# Nitrile sulfides. Part 12.[1,2] Generation of nitrile sulfides from 1,4,2-dithiazol-5-ones

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**Dedicated to Dr. Douglas Lloyd on the occasion of his 80th birthday**

## Abstract

Thermolysis of 1,4,2-dithiazol-5-ones in the presence of dimethyl acetylenedicarboxylate yielded dimethyl isothiazole-4,5-dicarboxylates, together with sulfur, carbon oxysulfide and nitriles. The proposed mechanism involves initial expulsion of carbon oxysulfide, followed by 1,3-dipolar cycloaddition of the resulting nitrile sulfide to the alkyne. The corresponding reaction of dithiazolone **3b** with ethyl propiolate afforded a *ca* 1:1.2 regioisomeric mixture of ethyl 3-phenylisothiazole-4- and 5-carboxylates, similar to that found for benzonitrile sulfide generated from 1,3,4-oxathiazol-2-one **1b**.

**Key words:** 1,4,2-Dithiazol-5-thione, 1,4,2-dithiazol-5-one, 1,3-dipolar cycloaddition, nitrile sulfide

## Introduction

The 1,3-dipolar cycloaddition reactions of nitrile sulfides ($R\text{-}C\equiv\overset{+}{N}S^-$)[3] are ideally suited for the synthesis of 5-membered heterocycles incorporating the $C=\overset{\sim}{N}S$ unit. Examples include high-yielding preparations of isothiazoles,[4] 1,2,4-thiadiazoles,[5] 1,3,4-oxathiazoles,[6] and 1,4,2-dithiazoles.[7] The most widely used method for the generation of nitrile sulfides involves thermal decarboxylation of 1,3,4-oxathiazol-2-ones **1**, and their chemistry has therefore been examined in some detail. Little attention, however, has been paid to the analogous 1,4,2-dithiazole-5-thiones **2** and 1,4,2-dithiazol-5-ones **3**, which would also afford nitrile sulfides on extrusion of carbon disulfide and carbon oxysulfide respectively. We have previously established[8] that thiones **2** are *not* useful nitrile sulfide precursors as they yield the 1,3-dithiolethione **4** rather than isothiazoles when heated with the acetylenic dipolarophile dimethyl acetylenedicarboxylate (DMAD). In

contrast we now report that nitrile sulfide-derived products *are* formed from the corresponding dithiazolones **3**.
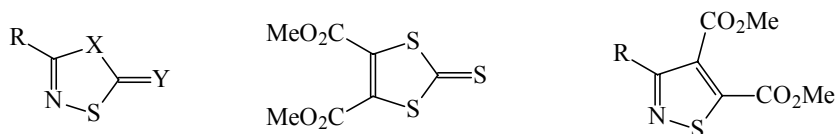


**1** X = Y = O                    **4**                    **5**
**2** X = Y = S
**3** X = S, Y = O
**a**, R = *p*-MeO$_6$H$_4$; **b**, R = C$_6$H$_5$; **c**, R = Me; **d**, R = *p*-MeC$_6$H$_4$; **e**, R = *p*-FC$_6$H$_4$;
**f**, R = *p*-ClC$_6$H$_4$; **g**, R = *m*-ClC$_6$H$_4$; **h**, R = CO$_2$Et

## Results and Discussion

The dithiazolones **3a-g** were prepared by oxidation of the corresponding thiones **2**, which are readily available from thiocarboxamides and trichloromethanesulfenyl chloride[8,9] (Scheme 1). Benzonitrile oxide, mercuric acetate, and potassium permanganate are reported[9,10] to be suitable reagents for achieving the thiocarbonyl to carbonyl conversion. We find that treatment with mercuric acetate (3 mol per mol of **2**) in acetic acid/chloroform/water at room temperature (5-20 h) provides a convenient and high yielding method.
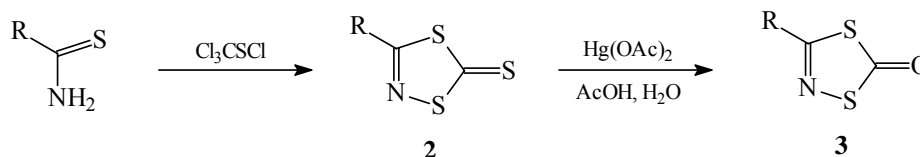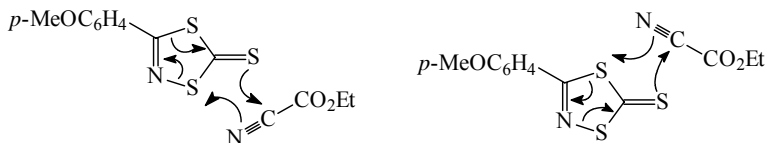


