Nitrile Sulphides. Part 1.[1] 1,3-Dipolar Cycloaddition to Carbonyl Groups activated by Trihaloalkyl Substituents; Synthesis and Crystal Structure of 1,3,4-Oxathiazoles

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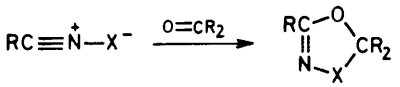
Nitrile sulphides, generated by the thermal decarboxylation of 1,3,4-oxathiazol-2-ones, undergo 1,3-dipolar cycloaddition to the carbonyl group in chloral, hexachloroacetone and α,α,α-trifluoroacetophenone to yield 2,2,5-trisubstituted 1,3,4-oxathiazoles (18—76%). Characterisation of the products is based on analytical and spectroscopic evidence, and is confirmed for 5-phenyl-2-trichloromethyl-1,3,4-oxathiazole and 5-(*p*-methoxyphenyl)-2-phenyl-2-trifluoromethyl-1,3,4-oxathiazole by *X*-ray crystal structure analyses. The oxathiazole rings are planar, with a localised C=N double bond.

THE synthesis of heterocycles *via* the 1,3-dipolar cycloaddition reactions of nitrile oxides (1) has been the subject of intensive study [2] over the last 20 years, the value of the method being well illustrated [3] by their reaction with carbonyl compounds yielding 1,3,4-dioxazoles (2), a group of compounds for which there are few preparative methods.[4] In contrast, the corresponding nitrile sulphides (3) have received much less attention, their reported cycloadditions being restricted to alkyne,[5] alkene,[6] and nitrile [7] dipolarophiles. We have examined their reaction with carbonyl compounds with a view to establishing a new route to 1,3,4-oxathiazoles (4), a rare class of heterocycles accessible only with difficulty by other means.[8]



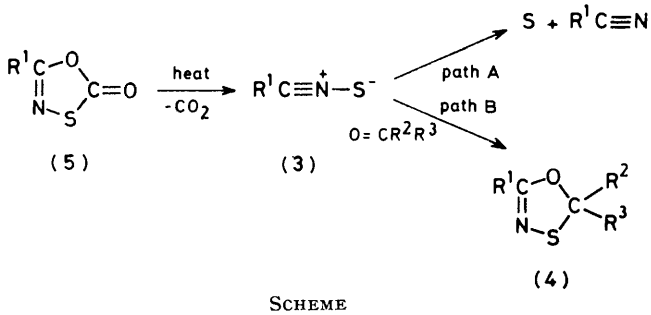
(1) X = O (2) X = O
(3) X = S (4) X = S

RESULTS AND DISCUSSION

For this investigation the nitrile sulphides were generated by the thermal decarboxylation of 1,3,4-oxathiazol-2-ones (5), while chloral, hexachloroacetone, and α,α,α-trifluoroacetophenone were selected as dipolarophiles in view of the established preference [3] of nitrile oxides for carbonyl groups which are activated by electron-withdrawing substituents.

The oxathiazolones were heated in xylene under reflux in the presence of an excess of the carbonyl compound [5 mol per mol of (5)] until h.p.l.c. analysis indicated their complete consumption. Removal of the solvent and excess of dipolarophile afforded the corresponding 1,3,4-oxathiazoles (4), (18—76%), together with sulphur and nitrile by-products which were separated by distillation and/or recrystallisation.

The identification of the products as 1,3,4-oxathiazoles follows from their analytical and spectroscopic data. The i.r. spectra are similar to those of the oxathiazolone precursors, but lack their carbonyl stretching band at 1 735—1 765 cm^{-1}; a new characteristic C=N peak appears at 1 615—1 655 cm^{-1}. The 1,3,4-oxathiazoles also have mass, ^1H, and ^{13}C n.m.r. spectra consistent with their structures. Comparison of the ^{13}C n.m.r. chemical shifts (Table 1) with those for the corresponding oxathiazol-2-ones (Table 2) supports the assignment of a



SCHEME

1,3,4-oxathiazole ring structure. The peaks attributable to the carbon at ring-position 5 and its substituent (R^1) show little or no variation; on the other hand significant shifts are observed for the carbon at position 2, consistent with replacement of the carbonyl group of (5) by CR^2R^3 in (4). The precise position of the C-2 absorption is also dependent on the nature of the C-2 substituents, being 95.6—95.9 p.p.m. for the oxathiazoles derived from chloral and trifluoroacetophenone, while those from hexachloroacetone lie between 111.9 and 112.2 p.p.m., thus reflecting the presence of the second trihaloalkyl group.

