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Direct synthesis of fused 1,2,3,4,5-pentathiepins

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Treatment of nucleophilic heterocycles like pyrroles and thiophenes, and their tetrahydro derivatives, with S_2Cl_2 and DABCO in chloroform at room temperature provides a simple one-pot synthesis of fused mono and bispentathiepins. *N*-Methylpyrrole and its 2-chloro and 2,5-dichloro derivatives and *N*-methylpyrrolidine all give the same dichloropentathiepin **1a**. *N*-Ethyl, isopropyl and *tert*-butylpyrrolidine behave similarly; the isopropylpyrrolidine also gives the bispentathiepin **6** which undergoes an intriguing rearrangement to the symmetrical monopentathiepin **1c**. *N*-Methyl and ethyl indole give either 2,3-dichloro derivatives **8** or the pentathiepinoindoles **9**, depending upon the reaction conditions. Thiophene and tetrahydrothiophene give the pentathiepin **10**. X-Ray crystal structures are provided for the pentathiepins **1a** and **1d**, and possible reaction pathways are suggested for the extensive cascade reactions reported.

Introduction

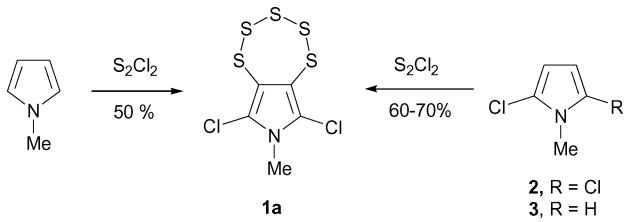
Sulfur is unique among the elements in forming medium to large rings of its atoms, which are stable. Several such rings up to S_{20} are known. The stability of these allotropes can survive the incorporation of a few atoms of other elements, such as carbon. In organic chemistry, seven-membered rings with one carbon–carbon double bond and five contiguous sulfur atoms, the 1,2,3,4,5-pentathiepins, have so far attracted most attention.[1] This is because of their special stability, their existence in natural products and their biological activity, and the high energy barrier for inversion of the chairlike C_2S_5 ring leading to chirality. Originally most attention was focused on benzopentathiepins bearing an aminoethyl group since the first naturally occurring examples varacin,[2] lissoclinotoxin A,[3,4] and *N*,*N*-dimethyl-7-(methylthio)varacin[5] have strong antimicrobial and antifungal activity, and selectively inhibit protein kinase C.[5] Furthermore, varacin is highly toxic towards human colon cancer HCT116.[2] More recently it was found that 7-methylbenzopentathiepin, lacking the aminoethyl group, is a potent thiol-dependent DNA cleaving agent.[6] The pentathiepin ring appears to be crucial for this biological activity.

Several synthetic benzopentathiepins are known[1] but heterocyclic fused systems are limited to isothiazolo,[7] pyrazolo,[8] 1,3-dithiolo,[9] trithiolobenzo[10] and 1,2,3-dithiazolocyclopenta[11] derivatives. Methods for the synthesis of pentathiepins are very limited, the most common being treatment of the preformed *o*-dithiols and their precursors and salts with disulfur dichloride, S_2Cl_2,[7] S_3Cl_2[12] or S_8 in liquid ammonia.[13] However, 1,2-disubstituted starting materials are not always readily available, especially for heterocycles.

We have found that nucleophilic heterocycles like pyrroles, indoles and thiophene, and their fully saturated derivatives, with S_2Cl_2 and a base in chloroform at room temperature give heterocyclic fused pentathiepins.[14] This unusual reaction was discovered as follows. We had previously shown that *N*-isopropyl groups reacted with S_2Cl_2 to give *N*-(1,2-dithiole-3-thiones).[15] However when *N*-isopropylpyrrolidine (Scheme 3) was similarly treated with S_2Cl_2 the isopropyl group remained intact but pentathiepin rings were fused onto the pyrrolidine ring to give **1c** and **6**. Clearly the pyrrolidine ring was more reactive than the isopropyl group, probably being initially dehydrogenated to the pyrrole ring, followed by pentathiepin fusion. This unusual reaction could thus provide an attractive route to fused pentathiepins and we have now studied it systematically, to find good reaction conditions, to uncover any intermediates which could indicate the reaction pathway, and to explore its scope.

Results and discussion

The reaction of *N*-methylpyrrole with S_2Cl_2 and a base was investigated in detail and dichloropentathiepinopyrrole **1a** was the major product (Scheme 1). Mass spectrometry, HRMS and microanalysis gave the formula $C_5H_3Cl_2NS_5$; **1a** is symmetrical, showing an *N*-methyl group in the ^{1}H and ^{13}C NMR spectra in addition to two different sp^2 carbons. The mass spectrum also showed a major loss of S_2, presumably for conversion of the pentathiepin into the corresponding 1,2,3-trithiole. Structure **1a** was confirmed by X-ray crystallography (see below).