**Scheme 1**

The dithiazolethione precursor **2h** for the ethoxycarbonyl-dithiazolone **3h** was prepared from the readily accessible *p*-methoxyphenyl analogue **2a** by reaction with ethyl cyanoformate. Subsequent treatment with Hg(OAc)$_2$ afforded **3h** (Scheme 2). The formation of **2h** is believed to involve cycloaddition of the electron-poor nitrile to the exocyclic sulfur and one of the ring sulfurs, and is accompanied by expulsion of *p*-methoxybenzonitrile. The mechanism may be concerted (Scheme 3), a process which has been designated[11] [2' + (1,2,3)]-cyclodismutation or cyclosubstitution. Alternatively, it may proceed in two steps, cycloaddition followed by fragmentation, *via* a bicyclic intermediate (**6** or **7**) involving a hyper-valent sulphur at one of the bridgeheads.[8]
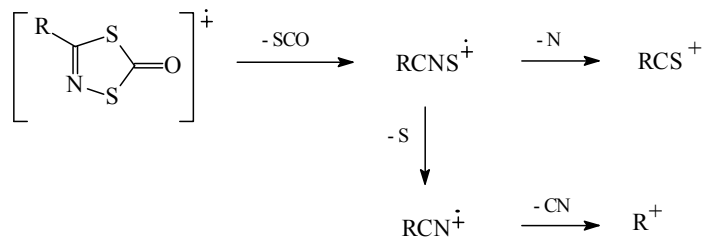
**2a**　　　　　　　　　　**2h**　　　　　　　　　**3h**

**Scheme 2**



**Scheme 3**



**6**　　　　　　　　　　　　**7**
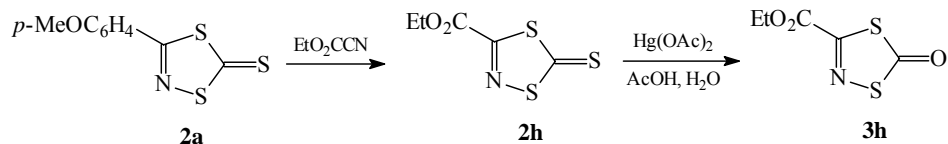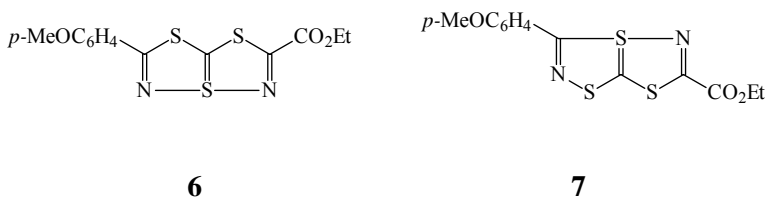
The products are readily identifiable from their spectroscopic properties. In the mass spectra there are prominent peaks for $RCNS^+$, $RCS^+$, $RCN^+$ and $R^+$, in addition to the molecular ion, suggesting fragmentation pathways involving initial expulsion of SCO.



**Scheme 4**

Cleavage at $C(3)S(4)$ and $C(5)S(1)$, or at $S(1)N(2)$ and $S(4)C(5)$ gives RCNS, and thereafter RCS and RCN by loss of N or S (Scheme 4). Electron impact induced fragmentation of oxathiazolones **1** to RCNS has also been reported.[12]
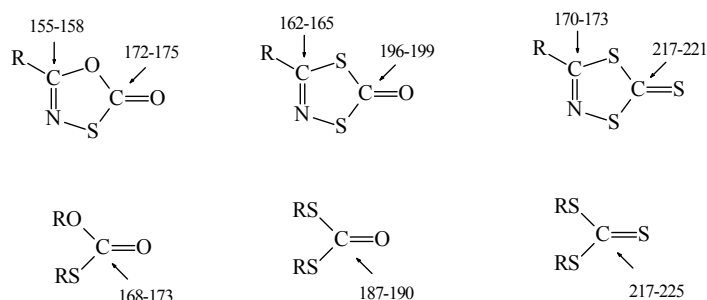
**Figure 1**

