60	154–155	—

[a] Ref. 6. [b] Ref. 1.

Although aliphatic amines react with the dithiazolium salt **1** no pure products could be isolated, and the analogous imines **5** could only be prepared from **1** by use of the corresponding



bis(trimethylsilyl)amines.[1] We prepared the *N*-Me, *N*-Pr^i and *N*-CH(Me)Ph imines in this way, but could not isolate the *N*-Bu^t compound analogously. The *N*-alkyl imines **5** are less stable than the *N*-aryl compounds **2**, and the *N*-Pr^i compound is less stable to storage than the *N*-Me compound.

Table 2 Conversion of $RN(TMS)_2$ into 5-alkylimino-4-chloro-5*H*-1,2,3-dithiazole **5** with dithiazolium chloride **1**

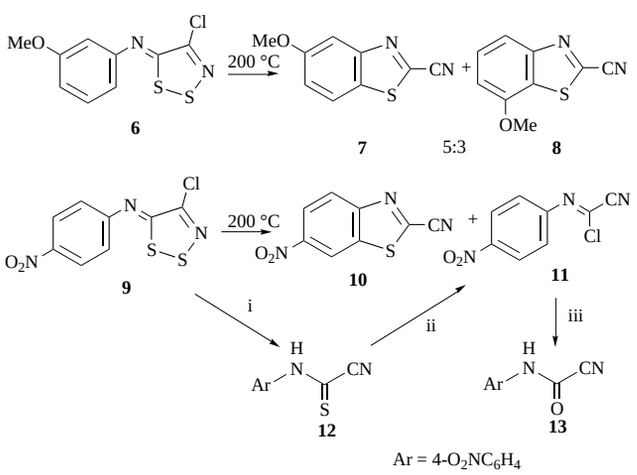
R in $RN(TMS)_2$	*t*/h	Yield of **5** (%)	Mp/°C	Lit. mp/°C
Methyl	2	48	112	112[a]
Isopropyl	1	38	58–60	—
1-Phenylethyl	3	30	39–40	—

[a] Ref. 1.

Thermolyses

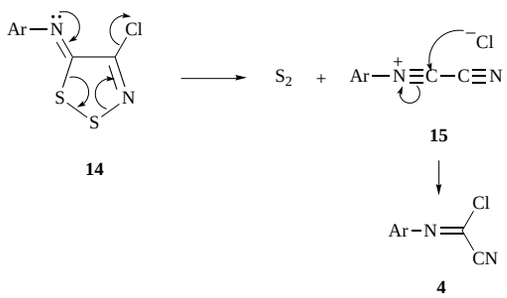
When the neat anilino derivative (**2**, Ar = Ph) was heated under argon at 250 °C for 2 min it melted and gave off gaseous hydrogen chloride; after chromatography, sulfur (S_8, 60%) and 2-cyanobenzothiazole (**3**, R = H) (50%) were isolated. We have proposed a possible mechanism for this reaction [2,3] involving the formation of a bond from an *ortho* carbon of the anilino ring to S(1) of the dithiazole, with extrusion of hydrogen chloride and the S(2) atom, possibly by electrocyclisation and fragmentation processes. The benzothiazole-2-nitrile sulfide may be an intermediate since the direct, unimolecular expulsion of a single sulfur atom is energetically unlikely.

This thermolysis reaction provides a new method for the synthesis of the benzothiazole ring system, and a simple way of converting aniline into 2-cyanobenzothiazole in two steps. We therefore investigated the thermolysis of most of the other imines in Table 1, noting the effect of electron-releasing and withdrawing substituents in the benzene ring. A *m*-methoxy group, in **6**, which releases electrons to the site of cyclisation, increased the rate of thermolysis which was complete within 30 s at 200 °C. The products, 5-methoxy- **7** and 7-methoxy-2-cyanobenzothiazole **8**, were formed in high combined yield (85%), in the ratio of 5:3; the slight selectivity in favour of the 5-methoxy isomer is possibly a steric effect. On the other hand, thermolysis of the *p*-nitro derivative **9** gave only a very low yield (9%) of the corresponding 2-cyano-6-nitrobenzothiazole **10**. The major, unexpected, product isolated from this reaction was a colourless crystalline solid with a molecular ion at *m*/*z* 209 containing one chlorine atom, thus corresponding to the loss of both sulfur atoms from the starting imine, in 54% yield. This product hydrolysed in damp ethanol to give *N*-(4-nitrophenyl)-cyanoformamide **13** suggesting that it is the cyanoimidoyl chloride **11**. The same product was prepared by the reaction of thionyl chloride with *N*-(4-nitrophenyl)cyanothioformamide **12**, obtained from the iminodithiazole **9** by alkaline hydrolysis (Scheme 1). Thermolysis of the analogous imine from *m*-



