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New Route to 2-Cyanobenzimidazoles*

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Abstract: *N*-Monosubstituted 1,2-diaminobenzenes **4** (R = Me, Ph, $PhCH_2$, and 3,4-$Me_2C_6H_3CH_2$) react with 4,5-dichloro-1,2,3-dithiazolium chloride **1** in dichloromethane at room temperature to give the corresponding 2-cyanobenzimidazoles **6**. If pyridine is added at the beginning of the reaction, the intermediate imino-1,2,3-dithiazoles **5** can be isolated. Upon thermolysis, most of the imines **5** give the 2-cyanobenzimidazoles **6** in fair to good yields. 1,2-Diaminobenzene can be converted in high yield into the mono-imine **5i** or the bis-imine **12**, R = H; thermolysis of **5i** gives 2-cyanobenzimidazole in high yield. Conversion of **5** into **6** involves the loss of both sulfur atoms and with the *N*-phenylimino derivative **5b** singlet diatomic sulfur, S_2, has been intercepted with norbornene and with 2,3-diphenylbutadiene to give the expected cycloadducts **7** and **8**.

The most common route to benzimidazoles is the acid catalysed condensation of 1,2-diaminobenzenes with carboxylic acids and their derivatives.[1] This general method has been widely applied to the synthesis of 2-alkyl, aryl, amino, hydroxy and mercapto derivatives, many of which have useful biological activity.[2] However this method has been used much less for benzimidazoles with carbon-based functional groups in the 2-position,[3] such as the 2-cyano compounds which are surprisingly rare,[4] in spite of their obvious potential as synthetic intermediates. We have discovered a very simple, direct route to 2-cyanobenzimidazoles in the reaction of 1,2-diaminobenzenes with 4,5-dichloro-1,2,3-dithiazolium chloride **1**.[5]

4,5-Dichloro-1,2,3-dithiazolium chloride **1**, which is readily prepared from chloroacetonitrile and disulfur dichloride, reacts with anilines in the presence of pyridine to give *N*-arylimines **2**.[6-8] These imines show

* Dedicated with admiration and affection to Alan Katritzky on the occasion of his 70th birthday.

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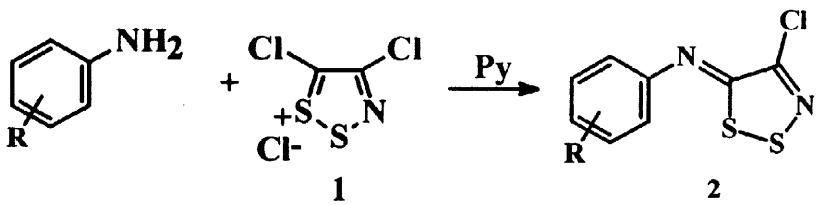
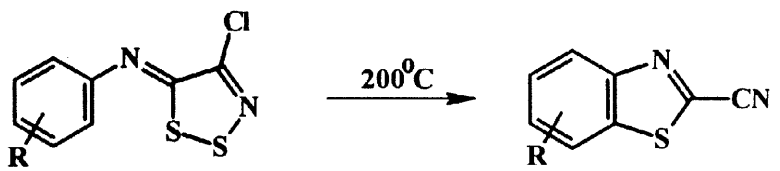


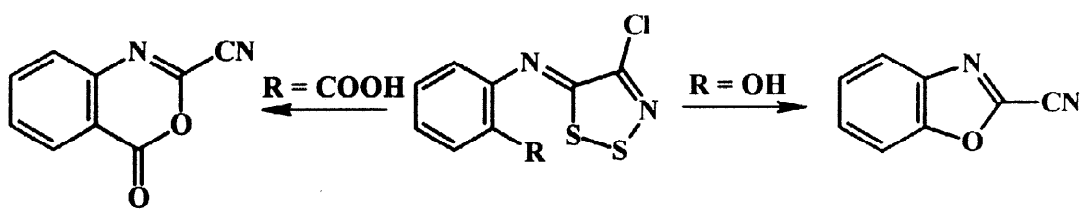
1 2

interesting biological activity[9] and have considerable synthetic utility.[7-10] For example, previous work showed that imines **2** cyclised from an *ortho*-carbon onto sulfur when vigorously heated, to give 2-cyanobenzothiazoles **3**, sulfur and hydrogen chloride.[7,8] At the same time, if the aryl ring had a nucleophilic *ortho*-substituent (e.g. R =

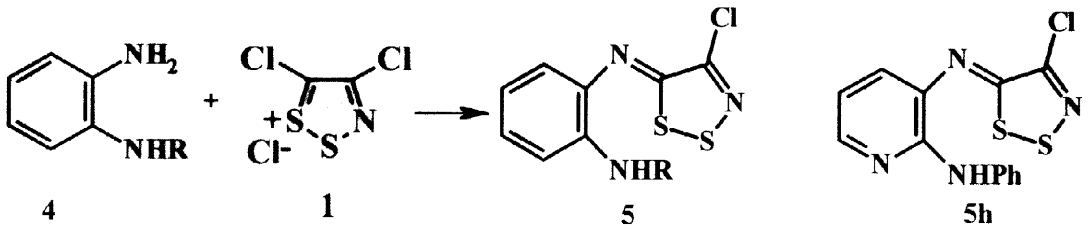


2 3

OH, COOH), cyclisation involved attack of this nucleophile at the imino-carbon to form a new heterocyclic ring with loss of both sulfur atoms from the dithiazole ring.[10b] It is now shown that with *o*-amino groups, as in **5**, 2-cyanobenzimidazoles are readily formed.