The $^{13}C$ NMR spectra show characteristic absorptions for the heterocyclic ring carbons at 196-199 and 162-165 ppm. Assignment to C-5 and C-3, respectively, was made with the aid of fully coupled spectra. In each case the chemical shifts fall between those of oxathiazolones **1** and dithiazolethiones **2** (Figure 1). A similar trend has been reported[13] for the carbonyl and thiocarbonyl groups in *O,S*-dialkyl thiocarbonates, *S,S*-dialkyl dithiocarbonates, and *S,S*-dialkyl trithiocarbonates.

The dithiazolones **3** prove to be much more stable than the corresponding oxathiazolones **1**, with >50 hours under reflux in mesitylene (*ca* 164 °C) being required for decomposition (5-6 half-lives). Under similar conditions the oxathiazolones are undetectable by HPLC after one hour.[14] Analysis of the reaction mixture from the thermolysis of compound **3a** indicated the presence of *p*-methoxybenzonitrile, and carbon oxysulfide was detected in the exit gas ($\nu_{max}$ 2080 cm$^{-1}$, *m/z* 60). The fragmentation can proceed by a thermally allowed $_\sigma 2_s + _\sigma 2_s + _\pi 2_s$ process.

To test for the involvement of nitrile sulfides in the decomposition the reaction was repeated in the presence of DMAD, a dipolarophile known to be reactive towards nitrilium betaines including nitrile sulfides.[3,4] Phenyl-dithiazolone **3b** was heated with DMAD (1:10) in mesitylene under reflux until HPLC analysis indicated its complete consumption (after 100 h). Removal of the solvent and excess dipolarophile by distillation under reduced pressure, followed by chromatography of the residue, afforded the isothiazole **5b** in 52% yield. Similarly methyl-dithiazolone **3c** afforded isothiazole **5c** (56%).

The effect of substituents on the progress of the reaction was examined for the series of 3-arylthiazolones **3a**, **3b**, **3d-3g**. Each was heated with DMAD (1:1) under identical conditions (in mesitylene, 163±1 °C) and the products analysed by HPLC (Table).
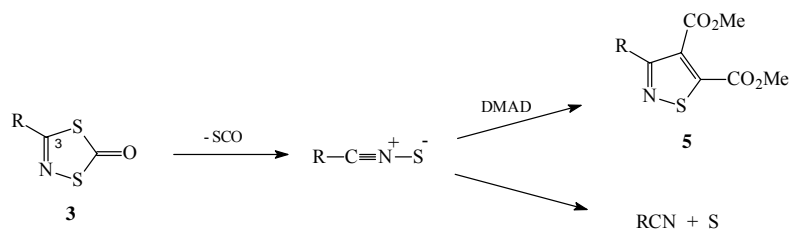


**Scheme 5**

The rate of reaction is influenced by the electronic nature of substituents in the aryl ring, with electron-donating groups accelerating the process. This effect is accompanied by a small increase in yield of isothiazole. A similar trend has been reported[4] for the fragmentation of the corresponding oxathiazolones **1**. These results are consistent with a pathway (Scheme 5) involving rate-determining cleavage of the dithiazolone at C(3)S(4) and at C(5)S(1), followed by 1,3-dipolar cycloaddition of the resulting nitrile sulfide to the alkyne. The formation of nitriles and sulfur as by-products is a common feature of nitrile sulfide reactions and can be attributed to fragmentation competing with cycloaddition.[3] The dependence of rate on substituent is consistent with a developing positive charge at the 3-position of the 1,4,2-dithiazolone in the transition state for the expulsion of SCO.

**Table 1.** Products[a] from the thermolysis of 1,4,2-dithiazol-5-ones 3 with DMAD at 163±1 °C

| Dithiazolone | Reaction time / h | Isothiazole **5** / % | Nitrile / % |
|---|---|---|---|
| **3a** R = $p$-MeOC$_6$H$_4$ | 75 | 60 | 30 |
| **3b** R = C$_6$H$_5$ | 100 | 66 (52) | [b] |
| **3c** R = Me | 50 | (56) | [b] |
| **3d** R = $p$-MeC$_6$H$_4$ | 90 | 60 | [b] |
| **3e** R = $p$-FC$_6$H$_4$ | 150 | 49 | 44 |
| **3f** R = $p$-ClC$_6$H$_4$ | 174 | 46 | 40 |
| **3g** R = $m$-ClC$_6$H$_4$ | 200 | 48 | 45 |
| **3h** R = CO$_2$Et | 250[c] | trace | [b] |

[a] Yields determined by HPLC (isolated yields); [b] not determined; [c] reaction incomplete.

