Cyclopenta-1,2,3-dithiazoles and Related Compounds

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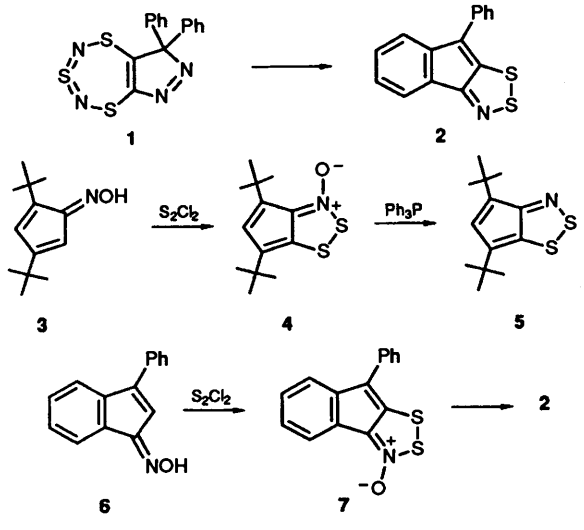
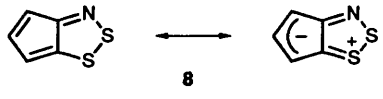
Treatment of 3-phenylinden-1-one oxime **6** with disulfur dichloride gives the indenodithiazole **2** directly in 58%; in the presence of Hünig's base the yield rises to 90%. Indenone oxime **9** and indanone oxime **11** with disulfur dichloride both give the chlorinated indenodithiazole **10**, in up to 80% with Hünig's base. Similarly, cyclopentanone oxime gives the deeply violet trichlorocyclopentadithiazole **13** (*ca.* 25%) at 4 °C in tetrahydrofuran with Hünig's base or in dimethylformamide without added base. A mechanism (see Scheme 1) is proposed for this extensive transformation in which a simple saturated oxime is converted into a highly functionalised heteroaromatic compound by the formation of 7 new bonds; this mechanism is based on the activation to chlorodeprotonation of all the cyclopentane positions, in turn, by the dithiazole ring. Analogously, cycloheptanone oxime **17** gives the red pentachlorocycloheptadithiazole **21**, by the formation of 10 new bonds, and now di-, tri-, and tetrachloro intermediates, **18–20**, can also be isolated; tetrahydrobenzocycloheptenone oxime **22** gives the analogous dichloro **23** and trichloro **24** compounds, and the acyclic oxime **25** gives the monocyclic dithiazole **27**, all in modest yield. The chlorine in compound **10** is displaced by morpholine and pyrrolidine, but similar displacements in the trichloro compound **13** are unsuccessful since its heterocyclic ring is destroyed by nucleophiles. The pentachloro compound **21** is more stable than **13** towards nucleophiles, but less stable towards *m*-chloroperbenzoic acid, and these observations are explained in terms of the dipolar structures **13a** and **21a**.

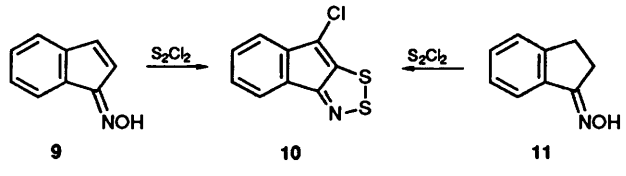
We recently described the pyrolysis of 3,3-diphenyl-3*H*-pyrazolotrithiadiazepine **1** which, in a few seconds at 200 °C, lost N_2 and the elements of HNS and underwent extensive rearrangement to give the deep red 8-phenylindeno[1,2-*d*]-1,2,3-dithiazole **2**.[1] We wished to synthesise this product independently to confirm its novel structure and hopefully to make it, and related compounds, available on a larger scale. This has now been done, based upon a reaction described by Hafner *et al.*[2] which gave the only other cyclopenta-1,2,3-diathiazole known, *i.e.* treatment of the cyclopentadienone oxime **3**, stabilised by two *tert*-butyl groups, with disulfur dichloride (sulfur monochloride, S_2Cl_2) in tetrahydrofuran (THF) at room temperature. The cyclised *N*-oxide **4** so formed was deoxygenated with triphenylphosphine to give the 1,2,3-dithiazole **5** as a violet oil. A similar synthesis of compound **2** would require the oxime **6** of 3-phenylinden-1-one, which was readily prepared by nitrosation[3] of the sodium salt of 3-phenylindene.[4] Treatment of the oxime **6** with disulfur dichloride in refluxing THF gave the desired, deoxygenated product **2** directly, in 58% yield. Presumably the corresponding *N*-oxide **7** had been formed, by reaction of the oxime nitrogen with S_2Cl_2 followed by cyclisation, and deoxygenated by S_2Cl_2 acting as a reducing agent. Thus the stabilising *tert*-butyl groups in the previous example of this reaction are not necessary for the method to be successful.



This simple one-step conversion of an oxime into a dithiazole seemed worthy of further investigation, for its potential synthetic utility and for the interest of the cyclopentadithiazole structure **8** which could be a 10π electron aromatic system, isoelectronic with azulene. Extensive delocalisation in compound **2** is suggested by its deep red colour and its high thermal stability.



Cyclopentadithiazoles.—The indenone oxime **9** similarly gave a dithiazole with S_2Cl_2, but now the unsubstituted position in the cyclopentadiene ring had been chlorinated to give 8-chloroindenodithiazole **10**, as a red crystalline solid; the yield was relatively low (26%), and none of the unchlorinated product was detected. Presumably the reaction pathway is similar to that for formation of the 8-phenyl compound **2**, with the introduction of chlorine either by electrophilic chlorination of the deoxygenated material or by nucleophilic attack by chloride ion on the protonated *N*-oxide.