1a **2**, R = Cl **3**, R = H

Scheme 1

The reaction time and temperature, and the nature and quantity of base were important for the yield of **1a**. Our standard procedure was to mix the pyrrole (5 mmol), base and S_2Cl_2 in chloroform (50 ml) at −35 °C and to stir the mixture for 2 d at the temperature indicated in Table 1 (nearly always room temperature) followed by a shorter period of heating under reflux. The final period of refluxing was not essential but it appears to facilitate the work-up. The conditions and yields of **1a** are given in Table 1. In the absence of base, or with

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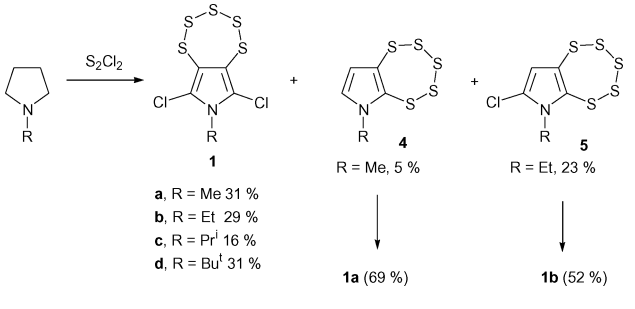
Table 1 Reaction of *N*-methylpyrrole (5 mmol) with disulfur dichloride and a base in chloroform

No.	Reagents		Temperature of stirring/°C	Reflux time/h	Yield of **1a** (%)
	Base/mmol	S_2Cl_2/mmol			
1	Pyridine (2 mmol)	20	20	3	12
2	Pyridine (25 mmol)	25	20	0	30
3	$EtNPr^i_2$ (25 mmol)	25	20	0	15
4	Et_3N (25 mmol)	25	20	0	29
5	DABCO (5 mmol)	25	20	5	20
6	DABCO (20 mmol)	25	20	0	44
7	DABCO (20 mmol)	20	20	0	21
8	DABCO (25 mmol)	25	20	1	45
9	DABCO (25 mmol)	25	20	0	50
10	DABCO (25 mmol)	25	0	0	27
11	DABCO (30 mmol)	30	20	0	38

sodium carbonate or HMDS, the yields of **1a** were lower than those shown. Diazabicyclooctane (DABCO) (5-fold excess) was found to be the most effective base, used with S_2Cl_2 (5-fold excess) at room temperature, giving up to 50% of pentathiepin **1a**. This pentathiepin was stable to further reaction with S_2Cl_2 and DABCO mixtures in the same conditions. Since the precise stoichiometry of these, and the other reactions reported here, are not yet known, all yields are based on the assumption that the S_2Cl_2 is in excess, and are thus minimum values based on the heterocyclic starting material. In trying to find reaction intermediates in the synthesis of **1a**, we used less than 5-fold excess of S_2Cl_2 (entries 1 and 7), but only **1a** was found, in lower yields.

In the formation of **1a** from *N*-methylpyrrole, a pentathiepin ring has been fused to the pyrrole ring and both pyrrole α-positions have been chlorinated. To see if the pentathiepin fusion is possible if one or both α-positions are already chlorinated we treated 2,5-dichloro **2** and 2-chloro derivatives **3** in the same way, and **1a** was again formed. When equimolar mixtures of S_2Cl_2 and DABCO were in 3, 4, 5 and 6-fold excess over **2**, the yields of **1a** were 40, 53, 62 and 70% respectively. Analogously, **3** gave **1a** with a 5-fold excess of S_2Cl_2 and DABCO in 60% yield. Thus β-substitution of the pyrroles **2** and **3** by S_2Cl_2 followed by further substitution at sulfur and cyclisation to give the stable pentathiepin **1a** ring would appear to be a possible reaction pathway.

Since S_2Cl_2 could also, in principle, oxidize the pyrrolidine to pyrrole, we studied the same reaction of *N*-alkyl derivatives of pyrrolidine, which are readily available from the reaction of dichloro- or dibromobutanes and corresponding amines.[16] *N*-Methyl-, *N*-ethyl, *N*-isopropyl- and *N*-*tert*butyl-pyrrolidines all gave the corresponding *N*-alkyl dichloropentathiepinopyrrole **1** as the main product in low to moderate yield (16–31%) (Scheme 2). Additionally *N*-methylpyrrolidine gave a small amount (5%) of unchlorinated compound **4** with the pentathiepin ring fused across the 2,3-pyrrole bond and *N*-ethylpyrrolidine gave rather more (23%) of a similarly fused product **5** but now chlorinated in the free α-position of pyrrole (Scheme 2). The spectral data of **1b**, **c** and **d** were similar to those of **1a**. Mass spectrometry, HRMS and microanalysis

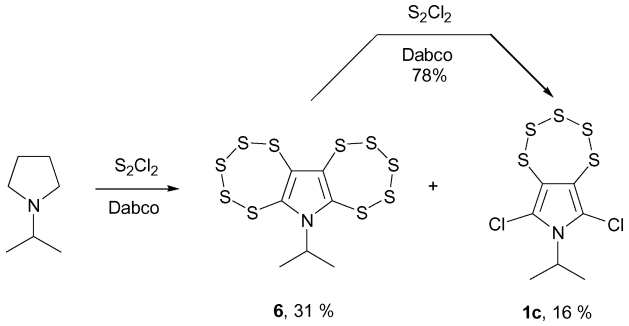


Scheme 2

gave the molecular formula $C_5H_5NS_5$ for **4** and ^1H and ^{13}C NMR confirmed its lack of symmetry. The unsymmetrical structure of **5** and the position of the polysulfur ring and the single hydrogen atom were confirmed by NOE and HMBC experiments. Saturation at 4.18 ppm (CH_2 group) or at 1.32 ppm (Me group) caused no change at 6.42 ppm (CH group of pyrrole), and there is thus no interaction of these groups through space. A heteronuclear multiple bond correlation experiment[17] confirmed the position of the pyrrole CH group: there are two intensive connectivities of the methylene group (4.18 ppm) to C–S and C–Cl (117.58 and 131.14 ppm), but no connection of the pyrrole C–H (6.42 ppm) to these carbons which confirms that the C–H is in the β-position of the pyrrole ring, **5**.