The 3-ethoxycarbonyl-dithiazolone **3h** proved to be more stable. Even after prolonged heating (250 h) with DMAD in refluxing mesitylene the reaction was incomplete, and HPLC and NMR analysis of the reaction mixture revealed a complex mixture containing only traces of the expected isothiazole **5h**, together with various DMAD-derived by-products. A similar effect has been reported[16] for ethoxycarbonyl-oxathiazolone **1h**; whereas aryl-oxathiazolones, *eg* **1b**, fragment readily in refluxing xylene at 135 °C, the ethoxycarbonyl analogue **1h** requires temperatures in the range 160-190 °C. It has also been reported[4] that DMAD forms oligomers on prolonged heating. As nitrile sulfide cycloadditions to electron-poor dipolarophiles are regarded[4] as dipole HOMO-controlled reactions, it is not surprising that EtO$_2$C-C≡N$^+$S$^-$ shows lower reactivity than aryl and alkyl nitrile sulfides.

Further evidence for the involvement of nitrile sulfides as discrete intermediates was provided by comparison of the reactions of dithiazolone **3b** and oxathiazolone **1b** with ethyl propiolate to afford regioisomeric mixtures of 3-phenylisothiazole-4- and 5-carboxylates **8** and **9**. Two pathways can be considered: extrusion of SCO or CO$_2$ generating benzonitrile sulfide, followed by its cycloaddition to the dipolarophile [Scheme 6, path (a)]; or direct reaction between dipolarophile and precursor to form intermediate adducts **10** and **11**, which

subsequently collapse to form SCO or $CO_2$ and the observed isothiazoles [path (b)]. The regioselectivity is expected to be independent of source for path (a), but not for path (b). In parallel experiments solutions of the precursors **1b** or **3b** and excess ethyl propiolate were heated in mesitylene at ~163 °C and the reaction mixtures monitored by GC and NMR spectroscopy. Dithiazolone **3b** required 100 hours for the reaction to be complete and afforded a multi-component mixture of products including isothiazoles **8** and **9**, together with oligomers of ethyl propiolate; the regioisomer ratio was measured as **8**:**9** = 1: 1.2 $\tilde{\pm}$1. The corresponding reaction of oxathiazolone **1b** was complete in 1 hour and proved to be much cleaner, affording **8** and **9** in the ratio 1: 1.23 $\tilde{\pm}\tilde{5}$ A similar ratio (1:1.1) was observed by Howe *et al*[4] for the latter reaction at 150 °C. The consistent regioselectivity obtained from the two precursors is consistent with path (a) involving benzonitrile sulfide as an intermediate, rather than path (b).
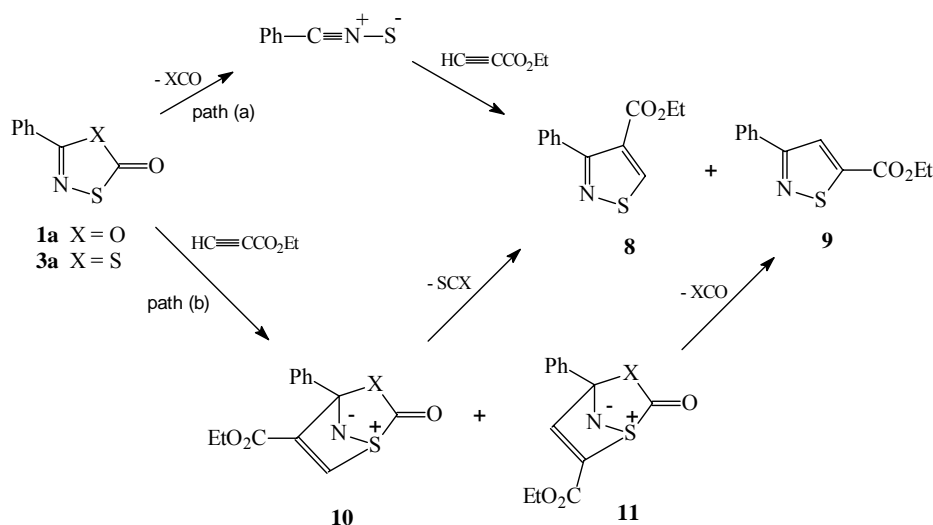


**Scheme 6**

In conclusion the thermolytic behaviour 1,4,2-dithiazol-5-ones parallels that of 1,3,4-oxathiazol-2-ones. Both provide a source nitrile sulfides, although the latter are more accessible and require lower reaction temperatures, and are therefore the more convenient precursors.