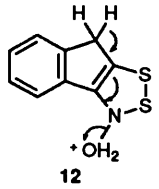


It was of interest to see if the S_2Cl_2 reaction could be extended to more saturated oximes, and so the indanone oxime **11** was treated similarly. This did indeed give the same chloroindeno-

Table 1 Yield of the dithiazole **13** from cyclopentanone oxime and S_2Cl_2 in THF at 4 °C for 72 h in the presence of bases

Base	Equiv of S_2Cl_2 and of base	Yield of **13** (%)
NaOAc	3.75	5
4-Dimethylaminopyridine	3.75	5
Pyridinium toluene-*p*-sulfonate	3.75	12
Pyridine	3.75	12
Pyridine	10.0	17
2,6-Lutidine	3.75	14
Et_3N	3.75	17
$EtNPr^i_2$	3.75	22
$EtNPr^i_2$	10.0	25
No base	—	Trace

dithiazole **10**, as the only product isolable from a complex reaction, though in even lower yield (14%); the S_2Cl_2 has presumably acted as an oxidising and chlorinating agent. In this case the oxime oxygen is likely to be lost by acid-catalysed dehydration of an *N*-hydroxy species (see **12**), to give the unchlorinated product **10** (H for Cl) as an intermediate and this tends to support the notion of chlorine being introduced in a final, electrophilic reaction.



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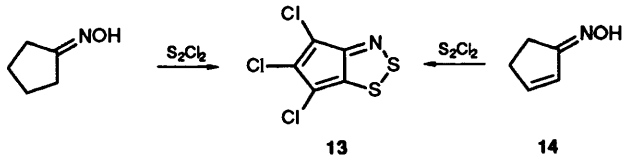
The S_2Cl_2 reaction was attempted on even more saturated systems and the culmination of this was treatment of cyclopentanone oxime with S_2Cl_2 in refluxing THF. This resulted in the fully unsaturated, fully chlorinated compound **13** as deep violet crystals, though in only 8% yield. In this remarkable reaction a very simple oxime has been converted, by the formation of seven new bonds, into a highly functionalised heteroaromatic compound **13**; a mechanism for this is proposed later. Although the product is easily isolated and purified the reaction is complex (TLC) and no other products or intermediates could be isolated.

We next investigated ways to increase the yields of these reactions of oximes with S_2Cl_2 by variation in reactant ratios, solvents, reaction time and temperature, and particularly the influence of bases. When the indenone oxime **9** was treated with S_2Cl_2 (2 equiv.) in THF for 48 h at 4 °C in the presence of base (2 equiv.) the yield of product **10** increased considerably, to 40% with pyridine and to 60% with ethyldiisopropylamine (Hünig's base). Similarly with the indanone oxime **11** and S_2Cl_2 (3.75 equiv.) in THF at 4 °C the yield of **10** increased to 24% (potassium acetate, 2 equiv., 24 h), 40% (pyridine, 3 equiv., 70 h) and 80% (Hünig's base, 3 equiv., 72 h). Surprisingly, the highest yield was obtained starting with the more saturated oxime. When these best conditions were applied to 3-phenylindenone oxime **6** (oxime : S_2Cl_2 : Hünig's base = 1 : 3 : 3; THF, 4 °C, 72 h) the yield of dithiazole **2** increased to 90%.

Unfortunately, these reaction conditions were not as beneficial when applied to cyclopentanone oxime; the yield of trichlorodithiazole **13** was at best increased about three-fold, to 25%, with the non-nucleophilic Hünig's base. The yields with this and other bases are given in Table 1 for reactions of the oxime with S_2Cl_2 in THF at 4 °C for 72 h. The better yields obtained with the less nucleophilic bases possibly arise from reduced reaction between the base and the very electrophilic sulfur species present in the reaction mixture. All of the bases were treated with S_2Cl_2 under the reaction conditions, but in the absence of oxime, and all of them, including Hünig's base, were found to react to some extent with S_2Cl_2 to give insoluble products and sulfur. This could not be compensated for by using a large excess of S_2Cl_2, since the yields were then lower. The effect of changing solvent is shown in Table 2.

The need for a base is clear, for all solvents other than dimethylformamide (DMF) where the yield is the same with and without Hünig's base; presumably dimethylamine is liberated from DMF during the course of the acid-generating reaction. Running the oxime–S_2Cl_2 reaction in dry DMF for 3 days in the cold room was the simplest route to trichlorocyclopenta-1,2,3-dithiazole **13**. But in view of the relatively low yield, other ways of increasing this were explored, though with little success.

Since the oxime hydroxy group was eliminated in the reaction, this was converted into a better leaving group, as the *O*-acetyl, toluene-*p*-sulfonyl, and methyl derivatives. All showed some reactivity towards S_2Cl_2 in DMF at 4 °C for 72 h, but in each case the yield of product **13** was lower than with the oxime itself. Similarly, conversion of the oxime into its sodium or tetrabutylammonium salt, to enhance its reactivity towards S_2Cl_2, led to no increase in product yield. However, the addition of a catalytic amount of tetrabutylammonium chloride to the reaction in DMF did give a slight increase in yield of **13** (29%), the highest obtained for this product. Substantially more dissolved chloride was not beneficial; lithium chloride (3 equiv.) caused a marked reduction in yield, possibly because chloride ion reverses a key reaction.



13 **14**

It was hoped that cyclisation of the initial oxime–S_2Cl_2 intermediate, to form the heterocyclic ring, would be favoured by the presence of a double bond in the carbocyclic ring. Therefore the oxime **14** of cyclopent-2-enone was treated with S_2Cl_2 in DMF; this did give the same dithiazole **13**, but in exactly the same yield (25%) as before.

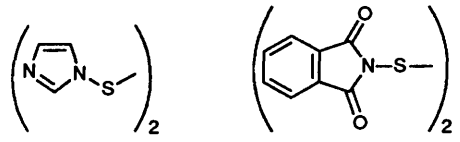
Further attempts to improve the yield of **13** by slow addition of S_2Cl_2 to cyclopentanone oxime, and *vice versa*, over periods from a few hours to a few days, and slow, separate and synchronous addition of both reactants to vigorously stirred DMF, all resulted surprisingly in much lower yields.