Scheme 1 *Reagents and conditions:* i, NaOH, H_2O, Me_2CO; ii, $SOCl_2$; iii, H_2O, EtOH

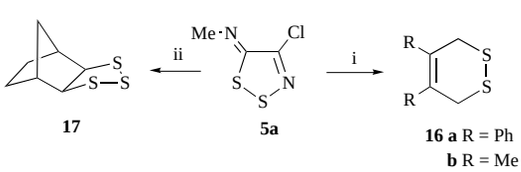
nitroaniline gave the corresponding cyanoimidoyl chloride (63%) together with a 12% yield of a mixture of 5-nitro- and 7-nitro-2-cyanobenzothiazoles which could not be separated by chromatography. The ratio of the two products was 3:1, according to the integration of the ^{1}H NMR spectrum, indicating a somewhat bigger steric effect than in the methoxy case, as would be expected. Whatever the fine details of the reaction mechanism, it seems reasonable that an electron rich benzene ring favours its substitution to form a benzothiazole, whilst an electron deficient ring is not attacked, and the predominant reaction then takes place entirely in the dithiazole ring, with loss of sulfur and shift of chlorine, to form the cyanoimidoyl chloride **4**. The two sulfur atoms could be extruded as singlet diatomic sulfur, as in **14**, to give a nitrilium chloride **15** which then collapses to the observed product (Scheme 2).



Scheme 2

S_2 generation

To favour formation of the cyanoimidoyl chloride and, hopefully, S_2 we needed to suppress benzothiazole formation, for example by blocking the *ortho* positions of the *N*-aryl group or replacing this group by *N*-alkyl. With electron withdrawing *ortho* substituents (2,6-dichloro and 2,4,6-trichloro) the imines **2** were thermally very stable, up to about 300 °C. With electron releasing groups (2,4,6-trimethyl and 2,4,6-triethyl) the imines decomposed at 185–190 °C within 4 min to give S_8 in good yield (*ca*. 70%) and the corresponding cyanoimidoyl chloride **4** in low yield (*ca*. 25%). On the assumption that the S_8 isolated was formed from diatomic sulfur generated by opening of the dithiazole ring, we turned to the less stable *N*-alkyl imines **5** in the hope that they would decompose at a lower temperature, more appropriate to the generation and interception of S_2. The 1-phenylethyl imine **5c** was surprisingly stable and did not decompose significantly at 200 °C; the isopropyl compound **5b** decomposed at 180 °C in 5 min, and the methyl compound **5a** decomposed at 140–150 °C in 5 min. We therefore heated the *N*-methyl imine **5a** at this last temperature, in sealed tubes, with 2,3-diphenylbutadiene, 2,3-dimethylbutadiene and norbornene (Scheme 3).[7] The dienes gave the known S_2 Diels–Alder adducts



Scheme 3 *Reagents and conditions:* i, $H_2C{=}C(R){-}C(R){=}CH_2$, *ca*. 150 °C; ii, norbornene, 140–150 °C

16a and **16b** in isolated yields of 29% and 19% respectively. This compares favourably with most other S_2 precursors but not with Harpp's high-yielding dibenzyloxy disulfides.[8] 3,6-Dihydro-1,2-dithiines **16** are known to polymerise readily at this temperature [9] and their initial yields may have been much higher. Under the same conditions norbornene gave the trisulfide **17** in good yield (62%); this is known to be the ultimate product of the reaction of S_2 with norbornene.[10] We showed that these S_2 adducts, **16** and **17**, were not formed from S_8 and the alkenes under the same conditions.

Thus the application of 4,5-dichloro-1,2,3-dithiazolium chloride **1** chemistry described in this paper provides a simple

route to 2-cyanobenzothiazoles **3** from anilines in two steps, a synthesis of *N*-chlorocyanomethylidene anilines **4**, and a new and useful precursor, **5a**, of diatomic sulfur.

Experimental

Light petroleum refers to the fraction with bp 40–60 °C. Solvents were dried and purified in standard ways. Disulfur dichloride was distilled from elemental sulfur under reduced pressure and stored under nitrogen. 4,5-Dichloro-1,2,3-dithiazolium chloride **1** was prepared by Appel's method[1] but on a smaller scale (one-tenth or less) and with the addition of a catalytic amount (*ca*. 1%) of Adogen 464 to the reaction mixture.