# Experimental Section

**General Procedures.** The analytical methods for monitoring the reactions and the instruments used for recording IR, ^{1}H and ^{13}C NMR, and mass spectra were as previously described.[8] Authentic samples of the dimethyl isothiazole-4,5-dicarboxylates **5a-d**,**f-h** were prepared by heating the corresponding 1,3,4-oxathiazol-2-one with DMAD using the established literature procedure.[4] Similarly prepared was *dimethyl 3-p-fluorophenylisothiazole-4,5-dicarboxylate* (**5e**), m.p. 66-67 °C (Found: C, 53.1; H, 3.4; N, 4.7. $C_{13}H_{10}FNO_4S$ requires: C, 52.9; H, 3.4; N, 4.7%).

Ethyl 3-phenylisothiazole-4- and 5-carboxylates **7** and **8** were prepared from oxathazolone **1a** and ethyl propiolate as previously reported.[4]

## Preparation of 1,4,2-dithiazole-5-thiones. (2)

The dithiazolethiones **2a, 2b, 2d, 2f** were prepared from trichloromethanesulfenyl chloride and the appropriate thioamide as described in the literature.[8] The following were prepared similarly:

**3-Methyl-1,4,2-dithiazole-5-thione (2c).** (9%) m.p. 30-31 °C (Found: C, 23.9; H, 1.9; N, 9.1. $C_3H_3NS_3$ requires: C, 24.1; H, 2.0; N, 9.4%); $\delta_C$ 220.9 (C-5), 171.9 (C-3), and 21.2 ($CH_3$); $m/z$ 149 ($M^+$).

**3-(*p*-Fluorophenyl)-1,4,2-dithiazole-5-thione (2e).** (22%) mp 137-138 °C (Found: C, 41.8; H, 1.7; N, 6.3. $C_8H_4FNS_3$ requires: C, 41.9; H, 1.8; N, 6.1%); $m/z$ 229 ($M^+$).

**3-(*m*-Chlorophenyl)-1,4,2-dithiazole-5-thione (2g).** (19%) mp 103 °C (Found: C, 39.0; H, 1.7; N, 5.6. $C_8H_4ClNS_3$ requires: C, 39.1; H, 1.6; N, 5.7%); $m/z$ 245, 247 ($M^+$).

**3-Ethoxycarbonyl-1,4,2-dithiazole-5-thione (2h).** A solution of 3-(*p*-methoxyphenyl)-1,4,2-dithiazol-5-thione **2b** (2.0 g, 8.30 mmol) and ethyl cyanoformate (2.46.g, 24.9 mmol) in dry xylene (40 mL) was heated under reflux for 47 h. The solvent and excess dipolarophile were removed under reduced pressure, and *p*-methoxybenzonitrile isolated from the residue by vacuum distillation (Kugelrohr). Chromatography of the residue on silica afforded unchanged **2b** (280 mg, 1.16.mmol, 14% recovery) and 3-ethoxycarbonyl-1,4,2-dithiazole-5-thione **2h** (1.13 g, 66%, 76% based on consumed **2b**) as yellow needles, m.p., mixed mp 44 °C (from ethanol) (lit.,[8] 44 °C).

## Preparation of 1,4,2-dithiazole-5-ones (3)

These were prepared from the corresponding 1,4,2-dithiazole-5-thione by treatment with mercuric acetate as described below for 3-(*p*-methoxyphenyl)-1,4,2-dithiazol-5-one. The products were purified by chromatography on silica and, for solids, recrystallisation from ethanol.