Whilst investigating the effect of reaction temperature and time on the conversion of cyclopentanone oxime into the dithiazole **13** in DMF, we found that 3 days at 4 °C was optimum; the yield decreased with longer reaction times and at higher temperatures. For example, after 1 week of stirring at 4 °C very little of the product remained. When larger amounts of S_2Cl_2 and base were used the yield reached its maximum value more rapidly. Presumably, some component of the mixture, most probably S_2Cl_2, was destroying the dithiazole **13**. This was readily confirmed by treating **13** in DMF with cyclopentanone oxime (no reaction), Hünig's base (no reaction), and S_2Cl_2 (decomposition). Indeed the other 1,2,3-dithiazoles produced in this work, such as **2** and **10**, were also decomposed by S_2Cl_2.

In view of this last observation, we decided to replace S_2Cl_2 by milder reagents of the type, X–S–S–X, which would hopefully react with the oxime but not the dithiazole. Three such analogues were prepared from S_2Cl_2: EtOSSOEt,[5] the

Table 2 Yield of dithiazole **13** from cyclopentanone oxime and S_2Cl_2 (4 equiv.) in various anhydrous solvents at 4 °C for 72 h

Solvent	Yield with $EtNPr^i_2$ (4 equiv.) present	Yield without added base
THF	24%	Trace
Et_2O	20%	Trace
CH_2Cl_2	4%	Trace
$CHCl_3$	5%	Trace
C_6H_6	4%	Trace
C_6H_5Me	3%	Trace
DMF	25%	
AcOH	Decomposition	
DMSO	Decomposition	



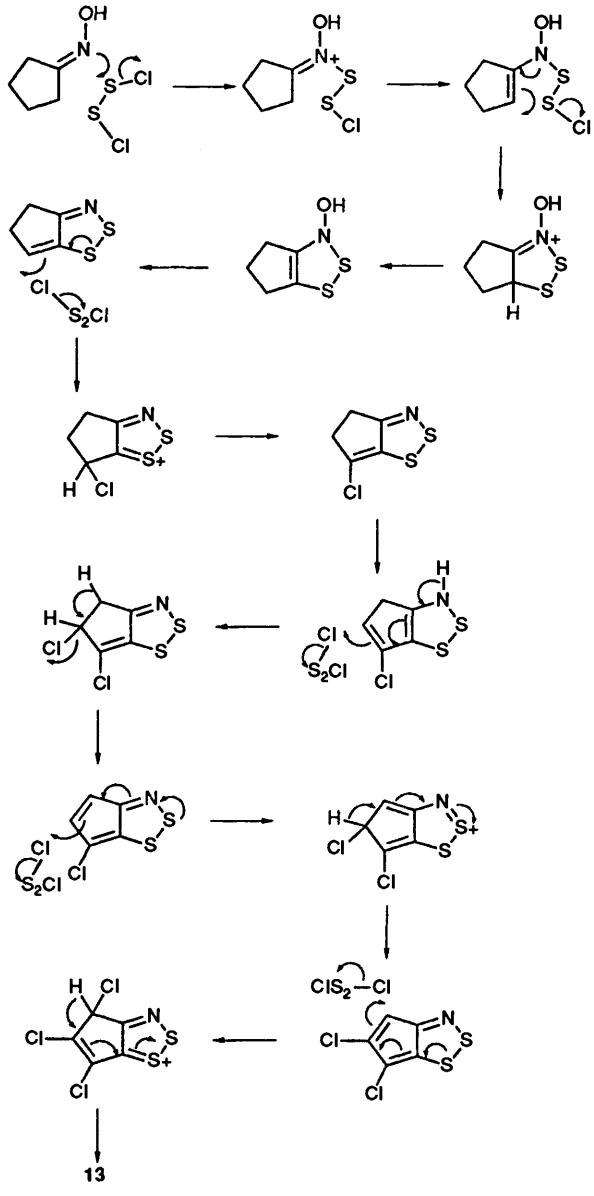
15 **16**

imidazole **15**[6] and the phthalimide **16**.[6] All of these were unreactive towards cyclopentanone oxime in DMF at room temperature. More vigorous conditions, such as heating of the reaction mixture or using the sodium salt of the oxime, resulted in extensive decomposition, and none of the parent dithiazole **8** was isolated.

One final attempt was made to minimise S_2Cl_2-induced decomposition of the product **13**. Only 1 equiv. of S_2Cl_2 is required to form the dithiazole ring, the rest of the S_2Cl_2 (4 equiv. based on the mechanism below) acting as an oxidising and chlorinating agent. We therefore carried out the reaction using just 1 equiv. of S_2Cl_2 together with an excess of *N*-chlorosuccinimide; this gave the dithiazole **13** in undiminished, but not significantly improved, yield (26%). We repeated this reaction with *N*-bromosuccinimide in the hope of producing the tribromo compound analogous to **13**, but no clean products could be isolated. Also unsuccessful was an attempt to produce the unhalogenated cyclopentathiazole **8** by using S_2Cl_2 and an excess of manganese dioxide as oxidant.

Reaction Mechanism.—The conversion of cyclopentanone oxime and S_2Cl_2 into the dithiazole **13**, which is probably catalysed by the hydrochloric acid generated and by the added base, requires the formation of the heterocyclic ring and introduction of two double bonds and three chlorine atoms, seven new bonds in all. A possible mechanism for this is proposed in Scheme 1. This mechanism could, with minor variations, account for the formation of the dithiazoles **2**, and **10**, and others mentioned below. As well as forming the heterocyclic rings, S_2Cl_2 functions as an oxidising–chlorinating agent, facilitated by the ability of the dithiazole sulfur atoms to activate all the positions of the cyclopentane ring to chlorodeprotonation. In all, 5 equiv. of S_2Cl_2 are required, and the relatively low yield presumably stems from the large number of reaction steps involved as well as the sensitivity of the product towards S_2Cl_2.