Ultraviolet and infra-red spectra were recorded on a Pye-Unicam SP 800 B and on a Perkin-Elmer 298 spectrometer, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX 270 or a Bruker WM 250 machine in $CDCl_3$ solution. *J*-Values are given in Hz. Mass spectra were measured on a VG Micromass 7070 B or an AE1 MS12 mass spectrometer using electron impact ionisation.

N-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)anilines 2: typical general procedure

4,5-Dichloro-1,2,3-dithiazolium chloride **1** (1.04 g, 5.0 mmol) was added to the aniline (5.0 mmol) in dichloromethane (20 ml) and stirred at room temperature until all the amine was consumed (see time in Table 1). Then pyridine (0.81 ml, 10 mmol) was added and the mixture stirred for a further 2 h, filtered and the product **2** isolated by flash column chromatography with gradient elution from light petroleum to dichloromethane to give the following compounds (see Table 1).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)aniline 2, Ar = C_6H_5.** Yellow needles, λ_{max}(EtOH)/nm 373 (log ε 3.77); $\upsilon_{max}(CCl_4)/cm^{-1}$ 1703, 1598, 1485, 1220, 1143, 908, 861, 846, 693 and 661; δ_H 7.19–7.29 (2 H, m) and 7.43–7.50 (3 H, m); δ_C 119.4, 126.5, 129.8, 147.9, 150.9 and 158.4.

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-4-methylaniline 2, Ar = 4-MeC_6H_4.** Yellow crystals (Found: C, 44.55; H, 2.8; N, 11.6. Calc. for $C_9H_7ClN_2S_2$: C, 44.5; H, 2.9; N, 11.5%); $\upsilon_{max}(CCl_4)/cm^{-1}$ 2984, 1704, 1614, 1588, 1503, 1265, 1223, 1137, 864 and 569; δ_H 2.38 (3 H, s, Me), 7.15 (2 H, d, *J* 8.3, 3-H and 5-H) and 7.27 (2 H, d, *J* 8.3, 2-H and 6-H); δ_C 20.8, 135.7, 138.7, 140.3, 147.0, 148.2 and 159.1; *m/z* 242 (M^+, 66%), 227 ($M^+ - CH_3$, 13), 207 ($M^+ - Cl$, 2), 181 ($M^+ - ClCN$, 30), 149 ($M^+ - ClCNS$, 25), 143 ($M^+ - ClS_2$, 22), 117 ($M^+ - ClCNS_2$, 100), 91 ($M^+ - C_2N_2S_2Cl$, 50) and 90 ($M^+ - HCl$, $N_2C_2S_2$, 17).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,4-dimethylaniline 2, Ar = 2,4-$Me_2C_6H_3$** (Found: C, 46.7; H, 3.2; N, 10.7. $C_{10}H_9ClN_2S_2$ requires C, 46.8; H, 3.5; N, 10.9%); δ_H 2.23 (3 H, s), 2.30 (3 H, s) and 7.02–7.12 (3 H m); δ_C 17.5, 21.1, 115.5, 127.4, 130.6, 131.8, 136.3, 147.2, 147.9 and 156.9; *m/z* 258 (M^+, 13%) and 256 (M^+, 31), 163 (80), 131 (100) and 116 (60).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,4,6-trimethylaniline 2, Ar = 2,4,6-$Me_3C_6H_2$** (Found: C, 49.0; H, 4.1; N, 10.2. $C_{11}H_{11}ClN_2S_2$ requires C, 48.8; H, 4.1; N, 10.35%); δ_H 2.07 (6 H, s), 2.27 (3 H, s) and 6.90 (2 H, s); δ_C 17.2, 20.7, 125.2, 129.5, 134.5, 146.2, 148.8 and 160.8; *m/z* 272 (M^+, 23%) and 270 (M^+, 55), 145 (100) and 130 (68).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,4,6-triethylaniline 2, Ar = 2,4,6-$Et_3C_6H_2$** (Found: C, 53.7; H, 5.4; N, 8.9. $C_{14}H_{17}ClN_2S_2$ requires C, 53.7; H, 5.5; N, 9.0%); δ_H 1.15 (6 H, t), 1.20 (3 H, t), 2.43 (4 H, q), 2.61 (2 H, q) and 7.04 (2 H, s); δ_C 15.4, 16.3, 25.3, 29.2, 127.7, 128.6, 132.1, 142.1, 149.3 and 161.8.