The mass spectra of the oxathiazoles showed, in addition to the parent ion, peaks corresponding to R^1CNS and R^1CN fragments, thus suggesting a major fragmentation pathway involving retro-1,3-dipolar cycloaddition to dipolarophile and 1,3-dipole and its subsequent cleavage to nitrile and sulphur. Similar behaviour is exhibited by compound (5) and the corresponding, nitrile oxide derived, 1,3,4-dioxazoles (2).[9]

The structures of 5-phenyl-2-trichloromethyl-1,3,4-oxathiazole (4A) and 5-(*p*-methoxyphenyl)-2-phenyl-2-trifluoromethyl-1,3,4-oxathiazole (4B) have been determined by *X*-ray analysis.

These appear to be the first crystal-structure determinations of the 1,3,4-oxathiazole ring. The molecular shapes found are illustrated in Figure 1 and important bond lengths and angles are compared in Figure 2.

TABLE 1

^{13}C N.m.r. data (p.p.m. from Me_4Si; $CDCl_3$ solvent) for 1,3,4-oxathiazoles (4)

R^1	R^2	R^3	C-2	C-5	C or R^1	C of R^2 and R^3
Ph	CCl_3	H	95.9	157.1	131.4, 128.4, 127.9 (5 Ph ring CH); 125.9 (Ph ring C)	99.7 (CCl_3)
Ph	CCl_3	CCl_3	112.2	156.1	131.8, 128.6, 128.0 (5 Ph ring CH); 125.5 (Ph ring C)	100.3 (2 CCl_3)
4-$MeOC_6H_4$	CCl_3	H	95.9	157.3	162.3, 118.9 (Ar ring C); 129.9, 114.1 (4 Ar ring CH); 55.4 (OMe)	100.1 (CCl_3)
4-$MeOC_6H_4$	CCl_3	CCl_3	112.1	156.1	162.4, 118.1 (Ar ring C); 129.9, 114.1 (4 Ar ring CH); 55.4 (OMe)	100.4 (2 CCl_3)
4-$MeOC_6H_4$	CF_3	Ph	95.6 (J_{C-C-F} 33 Hz)	156.0	162.2, 118.7 (Ar ring C); 129.7, 113.9 (4 Ar ring CH); 55.2 (OMe)	134.9 (Ph ring C) 129.7, 128.6, 126.0 (5 Ph ring CH); 123.7 (CF_3, J_{C-F} 284 Hz)
4-ClC_6H_4	CCl_3	CCl_3	112.4	155.2	138.3, 124.0 (Ar ring C); 129.3, 129.1 (4 Ar ring CH)	100.2 (2 CCl_3)
4-ClC_6H_4	CF_3	Ph	96.2 (J_{C-C-F} 33 Hz)	155.2	137.9, 124.6 (Ar ring C); 129.2, 128.9 (Ar ring CH)	134.6 (Ph ring C); 129.9, 128.7, 126.0 (5 Ph ring CH); 123.5 (CF_3, J_{C-F} 284 Hz)
Me	CCl_3	H	95.9	157.6	15.0 (CH_3)	99.9 (CCl_3)
Me	CCl_3	CCl_3	112.1	156.5	15.0 (CH_3)	100.4 (2 CCl_3)
$CH_3(CH_2)_2$	CCl_3	CCl_3	111.9	159.8	31.0, 19.1 (CH_2); 13.5 (CH_3)	100.3 (2 CCl_3)
$CH_3(CH_2)_{10}$	CCl_3	H	95.7	161.0	31.8, 29.4, 29.3, 29.2, 29.0, 28.8, 25.7, 22.5 (10 CH_2); 14.0 (CH_3)	99.8 (CCl_3)
$CH_3(CH_2)_{10}$	CCl_3	CCl_3	112.0	160.0	31.8, 29.5, 29.3, 29.2, 29.0, 28.8, 25.5, 22.6 (10 CH_2); 14.0 (CH_3)	100.4 (2 CCl_3)

There are no significant differences in the oxathiazole ring between the two compounds, and bond lengths are consistent with a localised C=N double bond. The oxathiazole rings are nearly planar, with a very slight fold across S · · · O; in (4A) the maximum deviation

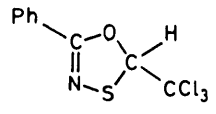
TABLE 2

^{13}C N.m.r. data (p.p.m. from Me_4Si; $CDCl_3$ solvent) of 1,3,4-oxathiazol-2-ones (5).