A separate experiment showed that the unsymmetrical pentathiepin **5** was converted into the symmetrical pentathiepin **1b** by S_2Cl_2–DABCO in good yield (52%); this is a new and unexpected rearrangement of a 2,3- to a 3,4-fused pentathiepin accompanied by ring-chlorination, of considerable mechanistic significance (see Scheme 8).

As we saw above, *N*-isopropylpyrrolidine gave an initially unexpected mixture of two pentathiepins with the *N*-isopropyl groups intact, dichloromonopentathiepin **1c** and the bispentathiepin **6** (Scheme 3). The latter, a yellow oil, is believed to be the first bispentathiepin reported. Both are symmetrical, and their structures were confirmed by their spectroscopic properties and the X-ray crystal structure determination of **1c**.

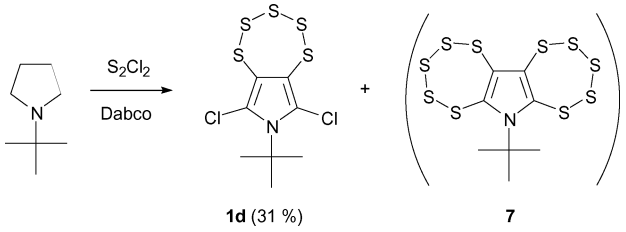


Scheme 3

Separate experiments showed that **6** was also converted into **1c** by S_2Cl_2–DABCO in high yield (78%) and **1c** was unchanged by further treatment. This conversion of **6** into **1c** is presumably mechanistically related to the rearrangement of the monopentathiepin **5** to **1b** above. A possible mechanism is proposed (Scheme 9).

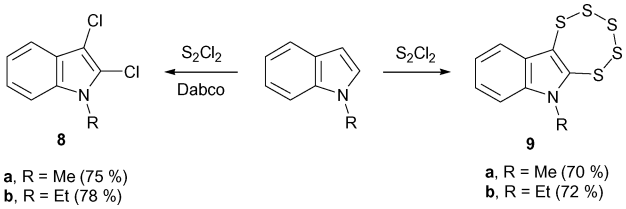
With *N*-*tert*-butylpyrrolidine, the only fully characterised product was the dichloropentathiepin **1d** (31%); the bispentathiepin **7**, analogous to **6**, was detected in traces and its structure was indicated by mass and HMRS spectra (Scheme 4).

Structurally similar *N*-alkylindoles, with only the 2,3-indole bond available for pentathiepin fusion, were also treated with



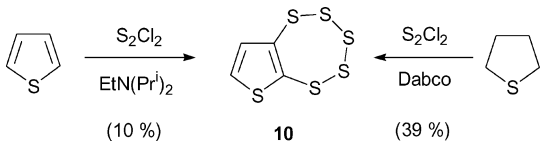
Scheme 4

S_2Cl_2–DABCO in the same way. However the major products from the *N*-methyl- and *N*-ethyl compounds were the 2,3-dichloroindoles **8a**, **b** (75 and 78%) (Scheme 5); some unchlorinated pentathiepin **9b** was formed in the case of *N*-ethylindole but in very low yield (8%). But with a deficiency of S_2Cl_2 (0.8 equiv) and in the absence of a base the only products were unchlorinated pentathiepins **9** in 70 and 72% yields. The reactions of Scheme 5 underline the influential role of the base DABCO, possibly resulting from complexes formed between it and S_2Cl_2 *e.g.* **11** and **12**. No characterisable products were obtained when *N*-unsubstituted indole, as well as *N*-unsubstituted pyrrole and pyrrolidine, were treated similarly with S_2Cl_2–DABCO. Possibly the first step in these reactions is sulfuration of the N–H bond followed by decomposition or oligomerisation. The parent pentathiepinoindole (**9**, R = H) has been reported as a minor product (4%) when isatin was heated with P_4S_{10} in pyridine.[18]



Scheme 5

We have tried to extend these S_2Cl_2 reactions to oxygen and sulfur nucleophilic five membered heterocycles, and their tetrahydro derivatives, with more limited success. Furan and THF decomposed under the reaction conditions, probably with opening of the oxygen ring, as was found for THF.[19] Thiophene gave a mixture of oligomers with no pentathiepin products; apparently the ring is very reactive towards S_2Cl_2 and about half of its hydrogen atoms appeared, from NMR spectra, to be substituted by sulfur. A reduced ratio of S_2Cl_2 and DABCO did not improve the situation but simply gave similar oligomers in lower yield. However, replacement of DABCO by *N*-ethyldiisopropylamine in the thiophene reaction did give unsymmetrical pentathiepinothiophene **10** but only in low yield (Scheme 6); triethylamine as the base resulted in complete decomposition of thiophene. Tetrahydrothiophene gave a higher yield of **10** than thiophene, and the yield increased as the mixture of S_2Cl_2 and DABCO was reduced, from a 6-fold excess (24%) to a 4-fold excess (39%), which suggests the possible conversion of **10** by these reagents to the mixture of oligomers; this was confirmed by a blank experiment.