2-Bromo-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)aniline 2, Ar = 2-BrC_6H_4. Yellow needles (Found: C, 31.3; H, 1.8; N, 9.1. $C_8H_4BrClN_2S_2$ requires C, 31.2; H, 1.3; N, 9.1%); $\upsilon_{max}(CCl_4)/cm^{-1}$ 1704, 1604, 1585, 1465, 873, 850 and 675; δ_H 7.07–7.13 (2 H, m), 7.39 (1 H, dt, *J* 1.2, 7.3) and 7.70 (1 H, ddd, *J* 0.7, 1.2, 7.6); *m/z* 306 (M^+, 66%), 245 ($M^+ - ClCN$, 48), 227 ($M^+ - Br$, 12), 213 ($M^+ - ClCNS$, 12), 207 ($M^+ - ClS_2$, 12), 181 ($M^+ - ClCNS_2$, 50), 166 ($M^+ - ClBrCN$, 10), 155 ($M^+ - ClC_2N_2S_2$, 20), 102 (37), 86 (50), 84 (77), 76 ($C_6H_4^+$, 50), 75 ($C_6H_3^+$, 35), 64 (S^{2+}, 81) and 49 (100).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,6-dichloroaniline 2, Ar = 2,6-$Cl_2C_6H_3$** (Found: C, 32.2; H, 0.7; N, 9.3. $C_8H_3Cl_3N_2S_2$ requires C, 32.3; H, 1.0; N, 9.4%); δ_H 7.22 (2 H, m) and 7.56 (1 H, m); δ_C 123.8, 126.7, 129.3, 145.0, 146.1 and 164.8; *m/z* 300 (M^+, 7%), 298 (M^+, 18) and 296 (M^+, 18), 235 (25) and 203 (58).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2,4,6-trichloroaniline 2, Ar = 2,4,6-$Cl_3C_6H_2$** (Found: C, 29.0; H, 0.6; N, 8.4. $C_8H_2Cl_4N_2S_2$ requires C, 28.9; H, 0.6; N, 8.4%); δ_H 7.40 (2 H, s); δ_C 125.4, 128.8, 130.7, 145.2, 146.5 and 164.2; *m/z* 336 (M^+, 2%), 334 (M^+, 8), 332 (M^+, 15) and 330 (M^+, 10) and 271 (13).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-hydroxyaniline 2, Ar = 2-HOC_6H_4.** Yellow crystals (Found: C, 39.0; H, 1.95; N, 11.3. $C_8H_5ClN_2OS_2$ requires C, 39.3; H, 2.1; N, 11.5%); $\upsilon_{max}(CCl_4)/cm^{-1}$ 3431, 3049, 1612, 1590, 1482, 1294, 1258, 1240, 1193, 1142, 871, 861 and 612; δ_H 7.02 (1 H, dd, *J* 1.2, 8.1, 5-H), 7.09 (1 H, dd, *J* 1.2, 8.1, 3 H), 7.10 (1 H, s, OH), 7.28 (1 H, dd, *J* 1.2, 8.1, 4-H) and 7.51 (1 H, dd, *J* 1.2, 8.1, 6-H); *m/z* 244 (M^+, 23%), 208 ($M^+ - Cl$, 14), 145 ($M^+ - ClS_2$, 100), 144 ($M^+ - HClS_2$), 119 ($M^+ - ClCNS_2$, 21), 91 (PhN^+, 16) and 64 (S_2^+, 19).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-methoxyaniline 6.** Orange oil; $\upsilon_{max}(CDCl_3)/cm^{-1}$ 3011, 2942, 2838, 1587, 1482, 1285, 1267, 1160, 864 and 693; δ_H 3.82 (3 H, s), 6.75 (1 H, d, *J* 2.2), 6.80 (1 H, dd, *J* 2.4, 8.1), 6.78–6.83 (1 H, m) and 7.36 (1 H, t, *J* 8.1); *m/z* 258 (M^+, 65%), 243 ($M^+ - CH_3$, 10), 223 ($M^+ - Cl$, 22), 165 ($M^+ - ClCNS$, 22), 159 ($M^+ - ClS_2$) and 133 ($M^+ - ClCNS_2$, 100). Dry hydrogen chloride gas was passed through a solution of this imine in dichloromethane for a few minutes. The yellow precipitate was filtered off to give 4-*chloro*-5-(3-*methoxyphenylamino*)-1,2,3-*dithiazolium chloride*, mp 86–87 °C (Found: C, 36.6; H, 2.6; N, 9.5. $C_9H_8Cl_2N_2OS_2$ requires C, 36.6; H, 2.7; N, 9.5%).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-4-methoxyaniline 2, Ar = 4-$MeOC_6H_4$.** δ_H 3.85 (3 H, s), 6.99 (2 H, d, *J* 8.8) and 7.28 (2 H, d, *J* 8.8).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-nitroaniline 2, Ar = 2-$O_2NC_6H_4$.** Yellow needles (Found: C, 35.2; H, 1.3; N, 15.6. $C_8H_4ClN_3O_2S_2$ requires C, 35.1; H, 1.5; N, 15.4%); $\upsilon_{max}(CDCl_3)/cm^{-1}$ 1603, 1530, 1347, 881, 851, 699 and 679; δ_H 7.13 (1 H, dd, *J* 1.2, 8.3, 6-H), 7.34 (1 H, ddd, *J* 1.2, 7.6, 8.1, 4-H), 7.68 (1 H, ddd, *J* 1.5, 7.6, 8.1, 5-H) and 8.11 (1 H, dd, *J* 1.5, 8.3, 3-H); *m/z* 273 (M^+, 62%), 153 ($M^+ - CN_2OS_2$, 32), 148 ($M^+ - ClCNS_2$, 92), 136 ($M^+ - HS_2NO_2CN$, 66), 125 ($ClCNS_2^+$, 23), 120 (44), 118 ($M^+ - ClCN_2OS_2$, 30), 102 ($M^+ - ClCN_2O_2S_2$, 11), 90 (CNS_2^+, 92) and 64 (S_2^+, 100).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-nitroaniline 2, Ar = 3-$O_2NC_6H_4$** (Found: C, 35.25; H, 1.5; N, 15.5. Calc. for $C_8H_4ClN_3O_2S_2$: C, 35.1; H, 1.5; N, 15.35%); $\upsilon_{max}(CCl_4)/cm^{-1}$ 1596, 1536 and 1355; δ_H 7.52 (1 H, ddd, *J* 1.2, 2.0, 7.8, 6-H), 7.65 (1 H, dt, *J* 0.7, 7.8, 5-H) and 8.08–8.14 (2 H, m, 2-H and 4-H); *m/z* 273 (M^+, 51%), 212 ($M^+ - ClCN$, 26), 132 ($M^+ - ClCNOS_2$, 18), 76 ($C_6H_4^+$, 16), 75 ($C_6H_3^+$, 16), 64 (S_2^+, 100) and 50 ($C_4H_2^+$, 17).