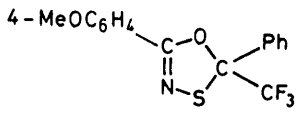
R^1	C-2	C-5	C of R^1
Ph	173.7	157.4	132.6, 129.0, 127.4 (5 Ph ring CH); 125.8 (Ph ring C)
4-$MeOC_6H_4$	174.1	157.3	163.3, 118.5 (Ar ring C); 129.3, 114.5 (Ar ring CH); 55.5 (OMe)
4-ClC_6H_4	173.3	156.5	139.1, 124.3 (Ar ring C); 129.5, 128.7 (Ar ring CH)
Me	174.2	158.7	16.4 (CH_3)
$CH_3(CH_2)_2$	174.4	161.8	32.3, 18.9 (CH_2); 13.4 (CH_3)
$CH_3(CH_2)_{11}$	174.0	161.7	31.6, 30.2, 29.4, 29.1, 28.9, 28.6, 25.1, 22.4 (10 CH_2); 13.8 (CH_3)

from the best plane of the five ring atoms is 0.08 Å and in (4B), 0.01 Å. The aryl groups at C(5) are not coplanar with the five-membered rings; in (4A) the torsion angle C(7)–C(6)–C(5)–N(4) is −16.7° and in (4B), −12.0°. [For atom numbering see Figure 1]. Bond lengths and angles in other parts of the molecule are in agreement with those in similar compounds. There are no intermolecular contacts between non-hydrogen atoms less than 3.3 Å in either compound.

The formation of nitrile and sulphur by-products is a common feature of nitrile sulphide chemistry and is attributed [7] to fragmentation (Scheme, path A) competing with cycloaddition (path B). As has been observed for other nitrile sulphide cycloadditions, we find that the balance between the two pathways, and consequently the yield of the cycloadduct, is dependent on the reactivity of the nitrile sulphide and on the nature of the dipolarophile. Electron-donating substituents in the dipole favour cycloaddition; thus the adduct yield rises from 35% for R^1 = 4-ClC_6H_4 to 57% for R^1 = 4-$MeOC_6H_4$ for reaction with hexachloroacetone. Electron-withdrawing groups in the dipolarophile also favour cycloadduct formation, but the slightly greater yields obtained for chloral compared with hexachloroacetone, in spite of the presence of two electron-withdrawing trihalogenoalkyl groups in the latter, suggest that steric factors may also play an important role.



(4A)



(4B)

EXPERIMENTAL

Mass spectra (70 eV ionisation potential) were measured using an AEI MS902 instrument. Varian HA 100 and CFT 20 spectrometers were used to record ^1H and ^{13}C n.m.r. spectra respectively. I.r. spectra were recorded with a Perkin-Elmer model 257 spectrophotometer. The reactions were followed and the yields of the products determined by high-performance liquid chromatography (h.p.l.c.) analysis, utilising a 15 × 0.5 cm alumina column (25% water deactivated) with 80% hexane–20% dichloromethane (25% water saturated) as eluant.

Preparation of the 1,3,4-*Oxathiazol*-2-*ones* (5).—The

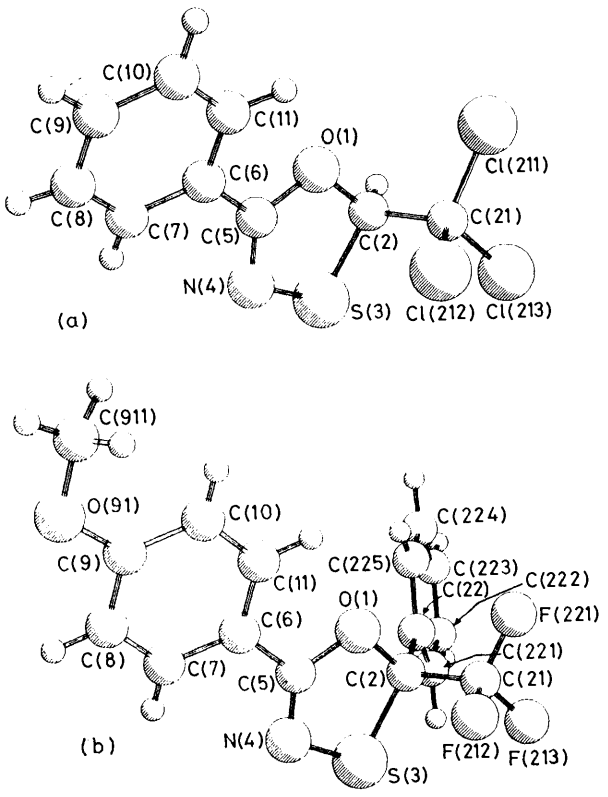


FIGURE 1 One molecule of compound (4A) (a) and compound (4B) (b) as found in the crystals and showing the atom numbering used in the crystallographic tables