The standard method for preparing the *N*-arylimines **2** involves stirring the primary amine with the salt **1** in DCM at room temperature, followed by the addition of pyridine (2 equiv) after 30min.[7] This proved to be unsuitable for the preparation of some of the *o*-aminophenylimines **5**, since these started to cyclize to the benzimidazoles **6** under the developing acidic conditions. However, if pyridine (2 equiv) was added at the beginning of the reaction, preferably with tetrahydrofuran (THF) as solvent, the intermediate imines **5** could be isolated, mostly in very good yield, after 1 to 5 hours at room temperature. An analogous procedure was used for the synthesis of the anilinopyridylimino-1,2,3-dithiazole **5h**.

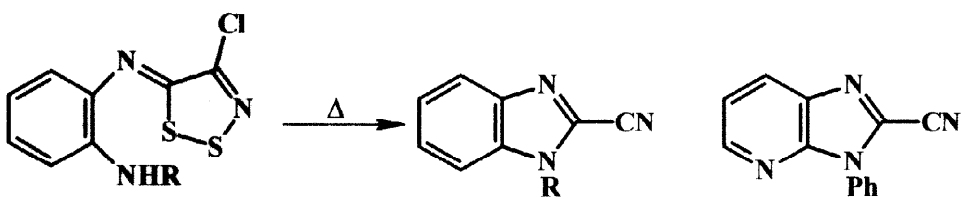


4 1 5 5h

a R = Me (36%) **d** R = 2,4-$(O_2N)_2C_6H_3$ (68%) **g** R = cyclohexyl (70%)
b R = Ph (79%) **e** R = 4-Me-2-pyridyl (62%) **i** R = H (70%)
c R = 4-ClC_6H_4 (79%) **f** R = 3-O_2N-2-pyridyl (80%)

However when R = $PhCH_2$ or 3,4-$Me_2C_6H_3CH_2$ we failed to isolate the imines **5** even in these conditions because of their rapid cyclisation to the benzimidazoles **6** (see below).

Table 1. Thermolysis of *N*-Arylimines **5** to give Benzimidazoles **6**



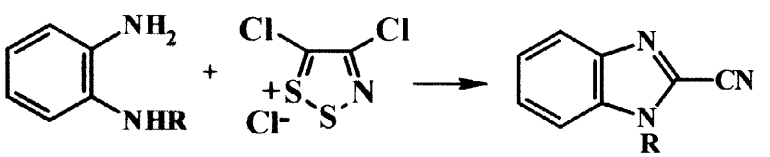
5 6 6h

5	R	Reaction temperature, °C	Solvent	Reaction time, min	Yield (%) of **6**
5a	CH_3	80°	C_6H_6	10	70
5b	C_6H_5	110°	C_6H_5Me	10	69
5c	4-ClC_6H_4	139°	$C_6H_4Me_2$	60	75
5e	4-Me-2-pyridyl	150°	neat	45	30
5g	C_6H_{11}-cyclo	155-160°	neat	120	32
5h	see text	139°	$C_6H_4Me_2$	150	85
5i	H	139°	$C_6H_4Me_2$	120	80

Upon thermolysis most of the imines **5** gave the corresponding 2-cyanobenzimidazoles **6** in fair to good yields (Table 1). Reaction conditions ranged from boiling in benzene for 10 min (**5a**) to heating neat at 160°C for 2h (**5g**). As expected, the more nucleophilic imines rearranged at lower temperatures, and the very poorly nucleophilic dinitroanilino compound **5d** and nitropyridylamino compound **5f** failed to react at temperatures up to 180°C. Imine **5h** gave the imidazo[5,4-*b*]pyridine **6h** analogously, in high yield. The thermolysis results are given in Table 1.

In some cases the *N*-arylimines **5** were found to rearrange to the benzimidazoles **6** in solution (DCM) at room temperature; thus **6a**, **6b**, and **6c** were isolated in 31, 93 and 80% yield respectively. This was traced to the pronounced catalytic effect of hydrogen chloride upon this rearrangement. Addition of pyridine (2 equiv) to the reaction mixture suppressed the spontaneous reaction, and if a little dry hydrogen chloride gas was bubbled into the reaction solution, benzimidazole formation was very rapid.

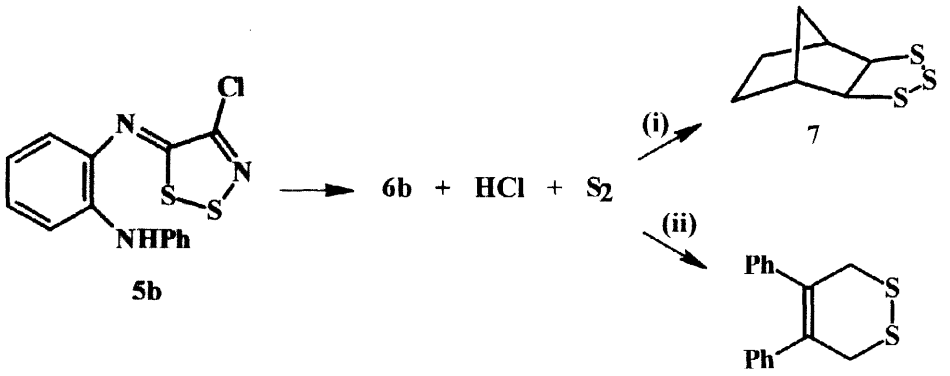
By omission of pyridine it was possible to convert the amines **4** into the benzimidazoles **6** in one step, without isolation of the imines **5**. This worked for amines without electron withdrawing groups, at room temperature in DCM over 24-48h; thus **4** (R = Me, Ph, $PhCH_2$ and 3,4-$Me_2C_6H_3CH_2$) gave the corresponding benzimidazoles **6** in yields of 30-70%.