***N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-4-diethylamino-aniline 2, Ar = 4-$Et_2NC_6H_4$.** Dark red crystals (Found: C, 48.3; H, 4.55; N, 14.2. $C_{12}H_{14}ClN_3S_2$ requires C, 48.1; H, 4.7; N, 14.0%); λ_{max}(EtOH)/nm 274 (log ε 4.06), 326 (3.79) and 444 (4.14); $\upsilon_{max}(CCl_4)/cm^{-1}$ 2976, 1608, 1573, 1515, 1357, 1268, 1125, 857 and 509; δ_H 1.20 (6 H, t, *J* 7.1, CH_3), 3.41 (4 H, q, *J* 7.1, CH_2), 6.73 (2 H, d, *J* 9.0, 3-H and 5-H) and 7.36 (2 H, d, *J* 9.3, 2-H and 6-H); *m/z* 299 (M^+, 72%), 284 ($M^+ - CH_3$, 100), 206 ($M^+ - ClCNS$, 17), 191 ($M^+ - ClCNSCH_3$, 49) and 159 ($M^+ - ClCNS_2CH_3$, 13).

2-[*N*-(4-Chloro-5*H*-1,2,3–dithiazol-5-ylidene)amino]pyridine

2, Ar = 2-pyridyl. Yellow crystals (Found: C, 36.5; H, 1.8; N, 18.4. $C_7H_4ClN_3S_2$ requires C, 36.6; H, 1.8; N, 18.4%); λ_{max}(EtOH)/nm 245 (log ε 4.00), 292 (3.68), 387 (4.04), 404 (4.13) and 425 (3.94); $\upsilon_{max}(CCl_4)/cm^{-1}$ 3059, 1569, 1523, 1453, 1449, 1435, 1288, 1269, 1171, 895 and 867; δ_H 7.30 (1 H, ddd, *J* 1.0, 5.1, 7.3, 5-H), 7.69 (1 H, m, 3-H), 7.92 (1 H, ddd, *J* 1.7, 7.3, 8.1, 4-H) and 8.62 (1 H, ddd, *J* 1.0, 1.7, 5.1, 6-H); *m/z* 231 (M^+, 28%), 194 (M^+ − Cl, 83), 78 ($C_5H_4N^+$, 100), 64 (S_2^+, 21) and 51 (24).