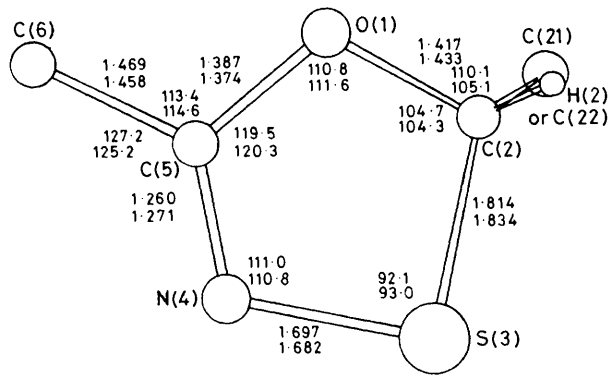


FIGURE 2 Bond lengths (in Å) and angles (in degrees) in the 1,3,4-oxathiazole ring in (4A) (above) and (4B). Estimated standard deviations range from 0.004 Å for the N–S bond to 0.006 Å for the C–C bonds in both compounds, and from 0.3° for the angle at sulphur to 0.6° for angles at carbon

following were prepared from chlorocarbonylsulphenyl chloride and the appropriate amide as described in the literature and had correct characteristics: 5-phenyl-1,3,4-oxathiazol-2-one,[10] 5-(*p*-chlorophenyl)-1,3,4-oxathiazol-2-one,[10] 5-methyl-1,3,4-oxathiazol-2-one.[11]

5-(p-*Methoxyphenyl*)-1,3,4-*oxathiazol*-2-*one*. This compound was prepared (54%) from *p*-methoxybenzamide and ClCOSCl by the same route and the product recrystallised from ethanol; it had m.p. 112 °C (Found: C, 51.4; H, 3.3; N, 6.5. $C_9H_7NO_3S$ requires C, 51.7; H, 3.4; N, 6.7%); $\nu_{max.}$ (Nujol) 1 750 cm^{-1} (C=O); *m/e* 209 (M^+), 165 ($MeOC_6H_4CNS^+$), 135 ($MeOC_6H_4CO^+$), and 133 ($MeOC_6H_4CN^+$).

5-*Propyl*-1,3,4-*oxathiazol*-2-*one*. This compound was similarly prepared in 59% yield from ClCOSCl and butanamide; it had b.p. 69—70 °C at 12 mmHg (Found: C, 41.1; H, 4.8; N, 9.9. $C_5H_7NO_2S$ requires C, 41.4; H, 4.9; N, 9.7%); $\nu_{max.}$ (film) 1 760 cm^{-1} (C=O); *m/e* 145 (M^+), 71 ($C_3H_7CO^+$), and 43 (C_3H_7).

5-*Undecyl*-1,3,4-*oxathiazol*-2-*one*. This compound was prepared in 75% yield from dodecanamide and ClCOSCl; it had m.p. 37—38.5 °C (Found: C, 60.9; H, 9.2; N, 5.0. $C_{13}H_{23}NO_2S$ requires C, 60.7; H, 9.0; N, 5.4%); $\nu_{max.}$ (Nujol) 1 765 cm^{-1} (C=O); *m/e* 257 (M^+), 213 ($C_{11}H_{23}CNS^+$), and 183 ($C_{11}H_{23}CO^+$).

Synthesis of 1,3,4-*Oxathiazoles* (4).—The general method was to heat under reflux a solution of the 1,3,4-oxathiazol-2-one and the carbonyl compound (5 mol per mol of oxathiazolone) in dry xylene, as described below for 5-(*p*-chlorophenyl)-2-phenyl-2-trifluoromethyl-1,3,4-oxathiazole. The reaction was continued until h.p.l.c. analysis showed that all the starting material had been consumed. After evaporation under reduced pressure to remove the solvent and excess dipolarophile, the oxathiazole was separated from nitrile and sulphur by-products by distillation and/or recrystallisation.