4 **1** **6**

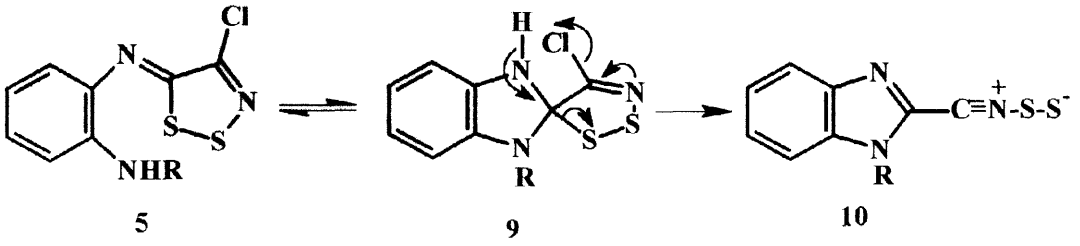
a R = Me **b** R = Ph **k** R = $PhCH_2$ **l** R = 3,4-$Me_2C_6H_3CH_2$

The transformation of **5** into **6** requires the formal loss of S_2 and HCl and it is possible that the sulfur atoms are actually extruded as singlet diatomic sulfur, S_2.[11] Whenever 2-cyanobenzimidazoles were formed S_8 was also formed and could be isolated in high yield, up to 95% from **5a**, **b**, and **c**. In an attempt to intercept S_2 the imine **5b** was heated in neat norbornene at 140-150°C for 4h in a sealed tube; benzimidazole **6b** was isolated (72%) together with the 1,2,3-trithiole **7** (78%) which is known to be characteristic of the reaction of S_2 with norbornene.[12] Decomposition of imine **5b** in the presence of norbornene in boiling toluene, did not give the trithiole **7** although benzimidazole **6b** was formed (69%). Similarly, in the presence of 2,3-diphenylbutadiene the S_2 Diels-Alder adduct **8**[11] (25%) was obtained after reaction at 140-150°C for 3h in a sealed tube; in toluene solution **8** was not produced although the benzimidazole **6b** was again formed. Similar results were obtained



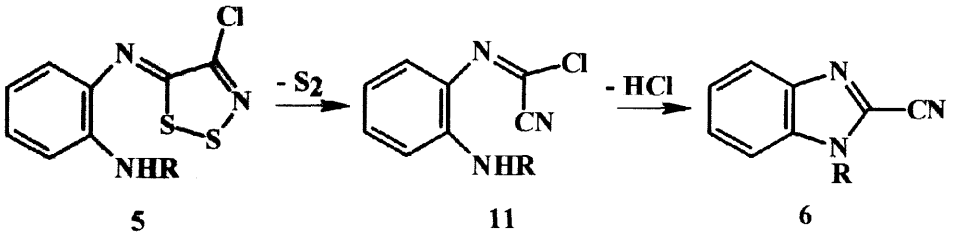
(i) norbornene (ii) 2,3-diphenylbuta-1,3-diene

with the (less stable) methylamino-imine **5a**. In experiments where S_8 was formed but S_2 was not intercepted, it is possible that the reaction may involve reversible attack of the *o*-amino group on the dithiazole ring to give the spiro compound **9** which aromatises with loss of HCl to give the nitrile disulfide **10** which could undergo extension of the sulfur chain, with final formation of S_8 (Scheme 1). At the higher temperature the spiro compound **9** might fragment completely to the 2-cyanobenzimidazole, HCl and S_2; alternatively, S_2 could be extruded directly from **5**, with formation of the cyanoimidoyl chloride **11** which then cyclises to the benzimidazole **6** (Scheme 2). We have previously isolated such cyanoimidoyl chlorides, in the absence of a neighbouring nucleophile, from high temperature decomposition of *N*-arylimino-1,2,3-dithiazoles.[7,8]



$$10 \xrightarrow[-6]{10} \text{Het-C}\equiv\overset{+}{\text{N}}\text{-S}_3\text{-S}^- \xrightarrow[-6]{10} \text{Het-C}\equiv\overset{+}{\text{N}}\text{-S}_5\text{-S}^- \xrightarrow[-6]{10} \text{Het-C}\equiv\overset{+}{\text{N}}\text{-S}_7\text{-S}^- \longrightarrow \text{Het-C}\equiv\text{N} + \text{S}_8$$

