Nitrile Sulphides. Part 3.[1,2] Thermal Fragmentation of 1,3,4-Oxathiazoles: Formation of Nitrile Sulphides in a Retro-1,3-dipolar Cycloaddition Reaction

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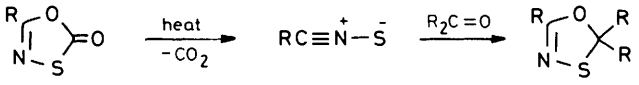
On thermolysis at *ca.* 160 °C 1,3,4-oxathiazoles undergo retro-1,3-dipolar cycloaddition forming nitrile sulphides and carbonyl-containing fragments. The nitrile sulphides either decompose to sulphur and nitriles or are trapped as their 1,3-dipolar cycloadducts in the presence of dipolarophiles (dimethyl acetylenedicarboxylate, ethyl cyanoformate, benzonitrile, ethyl propiolate). Similar ratios (1.32, 1.34, 1.33, 1.31) of 4- and 5-ethoxycarbonyl-3-(*p*-methoxyphenyl)isothiazole obtained from four sources [(**2a**), (**3a**), (**3b**), (**3c**)] of *p*-methoxybenzonitrile sulphide with ethyl propiolate provide strong evidence for product formation from a discrete intermediate nitrile sulphide rather than *via* direct interaction of precursor with dipolarophile. 2-Dichloromethylene-1,3,4-oxathiazoles, prepared by dehydrochlorination of 2-trichloromethyloxathiazoles, likewise fragment to nitrile sulphides, but attempts to trap dichloroketene were unsuccessful.

We have previously described[3] the 1,3-dipolar cycloaddition reactions of nitrile sulphides (**1**), generated by thermal decarboxylation of 1,3,4-oxathiazol-2-ones (**2**), with aldehydes and ketones bearing trihalogenomethyl substituents. By this means 1,3,4-oxathiazoles (**3**) were formed from chloral, hexachloroacetone, and α,α,α-trifluoroacetophenone. We now report that the oxathiazoles are themselves thermally labile, fragmenting on more vigorous heating to regenerate the nitrile sulphides in a retro-1,3-dipolar cycloaddition reaction.



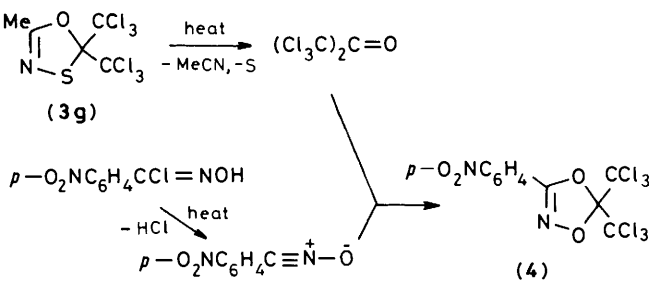
(**2**) (**1**) (**3**)

a; R = *p*-$MeOC_6H_4$
b; R = *p*-MeC_6H_4

Results and Discussion

During the synthesis of compound (**3a**) from 5-(*p*-methoxyphenyl)-1,3,4-oxathiazol-2-one (**2a**) and hexachloroacetone in xylene under reflux it was noted that the yield of product decreased on more prolonged heating. An investigation of the thermal stabilities of 2,2,4-trisubstituted-1,3,4-oxathiazoles was therefore undertaken. Compound (**3a**) was heated in mesitylene under reflux until high-pressure liquid chromatography (h.p.l.c.) analysis indicated complete consumption of the starting material (after 1 h). The products were identified as sulphur, *p*-methoxybenzonitrile (98%, h.p.l.c.), and hexachloroacetone (99%, g.l.c.). Other oxathiazoles behaved similarly. In the case of the methylbis(trichloromethyl)oxathiazole (**3g**) the formation of hexachloroacetone was confirmed by isolation of its dioxazole 1,3-dipolar cycloadduct (**4**) on reaction with *p*-nitrobenzonitrile oxide, generated *in situ* by dehydrochlorination of the corresponding hydroximoyl chloride (Scheme 1).[4]