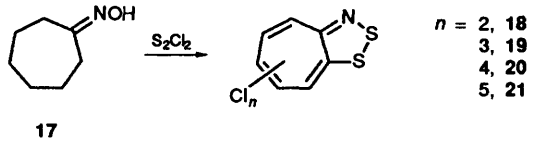
Cycloheptadithiazoles.—In view of the extensive oxidation and chlorination sequence accompanying the reaction of cyclopentanone oxime with S_2Cl_2, it would be of interest to see if a similar, even longer, sequence occurred with cycloheptanone oxime, though now the analogous product, with an extra double bond, is potentially a 12π antiaromatic species. Therefore, the reaction of cycloheptanone oxime **17** with S_2Cl_2 was studied and, in spite of the large number of reaction steps involved, some stable crystalline products have been isolated, though in low



Scheme 1 The formation of dithiazole **13**

yield. Their formation can be rationalised by a reaction sequence very similar to that in the Scheme above.

Thus, when the oxime **17**, S_2Cl_2 and Hünig's base (1:15:15

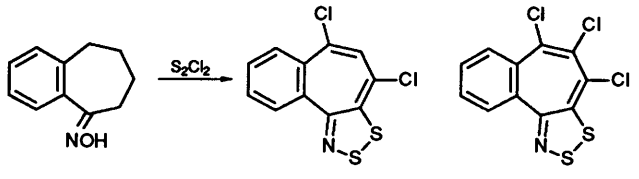


17

respectively) were stirred in THF for 4 °C for 1 day the main product of the reaction was a yellow, partially unsaturated dichloro compound which was not stable in solution and transformed into **18** when set aside for several days. When this oxime–S_2Cl_2 reaction was repeated exactly, but for 3 days, the products were chlorinated derivatives of the fully unsaturated cyclohepta[1,2-*d*]-1,2,3-dithiazole. A dichloro compound **18** (4%) and a trichloro compound **19** (5%) were green, a tetrachloro compound **20** (2%) was brownish green, and the pentachloro compound **21** (2%) was red. Several chromatography column separations were necessary to purify these products and the amounts actually formed were considerably greater than indicated. Cycloheptanone oxime **17** did not react with S_2Cl_2 in

THF at 4 °C when Hünig's base was replaced by polypyridine, but on refluxing this mixture the trichloro compound **19** and pentachloro compound **21** were formed, suggesting that some control over the products formed would be possible by variation of the reaction conditions. When the initial reaction of **17** was repeated, but with the addition of *N*-chlorosuccinimide (10 equiv.), the pentachloro compound **21** was isolated in 14% yield, together with 7% of the tetrachloro compound **20**. From the coupling patterns in the ^{1}H NMR spectra compound **18** is the 4,6- or 6,8-dichloro isomer, compound **19** is probably the 4,6,8-trichloro isomer, and compound **20** is the 4,6,7,8- or 4,5,6,8-tetrachloro isomer. These structures are consistent with our proposed mechamism.

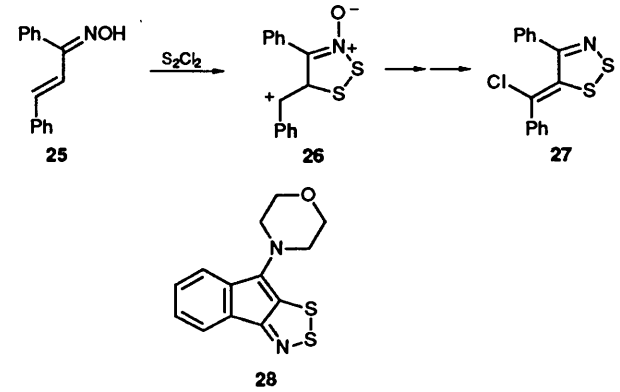
When two of the cycloheptanone ring positions were blocked by benzo fusion, the oxime–S_2Cl_2 reaction was much cleaner: tetrahydrobenzocycloheptenone oxime **22**, S_2Cl_2 and Hünig's base (1:12:12 respectively) were stirred in THF at room temperature for 2 days, and then heated under reflux for 4 h. Chromatography gave one product, an orange–red dichlorobenzocyclohepta[1,2-*d*]-1,2,3-dithiazole in relatively high (35%) yield. This structure is based upon microanalysis, mass spectrometry, ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy (11 signals, 5 corresponding to C–H carbons); the positions of the chlorine atoms are not known for certain, but the 8,10-dichloro isomer **23** seems most likely from mechanistic considerations. When the reaction was repeated in the presence of *N*-chlorosuccinimide the red 8,9,10-trichloro compound **24** was isolated in 29% yield.



22 **23** **24**

Finally, an acyclic example of the oxime–S_2Cl_2 reaction was sought, to extend its scope; benzylideneacetophenone oxime **25** was chosen in the hope that stabilisation of the intermediate carbocation **26** by the phenyl ring would lead to a cleaner, higher-yielding reaction. Thus, the oxime **25** was treated with S_2Cl_2 in DMF or in THF containing Hünig's base; it reacted more rapidly than the cyclic oximes, but in substantially the same way to give the monocyclic dithiazole **27** as a stable, orange crystalline compound. Again deoxygenation, dehydrogenation and chlorination have all occurred, but still in modest overall yield (22–23%); the dithiazole **27** is sensitive to S_2Cl_2.