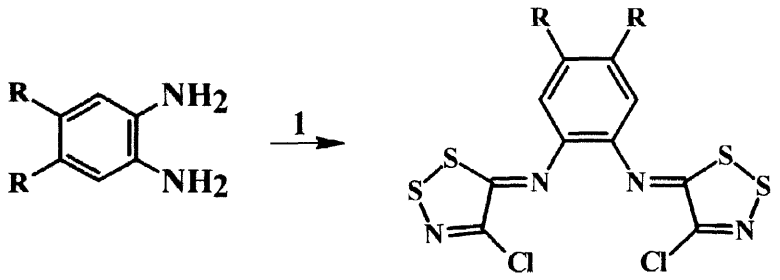
Scheme 1



5 11 6

Scheme 2

In all of above reactions the starting 1,2-diamines are mono-*N*-substituted and react with 4,5-dichloro-1,2,3-dithiazolium chloride **1** only at the primary amino group, to form the corresponding mono-imines **5**. With 1,2-diaminobenzene itself there is the possibility of reaction at both amino groups to form a bis-imine; this happens readily in DCM at room temperature with a 3-fold excess of **1**, to give the bis-imine **12**, R = H, in high yield (81%). Very little of the mono-imine **5i** is isolated under our standard conditions, even with a deficiency of the dithiazolium salt **1**. However, under much more *dilute* conditions the mono-imine **5i** could be isolated in good yield (67-73%, 5 experiments), together with minor amounts (5-8%) of the bis-imine **12**, R = H. This could be achieved with the reagent **1** (1 equiv.) and pyridine (2 equiv.) exactly as for the other amines **4**



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but in 50 ml of THF rather than 5 ml; alternatively a 3-fold excess of 1,2-diaminobenzene over the reagent was used in dilute THF or DCM without the addition of pyridine; the same yields as above were obtained, whether the reagent **1** was added in one portion or was added slowly over 10 h.

Thermolysis of the mono-imine **5i** in boiling xylene for 2h gave the *N*-unsubstituted 2-cyanobenzimidazole **6i** in high yield (80%) together with sulfur. There was no reaction in boiling toluene over the same period of time. The known 2-cyanobenzimidazole is high melting and insoluble and was isolated from the reaction mixture *without* chromatography. Thus this two step preparation of 2-cyanobenzimidazoles from 1,2-diaminobenzenes is probably general for ring substituted *N*-unsubstituted and *N*-mono-substituted derivatives.

1,2-Diamino-4,5-dimethylbenzene gave an 83% yield of the corresponding bis-imine **12**, R = Me, after stirring in DCM with the dithiazolium salt **1** (3 equiv.) for 6h before the addition of pyridine (4 equiv.); shorter reaction times gave more complex mixtures including minor amounts of the mono-imine. 2,3-Diaminopyridine similarly gave a good yield (73%) of the corresponding bis-imine **13**. When 1,2-diamino-4,5-dimethylbenzene

was treated with **1** (1 equiv.) and pyridine (2 equiv.) and the mixture was stirred for 5 days at room temperature, a low yield (16%) of 2-cyano-5,6-dimethylbenzimidazole was formed, again probably *via* the corresponding mono-imine.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 instrument in KBr pellets. ^{1}H NMR spectra were recorded on a Bruker WM 250 spectrometer (250 MHz) and ^{13}C NMR spectra were recorded on a Bruker AM 300 (75.5MHz). Mass spectra were recorded on a AEI MS12 instrument using electron impact ionisation. Light petroleum refers to the fraction bp 40-60°C.

1,2-Diaminobenzene and its *N*-phenyl and *N*-(4-chlorophenyl) derivatives were commercial compounds; the *N*-methyl,[13] *N*-cyclohexyl,[14] *N*-benzyl,[14] *N*-(2,4-dinitrophenyl),[15] *N*-(3-nitropyridin-2-yl),[15] *N*-(4-methylpyridin-2-yl),[16] and *N*-(3,4-dimethylbenzyl)[16] derivatives and 3-amino-2-phenylaminopyridine[17] and 4,5-dichloro-1,2,3-dithiazolium chloride **1**[6] were made by literature procedures.

***5-[N-(2-Substituted aminophenyl)imino]-4-chloro-5H-1,2,3-dithiazoles* 5: general procedure**. 4,5-Dichloro-1,2,3-dithiazolium chloride **1** (205mg, 1mmol) was added to a mixture of amine (1 mmol) and pyridine (158mg, 2mmol) in tetrahydrofuran(5ml) (50 ml for **5i**). The mixture was stirred for the time indicated at ambient temperature. The solvents were removed under reduced pressure and the product **5** was isolated by flash chromatography on silica with gradient elution from light petroleum to dichloromethane.

5-[N-(2-Methylaminophenyl)imino]-4-chloro-5H-1,2,3-dithiazole, **5a**, reaction time 1h, (92mg, 36%), mp 83-84°C.[18] ν_{max} (KBr)/cm^{-1}: 3365 (NH), 3050 (CH), 1590 (C=N), 770 (C-Cl). δ_H ($CDCl_3$)/ppm: 2.82 (3H, s, CH_3); 4.93 (1H, s, NH), 6.66-7.23 (4H, m, Ar). *m/z* 257 (M^+, 11%), 221 (M^+-HCl, 3), 206 (8), 192 (1), 158 (100), 131 (21), 119 (4), 104 (12), 77 (26), 64 (S_2^+, 12).