Isolation of nitriles, sulphur, and carbonyl-containing decomposition products was reminiscent of the behaviour of the original oxathiazolones (**2**)[5] and suggested that nitrile sulphides might be involved as transient intermediates in each case. The thermolysis of compound (**3a**) was therefore repeated in the presence of a ten-fold excess of dimethyl acetylenedicarboxylate (DMAD), a well established dipolarophile. The products were



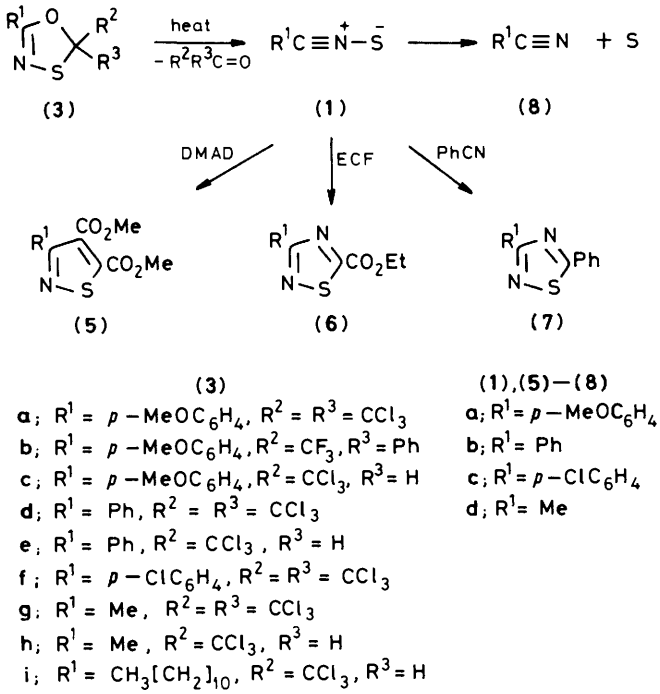
(**3g**) (**4**)

Scheme 1.

identified as sulphur, hexachloroacetone (99%), *p*-methoxybenzonitrile (8%), and the isothiazole (**5a**) (88%). The formation of the latter strongly indicates the involvement of an intermediate nitrile sulphide. Further evidence was provided when ethyl cyanoformate (ECF) and benzonitrile yielded the 1,2,4-thiadiazoles (**6a**) (92%) and (**7a**) (34%). The other oxathiazoles, (**3b**—**h**), reacted similarly (Scheme 2 and Table 1).

The oxathiazoles (**3**) prove to be similar to the oxathiazolones (**2**) as sources of nitrile sulphides. For example, nitriles are formed as by-products resulting from fragmentation of (**1**) competing with the cycloaddition (Scheme 2). The rate of oxathiazole disappearance is unaffected by the presence of dipolarophile, but is dependent on the electronic nature of R^1. Electron-donating substituents increase the rate, consistent with a developing positive charge at C-5 in the transition state. There are also significant differences in stability within each oxathiazole series, with reaction times increasing as the carbonyl fragment varies from hexachloroacetone (*ca.* 1 h) through trifluoroacetophenone (4 h) to chloral (18 h). The comparable figure for the parent oxathiazolones is *ca.* 0.5 h.

Compounds (**3a**) and (**3f**) in neat benzonitrile (*ca.* 190 °C) yielded 3,5-diphenyl-1,2,4-thiadiazole (**7b**) (2—3%) in addition to the anticipated unsymmetrically substituted derivatives (**7a**) and (**7c**). Thermal decarboxylation of compound (**2b**) in the same solvent has also been reported[6] to give (**7b**); the most likely explanation for the formation of this unexpected by-product is generation of benzonitrile sulphide, perhaps from benzonitrile and atomic sulphur or by direct sulphur-atom transfer from *p*-methylbenzonitrile sulphide, and its 1,3-dipolar



(3)

a; R^1 = p-$MeOC_6H_4$, R^2 = R^3 = CCl_3
b; R^1 = p-$MeOC_6H_4$, R^2 = CF_3, R^3 = Ph
c; R^1 = p-$MeOC_6H_4$, R^2 = CCl_3, R^3 = H
d; R^1 = Ph, R^2 = R^3 = CCl_3
e; R^1 = Ph, R^2 = CCl_3, R^3 = H
f; R^1 = p-ClC_6H_4, R^2 = R^3 = CCl_3
g; R^1 = Me, R^2 = R^3 = CCl_3
h; R^1 = Me, R^2 = CCl_3, R^3 = H
i; R^1 = $CH_3[CH_2]_{10}$, R^2 = CCl_3, R^3 = H

(1),(5)—(8)

a; R^1 = p-$MeOC_6H_4$
b; R^1 = Ph
c; R^1 = p-ClC_6H_4
d; R^1 = Me

Scheme 2.