Even though the yields are variable, the oxime–S_2Cl_2 reactions described above provide ready access to the relatively rare 1,2,3-dithiazole ring system.[7]

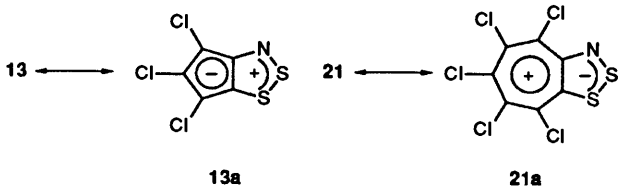


25 **26** **27** **28**

Dithiazole Reactions.—The chlorine atom in the dithiazoles **10** and **27** and all the chlorines in the other dithiazoles could be activated towards nucleophilic displacement by the electron-withdrawing 'imine' bond of the dithiazole ring. Treatment of the red compound **10** with an excess of morpholine in THF at room temperature or at reflux slowly gave a new deep purple compound (20%) assigned structure **28** from microanalysis, mass spectrometry and ^{1}H NMR spectroscopy. A second more polar, unstable red compound was detected in solution by TLC during the reaction. Pyrrolidine reacted with **10** at room temperature in THF over 24 h to give a higher yield (45%) of the analogous pyrrolidino compound. (The unchlorinated dithiazole **2** was inert to pyrrolidine in refluxing THF.) Similar reactions of the trichlorodithiazole **13** with pyrrolidine, piperidine or morpholine at room temperature led to extensive decomposition, as did treatment with KOH, LiSMe, KSCN, and PhSH. There was no reaction however with aniline, *p*-nitroaniline, *p*-methoxyaniline, all in dichloromethane at room temperature, potassium carbonate in ethanol, or with sodium iodide in refluxing acetone.

Attempted *S*-oxidation of dithiazole **13**, by analogy with other 1,2,3-dithiazoles,[1,8] with *m*-chloroperbenzoic acid, magnesium monoperphthalate, oxone, dinitrogen tetroxide, or sodium periodate all led to extensive decomposition and no products could be isolated.

This ready decomposition of the trichlorocyclopentadienodithiazole **13** by nucleophiles is in striking contrast to the more stable pentachlorocycloheptatrienodithiazole **21**. When treated with morpholine in dichloromethane or tetrahydrofuran at room temperature, the former decomposes to 'base-line' material over a few hours whilst the latter is unchanged. Displacement of chlorine by morpholine is not observed with either under these conditions, and decomposition of **13** is probably initiated by nucleophilic attack on heterocyclic sulfur. This difference between **13** and **21** can be explained by considering the resonance contributions of the cyclopentadienyl anion **13a** and the tropylium cation **21a** to their respective structures. Although the former is potentially 10π aromatic and the latter 12π antiaromatic, the heterocyclic ring in **13a** would presumably be much more susceptible to nucleophilic attack, and hence decomposition, than in **21a**. Conversely, the colour of **21** is destroyed much faster by *m*-chloroperbenzoic acid in cold dichloromethane than is that of **13**.



13a **21a**

This reversed polarisation of the 5-5 and 5-7 fused ring systems would also explain the varying ease of chlorination of the carbocyclic rings in the two systems. In the former, complete chlorination of the electron rich 5-membered ring is observed (products **10** and **13**) without the isolation of partly chlorinated products. In the latter, chlorination of the electron-poor 7-membered ring would be slower and incompletely chlorinated intermediates, such as **18–20** and **23**, can now be isolated.

Experimental

M.p.s were determined using a Kofler hot-stage apparatus and are uncorrected. UV and visible spectra were recorded using a Pye Unicam SP 800B spectrometer. IR spectra were recorded either on Perkin-Elmer 298 or Perkin-Elmer 1710 instruments.

^{1}H NMR spectra were recorded on a JEOL GSX 270 or a Bruker WM 250 spectrometer. ^{13}C NMR spectra were recorded on a Bruker WM 250 operating at 63 MHz, with broad-band decoupling and assignment of secondary, tertiary and quaternary carbons by the DEPT pulse sequence. Mass spectra were recorded on a AE MS12 or a VG micromass 7070B mass spectrometer; M refers to the isotopomer with the most abundant isotopes (^{35}Cl and ^{32}S). Column chromatography was on silica gel (C60). Light petroleum refers to the fraction b.p. 40–60 °C.

3-*Phenylinden*-1-*one Oxime* **6**.—3-Phenylindene[4] (3.65 g, 19 mmol) in liquid ammonia (100 cm^3) was treated with sodium amide (0.76 g, 20 mmol) followed by pentyl nitrite (2.68 g, 22 mmol). The mixture was stirred for 1 h and then ammonium chloride (3.1 g) was added and the solvent allowed to evaporate. The residue was dissolved in an ether–water bilayer and the aqueous portion was extracted with ether. The combined ether extracts were dried ($MgSO_4$) and evaporated and the residue subjected to flash chromatography; dichloromethane eluted the *title compound* (2.74 g, 65%) as a yellow solid, m.p. 111–113 °C (from light petroleum–dichloromethane) (Found: C, 81.4; H, 5.05; N, 6.2. $C_{15}H_{11}NO$ requires C, 81.45; H, 5.0; N, 6.3%); ν_{max}/cm^{-1} (CCl_4) 2959s, 3207s, 1360w and 965vs; δ_H(250 MHz; $CDCl_3$) 7.2–7.8 (10 H, m, ArH) and 10.1–10.4 (1 H, s, OH); *m*/*z* (100 °C) 221 (M^+, 100%) and 204 (M^+ − OH, 16).