Scheme 6

The unsymmetrical nature of **10** followed from its spectroscopic properties which were similar to those of the analogous pyrrole **4**. The symmetrical isomer of **10**, with the pentathiepin ring fused across the 3,4-thiophene bond, has previously been prepared from 3,4-dibromothiophene by conversion into the 3,4-dithiol followed by S_2Cl_2 treatment in 2% overall yield.[7]

Unexpectedly benzo[*b*]thiophene did not react with S_2Cl_2–base mixtures.

Table 2 Selected bond lengths (Å) and angles (°) in crystals of **1a** and **1d**

	1a	1d
S(1)–S(2)	2.053(1)/2.051(1)[a]	2.0527(8)
S(2)–S(3)	2.056(1)/2.050(1)	2.0558(8)
S(3)–S(4)	2.044(1)/2.053(1)	2.0579(8)
S(4)–S(5)	2.059(1)/2.055(1)	2.0587(7)
S(1)–C(2)	1.735(3)/1.739(3)	1.743(2)
S(5)–C(3)	1.740(3)/1.740(3)	1.746(2)
Cl(1)–C(1)	1.705(3)/1.705(3)	1.709(2)
Cl(2)–C(4)	1.705(3)/1.705(3)	1.709(2)
N(1)–C(1)	1.360(4)/1.369(4)	1.389(2)
N(1)–C(4)	1.363(3)/1.375(4)	1.386(2)
N(1)–C(5)	1.470(4)/1.468(4)	1.526(2)
C(1)–C(2)	1.366(4)/1.363(4)	1.372(3)
C(2)–C(3)	1.435(4)/1.425(4)	1.426(3)
C(3)–C(4)	1.361(4)/1.369(4)	1.375(3)
C(2)–S(1)–S(2)	103.8(1)/103.3(1)	104.47(7)
S(1)–S(2)–S(3)	104.14(5)/104.74(5)	104.64(3)
S(2)–S(3)–S(4)	105.03(5)/104.04(5)	103.54(3)
S(3)–S(4)–S(5)	104.86(5)/102.7(1)	103.97(3)
C(3)–S(5)–S(4)	102.70(9)/106.8(2)	104.85(7)
C(1)–N(1)–C(4)	106.7(2)/106.8(2)	105.07(15)
C(1)–N(1)–C(5)	126.9(3)/126.2(3)	123.94(15)

[a] For **1a** bond lengths and angles are listed for two independent molecules.

Unexpectedly benzo[*b*]thiophene did not react with S_2Cl_2–base mixtures.

The structures of **1a** and **1d** were confirmed by X-ray analysis.† Both pentathiepin rings are characterized by the expected chair-type conformation (Fig. 1, Table 2). The geometrical parameters for both compounds are close to the previously investigated, analogous thienopentathiepin.[1,20] The S–S bond lengths vary in the narrow range of 2.044(1)–2.056(1) Å (for two independent molecules) in **1a** and 2.0527(8)–2.0587(7) Å in **1d**. The increase of the inductive effect of the alkyl substituent in **1d** leads to some elongation of the N–C bonds in comparison with those in **1a**.

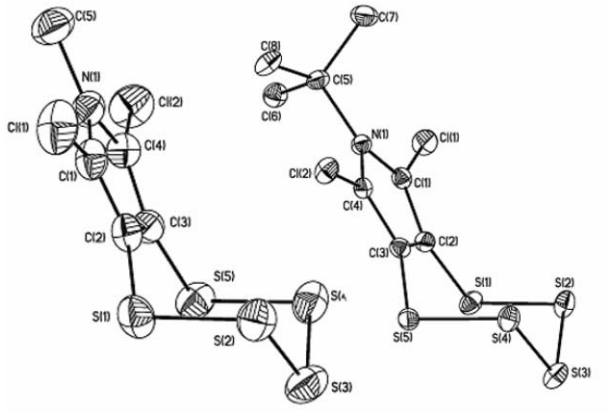


Fig. 1 General view of one independent molecule in **1a** and of **1d** with thermal ellipsoids ($p = 50\%$).

Analysis of the packing in both crystals showed that the molecules are assembled into centrosymmetric dimers. The intermolecular contacts in **1a** and **1d** have revealed that in these dimers, sulfur atoms S(2) and S(4) participate in shortened contacts with chlorine and the pyrrole π-system of the neighbouring molecule with the S(2)···Cl(2A) and S(4)···C(1A) distances

† CCDC reference numbers 274835 and 274836. See http://dx.doi.org/10.1039/b508186f for crystallographic data in CIF or other electronic format.

varying in the range of 3.595(1)–3.620(1) Å and 3.447(3)–3.467(3) Å, respectively see for *e.g.* (Fig. 2). It is noteworthy that these contacts are characterized by specific directionality with the average Cl(2)S(2A)S(1A) and C(1)S(4A)S(5A) angles equal to 164.5 and 154°, respectively. In addition to the above contacts, the S···Cl contacts (3.438(1) and 3.469(1) Å) between dimers assembles the molecules into a 3-dimensional framework.