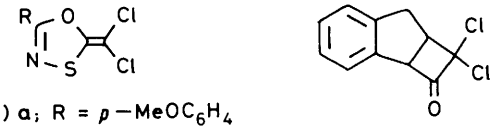
Table 1. Products and reaction conditions[a] for the thermolyses of 1,3,4-oxathiazoles (3) in the presence of dipolarophiles

Oxathiazole	Dipolarophile	Reaction time/h	Cycloadduct (%)[b]	Nitrile (%)[b]
(3a)	DMAD	0.8	(5a) (88)	(8a) (8)[c]
	ECF	1	(6a) (92, isolated)	
	PhCN	0.3	(7a) (34)	(8a) (60)
			(7b) (3)	
(3b)	DMAD	4	(5a) (80)	(8a) (12)[d]
(3c)	DMAD	18	(5a) (60)	(8a) (33)[e]
(3d)	DMAD	2	(5b) (64)	
	PhCN	0.5	(7b) (28)	
(3e)	DMAD	22	(5b) (52)	
	ECF	26	(6b) (75, isolated)	
	PhCN	2.5	(7b) (22)	
(3f)	DMAD	2.8	(5c) (69)	
	ECF	3	(6c) (70, isolated)	
	PhCN	0.8	(7c) (20)	
			(7b) (2)	
(3g)	DMAD	0.6	(5d) (92)	
(3h)	DMAD	10.5	(5d) (34)	

[a] Reactions carried out in refluxing mesitylene at 161 ± 1 °C using 10 mol dipolarophile per mol of (3), except for benzonitrile when the solvent was omitted and the temperature was *ca.* 190 °C. [b] Yields determined by h.p.l.c. unless otherwise stated. [c] Hexachloroacetone (99%, g.l.c.) also formed. 98% (8a) and 99% $(Cl_3C)_2CO$ formed after 1 h in the absence of dipolarophile. [d] 96% (8a) and 79% CF_3COPh formed after 4 h in the absence of dipolarophile. [e] 95% (8a) formed after 18 h in the absence of dipolarophile.

cycloaddition to the solvent. This explanation may also be invoked to explain the observations of the present study.

The range of oxathiazoles available for study was extended by dehydrochlorination of the 2-trichloromethyl derivatives. Treatment of oxathiazoles (3c), (3e), (3h), and (3i) with sodium ethoxide in ethanol at room temperature for 1—3 h yielded the 2-dichloromethylene compounds (9a—d) in good yields (70—84%). Attempts to achieve the dehydrochlorination with triethylamine failed. The products were identified from their analytical and spectroscopic data. The i.r. spectra show a C=C peak at 1 610—1 630 cm^{-1} in addition to the characteristic C=N absorption at 1 650—1 660 cm^{-1} found for other oxathiazoles.[3] In the ^{13}C n.m.r. spectra the introduction of the olefinic double bond results in a shift of the absorption for C-2 to *ca.* 155 p.p.m. from the value of 96 p.p.m. for the 2-trichloromethyl precursors, while that for C-5 remains almost unaltered (158, *cf.* 157 p.p.m.); the exocyclic CCl_2 signal appears at 88—89 p.p.m. Their mass spectra are very similar to those of other oxathiazoles with major fragments corresponding to RCNS and RCN, presumably resulting from electron-impact-induced cycloreversion. This suggested that oxathiazoles (9) might also be able to act as nitrile sulphide precursors. On thermolysis in mesitylene compound (9a) did decompose to give nitrile (8a) (96%), but only after prolonged heating (168 h) under reflux. Repetition of the reaction in the presence of DMAD in excess (1:10) yielded the expected isothiazole (5a) (27%) thus confirming the involvement of the nitrile sulphide (1a). Benzonitrile sulphide (1b) generated from the oxathiazole (9b) was also trapped by benzonitrile, the thiadiazole (7b) being formed in low yield (6%). By analogy with the other oxathiazoles examined it was anticipated that dichloroketene would be formed concomitantly. Attempts to trap it with indene, with which it is known[7] to react readily, failed. On being heated in neat indene at 180 °C for 56 h, compound (9a) yielded the nitrile (8a) (96%), but the adduct (10) could not be detected by h.p.l.c. or g.l.c. Compound (10) is stable at these