5-(*p-Chlorophenyl*-2-*phenyl*-2-*trifluoromethyl*-1,3,4-*oxathiazole*. A mixture of 5-(*p*-chlorophenyl)-1,3,4-oxathiazol-2-one (2.0 g, 9.4 mmol) and α,α,α-trifluoroacetophenone (8.2 g, 47 mmol) in dry xylene (50 ml) was heated under reflux until h.p.l.c. analysis indicated complete consumption of the oxathiazolone (12.5 h). The solvent and excess trifluoroacetophenone were removed under reduced pressure to leave a yellow oil, from which 4-chlorobenzonitrile (0.52 g, 65%) was isolated by vacuum distillation (80 °C, 0.003 mmHg). On dissolving the residue in hexane and cooling, a pale yellow solid was formed which, after treatment with charcoal and recrystallisation from hexane, afforded 5-(*p*-chlorophenyl)-2-phenyl-2-trifluoromethyl-1,3,4-oxathiazole (0.30 g, 18%) as white crystals, m.p. 77 °C (Found: C, 52.4; H, 2.6; N, 4.0. $C_{15}H_9ClF_3NOS$ requires C, 52.4; H, 2.6; N, 4.1%); $\nu_{max.}$ (Nujol) 1 625 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 7.84 (d, 2 H, *J* 8.5 Hz, ArH), 7.2—7.5 (m, 7 H, ArH); *m/e* 345 and 343 (M^+), 276 and 274 ($[M - CF_3]^+$), 171 and 169 ($ClC_6H_4CNS^+$), 139 and 137 ($ClC_6H_4CN^+$).

2,2-*Bis*(*trichloromethyl*)-5-(p-*chlorophenyl*)-1,3,4-*oxathiazole*. After a reaction period of 28 h this compound (35%), together with 4-chlorobenzonitrile (58%), was obtained as white crystals, m.p. 104.5 °C (from hexane, charcoal) (Found: C, 27.5; H, 0.9; N, 3.2. $C_{10}H_4Cl_7NOS$ requires C, 27.6; H, 0.9; N, 3.2%); $\nu_{max.}$ (Nujol) 1 625 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 7.84 (d, 2 H, *J* 8.5 Hz, ArH), and 7.40 (d, 2 H, *J* 8.5 Hz, ArH); *m/e* 433, 431, 429 and 427 (M^+), 314, 312 and 310 [$(M - CCl_3)^+$], and 165 ($ClC_6H_4CN^+$).

5-*Phenyl*-2-*trichloromethyl*-1,3,4-*oxathiazole*. After a reaction period of 26 h this compound was obtained (59%) as white crystals, m.p. 67—68 °C (from hexane, charcoal) (Found: C, 38.1; H, 2.1; N, 5.0. $C_9H_6Cl_3NOS$ requires C, 38.3; H, 2.1; N, 5.0%); $\nu_{max.}$ (Nujol) 1 615 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 7.3—8.2 (m, 5 H, PhH) and 6.44 (s, 1 H, $CHCCl_3$); *m/e* 285, 283 and 281 (M^+), 166 and 164 ($[M - CCl_3]^+$), 135 ($PhCNS^+$), 105 ($PhCO^+$), 103 ($PhCN^+$), and 77 (Ph^+).

2,2-*Bis*(*trichloromethyl*)-5-*phenyl*-1,3,4-*oxathiazole*. After a reaction period of 8 h this compound was obtained (54%) as white needles, m.p. 53—54 °C (from hexane) (Found: C,

29.8; H, 1.2; N, 3.4. $C_{10}H_5Cl_6NOS$ requires C, 30.0; H, 1.3; N, 3.5%); $\nu_{max.}$ (Nujol) 1 630 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 7.4—8.1 (m, 5 H, PhH); *m/e* 403, 401, 399 and 397 (M^+), 284, 282 and 280 ($[M - CCl_3]^+$), 135 ($PhCNS^+$), 105 ($PhCO^+$), 103 ($PhCN^+$), and 77 (Ph^+).