4-Chloro-5-methylimino-5*H*-1,2,3-dithiazole 5a. Prepared by the method of Appel *et al.*[1]

4-Chloro-5-isopropylimino-5*H*-1,2,3-dithiazole 5b. A solution of bis(trimethylsilyl)isopropylamine[11] (0.54 g, 2.7 mmol) in dichloromethane (2 ml) was added to the dithiazolium chloride **1** (0.58 g, 2.7 mmol) at room temperature and the mixture was stirred for 1 h. The solvent was removed under reduced pressure and column chromatography of the residue, with hexane–chloroform (2:1) as eluent, gave the *title compound* **5b** as a pale yellow solid (see Table 2) (Found: C, 30.85; H, 3.6; N, 14.3; S, 32.9. $C_5H_7ClN_2S_2$ requires C, 30.8; H, 3.6; N, 14.4; S, 32.9%); δ_H 1.53 (6 H, d, CH_3) and 5.09 (1 H, m, CH); δ_C 21.5 (CH), 54.6 (CH_3), 149.3 (C–Cl) and 174.5 (C=N); *m/z* 194 (M^+).

4-Chloro-5-(1-phenylethylimino)-5*H*-1,2,3-dithiazole 5c. Prepared similarly (see Table 2) (Found: C, 46.7; H, 3.20; N, 10.7. $C_{10}H_9ClN_2S_2$ requires C, 46.6; H, 3.25; N, 10.8%); δ_H 1.89 (3 H, d, *J* 6.5), 6.10 (1 H, q, *J* 6.6) and 7.46 (5 H, m); δ_C 17.8, 60.9, 126.7, 127.8, 129.2, 129.8, 136.7 and 148.9; *m/z* 256 (M^+).

Thermolyses of *N*-arylimines 2

The imines (25 mg to 1 g) were heated under argon under the given conditions and the products were isolated by dry-column flash chromatography on silica with light petroleum–dichloromethane mixtures as eluents.

Imine **2**, Ar = C_6H_5, at 250 °C for 2 min gave sulfur (60%), starting imine (11%) and 2-cyanobenzothiazole **3** (R = H) (50%), mp 77–78 °C (lit.,[12] 71–73 °C); $\upsilon_{max}(CCl_4)/cm^{-1}$ 1477, 1459, 1317, 1265, 1151, 1136, 1125, 741 and 729; δ_H 8.24 (1 H, m), 7.99 (1 H, m) and 7.65 (2 H, m); *m/z* 160 (M^+, 100%) and 108 (M^+ − NCCN, 26).

Imine **2**, Ar = 4-MeC_6H_4, at 190 °C for 4 min gave sulfur (80%) and 2-*cyano*-6-*methylbenzothiazole* (62%), mp 86–88 °C (Found: C, 62.1; H, 3.5; N, 16.1; S, 18.1. $C_9H_6N_2S$ requires C, 62.0; H, 3.5; N, 16.1; S, 18.4%); υ_{max}(NaCl)/cm^{-1} 2260 (CN); δ_H 2.53 (3 H, s) and 7.44–8.04 (3 H, m); δ_C 21.0 (CH_3), 113.0 (CN), 121.1, 124.4, 129.7, 135.0, 135.5, 139.4 (*C*–CH_3) and 150.2 (C=N); *m/z* 174 (M^+).

Imine **2**, Ar = 2,4-$Me_2C_6H_3$, at 185 °C for 4 min gave sulfur (75%) and 2-*cyano*-4,6-*dimethylbenzothiazole* (57%), mp 99–101 °C (Found: C, 63.6; H, 4.1; N, 14.9. $C_{10}H_8N_2S$ requires C, 63.8; H, 4.3; N, 14.9%); υ_{max}(NaCl)/cm^{-1} 2260 (CN); δ_H 2.48 (3 H, s), 2.69 (3 H, s), 7.20 (1 H, s) and 7.50 (1 H, s); δ_C 17.9 (Me), 21.6 (Me), 113.2 (CN), 118.4, 129.9, 133.6, 134.7, 135.5, 139.4 and 149.9 (C=N); *m/z* 188 (M^+, 84%) and 173 (100).