5-[N-(2-Phenylaminophenyl)imino]-4-chloro-5H-1,2,3-dithiazole, **5b**, reaction time 4h, (250mg, 79%), mp 65°C. (Found: C, 52.42; H, 3.09; N, 13.25. $C_{14}H_{10}ClN_3S_2$ requires C, 52.57; H, 3.15; N, 13.14%). ν_{max} (KBr)/cm^{-1}: 3360 (NH), 2925 (CH), 1580 (C=N), 770 (C-Cl). δ_H ($CDCl_3$ +Py-d_5)/ppm: 7.2-7.6 (9H, m, Ar). *m z* 319 (M^+, 1%), 283 (M^+-HCl, 3), 256 (26), 220 (95), 193 (24), 160 (47), 128 (17), 115 (6), 64 (S_2^+, 100).

5-[N-(2-(4-Chlorophenylamino)phenyl)imino]-4-chloro-5H-1,2,3-dithiazole, **5c**, reaction time 20h, (280mg, 79%), mp 100-102°C (dec). (Found: C, 47.42; H, 2.48; N, 11.62. $C_{14}H_9Cl_2N_3S_2$ requires C, 47.46; H, 2.56; N, 11.86%). ν_{max} (KBr)/cm^{-1}: 3410 (NH), 2920 (CH), 1590 (C=N), 770 (C-Cl). δ_H ($CDCl_3$ +Py-d_5)/ppm: 6.95-7.2 (8H, m, Ar). *m/z* 353 (M^+, 1%), 317 (M^+-HCl, 1), 287 (1), 255 (95), 218 (85), 193 (27), 166 (51), 149 (49), 140 (24), 111 (66), 100 (40), 82 (41), 75 (100), 64 (S_2^+,39).

5 -[N-(2-(2,4-Dinitrophenylamino)phenyl)imino]-4-chloro-5H-1,2,3-dithiazole, **5d**, reaction time 2h, (280mg, 68%), mp 188-190°C. (Found: C 41.64; H 2.18. $C_{14}H_8ClN_5O_4S_2$ requires C 41.03; H 1.95%. ν_{max} (KBr)/cm^{-1}:

3315 (NH), 2920 (CH), 1580 (C=N), 1520 and 1340 (NO_2), 740 (C-Cl). $\delta_H((CD_3)_2SO)$/ppm: 7.4-7.8 (7H, m, Ar). *m/z*: 409 (M^+,1%), 373 (M^+-HCl, 2), 341 (80), 330 (75), 310 (49), 239 (61), 218 (35), 179 (42), 165 (30), 75 (100), 64 (S_2^+, 45).

5-[N-(2-(4-Methylpyridin-2-ylamino)phenyl)imino]-4-chloro-5H-1,2,3-dithiazole, **5e**, reaction time 4h, (210mg, 62%), mp 115-116°C. (Found: C, 50.02; H, 3.02; N, 16.48. $C_{14}H_{11}ClN_4S_2$ requires C, 50.22; H, 3.31; N, 16.73%). n_{max} (KBr)/cm^{-1}: 3310 (NH), 2910 (CH), 1570 (C=N), 765 (C-Cl). d_H ($(CD_3)_2SO$)/ppm: 2.4 (3H, s, CH_3), 7.25 and 8.6 (7H, m, Ar and Py). d_C ($(CD_3)_2SO$)/ppm: 13.76, 116.14, 116.18, 123.25, 125.32, 126.73, 131.86, 136.20, 136.38, 142.60, 146.68, 147.87, 152.30, 160.06. *m/z* 334 (M^+, 2%), 298 (M^+-HCl, 2), 284 (23), 257 (6), 229 (7).

5-[N-(2-(3-Nitropyridin-2-ylamino)phenyl)imino]-4-chloro-5H-1,2,3-dithiazole, **5f**, reaction time 1.5h, (290mg, 80%), mp 178-180°C. Found: C, 42.33; H, 2.36; Cl, 9.24; N, 18.93; S, 17.72. $C_{13}H_8ClN_5O_2S_2$ requires C, 42.68; H, 2.20; Cl, 9.69; N, 19.40; S, 17.53%. ν_{max} (KBr)/cm^{-1}: 3360 (NH), 1610 (C=N), 1505 and 1310 (NO_2), 750 (C-Cl). δ_H ($(CD_3)_2SO$)/ppm: 7.24 and 8.65 (7H, m, Ar), 10.56 (1H, s, NH). δ_C ($(CD_3)_2SO$)/ppm: 114.97, 115.99, 120.54, 123.38, 127.19, 129.22, 132.39, 132.46, 142.52, 147.56, 148.41, 154.81, 159.47. *m/z*: 365 (M^+, 1%), 329 (M^+-HCl, 1), 267 (78), 221 (64), 194 (50), 169 (30), 141 (37), 64 (S_2^+, 53).