(9) a; R = p-$MeOC_6H_4$
b; R = Ph
c; R = Me
d; R = $CH_3[CH_2]_{10}$

(10)

temperatures. There is no reaction between indene and the nitrile sulphide (1a) generated from oxathiazoles (9a) or (2a); in each case only the nitrile was detected. It is therefore considered likely that the ketene, if formed, is reacting by another pathway before trapping can take place. Dichloroketene is known to be of limited thermal stability.[8] The 2-chloromethyleneoxathiazoles are the least useful source of nitrile sulphides, giving generally low yields of cycloadducts and requiring long reaction times at high temperatures.

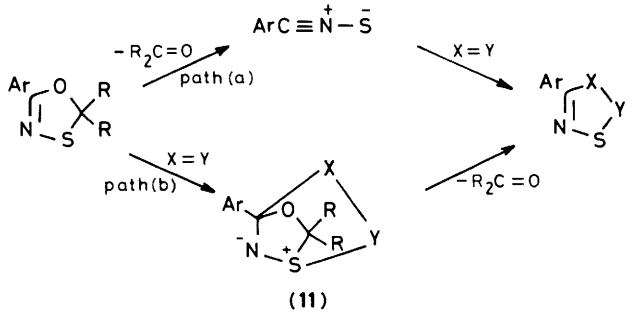
The variety of sources of *p*-methoxybenzonitrile sulphide provided by the oxathiazoles (3a—c) and the corresponding oxathiazolone (2a) presented the opportunity to test for any variation in regioselectivity in the cycloaddition reaction, and thereby gain insight into the mechanism of product formation. Two reaction pathways were considered: initial loss of the carbonyl fragment generating a free nitrile sulphide intermediate, followed by its 1,3-dipolar cycloaddition to the dipolarophile [Scheme 3, path (a)]; or direct interaction between dipolarophile and precursor to form an intermediate adduct (11), which subsequently collapses to product, expelling the carbonyl fragment [path (b)]. The regioselectivity might be expected to be independent of source for path (a) but not for path (b).

Ethyl propiolate (EP) was selected as dipolarophile as it was known[9] to react with benzonitrile sulphide forming similar amounts of the 4- and 5-ethoxycarbonylisothiazole, (12) and (13). The ratio (12):(13) was therefore considered to be a sensitive probe for any dependence of regioselectivity on source.

Table 2. Products from the thermolysis of *p*-methoxyphenyloxathiazoles (**3a**—**c**) and the oxathiazolone in the presence of ethyl propiolate[a]

Oxathiazole	Isothiazole cycloadducts (%)[b] (12)	(13)	Isomer ratio (12)/(13)	Nitrile (%)[b]
(**3a**)	47	35	1.34	16
(**3b**)	44	33	1.33	23
(**3c**)	17	13	1.31	68
(**2a**)	49	37	1.32	12

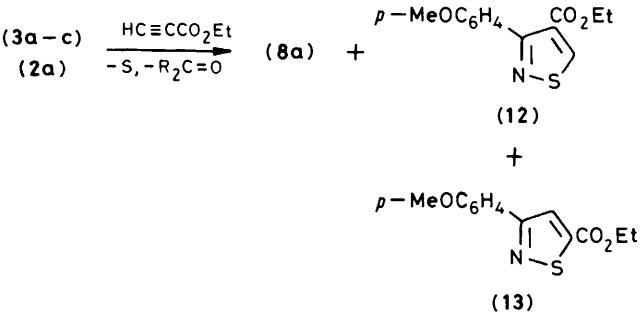
[a] Reactions carried out in refluxing mesitylene at 161 ± 1 °C using 10 mol EP per mol of (**3**) or (**2**). [b] Yields determined by h.p.l.c.



(**11**)

Scheme 3.

The ratio of regioisomers is found to be independent of source, consistent with cycloadduct formation *via* a free nitrile sulphide [Scheme 3, path (a)], and the involvement of intermediates such as (**11**) can therefore be discounted.