5-(*p-Methoxyphenyl*)-2-*trichloromethyl*-1,3,4-*oxathiazole*. After a reaction period of 5 h this compound was obtained (76%) as white crystals, m.p. 82—83 °C (from hexane) (Found: C, 38.5; H, 2.6; N, 4.4. $C_{10}H_8Cl_3NO_2S$ requires C, 38.4; H, 2.6; N, 4.5%); $\nu_{max.}$ (Nujol) 1 615 cm^{-1} (C=N); δ_H ($CDCl_3$ Me_4Si) 7.83 (d, 2 H, *J* 9 Hz, ArH), 6.88 (d, 2 H, *J* 9 Hz, ArH), 6.43 (s, 1 H, $CHCCl_3$), and 3.80 (s, 3 H, OMe); *m/e* 315, 313 and 311 (M^+), 194 ($[M - CCl_3]^+$), 165 ($MeOC_6H_4CNS^+$), 135 ($MeOC_6H_4CO^+$), and 133 ($MeOC_6H_4CN^+$).

2,2-*Bis*(*trichloromethyl*)-5-(p-*methoxyphenyl*)-1,3,4-*oxathiazole*. After a reaction period of 5 h this compound was obtained in 57% yield and purified by chromatography (silica–hexane), m.p. 87—88 °C (from hexane) (Found: C, 31.0; H, 1.7; N, 3.2. $C_{11}H_7Cl_6NO_2S$ requires C, 30.7; H, 1.6; N, 3.3%); $\nu_{max.}$ (Nujol) 1 620 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 7.86 (d, 2 H, *J* 9 Hz, ArH), 6.92 (d, 2 H, *J* 9 Hz, ArH), and 3.82 (s, 3 H, OMe); *m/e* 433, 431, 429 and 427 (M^+), 314, 312 and 310 ($[M - CCl_3]^+$), 165 ($MeOC_6H_4CNS^+$), 135 ($MeOC_6H_4CO^+$), and 133 ($MeOC_6H_4CN^+$).

5-(p-*Methoxyphenyl*)-2-*phenyl*-2-*trifluoromethyl*-1,3,4-*oxathiazole*. After a reaction period of 4 h this compound (28%), together with 4-methoxybenzonitrile (59%), was obtained as white crystals, m.p. 86—87 °C (from hexane) (Found: C, 56.4; H, 3.5; N, 4.0. $C_{16}H_{12}F_3NO_2S$ requires C, 56.6; H, 3.6; N, 4.1%); $\nu_{max.}$ (Nujol) 1 620 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 7.89 (d, 2 H, *J* 9 Hz, ArH), 7.3—7.5 (m, 5 H, PhH), 6.91 (d, 2 H, *J* 9 Hz, ArH), and 3.81 (s, 3 H, OMe); *m/e* 339 (M^+), 270 ($[M - CF_3]^+$), 165 ($MeOC_6H_4CNS^+$), 135 ($MeOC_6H_4CO^+$), and 133 ($MeOC_6H_4CN^+$).

5-*Methyl*-2-*trichloromethyl*-1,3,4-*oxathiazole*. After a reaction period of 5 h this compound was obtained (62%) as white crystals, m.p. 44.5—50 °C (from hexane, charcoal) (Found: C, 21.5; H, 1.7; N, 6.2. $C_4H_4Cl_3NOS$ requires C, 21.8; H, 1.8; N, 6.3%); $\nu_{max.}$ (Nujol) 1 650 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 6.30 (s, 1 H, $CHCCl_3$), and 2.12 (s, 3 H, Me); *m/e* 223, 221 and 219 (M^+), 102 ($[M - CCl_3]^+$), 73 ($MeCNS^+$), 43 ($MeCO^+$), and 41 ($MeCN^+$).

2,2-*Bis*(*trichloromethyl*)-5-*methyl*-1,3,4-*oxathiazole*. After a reaction period of 6 h this compound was obtained (56%) as white needles, m.p. 70 °C (from hexane) (Found: C, 17.5; H, 0.9; N, 3.9. $C_5H_3Cl_6NOS$ requires C, 17.8; H, 0.9; N, 4.1%); $\nu_{max.}$ (Nujol) 1 655 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 2.23 (s, 3 H, Me); 341, 339, 337 and 335 (M^+), 218 ($[M - CCl_3]^+$), 73 ($MeCNS^+$), 43 ($MeCO^+$), and 41 ($MeCN^+$).

2,2-*Bis*(*trichloromethyl*)-5-*propyl*-1,3,4-*oxathiazole*. After a reaction period of 5 h this compound was obtained (44%) as a colourless oil, b.p. 135 °C at 0.003 mmHg (Found: C, 22.7; H, 1.6; N, 3.7. $C_6H_7Cl_6NOS$ requires C, 23.0; H, 1.9; N, 3.8%); $\nu_{max.}$ (film) 1 655 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 2.43 (t, 2 H, CH_2), 1.6—1.9 (m, 2 H, CH_2), and 1.00 (t, 3 H, Me); *m/e* 369, 367, 365 and 363 (M^+), 101 ($PrCNS^+$).