5-[N-(2-Cyclohexylamino)phenylimino]-4-chloro-5H-1,2,3-dithiazole, **5g**, reaction time 2h, (230mg, 70%), mp 71-73°C. Found: C, 52.04; H, 5.45; N, 12.86. $C_{14}H_{16}ClN_3S_2$ requires C, 51.61; H, 4.92; N, 12.90%. ν_{max} (KBr)/cm^{-1}: 3380 (NH), 3070 and 2921 (C-H), 1660 (C=N), 740 (C-Cl). $\delta_H(CDCl_3)$/ppm: 1.65 (10H, br. s, CH), 3.45 (1H, m, CH), 5.25 (1H, s, NH), 6.75 - 7.4 (4H, m, Ar). $\delta_C(CDCl_3)$/ppm: 24.48, 25.76, 32.85, 50.86, 110.85, 114.84, 115.87, 129.24, 131.39, 143.30, 149.41, 151.03. *m/z*: 325 (M^+, 2%), 226 (4), 200 (81), 182 (59), 144 (61), 119 (40), 85 (83), 64 (S_2^+, 48).

5-[N-(2-Phenylamino)pyridin-3-ylimino]-4-chloro-5H-1,2,3-dithiazole, **5h**, reaction time 5h, (110mg, 35%), mp 108-110°C. Found: C, 48.79; H, 2.99; N, 17.23. $C_{13}H_9ClN_4S_2$ requires C, 48.67; H, 2.83; N, 17.47%. ν_{max} (KBr)/cm^{-1}: 3360 (NH), 3050 (CH), 1595 (C=N), 775 (C-Cl). $\delta_H(CDCl_3)$/ppm: 6.80 - 8.20 (8H, m, Ar). $\delta_C(CDCl_3)$/ppm: 113.42, 119.29, 122.21, 122.55, 127.83, 128.92, 139.68, 146.59, 149.41, 151.03, 154.54. *m/z*: 320 (M^+, 8%), 284 (M^+-HCl, 5), 255 (1), 226 (20), 221 (100), 194 (28), 77 (12), 64 (S_2^+, 19).

5-[N-(2-Aminophenyl)imino]-4-chloro-5H-1,2,3-dithiazole, **5i**, reaction time 22h , (170mg, 70%), mp 117-119°C (dec). (Found: C, 39.28; H, 2.25; N, 16.94. $C_8H_6ClN_3S_2$ requires C, 39.43; H, 2.48; N, 17.24%). ν_{max} (KBr)/cm^{-1}: 3400 and 3270 (NH_2), 1565 (C=N), 730 (C-Cl). δ_H ($CDCl_3$)/ppm: 4.35 (2H, s, NH_2), 6.81-7.35 (4H, m, Ar). $\delta_C(CDCl_3)$/ppm: 115.82, 116.16, 117.77, 128.91, 133.26, 142.56, 149.32, 153.24. *m/z*: 243 (M^+, 28), 210 (2), 179 (3), 144 (100), 118 (38), 91 (25), 64 (S_2^+, 38).

Thermolysis of imines 5. Imine **5** (1 mmol) was heated under argon in 5ml of boiling benzene (for **5a**), toluene (for **5b**), xylene (for **5c**, **5h** and **5i**) or without solvent in a sealed tube (for the other imines). Solvents were evaporated, and the products were isolated by flash chromatography with gradient elution from light petroleum

to dichloromethane and recrystallised from the mixture of light petroleum-dichloromethane. Product **5i** was isolated by filtration of the cooled reaction mixture and recrystallisation from methanol. The temperature,time, and yields of reactions are given in Table 1.

2-Cyano-1-methylbenzimidazole, **6a**, mp 177-179°C (lit.[19] mp 178-179°C). n_{max} (KBr)/cm^{-1}: 3060 (CH), 2240 (CN), 1540 (C=N). $d_H((CD_3)_2SO)$/ppm: 2.42(3H, s, CH_3), 6.95-7.34(4H, m, Ar). $d_C((CD_3)_2SO)$/ppm: 31.30, 111.52, 111.60, 120.55, 124.00, 125.91, 126.78, 134.74, 141.75. *m/z*: 157 (M^+, 100%), 129 (8), 103 (6), 90 (7), 77 (22).

2-Cyano-1-phenylbenzimidazole, **6b**, mp 85-87°C. Found: C, 76.44; H, 4.30; N, 19.15. $C_{14}H_9N_3$ requires C, 76.70; H, 4.13; N, 19.17%. ν_{max} (KBr)/cm^{-1}: 3060 (CH), 2235 (CN), 1610 (C=N). $\delta_H((CD_3)_2SO)$/ppm: 7.35 - 7.78 (9H, m, Ar). $\delta_C((CD_3)_2SO)$/ppm: 111.04, 111.07, 121.50, 124.72, 125.79, 126.14, 126.91, 129.82, 130.14, 133.66, 134.75, 142.36. *m/z*: 219 (M^+, 100%), 193 (M^+ - CN, 11%), 166 (8), 139 (7), 129 (2), 115 (11), 84 (7).

2-Cyano-1-(4-chlorophenyl)benzimidazole, **6c**, mp 128-130°C. Found: C, 66.27; H, 3.39; N, 16.19. $C_{14}H_8ClN_3$ requires C, 66.01; H, 3.14; N, 16.50%. ν_{max} (KBr)/cm^{-1}: 3040 (CH), 2240 (CN), 1590 (C=N), 760 (C-Cl). $\delta_H((CD_3)_2SO)$/ppm: 7.45-7.55 and 7.75-7.95 (8H, m, Ar). $\delta_C((CD_3)_2SO)$/ppm: 111.43, 111.48, 121.00, 124.80, 126.23, 127.14, 128.30, 130.20, 132.34, 134.53, 134.61, 141.75. *m/z*: 253 (M^+, 100), 226 (3), 218 (15), 193 (4), 166 (7), 149 (10), 140 (4), 111 (11), 100 (7), 90 (2), 82 (6).