Scheme 4.

Accordingly oxathiazoles (**3a**—**c**) and (**2a**) were heated in mesitylene (161 °C) in the presence of EP [10 mol per mol (**3**) or (**2a**)] and the products were analysed by h.p.l.c. (Scheme 4 and Table 2).

These results support the kinetic work of Howe *et al.*[9] which established that the rate of consumption of oxathiazolones (**2**) is independent of alkyne concentration and that the observed rate constants for the formation of isothiazole and of nitrile are first order and equal to that for the disappearance of compound (**2**). These complementary studies firmly establish the role of free nitrile sulphides as intermediates in such reactions.

The yield of nitrile by-products proved to be strongly dependent on the starting material, ranging from 12% from (**2a**) to 63% from (**3c**). This variation is not consistent with nitrile formation solely by unimolecular decomposition of the nitrile sulphide for which the yield should be independent of source. Howe and Shelton[10] have reached the same conclusion based on the dependence of yield on concentration. The possibility that there exists an alternative, as yet unidentified, pathway to the nitrile cannot be discounted.

Although there have been a number of recent reports of retro-1,3-dipolar cycloaddition reactions, *e.g.* yielding nitrile oxides,[11] the present work represents the first case involving a nitrile sulphide.

Experimental

The analytical methods for monitoring the reactions and the instrumentation used for recording i.r., ^1H and ^{13}C n.m.r., and mass spectra were as previously described.[3] 5-(*p*-Methoxy phenyl)-1,3,4-oxathiazol-2-one (**2a**)[3] the oxathiazoles (**3a**—**i**),[3] isothiazoles (**5b**—**d**),[9] thiadiazoles (**6b**), (**6c**), (**7b**), and (**7c**),[6] *p*-nitrobenzohydroximoyl chloride,[12] and 1,1-dichloro-1,2a,7,7a-tetrahydrocyclobut[*a*]inden-2-one (**10**)[13] were prepared by established literature routes. Light petroleum refers to the fraction boiling in the range 40—60 °C.

3-(*p-Nitrophenyl*)-5,5-*bis*(*trichloromethyl*)-1,4,2-*dioxazole* (**4**). —Triethylamine (0.51 g, 4.0 mmol) dissolved in diethyl ether (20 ml) was added dropwise to a solution of *p*-nitrobenzohydroximoyl chloride (1.0 g, 5.0 mmol) and hexachloroacetone (6.6 g, 25.0 mmol) in diethyl ether (50 ml) and the mixture was heated under reflux until h.p.l.c. analysis indicated complete consumption of the hydroximoyl chloride (0.5 h). After separation of triethylamine hydrochloride by filtration, concentration of the filtrate, and Kugelrohr distillation (60 °C; 1.0 mmHg) to remove remaining traces of solvent and dipolarophile, the residue was recrystallised from diethyl ether to give 3-(*p-nitrophenyl*)-5,5-*bis*(*trichloromethyl*)-1,4,2-*dioxazole* (**4**) (56%) as pale yellow needles, m.p. 144 °C (Found: C, 28.2; H, 1.0; N, 6.3. $C_{10}H_4Cl_6N_2O_4$ requires C, 28.0; H, 0.9; N, 6.5%); δ_C ($CDCl_3$; 20 MHz) 159.0 (C-3), 150.2 and 125.7 (ArC), 128.3 and 124.2 (4 ArCH), 115.3 (C-5), and 96.8 p.p.m. (2 CCl_3).

3-(p-*Methoxyphenyl*)-5-*phenyl*-1,2,4-*thiadiazole* (**7a**) was prepared (52%) by the literature route[6] for 3,5-diaryl-1,2,4-thiadiazoles from 5-(*p*-methoxyphenyl)-1,3,4-oxathiazol-2-one and benzonitrile. It had m.p. 123 °C (white needles from ethanol) (Found: C, 66.9; H, 4.4; N, 10.2. $C_{15}H_{12}N_2OS$ requires C, 67.1; H, 4.5; N, 10.4%); δ_C ($CDCl_3$; 20 MHz) 187.6 (C-5), 173.4 (C-3), 161.2, 130.7, and 125.8 (ArC), 131.6, 129.8, 129.0, 127.3, and 113.9 (9 ArCH), and 55.2 p.p.m. (OCH_3).