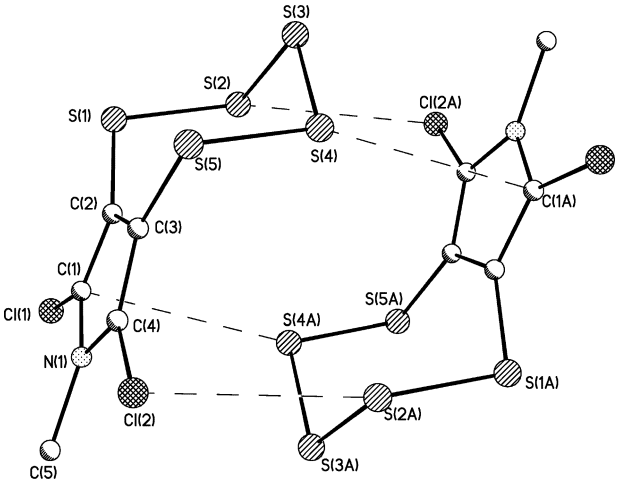
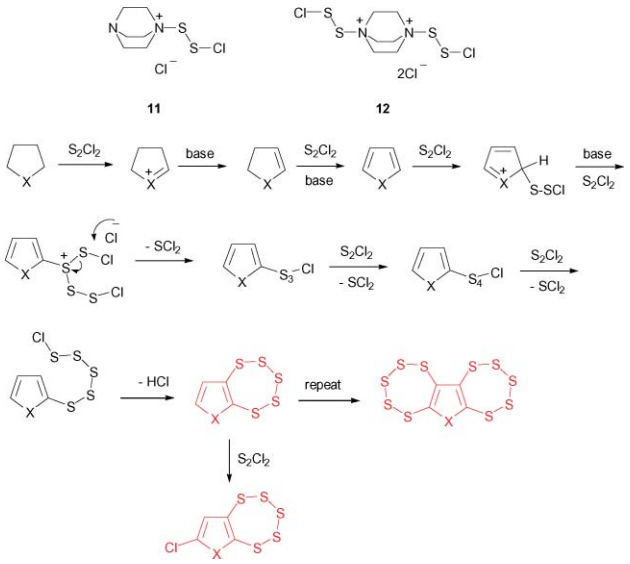


Fig. 2 The formation of dimers in the crystal structures of **1a**. Symmetry code: (A) $-x$, $1-y$, $-z$.

To estimate the nature of these contacts we have carried out the single point calculation of one of the dimers, using the experimental geometry of the dimer in the crystal of **1d** which is characterized by the shortest S(4)···C(1A) distance (3.466(1) Å). The electron density function obtained with the B3LYP/6-311G* calculation (Gaussian98W program package) was analyzed in terms of the R. F. Bader "Atoms in Molecule" (AIM) theory. The charge transfer in terms of the AIM theory implies the presence of a bond path and thus the presence of the critical point [CP] (3, −1) of the electron density function (ρ(r)) between the corresponding atoms. The critical point search has revealed the presence of CP (3, −1) for S···Cl and S···C contacts, and thus they both correspond to charge transfer from the chlorine lone pair or pyrrole π-system to antibonding S–S orbitals. It should be noted that the values of the electron density function in the CP (3, −1) for S···Cl and S···C contacts are both 0.043 *e* Å^{-3} which in turn means that the energies of these interactions are comparable.

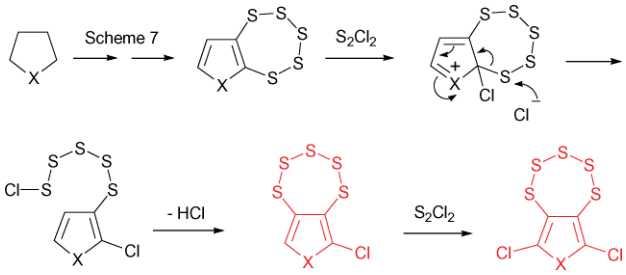
Possible reaction pathways

The various fairly complex cascade reactions described above convert simple saturated and aromatic heterocycles into polycyclic pentathiepins and their chlorinated and rearranged derivatives; this strikingly illustrates the extensive reactivity of S_2Cl_2 and its complexes with bases, particularly DABCO.[21] This reactivity encompasses dehydrogenation of tetrahydroaromatics, the chlorination and sulfuration of aromatics and their conversion into –SSCl derivatives,[22] pentathiepin ring formation and pentathiepin to pentathiepin rearrangements. We have also proposed[20] that $-S_nCl$ chains can be extended to give $-S_{(n+1)}Cl$ chains by the addition of S_2Cl_2 and loss of SCl_2 (see Scheme 7) to give ultimately the thermodynamically stable[1] pentathiepin ring. Too little is known as yet about the nature and timing of all these steps to give precise reaction mechanisms, but possible overall reaction pathways are suggested in Schemes 7–9,[23] where X represents a nucleophilic heteroatom and S_2Cl_2 includes possible S_2Cl_2–base complexes such as **11** and **12**.[21] In Scheme 9 the final cyclisation could have occurred earlier in the sequence. Scheme 9 shows two possible routes from bispentathiepins to the new monopentathiepin. In addition to this unexpected reaction, initiated by *ipso* chlorination of the 5-membered ring

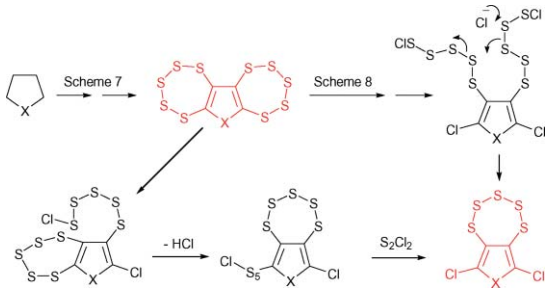


Scheme 7

with opening of the polysulfur ring (see Scheme 8), we also propose that pentathiepin rings can be built up independently of other pentathiepins since pentathiepin formation is not always accompanied by α-chlorination (Scheme 9).