2-*Trichloromethyl*-5-*undecyl*-1,3,4-*oxathiazole*. After a reaction period of 6.5 h this compound was obtained as a pale yellow oil (60%) and purified by chromatography (silica–hexane) (Found: *m/e* 359.065 016. $C_{14}H_{24}{}^{35}Cl_3NOS$ requires *M*, 359.064 412); $\nu_{max.}$ (film) 1 650 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 6.28 (s, 1 H, $CHCCl_3$), 2.40 (t, 2 H, CH_2), 1.6—1.8 (m, 2 H, CH_2), 1.1—1.6 (m, 16 H, CH_2), and 0.87 (t, 3 H, Me); *m/e* 363, 361 and 359 (M^+), 242 ($[M - CCl_3]^+$). An attempted distillation of the product at 175 °C/0.003 mmHg yielded a pale yellow oil; i.r. spectroscopy indicated that it contained some nitrile, $\nu_{max.}$ (film) 2 210 cm^{-1} (C=N), arising from the thermal fragmentation of the oxathiazole.[7]

2,2-*Bis*(*trichloromethyl*)-5-*undecyl*-1,3,4-*oxathiazole*. After a reaction period of 7 h this compound was obtained as a pale yellow oil (31%) and purified by chromatography (silica–hexane) (Found: *m/e* 474.963 078. $C_2H_2{}^{35}Cl_6NOS$ requires *M* 474.963 146); $\nu_{max.}$ (film) 1 655 cm^{-1} (C=N); δ_H ($CDCl_3$, Me_4Si) 2.50 (t, 2 H, CH_2), 1.9—1.6 (m, 2 H, CH_2), 1.1—1.5 (m, 16 H, CH_2) and 0.87 (t, 3 H, Me); *m/e* 481, 479, 477 and 475 (M^+), 362 and 360 ($[M - CCl_3]^+$). An attempted distillation of the product at 170—180 °C/0.003 mmHg yielded a yellow oil; i.r. spectroscopy indicated that it contained some nitrile, $\nu_{max.}$ (film) 2 210 cm^{-1} (C=N), arising from the thermal fragmentation of the oxathiazole.[7]

X-*Ray Crystal Structure Analysis of* 5-*Phenyl*-2-*trichloromethyl*-1,3,4-*oxathiazole* (4A) *and* 5-(p-*Methoxyphenyl*)-2-*phenyl*-2-*trifluoromethyl*-1,3,4-*oxathiazole* (4B).—Crystallisation of (4A) from hexane gave monoclinic needles, elongated along *c*, and of (4B) from hexane gave monoclinic prisms.

Crystal Data for (4A).—$C_9H_6Cl_3NOS$, $M = 282.6$, monoclinic, $a = 11.507(8)$, $b = 9.356(2)$, $c = 10.560(9)$ Å, $\beta = 78.54(1)°$, $U = 1\,114.2$ Å^3, $D_m = 1.65$ g cm^{-3}, $Z = 4$, $D_c = 1.68$ g cm^{-3}, space group $P2_1/c$ (by systematic absences), Mo-K_α radiation (graphite monochromatised) $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 9.7 cm^{-1}. Dimensions of crystal used for intensity data 0.2 × 0.2 × 0.7 mm.

Crystal Data for (4B).—$C_{16}H_{12}F_3NO_2S$, $M = 339.3$, monoclinic, $a = 12.282(5)$, $b = 7.311(2)$, $c = 17.181(7)$ Å, $\beta = 105.89(3)°$, $U = 1\,483.8$ Å^3, $D_m = 1.52$ g cm^{-3}, $Z = 4$, $D_c = 1.52$ g cm^{-3}, space group $P2_1/c$ (by systematic absences), Mo-K_α radiation (graphite monochromatised), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 2.6 cm^{-1}. Dimensions of crystal used for intensity data 0.15 × 0.20 × 0.25 mm.

After preliminary oscillation and Weissenberg photographs each crystal was mounted on the Stadi-2 diffractometer with *b* along the spindle; cell dimensions were refined and the intensity data recorded using an ω scan and $\theta_{max.} = 25°$. In each case two unique sets of reflections were recorded and subsequently averaged after Lp correction.