8-*Phenylindeno*[1,2-d]-1,2,3-*dithiazole* **2**.—Disulfur dichloride (1.12 cm^3, 14 mmol) was added to a stirred, cold (−50 °C) solution of 3-phenylinden-1-one oxime **6** (1 g, 4.52 mmol) and ethyldiisopropylamine (Hünig's base, 2.36 cm^3, 13.6 mmol) in tetrahydrofuran (75 cm^3) and the mixture was stirred at 4 °C for 72 h. The solvent was removed under reduced pressure and column chromatography of the residue (light petroleum) gave the title compound **2** (1.09 g, 90%) identical with that previously described.[1]

8-*Chloroindeno*[1,2-d]-1,2,3-*dithiazole* **10**.—(a) *From indan*-1-*one oxime*. Disulfur dichloride (2.04 cm^3, 25.5 mmol) was added to a stirred, cold (−50 °C) solution of indan-1-one oxime **11** (1 g, 6.8 mmol) and ethyldiisopropylamine (3.55 cm^3, 20.4 mmol) in tetrahydrofuran (75 cm^3) and the mixture was stirred at 4 °C for 72 h. The solvent was removed under reduce pressure and column chromatography of the residue (light petroleum) gave the *title compound* **10** (1.24 g, 80%) as a deep red solid, m.p. 107–109 °C (decomp) (from light petroleum–dichloromethane) (Found: C, 47.6; H, 1.7; N, 6.1. $C_9H_4ClNS_2$ requires C, 47.9; H, 1.8; N, 6.25%); λ_{max}/nm (EtOH) 287 (log ε 3.77), 305 (3.75), 347 (3.64) and 486 (3.27); ν_{max}(CCl_4)/cm^{-1} 1608s, 1537s, 1446s, 1245s and 1117m; δ_H(270 MHz; $CDCl_3$) 7.96 (1 H, d, *J* 7.65), 7.51 (1 H, d, *J* 7.65) 7.40 (1 H, d, *J* 7.65) and 7.30 (1 H, t, *J* 7.65); δ_C(63 MHz; $CDCl_3$) 165.30 (C = N), 147.50 (=C–S), 138.00 (=C–Cl), 130.80, 124.50, 123.00, 117.70, 125.3 and 116.5; *m*/*z* (160 °C) 225 (M^+, 100%), 193 (M^+ − S, 2), 190 (M^+ − Cl, 5) and 161 (M^+ − S_2, 12).

(b) *From inden*-1-*one oxime*. Disulfur dichloride (1.12 cm^3, 14 mmol) was added to a stirred, cold (−50 °C) solution of inden-1-one oxime **9** (1 g, 6.9 mmol) and ethyldiisopropylamine (2.4 cm^3, 13.8 mmol) in tetrahydrofuran (75 cm^3) and the mixture was stirred at 4 °C for 48 h. The solvent was removed under reduced pressure and column chromatography of the residue (light petroleum) gave the title compound **10** (0.95 g, 60%) identical with that previously described.

4,5,6-*Trichlorocyclopenta*[1,2-d]-1,2,3-*dithiazole* **13**.—*First method*. Disulfur dichloride (8.1 cm^3, 101 mmol) was added to a stirred, cold solution of cyclopentanone oxime (1 g, 10.1 mmol) and ethyldiisopropylamine (17.6 cm^3, 101 mmol) dissolved in tetrahydrofuran (75 cm^3) and the mixture was stirred at 4 °C for 72 h. The solvent was removed under reduced pressure and column chromatography of the residue (light petroleum) gave the *title compound* **13** (0.63 g, 25%) as a deep purple solid, m.p. 125–127 °C (from light petroleum–dichloromethane) (Found: C, 24.4; N, 5.5. $C_5Cl_3NS_2$ requires C, 24.5; N, 5.7%); λ_{max}(EtOH)/nm 360 (log ε 3.97) and 544 nm (3.07); ν_{max}(CCl_4)/cm^{-1} 1546s, 1284w, 1208s, and 1090w; δ_C(63 MHz; $CDCl_3$) 106.40, 110.10, 128.30, 144.50 (=C–S) and 160.60 (C=N); *m*/*z* (160 °C) 245 (M^+ + 2, 100%), 243 (M^+, 95) and 208 (M^+ − Cl, 26).

Second method. Disulfur dichloride (0.3 cm^3, 4 mmol) was added to a dimethylformamide (10 cm^3) solution of cyclopentanone oxime (0.1 g, 1.01 mmol) with cooling in an ice–salt bath and the mixture was stirred at 4 °C for 72 h. It was then added to ice (60 g) and extracted with ether (3 × 75 cm^3). The organic layer was dried ($MgSO_4$) and evaporated to dryness under reduced pressure. Column chromatography (light petroleum) gave compound **13** (62 mg, 25%).

Third method. To a solution of cyclopentanone oxime (0.1 g, 1.01 mmol) in dimethylformamide (10 cm^3) was added disulfur dichloride (0.08 cm^3, 1 mmol) followed by *N*-chlorosuccinimide (4 g, 30 mmol). After 24 h the reaction mixture was poured onto ice (60 g) and extracted with ether (3 × 75 cm^3). The organic layer was dried ($MgSO_4$) and evaporated to dryness. Column chromatography (light petroleum) of the residue gave compound **13** (64 mg, 26%).

From cyclopent-2-*enone oxime* **14**.—To a solution of cyclopent-2-enone oxime (0.097 g, 1 mmol) in dimethylformamide (10 cm^3) at 0 °C was added disulfur dichloride (0.32 cm^3, 4 mmol). After being stirred for 72 h the reaction mixture was worked up as above, to give compound **13** (51 mg, 25%).

Cyclohepta[1,2-d]-1,2,3-*dithiazole Derivatives*.—*First method*. Disulfur dichloride (9.47 cm^3, 118 mmol) was added to a cold (−50 °C) solution of cycloheptanone oxime **17** (1 g, 7.87 mmol) and ethyldiisopropylamine (20.6 cm^3, 118 mmol) in tetrahydrofuran (90 cm^3) and the mixture was stirred at 4 °C for 72 h. The solvent was removed under reduced pressure and repeated column chromatography of the residue (light petroleum) gave products **18**–**21**.