Imine **2**, Ar = 2,4,6-$Me_3C_6H_2$, at 185 °C for 4 min gave sulfur (67%) and N-(*chlorocyanomethylidene*)-2,4,6-*trimethylaniline* **4** (Ar = 2,4,6-$Me_3C_6H_2$) (22%) as a yellow oil; υ_{max}(NaCl)/cm^{-1} 2250 (CN); δ_H 2.39 (6 H, s, CH_3), 2.65 (3 H, s, CH_3) and 6.93–7.02 (2 H, m); δ_C 17.1 (CH_3), 20.7 (CH_3), 111.5 (CN), 117.1, 125.3, 128.9, 136.0 and 140.7; *m/z* 206 (M^+, 10%) and 208 (M^+, 3), 144 (19) and 130 (26).

Imine **2**, Ar = 2,4,6-$Et_3C_6H_2$, at 185 °C for 4 min gave sulfur (71%) and N-(*chlorocyanomethylidene*)-2,4,6-*triethylaniline* **4** (Ar = 2,4,6-$Et_3C_6H_2$) (31%) as a yellow oil (Found: C, 67.8; H, 6.7; N, 11.3; Cl, 14.2. $C_{14}H_{17}ClN_2$ requires C, 67.6; H, 6.9; N, 11.3; Cl, 14.3%); υ_{max}(NaCl)/cm^{-1} 2250 (CN); δ_H 1.16–1.31 (9 H, m, CH_3), 2.40–2.70 (6 H, m, CH_2) and 6.88–7.01 (2 H, m); *m/z* 248 (M^+).

Imine **6** at 200 °C for 30 s gave sulfur (83%), 2-cyano-7-methoxybenzothiazole **8** (33%), mp 106–108 °C (lit.,[13] 108–109 °C) (Found: M^+, 190.0201. $C_9H_6N_2OS$ requires *M*, 190.0201); $\upsilon_{max}(CCl_4)/cm^{-1}$ 2940, 2236, 1568, 1485, 1174, 1439, 1282, 1263, 1141, 1100 and 718; δ_H 4.03 (3 H, s, CH_3), 7.01 (1 H, dd, *J* 0.7, 8.1, 6-H), 7.59 (1 H, dd, *J* 8.1, 8.3, 5-H) and 7.83 (1 H, dd, *J* 0.7, 8.3, 4-H); *m/z* 190 (M^+, 100%), 175 (M^+ − CH_3, 45), 147 (M^+ − CH_3OC, 38), 95 (13) and 69 (20) followed by 2-cyano-5-methoxybenzothiazole **7** (52%), mp 99–100 °C (lit.,[13] 97.5–99 °C) (Found: C, 56.9; H, 3.05; N, 14.5. Calc. for $C_9H_6N_2OS$: C, 56.8; H, 3.2; N, 14.7%); $\upsilon_{max}(CCl_4)/cm^{-1}$ 2961, 2235, 1604, 1477, 1467, 1432, 1419, 1335, 1276, 1247, 1205, 1166, 1149, 1128, 1026 and 844; δ_H 3.92 (3 H, s, CH_3), 7.27 (1 H, dd, *J* 2.4, 9.0, 6-H), 7.62 (1 H, d, *J* 2.4, 4-H) and 7.82 (1 H, d, *J* 9.0, 7-H); *m/z* 190 (M^+, 100%), 175 (M^+ − CH_3, 41), 160 (M^+ − CH_2O, 11), 147 (M^+ − CH_3OC, 30), 95 (13) and 69 (15).