2-Cyano-1-(4-methylpyridin-2-yl)benzimidazole, **6e**, mp 151-153°C. Found: C, 71.95; H, 4.51; N, 23.63. $C_{14}H_{10}N_4$. requires C, 71.79; H, 4.27; N, 23.93%. ν_{max} (KBr)/cm^{-1}: 3070 (CH), 2240 (CN), 1545 (C=N). $\delta_H(CDCl_3)$/ppm: 2.63(3H, s, CH_3), 7.35 - 7.6 (7H, m, Ar). $\delta_C(CDCl_3)$/ppm: 15.08, 111.20, 113.01, 117.39, 121.80, 123.10, 123.22, 125.35, 127.89, 128.54, 128.90, 135.85, 137.70, 141.20. *m/z*: 206 (M^+-28, 100%), 173 (5), 160 (12), 125 (7), 97 (10), 71 (21), 69 (6).

2-Cyano-1-cyclohexylbenzimidazole, **6g**, mp 70-71°C. Found: C, 74.58; H, 6.64; N, 18.75. $C_{14}H_{15}N_3$ requires C 74.65; H 6.71; N 18.65%. ν_{max} (KBr)/cm^{-1}: 3060, 2930 and 2860 (CH), 2230 (CN), 1610 (C=N). $\delta_H(CDCl_3)$/ppm: 1.78 (10H, m, 5xCH_2), 4.51 (1H, m, CH), 7.58 (4H, m, Ar). $\delta_C(CDCl_3)$/ppm: 24.90, 25.77, 31.94, 58.13, 109.10, 111.81, 121.76, 124.07, 125.37, 125.82, 133.18, 143.00. *m/z*: 225 (M^+, 100%), 182 (10), 169 (23), 159 (11), 143 (28), 131 (10), 119 (12), 102 (6), 91 (6), 83 (7).

2-Cyano-3-phenyl -3H-imidazo[5,4-b]pyridine, **6h**, mp 150-151°C identical with an authentic specimen.[20]

2-Cyanobenzimidazole, **6i**, mp >300°C with spectroscopic properties identical with those of an authentic specimen.[4]

Rearrangement of imines 5a-c in dichloromethane.

A solution of imine **5a-c** (1mmol) in unpurified dichloromethane (5ml) was stirred at ambient tepmerature for 1-2h, until the imine had disappeared (TLC). The solvent was evaporated, and the products were isolated by flash chromatography with gradient elution from light petroleum to dichloromethane to give the benzimidazoles **6a** (31%), **6b** (93%), **6c** (80%), respectively.

Direct synthesis of benzimidazoles 6 from 1,2-diaminobenzenes.

4,5-Dichloro-1,2,3-dithiazolium chloride **1** (205mg, 1 mmol) was added to a solution of the diamine **4** (1 mmol) in dichloromethane (7.5 ml). The mixture was stirred at ambient temperature until the diamine had disappeared (TLC). The solvent was removed under reduced pressure, and the products were isolated by flash chromatography with gradient elution from light petroleum to dichloromethane to give the benzimidazoles **6a** (31%), **6b** (71%), **6k** (32%) and **6l** (29%).

1-Benzyl-2-cyanobenzimidazole, **6k**, mp 125-126°C. Found: C, 77.35; H, 5.07; N, 18.10. $C_{15}H_{11}N_3$ requires C, 77.25; H, 4.72; N, 18.03%. ν_{max} (KBr)/cm^{-1}: 3030 and 2940 (CH), 2230 (CN), 1580 (C=N). $\delta_H((CD_3)_2CO)$/ppm: 5.75 (2H, s, CH_2), 7.36 - 7.61 (9H, m, Ar). $\delta_C((CD_3)_2CO)$/ppm: 49.60, 112.05, 112.65, 122.26, 125.29, 127.37, 127.81, 128.29, 129.38, 130.04, 135.46, 136.65, 143.79. *m/z*: 233 (M^+, 100%), 206 (12), 136 (9), 103 (11), 91 (7), 71 (23).

2-Cyano-1-(3,4-dimethylbenzyl)benzimidazole, **6l**, mp 158-160°C. Found: C, 78.48; H, 5.44; N, 16.05. $C_{17}H_{15}N_3$. requires C, 78.16; H, 5.75; N, 16.09%. ν_{max} (KBr)/cm^{-1}: 3060 (CH), 2230 (CN), 1580 (C=N). $\delta_H((CD_3)_2SO_)$/ppm: 2.17 (3H, s, CH_3), 2.19 (3H, s, CH_3), 5.62 (2H, s, CH_2), 7.1 - 7.82 (7H, m, Ar). $\delta_C((CD_3)_2SO_)$/ppm: 18.97, 19.36, 48.06, 111.65, 112.04, 120.88, 123.50, 124.34, 124.68, 126.38, 128.35, 129.95, 132.84, 134.10, 136.39, 136.87, 141.95. *m/z*: 261 (M^+, 100%), 130 (8), 119 (6), 104 (9), 91 (7), 77 (20).

Thermolyses of imine 5b.