Dichlorocyclohepta[1,2-d]-1,2,3-*dithiazole* **18** (70 mg, 4%). A green solid, m.p. 98–100 °C (from light petroleum–dichloromethane); δ_H(270 MHz; $CDCl_3$) 5.45 (1 H, dd, *J* 13 and 2.25), 5.66 (1 H, dd, *J* 13 and 0.7), and 5.70 (1 H, dd, *J* 2.25 and 0.7); δ_C(63 MHz; $CDCl_3$) 119.60, 130.86 (2 × C–Cl), 129.76, 132.94, 133.51 [3 × C–H (from DEPT)], 159.24 (=C–S) and 159.98 (C=N); *m*/*z* (150 °C) 235 (M^+, 100%), 200 (M^+ − Cl, 21), 175 (M^+ − C_2HCl, 40) and 165 (M^+ − 2Cl, 12).

Trichlorocyclohepta[1,2-d]-1,2,3-*dithiazole* **19** (100 mg, 5%). A green solid, m.p. 140–142 °C (from light petroleum–dichloromethane); δ_H(270 MHz; $CDCl_3$) 5.83 (1 H, d, *J* 1.7) and 6.16 (1 H, d, *J* 1.7); δ_C(63 MHz; $CDCl_3$) 119.33, 126.68, 135.27 (3 × C–Cl), 133.21, 133.45 [2 × C–H (from DEPT)], 156.1 (=C–S) and 156.79 (C=N); *m*/*z* (170 °C) 271 (M^+ + 2, 100%), 269 (M^+, 93), 234 (M^+ − 35, 23) 209 (M^+ − C_2HCl, 41) and 199 (M^+ − 2 Cl, 25).

Tetrachlorocyclohepta[1,2-d]-1,2,3-*dithiazole* **20** (50 mg, 2%). A green brownish solid, m.p. 128–130 °C (from light petroleum–dichloromethane) (Found: C, 27.5; H, 0.35; N, 4.4. $C_7HCl_4NS_2$ requires C, 27.6; H, 0.33; N, 4.6%); ν_{max}(CCl_4)/cm^{-1} 1558w, 1505m, 1416w, 1173m and 1093m; δ_H(270 MHz; $CDCl_3$), 6.23 (1 H, S); δ_C(63 MHz; $CDCl_3$) 117.93, 127.18, 132.62, 137.29 (4 × C–Cl), 133.1 [=C–H (from DEPT)], 154.55 (=C–S), and 155.71 (C=N); *m*/*z* (150 °C), 307 (M^+ + 4, 57%), 305 (M^+ + 2, 100), 303 (M^+, 67), 270 (M^+ + 2 − Cl, 28), 268 (M^+ − Cl, 22) and 233 (M^+ − 2 Cl, 15).

4,5,6,7,8-*Pentachlorocyclohepta*[1,2-d]-1,2,3-*dithiazole* **21** (50 mg, 2%). A red solid, m.p. 120–122 °C (from light petroleum–dichloromethane) (Found: C, 25.4; N, 3.9. $C_7Cl_5NS_2$ requires C, 24.8; N, 4.1%); $\nu_{max}(CCl_4)/cm^{-1}$ 1558m, 1523w, 1303m and 1175m; δ_C(63 MHz; $CDCl_3$) 115.55, 124.63, 128.80, 131.20, 135.01 (5 × C–Cl), 152.58 (=C–S) and 156.65 (C=N); *m/z* (150 °C) 341 (M^+ + 4, 21%), 339 (M^+ + 2, 30), 337 (M^+, 18), **304** (M^+ + 2 − Cl, 23), 302 (M^+ − Cl, 16), 269 (M^+ + 2 − 2Cl, 24), 267 (M^+ − 2Cl, 22) and 149 (M^+ − C_4Cl_4, 100).

Second method. Disulfur dichloride (5.67 cm^3, 71 mmol) was added to a cold (−50 °C) solution of cycloheptanone oxime **17** (0.6 g, 4.72 mmol) and ethyldiisopropylamine (12.3 cm^3, 71 mmol) in tetrahydrofuran (50 cm^3). The mixture was stirred at 4 °C for 48 h and then a solution of *N*-chlorosuccinimide (6.31 g, 47.2 mmol) in tetrahydrofuran (25 cm^3) was added. The mixture was stirred at 4 °C for 24 h, allowed to warm up overnight and then refluxed for 4 h. The solvent was removed under reduced pressure and column chromatography (light petroleum) afforded 4,5,6,7,8-pentachlorocyclohepta[1,2-*d*]-1,2,3-dithiazole **21** (0.223 g, 14%) and tetrachlorocyclohepta[1,2-*d*]-1,2,3-dithiazole **20** (0.107 g, 7%), both compounds identical with those described above.

8,10-*Dichlorobenzocyclohepta*[1,2-d]-1,2,3-*dithiazole* **23**.—Disulfur dichloride (5.59 cm^3, 68.5 mmol) was added to a cold (−50 °C) solution of tetrahydrobenzocycloheptenone oxime **22** (1 g, 5.71 mmol) and ethyldiisopropylamine (11.94 cm^3, 68.5 mmol) dissolved in tetrahydrofuran (75 cm^3) and the solution was stirred at room temperature for 48 h and refluxed for 4 h. The solvent was removed under reduced pressure and column chromatography (light petroleum) of the residue gave the *title compound* **23** (0.57 g, 35%) as an orange–red solid, m.p. 118–120 °C (light petroleum–dichloromethane); $\nu_{max}(CCl_4)/cm^{-1}$ 1585m, 1557m, 1505w, 1482m and 1309m; δ_H(270 MHz; $CDCl_3$) 6.43 (1 H, s, ClC=CH), 7.40 (2 H, m), 7.59 (1 H, m) and 7.86 (1 H, m); δ_C(63 MHz; $CDCl_3$) 118.99, 131.97, 132.93, 133.78 (4 × quaternary C), 129.59, 130.60, 131.28, 132.16, 132.93 [5 × C–H (from DEPT)], 151.47 (=C–S) and 158.45 (C=N); *m/z* (210 °C) 287 (M^+ + 2, 74%), 285 (M^+, 100), 250 (M^+ − Cl, 15), 225 (M^+ − C_2HCl, 25) and 215 (M^+ − 2CL, 26).