Dimethyl 3-(p-*Methoxyphenyl*)*isothiazole*-4,5-*dicarboxylate* (**5a**) was prepared as described[9] for other isothiazoles from 5-(*p*-methoxyphenyl)-1,2,4-oxathiazol-2-one and DMAD. It had m.p. 88.5—89.5 °C (lit.,[14] 88—90 °C).

Ethyl 3-(p-*Methoxyphenyl*)*isothiazole*-4- and -5-*carboxylate* (**12**) *and* (**13**).—A solution of 5-(*p*-methoxyphenyl)-1,3,4-oxathiazol-2-one (**2a**) (4.3 g, 20.2 mmol) and ethyl propiolate (4.0 g, 40.8 mmol) in dry xylene (150 ml) was heated under reflux until h.p.l.c. analysis showed complete consumption of the oxathiazolone (5 h). The reaction mixture was concentrated to leave an amber oil which was subjected to medium-pressure liquid chromatography.[15] Elution with light petroleum–diethyl ether (1:1) afforded *ethyl* 3-(p-*methoxyphenyl*)*isothiazole*-5-*carboxylate* (**13**) (0.4 g, 8%) as white crystals, m.p. 78 °C (from methanol) (Found: C, 59.5; H, 5.0; N, 5.2. $C_{13}H_{13}NO_3S$ requires C, 59.3; H, 5.0; N, 5.3%); δ_H ($CDCl_3$; 100 MHz) 7.98 (1 H, s, 4-H), 7.83 (2 H, d, ArH), 6.92 (2 H, d, ArH), 4.39 (2 H, q, CH_2), 3.80 (3 H, s, OCH_3), and 1.39 (3 H, t, CH_3); δ_C ($CDCl_3$; 20 MHz) 167.6 (C-3), 160.6, 160.0, 157.3, and 126.9 (C=O, C-3, and 2 ArC), 128.1 and 114.1 (4 ArCH), 124.2 (C-4), 61.8 (CH_2), 55.1 (OCH_3), and 14.0 p.p.m. (CH_3); *m/z* 263 (M^+).

Further elution with the same solvent yielded *ethyl* 3-(p-*methoxyphenyl*)*isothiazole*-4-*carboxylate* (**12**) (0.7 g, 13%) as white needles, m.p. 75 °C (from methanol) (Found: C, 59.2; H,

5.0; N, 5.1%); δ_H ($CDCl_3$; 100 MHz) 9.26 (1 H, s, 5-H), 7.59 (2 H, d, ArH), 6.92 (2 H, d, ArH), 4.27 (2 H, q, CH_2), 3.81 (3 H, s, OCH_3), and 1.27 (3 H, t, CH_3); δ_C ($CDCl_3$; 20 MHz) 168.0 (C-3), 162.0 (C=O), 160.2 and 127.3 (ArC), 155.5 (C-5), 130.3 and 113.0 (4 ArCH), 128.8 (C-4), 60.9 (CH_2), 55.0 (OCH_3), and 13.9 p.p.m. (CH_3); *m/z* 263 (M^+).

Thermolysis of 1,3,4-*Oxathiazoles in the Absence of Dipolarophiles.*—The general method was to heat under reflux a solution of the oxathiazole in mesitylene (dried and redistilled) under nitrogen until h.p.l.c. analysis showed no remaining starting material. The products were identified and their yields determined by g.c. and/or h.p.l.c. analysis (see footnotes to Table 1).

A derivative of hexachloroacetone formed from 2,2-bis(trichloromethyl)-5-methyl-1,3,4-oxathiazole (**3g**) was prepared by reaction with *p*-nitrobenzohydroximoyl chloride. Thus a solution of the oxathiazole (**3g**) (2.4 g, 7.3 mmol) in mesitylene (10 ml) was heated under reflux for 0.5 h. After the mixture had cooled, a solution of *p*-nitrobenzohydroximoyl chloride (0.73 g, 3.65 mmol) in diethyl ether (20 ml) was added, followed dropwise by triethylamine (0.37 g, 3.65 mmol). The mixture was heated (*ca.* 40 °C) until no hydroximoyl halide remained (h.p.l.c.). Removal of triethylamine hydrochloride and concentration of the filtrate yielded a yellow solid from which was obtained (by recrystallisation from diethyl ether) 3-(*p*-nitrophenyl)-5,5-bis(trichloromethyl)-1,4,2-dioxazole (**4**) (0.35 g, 22%), m.p. and mixed m.p. 144 °C. The product gave an i.r. spectrum indistinguishable from that of authentic material.