**3-(*p*-Methoxyphenyl)-1,4,2-dithiazol-5-one (3a).** Mercuric acetate (11.8 g, 37 mmol) was added with stirring to a solution of 3-(*p*-methoxyphenyl)-1,4,2-dithiazole-5-thione (3.0 g, 12.4 mmol) in a mixture of chloroform (75 mL), glacial acetic acid (125 mL) and water (1 mL). After 6 h the yellow colour had faded, and the mixture was filtered to give an almost colourless filtrate, which was concentrated to afford a pink-white solid. Purification by chromatography and recrystallisation from ethanol yielded **3a** (90%) as white needles, mp 104 °C (lit.,[9] 106 °C); $\nu_{max}$(Nujol)/cm$^{-1}$ 1690 (C=O); $\delta_C$ 198.2 (C-5), 163.7, 162.2 (C-3, ArC), 126.3 (ArC), 128.7, 114.7 (ArCH), 55.3 (OMe); $m/z$ 225 ($M^+$), 165 [$(M$-COS$)^+$], 151 [$(M$-CNOS$)^+$], 133 [$(M$-CNOS$_2)]^+$, 60 (COS$^+$).

**3-Phenyl-1,4,2-dithiazol-5-one (3b).** (43%), mp 75-76 °C (from ethanol) (lit.,[9] 76 °C); $\nu_{max}$(Nujol)/cm$^{-1}$ 1690 (C=O); $\delta_C$ 197.6 (C-5), 164.2 (C-3), 133.3 (ArC), 131.6, 128.8, 127.0 (ArCH); $m/z$ 195 ($M^+$), 135 [$(M$-COS$)^+$], 121 [$(M$-CNOS$)]^+$, 103 [$(M$-COS$_2)^+$], 77 [$(M$-C$_2$NOS$_2)^+$], 60 (COS$^+$).

**3-Methyl-1,4,2-dithiazol-5-one (3c).** (38%), colourless oil; $\nu_{max}$(thin film)/cm$^{-1}$ 1685 (C=O); $m/z$ 133 ($M^+$), 73 [$(M$-COS$)^+$], 59 (MeCS$^+$).

**3-(*p*-Methylphenyl)-1,4,2-dithiazol-5-one (3d).** (97%), mp 77-78 °C (from ethanol) (Found: C, 51.8; H, 3.3; N, 6.7. $C_9H_7NOS_2$ requires C, 51.7; H, 3.4; N, 6.7%); $\nu_{max}$(Nujol)/cm$^{-1}$ 1690 (C=O); $\delta_C$ 197.9 (C-5), 164.2 (C-3), 142.2, 130.8 (ArC), 129.5, 126.9 (ArCH), 21.2 (Me); $m/z$ 209 ($M^+$), 149 [$(M$-COS$)^+$], 135 [$(M$-CNOS$)]^+$, 117 [$(M$-C$_2$NOS$_2)^+$], 60 (COS$^+$).

**3-(*p*-Fluorophenyl)-1,4,2-dithiazol-5-one (3e).** (53%), mp 80 °C (from ethanol) (Found: C, 45.1; H, 1.8; N, 6.6. $C_8H_4NFOS_2$ requires C, 45.1; H, 1.9; N, 6.6%); $\nu_{max}$(Nujol)/cm$^{-1}$ 1685 (C=O); $\delta_C$ 197.4 (C-5), 164.4 (ArC, $J_{CF}$ 55), 162.8 (C-3), 129.6 (ArC, $J_{CF}$ 3), 129.2 (ArCH, $J_{CF}$ 6), 116.0 (ArCH, $J$ 12); *m/z* 213 ($M^+$), 153 [$(M$-COS$)^+$], 139 [$(M$-CNOS)]$^+$, 121 [$(M$-COS$_2)$], 95 [$M$-C$_2$NOS$_2)^+$].

**3-(*p*-Chlorophenyl)-1,4,2-dithiazol-5-one (3f).** (43%), mp 133 °C (from ethanol) (lit.,[9] 132 °C); $\nu_{max}$(Nujol)/cm$^{-1}$ 1685 (C=O); $\delta_C$ 197.2 (C-5), 162.9 (C-3), 137.9, 131.8 (ArC), 129.3, 128.3 (ArCH); *m/z* 231, 229 ($M^+$), 171, 169 [$(M$-COS$)^+$], 157, 155 [$(M$-CNOS)]$^+$, 139, 137 [$(M$-COS$_2)^+$], 60 (COS$^+$).