Scheme 8



Scheme 9

All these cascade reactions show how readily and uniquely thermodynamically stable 1,2,3,4,5-pentathiepin rings can be fused onto certain heterocyclic rings in one-pot reactions and suggest many possible extensions of this simple procedure.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Specord M-80 instrument in KBr pellets. ^{1}H NMR were recorded on a Bruker WM 250 spectrometer (250 MHz) and ^{13}C NMR spectra were recorded on a Bruker AM 300 (75.5 MHz) in $CDCl_3$ solution. CH groups were identified by DEPT experiments. *J*-values are given in Hz. Mass spectra were recorded on a Finnigan MAT INCOS 50 instrument using electron impact ionisation. Light petroleum refers to the fraction bp 40–60 °C.

Table 3 Crystallographic data for **1a** and **1d**†

	1a	**1d**
Formula	$C_5H_3Cl_2NS_5$	$C_8H_9Cl_2NS_5$
M	308.28	350.36
T/K	298	110
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a/Å	8.781(2)	8.731(1)
b/Å	9.148(2)	9.435(1)
c/Å	13.906(3)	16.064(2)
α/deg	79.21(2)	
β/deg	87.89(2)	93.761(3)
γ/deg	84.47(2)	
V/Å^3, Z	1092.0(4), 4	1320.5(3), 4
μ/cm^{-1}	15.00	12.52
F(000)	616	712
Absorption correction	None	Semiempirical absorption correction from equivalent reflections
ρ_{calcd}/g cm^{-3}	1.875	1.762
$2\theta_{max}$/deg	54	60
Diffractometer	Siemens P3/PC	Smart CCD
Scan mode	$\theta/2\theta$	ω
No. of reflections measured (R_{int})	5037 (0.0178)	6930 (0.0136)
No. of independent reflections	4741	3674
No. of reflections with $I > 2\sigma(I)$	3411	3192
No. of parameters	237	145
R_1	0.0384	0.0362
wR_2	0.1022	0.0870
GOF	1.002	0.978
Max/min peak/e Å^{-3}	0.427/−0.417	0.512/−0.446

Crystallographic data for **1a** and **1d** are presented in Table 3. Both structures were solved by direct methods and refined by full-matrix least-squares against F^2 in the anisotropic (H-atoms isotropic) approximation, using the SHELXTL-97 package. The hydrogen atoms were located in the Fourier electron density synthesis. All calculations were performed using SHELXTL PLUS 5.0.

General procedure for the reactions with S_2Cl_2 and a base

Disulfur dichloride (2.8 ml, 35 mmol) was added dropwise at −30–35 °C to a stirred solution of the substrate (5 mmol) and DABCO (3.92 g, 35 mmol) dissolved in chloroform (100 ml). Then the mixture was stirred for 15 min at −20 °C and at room temperature for 48 h. Triethylamine (7.2 ml, 50 mmol) was added, the mixture was refluxed for up to 3 h, filtered and the solvent was removed under reduced pressure. The residue was separated by column chromatography (silica, light petroleum, and then light petroleum–DCM mixtures).

6,8-Dichloro-7-methyl-7*H*-[1,2,3,4,5]pentathiepino[6,7-*c*]pyrrole 1a. Yellow solid, mp 167–170 °C. (Found C, 19.8; H, 1.2; N, 4.2%. $C_5H_3Cl_2NS_5$ requires C, 19.5; H, 1.0; N, 4.5%); ν_{max}/cm^{-1} 1460, 1420, 1340, 1100, 780; δ_H 3.60 (s, 3H, CH_3); δ_C 123.82 and 121.53 (2 sp^2 tertiary C), 33.21 (CH_3). m/z (EI) 311 [(M^+ + 4, 2%, found M^+, 306.8238. $C_5H_3Cl_2NS_5$ requires M, 306.8246], 309 (M^+ + 2, 6), 307 (M^+, 9), 245 (39), 243 (48).

6-Methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]pyrrole 4. Yellow solid, mp 99–101 °C. (Found C, 24.8; H, 2.4; N, 5.8%. $C_5H_5NS_5$ requires C, 25.1; H, 2.1; N, 5.9%); ν_{max}/cm^{-1} 1495, 1440, 1360, 1300, 1180, 740; δ_H 6.58 (d, 1H, J 2.6, CH), 6.48 (d, 1H, J 2.6, CH), 3.80 (s, 3H, CH_3); δ_C 128.55 and 127.28 (2 sp^2 tertiary C), 123.86 and 115.31 (2 × CH), 35.80 (CH_3). m/z (EI) 239 (M^+, 47%, found M^+, 238.9016. $C_5H_5NS_5$ requires M, 238.9026), 207 (2), 175 (100), 142 (53), 128 (3), 111 (49).