Thermolysis of 1,3,4-*Oxathiazoles in the Presence of Dipolarophiles.*—The general procedure was to heat under reflux a solution of the oxathiazole (0.295 mmol) and dipolarophile (2.95 mmol) in mesitylene (10 ml) under nitrogen. The yields of the products were determined by h.p.l.c. and/or g.c. analysis (Tables 1 and 2), except in the cases described below for which the products were isolated.

5-(p-*Methoxyphenyl*)-2,2-*bis*(*trichloromethyl*)-1,3,4-*oxathiazole* (**3a**) *with ethyl cyanoformate.* The reaction mixture was concentrated under reduced pressure to leave a yellow solid which was recrystallised from ethanol to give *ethyl* 3-(p-*methoxyphenyl*)-1,2,4-*thiadiazole*-5-*carboxylate* (**6a**) (92%) as a white solid, m.p. 76 °C (Found: C, 54.7; H, 4.6; N, 10.7. $C_{12}H_{12}N_2O_3S$ requires C, 54.5; H, 4.6; N, 10.6%); δ_C ($CDCl_3$; 20 MHz) 178.4 (C-5), 174.3 (C-3), 158.3 (C=O), 161.5 and 124.8 (ArC), 129.9 and 113.8 (4 ArCH), 62.9 (CH_2), 55.1 (OCH_3), and 13.9 p.p.m. (CH_3); *m/z* 264 (M^+), 165 ($[M - C_4H_5NO_2]^+$), and 183 ($MeOC_6H_4CNS^+$).

5-*Phenyl*-2-*trichloromethyl*-1,3,4-*oxathiazole* (**3e**) *and ethyl cyanoformate.* The reaction mixture was concentrated to leave an orange oil. Chromatography (silica; $CHCl_3$) yielded an oil which crystallised from ethanol to give ethyl 3-phenyl-1,2,4-thiadiazole-5-carboxylate (**6b**) (75%) as white needles, m.p. 71—72 °C (lit.,[6] 70—71 °C); δ_C ($CDCl_3$; 20 MHz) 178.9 (C-5), 174.5 (C-3), 158.3 (C=O), 131.9 (PhC), 130.7, 128.6, and 128.3 (5 PhCH), 63.1 (CH_2), and 13.9 p.p.m. (CH_3); *m/z* 234 (M^+), 135 ($PhCNS^+$), and 103 ($PhCN^+$).

5-(p-*Chlorophenyl*)-2,2-*bis*(*trichloromethyl*)-1,3,4-*oxathiazole* (**3f**) *with ethyl cyanoformate.* Concentration of the reaction mixture yielded a brown solid which was recrystallised from ethanol to give ethyl 3-(*p*-chlorophenyl)-1,2,4-thiadiazole-5-carboxylate (**6c**) (70%) as white needles, m.p. 83.5 °C (lit.,[16] 82—84 °C); δ_C ($CDCl_3$; 20 MHz) 179.1 (C-5), 173.5 (C-3), 158.3 (C=O), 137.0 and 130.4 (ArC), 129.7 and 128.9 (4 ArCH), 63.2 (CH_2), and 14.0 p.p.m. (CH_3); *m/z* 270 and 268 (M^+), and 171 and 169 ($ClC_6H_4CNS^+$).