Both structures were solved by direct methods using the MULTAN system [12] and refined by least-squares using the XRAY system; [13] difference Fourier maps confirmed the presence of hydrogen atoms at the stereochemically expected positions. In the final cycles, positional parameters were refined for hydrogen atoms but their thermal parameters were fixed at $U = 0.06$ Å^2; positional and anisotropic thermal parameters were refined for all other atoms. Unit weights were used in (4B) and a weighting scheme dependent on both $|F_{obs.}|$ and sin θ in (4A).

The atomic scattering factors in the XRAY system were used. *R* Converged to 0.044 for 1 588 reflections with $I > 2\sigma(I)$ for (4A) and 0.043 for 1 223 reflections for (4B).

Positional parameters for atoms other than hydrogen are given in Table 3. The molecules (and atom numbering) are illustrated in Figure 1 (drawn by the programme PLUTO [14]), and selected bond lengths and angles in Figure 2. All positional and thermal parameters are deposited as supplementary publication No. SUP No. 23145 (28 pages).*

* For details of the Supplementary Publications Scheme see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1980, Index issue.

TABLE 3

Fractional co-ordinates for atoms other than hydrogen, with their standard deviations.

Atom	*x*	*y*	*z*
(*a*) for compound (4A)			
O(1)	0.438 1(2)	0.410 7(3)	0.297 8(3)
C(2)	0.396 4(3)	0.273 3(4)	0.273 6(4)
S(3)	0.488 8(1)	0.148 8(1)	0.340 0(1)
N(4)	0.583 8(3)	0.280 8(4)	0.359 7(4)
C(5)	0.545 4(3)	0.401 8(4)	0.334 4(3)
C(6)	0.605 2(3)	0.539 4(4)	0.335 5(3)
C(7)	0.699 9(3)	0.552 0(5)	0.398 0(4)
C(8)	0.760 9(4)	0.677 7(7)	0.392 0(5)
C(9)	0.731 3(5)	0.792 2(7)	0.325 5(5)
C(10)	0.638 2(5)	0.782 8(6)	0.263 2(5)
C(11)	0.574 9(4)	0.656 8(5)	0.270 0(4)
C(21)	0.402 4(3)	0.255 0(4)	0.130 0(4)
Cl(211)	0.308 9(1)	0.384 4(1)	0.080 6(1)
Cl(212)	0.545 7(1)	0.280 7(1)	0.042 6(1)
Cl(213)	0.352 8(1)	0.082 0(1)	0.102 2(1)
(*b*) for compound (4B)			
O(1)	0.738 6(2)	0.335 7(5)	0.715 4(2)
C(2)	0.825 1(4)	0.350 4(8)	0.790 4(3)
S(3)	0.951 2(1)	0.421 1(3)	0.760 7(1)
N(4)	0.882 6(3)	0.418 9(7)	0.661 4(2)
C(5)	0.779 6(4)	0.374 3(7)	0.650 5(3)
C(6)	0.696 0(4)	0.360 4(6)	0.571 9(3)
C(7)	0.719 8(4)	0.429 1(7)	0.502 8(3)
C(8)	0.643 6(4)	0.411 4(9)	0.428 8(3)
C(9)	0.540 8(4)	0.324 2(7)	0.421 0(3)
C(10)	0.514 7(4)	0.257 4(7)	0.489 2(3)
C(11)	0.592 3(4)	0.277 6(7)	0.564 3(3)
C(21)	0.838 7(5)	0.159 4(8)	0.825 2(3)
F(211)	0.746 5(3)	0.099 1(5)	0.841 5(2)
F(212)	0.865 7(3)	0.040 0(5)	0.775 3(2)
F(213)	0.923 0(3)	0.153 2(5)	0.893 8(2)
C(22)	0.789 7(4)	0.479 6(7)	0.847 2(3)
C(221)	0.870 6(5)	0.570 5(9)	0.905 9(3)
C(222)	0.838 7(7)	0.688 4(10)	0.957 3(4)
C(223)	0.726 0(7)	0.718 4(9)	0.950 8(4)
C(224)	0.645 6(6)	0.627 9(9)	0.893 3(4)
C(225)	0.677 2(5)	0.506 7(8)	0.841 5(3)
O(91)	0.471 6(3)	0.311 8(5)	0.344 5(2)
C(911)	0.370 0(6)	0.212 7(9)	0.332 7(4)

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