6,8-Dichloro-7-ethyl-7*H*-[1,2,3,4,5]pentathiepino[6,7-*c*]pyrrole 1b. Yellow solid, mp 103–105 °C. (Found C, 22.6; H, 1.8; N, 4.3%. $C_6H_5Cl_2NS_5$ requires C, 22.4; H, 1.6; N, 4.4%); ν_{max}/cm^{-1} 1450, 1380, 1330, 1110, 750 (C–Cl); δ_H 4.05 (q, 2H, J 7.2, CH_2), 1.36 (t, 3H, J 7.2, CH_3); δ_C 122.81 and 121.65 (2 sp^2 tertiary C), 41.98 (CH_2), 14.86 (CH_3). m/z (EI) 325 (M^+ + 4, 4%), 323 (M^+ + 2, 18%), 321 (M^+, 20%, found M^+, 320.8391. $C_6H_5Cl_2NS_5$ requires M, 320.8403), 261 ($M^+ + 4 - S_2$, 4%), 259 ($M^+ + 2 - S_2$, 18%), 257 ($M^+ - S_2$, 20%), 64 (S_2, 100%).

7-Chloro-6-ethyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]pyrrole 5. Yellow solid, mp 62–63 °C. (Found C, 24.8; H, 2.0; N, 5.2%. $C_6H_6ClNS_5$ requires C, 25.0; H, 2.1; N, 4.9%); ν_{max}/cm^{-1} 1480, 1440, 1410, 1380, 1300, 1140, 790 (C–Cl); δ_H ($CDCl_3$) 6.42 (s, 1H, CH), 4.18 (septet, 2H, J 6.9 and 7.3, CH_2), 1.32 (t, 3H, J 7.3, CH_3); δ_C ($CDCl_3$) 131.14, 117.58 and 105.14 (3 sp^2 tertiary C), 113.82 (CH), 41.61 (CH_2), 16.59 (CH_3). m/z (EI) 289 (M^+ + 2, 15%), 287 (M^+, 28%, found M^+, 286.8797. $C_6H_6ClNS_5$ requires M, 286.8792), 225 ($M^+ + 2 - S_2$, 44%), 223 ($M^+ - S_2$, 100%).

6,8-Dichloro-7-isopropyl-7*H*-[1,2,3,4,5]pentathiepino[6,7-*c*]pyrrole 1c. Yellow solid, mp 135–139 °C. (Found C, 24.7; H, 1.9; N, 4.5%. $C_7H_7Cl_2NS_5$ requires C, 25.0; H, 2.1; N, 4.2%); ν_{max}/cm^{-1} 2980 (CH), 1480, 1400, 1290, 1180, 1140, 795 (C–Cl); δ_H 5.01 (septet, 1H, J 6.5, CH), 1.61 (d, 6H, J 6.5, 2 CH_3); δ_C 115.31 and 78.01 (2 sp^2 tertiary C), 52.11 (CH), 21.66 (CH_3). m/z (EI) 339 (M^+ + 4, 1%), 337 (M^+ + 2, 3%), 335 (M^+, 4%, found M^+, 334.8550. $C_7H_7Cl_2NS_5$ requires M, 334.8559), 303 (15), 301 (22), 273 (17), 271 (22), 237 (85), 195 (100).

11-Isopropyl-11*H*-di[1,2,3,4,5]pentathiepino[6,7-*b*:6,7-*d*]pyrrole 6. Yellow oil. (Found C, 19.6; H, 1.8; N, 3.1%. $C_7H_7NS_{10}$ requires C, 19.8; H, 1.7; N, 3.3%); ν_{max}/cm^{-1} 2980 (CH), 1440, 1270, 1120; δ_H 4.84 (septet, 1H, J 7.2, CH), 1.59 (d, 6H, J 7.2, 2 CH_3); δ_C 122.79 and 87.53 (2 sp^2 tertiary C), 52.02 (CH), 21.13 (CH_3). m/z (EI) 425 (M^+, 5%, found M^+, 424.7788. $C_7H_7NS_{10}$ requires M, 424.7786), 393 (2), 361 (26), 337 (28), 297 (40), 271 (70), 229 (72), 96 (38), 64 (100).

6,8-Dichloro-7-*tert*-butyl-7*H*-[1,2,3,4,5]pentathiepino[6,7-*c*]pyrrole 1d. Yellow solid, mp 102–104 °C. (Found C, 27.7; H, 2.5; N, 3.8%. $C_8H_9Cl_2NS_5$ requires C, 27.4; H, 2.6; N, 4.0%); ν_{max}/cm^{-1} 1470, 1440, 1370, 1290, 1180, 1040; δ_H 1.87 (s, 9H, CH_3); δ_C 124.06 and 123.55 (2 sp^2 tertiary C), 65.84 (*C*–CH_3), 31.43 (CH_3). m/z (EI) 297 (M^+ + 4, 16%), 295 (M^+ + 2, 40%), 293 (M^+, 45%, found M^+, 348.8698. $C_8H_9Cl_2NS_5$ requires M, 348.8716), 233 ($M^+ + 4 - S_2$, 34%), 231 ($M^+ + 2 - S_2$, 84%), 229 ($M^+ - S_2$, 88%), 64 (S_2, 96%), 57 (100).