Synthesis of 2-*Dichloromethylene*-1,3,4-*oxathiazoles* (**9**).—Sodium (18.0 mmol) was added to a solution of the corresponding 2-trichloromethyl-1,3,4-oxathiazole (**3c**, **e**, **h**, or **i**) (18.0 mmol) in ethanol (100 ml) and the mixture was stirred until remaining starting material could not be detected by h.p.l.c. analysis (1.5—3 h). The reaction mixture was concentrated and chromatographed (alumina; toluene) to yield the 2-dichloromethylene-1,3,4-oxathiazole (**9**) which was purified by distillation and/or recrystallisation. By this method the following were prepared. 2-*Dichloromethylene*-5-(p-*methoxyphenyl*)-1,3,4-*oxathiazole* (**9a**) as white needles (77%) from hexane, m.p. 94—95 °C (Found: C, 43.2; H, 2.5; N, 4.9. $C_{10}H_7Cl_2NO_2S$ requires C, 43.2; H, 2.5; N, 5.1%); $\nu_{max.}$ (Nujol) 1 650 (C=N), 1 610 cm^{-1} (C=C); δ_C ($CDCl_3$; 20 MHz) 162.5 and 117.8 (ArC), 158.0 (C-5), 150.5 (C-2), 129.5 and 114.0 (4 ArCH), 88.6 (CCl_2), and 55.3 p.p.m. (CH_3); *m/z* 279, 277, and 275 (M^+), 165 ($MeOC_6H_4CNS^+$), and 133 ($MeOC_6H_4CN^+$).

2-*Dichloromethylene*-5-*phenyl*-1,3,4-*oxathiazole* (**9b**) as white needles (84%) from hexane, m.p. 77—78 °C (Found: C, 44.2; H, 2.0; N, 5.6. $C_9H_5Cl_2NOS$ requires C, 43.9; H, 2.1; N, 5.7%); $\nu_{max.}$ (Nujol) 1 650 (C=O) and 1 610 cm^{-1} (C=C); δ_C ($CDCl_3$; 20 MHz) 158.1 (C-5), 150.3 (C-2), 132.0, 128.6, and 127.7 (5 PhCH), 125.2 (PhC), and 89.1 p.p.m. (CCl_2); *m/z* 249, 247, and 245 (M^+), 135 ($PhCNS^+$), and 103 ($PhCN^+$).

2-*Dichloromethylene*-5-*methyl*-1,3,4-*oxathiazole* (**9c**) as white needles (80%) after Kugelrohr distillation and recrystallisation from hexane, m.p. 32—33 °C (Found: M^+, 182.931 192. $C_4H_3{}^{35}Cl_2NOS$ requires *M*, 182.931 241); $\nu_{max.}$ (Nujol) 1 660 (C=N) and 1 630 (C=C) cm^{-1}.

2-*Dichloromethylene*-5-*undecyl*-1,3,4-*oxathiazole* (**9d**) as a pale yellow oil (70%) (Found: M^+, 323.087 863. $C_{14}H_{23}{}^{35}Cl_2NOS$ requires *M*, 323.087 734); $\nu_{max.}$ (film) 1 655 (C=N) and 1 630 (C=C) cm^{-1}. An attempted Kugelrohr distillation (160 °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 thermal fragmentation of the oxathiazole.

Thermolysis of 2-*Dichloromethylene*-1,3,4-*oxathiazoles* (**9**).—When a solution of 2-dichloromethylene-3-(*p*-methoxyphenyl)-1,3,4-oxathiazole (**9a**) in mesitylene was heated under reflux for 168 h in the presence of DMAD [10 mol per mol of (**9a**)], as described above for other oxathiazoles, the isothiazole (**5a**) (27%) was produced together with *p*-methoxybenzonitrile (**8a**) (69%). In the absence of dipolarophile, only the nitrile (**8a**) (96%) was formed.

Thermolysis of compound (**9a**) (0.25 g) in indene (25 ml) at *ca.* 180 °C under nitrogen yielded the nitrile (**8a**) (96%) after 56 h. No trace of 1,1-dichloro-1,2a,7,7a-tetrahydrocyclobut[*a*]inden-2-one (**10**) could be detected by h.p.l.c. or g.l.c. (2.5% OVl; 160 °C) analysis. Under similar conditions after 1.5 h 5-(*p*-methoxyphenyl)-1,3,4-oxathiazol-2-one (**2a**) gave the nitrile (**8a**) (99%). The thermal stability of the tricycle (**10**) was confirmed when it was heated (170 °C) in *o*-dichlorobenzene for 48 h, after which time >95% remained.

When 2-dichloromethylene-5-phenyl-1,3,4-oxathiazole (**9b**) was heated in neat benzonitrile at 190 °C for 6 h 3,5-diphenyl-1,2,4-thiadiazole (**7b**) (6%) was produced.

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Received 14*th November* 1984; *Paper* 4/1930