8,9,10-*Trichlorobenzocyclohepta*[1,2-d]-1,2,3-*dithiazole* **24**.—Disulfur dichloride (2.74 cm^3, 34.3 mmol) was added to a cold (−50 °C) solution of tetrahydrobenzocycloheptenone oxime **22** (0.6 g, 3.43 mmol) and ethyldiisopropylamine (6.0 cm^3, 34.3 mmol) in tetrahydrofuran (50 cm^3) and the mixture was stirred for 5 min. A solution of *N*-chlorosuccinimide (2.29 g, 17.5 mmol) in tetrahydrofuran (25 cm^3) was then added and the mixture was stirred at room temperature for 48 h; it was then refluxed for 4 h. The solvent was removed under reduced pressure and column chromatography (light petroleum) of the residue afforded the *title compound* **24** (0.312 g, 29%) as red crystals, m.p. 121–122 °C (light petroleum–dichloromethane) (Found: C, 41.3; H, 1.2; N, 4.3. $C_{11}H_4Cl_3NS_2$ requires C, 41.2; H, 1.3; N, 4.4); ν_{max}/cm^{-1} 1593w, 1571w, 1558m, 1317m and 1166s; δ_H(270 MHz; $CDCl_3$), 7.43 (2 H, m), 7.48 (1 H, m) and 7.84 (1 H, m); δ_C(63 MHz; $CDCl_3$) 116.70, 130.05, 130.27, 133.93, 134.60 (all quaternary), 130.95, 131.25, 131.54, 132.22 [4 × C–H from DEPT], 153.93 (=C–S) and 157.22 (C=N); *m/z* (200 °C) 321 (M^+ + 2, 68%), 319 (M^+, 74), 284 (M^+ − Cl, 41) and 249 (M^+ − 2Cl, 100).

4-*Phenyl*-5-(α-*chlorobenzylidene*)-1,2,3-*dithiazole* **27**.—To a solution of benzylideneacetophenone oxime **25** (0.21 g, 1 mmol) in DMF (10 cm^3) was added disulfur dichloride (0.08 cm^3, 1 mmol) and the solution was stirred at room temperature for 1.5 h. After this, ice (60 g) was added to the mixture which was then extracted with ether (3 × 75 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated to dryness and column chromatography (light petroleum–dichloromethane, 2:1) of the residue gave the *title compound* **27** (47 mg, 23%) as a yellow solid, m.p. 126–127 °C (from light petroleum–dichloromethane) (Found: C, 59.1; H, 3.4; N, 4.4. $C_{15}H_{10}ClNS_2$ requires C, 59.3; H, 3.3; N, 4.6); ν_{max}/cm^{-1} 1546m, 1443s and 1296s; δ_H(250 MHz; $CDCl_3$) 6.91 (5 H, m) and 7.05 (5 H, m); δ_C(63 MHz; $CDCl_3$) 123.50, 134.03, 136.78 (3C, quaternary C), 127.79, 128.01, 128.56, 128.92, 129.12, 129.71, 144.10 (=C–S) and 160.21 (C=N); *m/z* (200 °C) 303 (M^+, 43%), 268 (M^+ − Cl, 75), 235 (M^+ − Cl − S, 24), 202 (M^+ − 25 − Cl, 31) and 103 ([Ph − C = N]$^+$, 100).

8-*Morpholinoindeno*[1,2-d]-1,2,3-*dithiazole* **28**.—8-Chloroindenodithiazole **10** (70 mg, 0.31 mmol) in tetrahydrofuran (15 cm^3) was treated with morpholine (270 mg, 3.1 mmol) and the mixture heated at reflux for 20 h. The solvent was removed under reduced pressure and the product isolated by dry flash chromatography. Light petroleum–dichloromethane (3:1) eluted the title compound **28** (12 mg, 14%) as a purple solid, m.p. 111–113 °C (from light petroleum–dichloromethane) (Found: C, 56.3; H, 4.5; N, 9.8. $C_{13}H_{12}N_2OS_2$ requires C, 56.5; H, 4.35; N, 10.1%); λ_{max}(EtOH)/nm 213 (log ε 3.85) and 310 (3.53); ν_{max}/cm^{-1} 1556m, 1514s, 1255m and 1119m; δ_H(250 MHz; $CDCl_3$) 3.36 (4 H, t), 3.90 (4 H, t), 7.22 (1 H, d), 7.30 (1 H, dd, ArH), 7.41 (1 H, dd, ArH) and 7.90 (1 H, d, ArH); *m/z* (150 °C) 276 (M^+, 100%), 218 (28) and 149 (34).

8-*Pyrrolidinoindeno*[1,2-d]-1,2,3-*dithiazole*.—8-Chloroindenodithiazole **10** (25 mg, 0.1 mmol) in tetrahydrofuran (15 cm^3) was treated with pyrrolidine (100 mg, 1.4 mmol) at room temperature and the mixture stirred for 8 h. The solvent was then removed under reduced pressure and the product isolated by dry flash chromatography. Light petroleum–dichloromethane (1:1) eluted the *title compound* (11 mg, 42%) as a red solid, m.p. 159–161 °C (from light petroleum–dichloromethane) (Found: C, 57.9; H, 4.4; N, 10.4. $C_{13}H_{12}N_2S_2$ requires C, 60.0; H, 4.6; N, 10.8%); λ_{max}(EtOH)/nm 312 (log ε 3.8) and 543 (3.23); $\nu_{max}(CCl_4)/cm^{-1}$ 1220m, 1504s and 1562m; δ_H(250 MHz; $CDCl_3$) 1.87–2.18 (4 H, m, 2 × CH_2), 3.82–4.11 (4 H, m, 2 × NCH_2) and 7.15–7.60 (4 H, m, ArH); *m/z* (170 °C) 260 (M^+, 100%).

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