2,3-Dichloro-1-methylindole 8a. Yellow solid, mp 55–57 °C. Lit.[24] mp 58 °C. ν_{max}/cm^{-1} 1520, 1460, 1430, 1360, 1340, 1240, 1000, 740 (C–Cl); δ_H 7.59 (m, 1H, PhH), 7.25 (m, 3H, PhH), 3.73 (s, 3H, CH_3); δ_C 135.02, 125.04, 121.92 and 102.63 (4 sp^2 tertiary C), 123.40, 121.28, 118.19 and 109.94 (4 × CH), 30.79 (CH_3). *m/z* 203 ($M^+ + 4$, 9%), 201 ($M^+ + 2$, 58%), 199 (M^+, 90%, found M^+, 198.9961. $C_9H_7Cl_2N$ requires M, 198.9956), 188 (M^+ + 4-Me, 10%), 186 (M^+ + 2-Me, 78%), 184 (M^+ − Me, 100%).

2,3-Dichloro-1-ethylindole 8b. Yellow oil. (Found C, 55.9; H, 4.3; N, 6.8%. $C_{10}H_9Cl_2N$ requires C, 56.1; H, 4.2; N, 6.5%); ν_{max}/cm^{-1} 2980 (CH), 1480, 1450, 1340, 1220, 1160, 1120, 740 (C–Cl); δ_H 7.65 (m, 1H, PhH), 7.27 (m, 3H, PhH), 4.25 (q, 2H, *J* 7.2, CH_2), 1.40 (t, 3H, *J* 7.2, CH_3); δ_C 133.37, 124.68, 121.84 and 102.19 (4 sp^2 tertiary C), 122.72, 120.55, 117.73 and 109.24 (4 × CH), 38.86 (CH_2), 14.86 (CH_3). *m/z* 217 ($M^+ + 4$, 10%), 215 ($M^+ + 2$, 55%), 213 (M^+, 92%, found M^+. $C_{10}H_9Cl_2N$ requires M, 213.0112), 202 (M^+ + 4-Me, 12%), 200 (M^+ + 2-Me, 75%), 198 (M^+ − Me, 100%).

6-Methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole 9a. Disulfur dichloride (1.2 ml, 20 mmol) was added dropwise at −30–35 °C to a stirred solution of 1-methylindole (2.55 g, 19.5 mmol) dissolved in chloroform (50 ml). Then the mixture was stirred for 15 min at −20 °C and at 0 °C for 48 h. The mixture was refluxed for 3 h, filtered and the solvent was removed under reduced pressure. The residue was separated by column chromatography (silica, light petroleum, and then light petroleum–DCM mixtures) to yield **9a** as a yellow solid (520 mg, 70%), mp 123–125 °C. Lit.[25] mp 124–125 °C. (Found C, 37.5; H, 2.3; N, 4.9%. $C_9H_7NS_5$ requires C, 37.3; H, 2.4; N, 4.8%); ν_{max}/cm^{-1} 2980 (CH), 1440, 1330, 1240, 1160, 820, 780, 740; δ_H 7.70 (m, 1H, PhH), 7.30 (m, 1H, PhH), 3.91 (s, 3H, CH_3); δ_C 141.84, 137.08, 129.47 and 126.01 (4 sp^2 tertiary C), 125.22, 122.70, 119.61 and 111.06 (4 × CH), 32.10 (CH_3). *m/z* 289 (M^+, 22%), 225 (100), 192 (42).

6-Ethyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole 9b. Yellow solid, mp 95–97 °C. (Found C, 39.3; H, 3.0; N, 4.8%. $C_{10}H_9NS_5$ requires C, 39.6; H, 3.0; N, 4.6%); ν_{max}/cm^{-1} 1460, 1420, 1340, 1220, 740 (CCl); δ_H 7.73 (m, 1H, PhH), 7.29 (m, 1H, PhH), 4.40 (10-tet, 2H, *J* 7.0 and 7.5, CH_2), 1.42 (t, 3H, *J* 7.5, CH_3); δ_C 140.37, 135.29, 129.07 and 119.05 (4 sp^2 tertiary C), 124.47, 121.92, 120.60 and 110.31 (4 × CH), 39.94 (CH_2), 16.10 (CH_3). *m/z* 303 (M^+, 28%, found M^+, 302.9352. $C_{10}H_9NS_5$ requires M, 302.9339), 239 (M − S_2, 100), 206 (42), 64 (46).

Thieno[2,3-*f*][1,2,3,4,5]pentathiepin 10. Yellow oil. (Found C, 22.8; H, 1.0%. $C_4H_2S_6$ requires C, 23.2; H, 0.8%); ν_{max}/cm^{-1} 3100 (CH), 1360, 1090, 880, 720; δ_H (acetone-d_6) 7.64 (d, 1H, *J* 5.5, CH), 7.36 (d, 1H, *J* 5.5, CH); δ_C 144.75 and 141.47 (2 sp^2 tertiary C), 134.05 and 130.16 (2 × CH). *m/z* 242 (M^+, 65%, found M^+, 241.8483. $C_4H_2S_6$ requires M, 241.8481), 178 (100), 146 (46), 114 (47).

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