**3-(*m*-Chlorophenyl)-1,4,2-dithiazol-5-one (3g).** (56%), mp 80 °C (from ethanol) (Found: C, 41.9; H, 1.7; N, 6.1. $C_8H_4ClNOS_2$ requires C, 41.8; H, 1.8; N, 6.1%); $\nu_{max}$(Nujol)/cm$^{-1}$ 1680 (C=O); $\delta_C$ 196.8 (C-5), 162.4 (C-3), 135.1, 134.5 (ArC), 131.5, 130.1, 126.7, 125.3 (ArCH); *m/z* 231, 229 ($M^+$), 171, 169 [$(M$-COS$)^+$], 157, 155 [$(M$-CNOS)]$^+$, 139, 137 [$(M$-COS$_2)$], 113, 111 [$M$-C$_2$NOS$_2)^+$].

**3-Ethoxycarbonyl-1,4,2-dithiazol-5-one (3h).** (48%), colourless oil; $\nu_{max}$(thin film)/cm$^{-1}$ 1735, 1690 (C=O); *m/z* 191 ($M^+$).

**Thermolysis of 1,4,2-dithiazol-5-ones in the presence of DMAD**

The general method was to heat under reflux (~163 °C) a solution of the dithiazolone **3** (1.0 mmol) and DMAD (1.0 mmol) in mesitylene (5 mL) until HPLC analysis indicated complete consumption of **3** ($\geq$6 half-lives). The yields were determined by HPLC (Table), except in the cases described below for which the products were isolated.

**3-Phenyl-1,4,2-dithiazol-5-one/DMAD.** To a solution of 3-phenyl-1,4,2-dithiazol-5-one **3b** (60 mg, 0.31 mmol) in mesitylene (20 mL) was added DMAD (440 mg, 3.10 mmol) and the mixture heated under reflux in a nitrogen atmosphere for 60 h. Concentration of the mixture afforded an amber oil from which was isolated by chromatography (silica, Et$_2$O) dimethyl 3-phenylisothiazole-4,5-dicarboxylate **5b** as white needles (from ethanol) (45 mg, 52%), m.p. and mixed m.p. 73 °C (lit.,[4] 73 °C).

**3-Methyl-1,4,2-dithiazol-5-one/DMAD.** A solution of 3-methyl-1,4,2-dithiazol-5-one **3c** (500 mg, 3.75 mmol) and DMAD (5.38 g, 37.5 mmol) in mesitylene (15 mL) was heated under reflux for 50 h. On cooling the solvent and excess DMAD were removed under reduced pressure, and the residue distilled (86-87 °C/0.5 mmHg, Kugelrohr) to afford dimethyl 3-methylisothiazole-4,5-dicarboxylate **5c** (455 mg, 56%) as a clear oil which crystallised on standing, mp 34-35 °C (lit.,[4] 34.5-35.5 °C).

**Thermolysis of 3-phenyl-1,4,2-dithiazol-5-one/5-phenyl-1,3,4-oxathaizol-2-one in the presence of ethyl propiolate**

A solution of 3-phenyl-1,4,2-dithiazol-5-one **2b** (102 mg, 0.523 mmol) and ethyl propiolate (520 mg, 5.31 mmol) in dry mesitylene (1.5 mL) was heated at 163$\overset{\sim}{\pm}$1 °C and the progress of the reaction monitored by HPLC. The isomer ratio (**8**:**9** = 1:1.2±0.1) was measured by GC (10% SE-30) and by comparison of the $^1$H NMR peaks at $\delta_H$ 9.31 (5-H of **8**) and $\delta_H$ 8.10 (4-H of **9**). The isomer ratio (**8**:**9** = 1:1.2±0.1) for the reaction of 5-phenyl-1,3,4-oxathaizol-2-one with ethyl propiolate was determined under similar conditions.

**Thermolysis of 3-(*p*-methoxyphenyl)-1,4,2-dithiazol-5-one (3a)**

3-(*p*-Methoxyphenyl)-1,4,2-dithiazol-5-one **3a** (200 mg) was heated without solvent in an evacuated tube at ~163 °C for 17 hours. Carbon oxysulfide was detected in the gaseous products by IR spectroscopy ($\nu_{max}$/cm$^{-1}$ 2080) and mass spectrometry (*m/z* 60). Examination of the residue showed by HPLC showed the presence of *p*-methoxybenzonitrile in addition to unreacted starting material.

# Acknowledgements

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