With norbornene. The imine **5b** (140 mg, 0.46 mmol) and norbornene (300 mg, 3.2 mmol) were heated at 140-150°C for 4 h in a sealed tube. Chromatography as above gave 1,2,3-trithiole **7** as a yellow oil (51 mg, 78%), *m/z*: 190 (M^+) with spectroscopic properties in agreement with the literature values,[11, 12] and benzimidazole **6b** (71mg, 69%), mp 85-87°C.

With 2,3-diphenylbuta-1,3-diene. The imine **5b** (140 mg, 0.46 mmol) and diene (650mg, 3.2 mmol) were heated at 140-150°C for 3 h in a sealed tube. Chromatographic separation as above gave 4,5-diphenyl-3,6-dihydro-1,2-dithiine **8** (30mg, 25%), mp100-103°C (lit.[21] mp 101-102°C), with spectroscopic properties in agreement with the literature values .[22]

N,N'-Bis(4-chloro-5H-1,2,3-dithiazolylidene)-1,2-diaminobenzene, **12**, R = H. To a solution of 1,2-diaminobenzene (250mg, 2.31 mmol) in dichloromethane (30 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (1.44 g, 6.93 mmol). The mixture was stirred at room temperature for 6 h and then pyridine (0.75ml, 9.24 mmol) was added. The mixture was stirred for a further 45 min and then filtered through a short pad of silica gel (C25 mesh), eluting with dichloromethane. The product was purified by flash chromatography on silica gel (C60 mesh), eluting with dichloromethane-light petroleum (b.p. 60-80°C) (1:1) to give the *title compound* (710mg, 81%) as yellow platelets, mp 148-149°C. Found: C, 31.51; H, 1.05; N, 14.62. $C_{10}H_4Cl_2N_4S_4$ requires C, 31.67; H, 1.06; N, 14.77%. ν_{max} (KBr)/cm^{-1}: 3068 (CH), 1599 and 1582(C=N). $\delta_H(CDCl_3)$/ppm: 7.33 (4H, m,

Ar). $\delta_C(CDCl_3)$/ppm: 119.25, 127.55, 141.73, 148.10, 159.03. *m/z*: 378 (M^+, 61%), 285 (65), 253 (36), 192 (69), 160 (90), 134 (38), 64 (S_2, 100).

N,N'-Bis(4-chloro-5H-1,2,3-dithiazolylidene)-4,5-dimethyl-1,2-diaminobenzene, **12**, R = CH_3. 1,2-Diamino-4,5-dimethylbenzene (250 mg, 1.84 mmol) was treated exactly as in the last experiment to give the *title compound* (620mg, 83%) as an orange solid, mp 175-178°C. Found: C, 35.3; H, 1.7; N, 13.7. $C_{12}H_8Cl_2N_4S_4$ requires C, 35.5; H, 2.0; N, 13.8%. ν_{max} (Nujol)/cm^{-1}: 1583(C=N). $\delta_H(CDCl_3)$/ppm: 7.11 (2H, s, Ar), 2.32 (6H, s, 2xAr-CH_3). $\delta_C((CD_3)_2SO)$/ppm: 159.1, 146.7, 139.1, 135.5, 120.0, 19.2. *m/z*: 406 (M^+, 61%), 342 (22), 307 (97), 243 (100), 234 (5), 214 (13), 188 (11), 174 (13), 162 (14), 103 (13), 77 (19), 64 (S_2, 56).

N,N'-Bis(4-chloro-5H-1,2,3-dithiazolylidene)-2,3-diaminopyridine, **13**. 2,3-Diaminopyridine (250 mg, 2.29 mmol) was treated exactly as in the last experiment to give the *title compound* (634mg, 83%) as an orange solid, mp 167-170°C. Found: C, 28.6; H, 0.7; N, 18.6. $C_9H_3Cl_2N_5S_4$ requires C, 28.5; H, 0.8; N, 18.5%. ν_{max} (Nujol)/cm^{-1}: 1601(C=N). $\delta_H(CDCl_3)$/ppm: 8.50 (1H, d J 5Hz, Ar), 7.70 (1H, d J 5Hz, Ar), 7.40 (1H, dd, J 3 and 5Hz, Ar). $\delta_C((CD_3)_2SO)$/ppm: 162.0, 157.5, 148.4, 146.2, 143.6, 142.2, 141.2, 130.0, 122.9. *m/z*: 379 (M^+, 23%), 344 (4), 286 (20), 280 (100), 228 (5), 216 (27), 193 (17), 187 (15), 161 (36), 135 (67), 103 (47), 64(S_2, 89).

2-Cyano-5,6-dimethylbenzimidazole. To a solution of 1,2-diamino-4,5-dimethylbenzene (500 mg, 3.68 mmol) in dichloromethane (30 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (0.77 g, 3.68 mmol). The mixture was stirred at room temperature for 30 min and then pyridine (0.59 ml, 7.36 mmol) was added. The mixture was stirred for a further 5 days and then filtered. The solid was thoroughly washed with dichloromethane-methanol (49:1). The combined filtrates were concentrated *in vacuo* to a gum. The product was purified by flash chromatography on silica gel (C60 mesh), eluting with dichloromethane-methanol (49:1) to give the title compound (103mg, 16%) as needles, m.p.>290°C, identical with an authentic specimen.[23]

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