Imine **9** at 200 °C for 2 min gave sulfur (77%), N-(*chlorocyanomethylidene*)-4-*nitroaniline* **11** (54%), mp 76–77 °C (Found: M^+, 208.9992. $C_8H_4ClN_3O_2$ requires *M*, 208.9992); $\upsilon_{max}(CDCl_3)/cm^{-1}$ 1573, 1345 and 1331; δ_H 7.19 (2 H, d, *J* 8.8) and 8.35 (2 H, dt, *J* 2.4, 9.0); *m/z* 209 (M^+, 69%), 179 (M^+ − NO, 14), 174 (M^+ − Cl, 100), 122 (M^+ − ClNCCN, 18), 76 ($C_6H_4^+$, 38), 75 ($C_6H_3^+$, 44) and 50 (40) followed by 2-*cyano*-6-*nitrobenzothiazole* **10** (9%), mp 55–56 °C (Found: C, 47.1; H, 1.5; N, 20.2. $C_8H_3N_3O_2S$ requires C, 46.8; H, 1.5; N, 20.5%); $\upsilon_{max}(CCl_4)/cm^{-1}$ 3109, 3082, 2862, 2242, 1655, 1606, 1592, 1529, 1488, 1347, 1111, 1049, 865, 857 and 676; δ_H 8.38 (1 H, dd, *J* 0.5, 9.0, 4-H), 8.52 (1 H, dd, *J* 2.2, 9.0, 5-H) and 8.96 (1 H, dd, *J* 0.5, 2.2, 7-H); *m/z* 205 (M^+, 100%), 175 (M^+ − NO, 29), 159 (M^+ − NO_2, 60), 147 (M^+ − SCN, 22), 107 [M^+ − $NO_2(CN)_2$, 42] and 63 [M^+ − $NO_2(CN)_2CS$, 29].

Imine **2**, Ar = 3-$O_2NC_6H_4$, at 200 °C for 1 min gave sulfur (70%), N-(*chlorocyanomethylidene*)-3-*nitroaniline* (63%), mp 56–57 °C (Found: C, 45.8; H, 1.9; N, 20.1. $C_8H_4ClN_3O_2$ requires C, 45.85; H, 1.9; N, 20.05%); $\upsilon_{max}(CCl_4)/cm^{-1}$ 3093, 2242, 1651, 1538, 1352, 1048, 820, 742 and 680; δ_H 7.44 (1 H, ddd, *J* 8.1, 2.0, 1.0, 6-H), 7.68 (1 H, t, *J* 8.2, 5-H), 8.00 (1 H, t, *J* 2.1, 2-H) and 8.22 (1 H, ddd, *J* 8.2, 2.1, 0.9, 4-H); *m/z* 209 (M^+, 58%), 174 (M^+ − Cl, 100), 163 (M^+ − NO_2, 14), 122 [M^+ − $Cl(CN)_2$, 12], 102 (M^+ − $ClCNNO_2$, 13), 76 ($C_6H_4^+$, 25), 75 (33) and 50 (24), followed by the starting imine (19%) and a mixture of 2-cyano-5-nitrobenzothiazole and 2-cyano-7-nitrobenzothiazole 12%; 3:1 ratio by ^{1}H NMR integration (Found: C, 47.0; H, 1.6; N, 20.3. $C_8H_3N_3O_2S$ requires C, 46.8; H, 1.5; N, 20.5%); *m/z* 205 (M^+, 100%).

Thermolysis of 4-chloro-5-methylimino-5*H*-1,2,3-dithiazole 5a

With 2,3-diphenylbuta-1,3-diene. The imine **5a** (0.3 g, 1.8 mmol) and diene (2.6 g, 12.6 mmol) were heated at 140–150 °C for 3 h in a sealed tube. Chromatographic separation (silica, heptane–dichloromethane) gave 4,5-diphenyl-3,6-dihydro-1,2-dithiine **16a** (0.14 g, 29%), mp 100–103 °C (lit.,[14] mp 101–102 °C); δ_H 3.58 (4 H, s) and 7.06–7.25 (10 H, m) (lit.,[15] 3.67 and 7.10–7.25).

With 2,3-dimethylbuta-1,3-diene. The imine **5a** (0.3 g, 1.8 mmol) and diene (1.0 g, 12.6 mmol) were heated at 150–160 °C for 3 h in a sealed tube. Chromatography as above gave 4,5-dimethyl-3,6-dihydro-1,2-dithiine **16b** as a yellow oil (49 mg, 19%); δ_H 1.75 (6 H, s, CH_3) and 3.21 (4 H, s, CH_2) (lit.,[16] 1.78 and 3.21).

With norbornene. The imine **5a** (0.3 g, 1.8 mmol) and norbornene (1.18 g, 12.6 mmol) were heated at 140–150 °C for 1.5 h in a sealed tube. Chromatography as above gave the trisulfide **17** as a yellow oil (0.11 g, 62%); *m/z* 190 (M^+); δ_H 1.27–1.70 (6 H, m), 2.56 (2 H, m) and 3.62 (2 H, d, *J* 1.8) (lit.,[9] 1.00–2.01, 2.45–2.48 and 3.62).

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