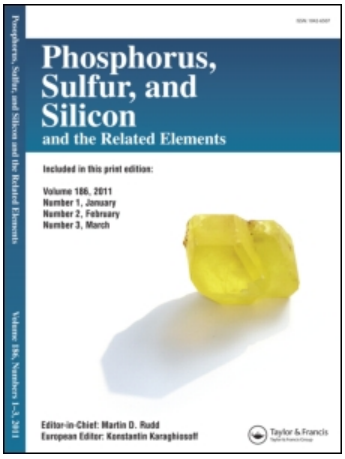


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R. Michael Paton[a]; Ian Stobie[a]; Roy M. Mortier[b]
[a] Department of Chemistry, University of Edinburgh, Edinburgh, Scotland [b] Organics Division, Imperial Chemical Industries PLC, Blackley, Manchester, England

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# GENERATION AND 1,3-DIPOLAR CYCLOADDITION REACTIONS OF α-ALKENYLNITRILE SULPHIDES

R. MICHAEL PATON and IAN STOBIE

*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland*

ROY M. MORTIER

*Imperial Chemical Industries PLC, Organics Division, PO Box 42, Hexagon House, Blackley, Manchester M9 3DA, England*

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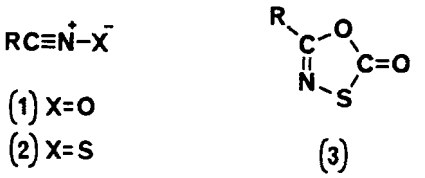
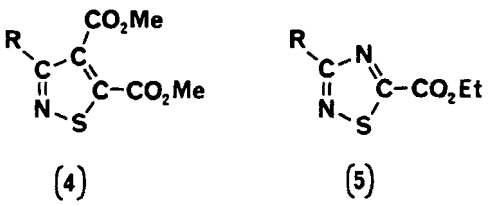
5-(Prop-1-enyl)-,5-isopropenyl- and 5-styryl-1,3,4-oxathiazol-2-ones, prepared from the corresponding amides and ClCOSCl, fragment on heating in xylene (*ca.* 135°C) to form α-alkenylnitrile sulphides which may be trapped with ethyl cyanoformate and dimethyl acetylenedicarboxylate as their 1,3-dipolar cycloadducts. Under the same conditions 5-vinyl-1,3,4-oxathiazol-2-one polymerises.

The 1,3-dipolar cycloaddition reactions of nitrile oxides (**1**) find widespread use[1] for the preparation of five membered heterocycles incorporating the C=N—O unit. In contrast the synthetic applications of the corresponding nitrile sulphides (**2**), which are uniquely suited for the introduction of C=N—S, have yet to be fully explored. Previous work has concentrated on extending the range of available heterocycles by varying the dipolarophile, with cycloadditions to alkynes,[2] alkenes,[3] nitriles[4] and carbonyl compounds[5] having been achieved so far. Some transformations have also been performed[2,6] on the substituents in the dipolarophile portion of nitrile sulphide derived cycloadducts, but less attention has been paid to the incorporation of reactive groups in the dipole. We now report the generation and cycloaddition reactions of some α-alkenylnitrile sulphides.

## RESULTS AND DISCUSSION

The thermal decarboxylation of 1,3,4-oxathiazol-2-ones (**3**) is the most widely used route to (**2**), and in view of the ready availability of their amide precursors this was the approach chosen for the generation of the α-alkenylnitrile sulphides. (**3**) were prepared from the carboxamides and chlorocarbonylsulphenyl chloride following the method reported[7] for simple oxathiazolones, but modified to take account of the tendency of the α-alkenyl compounds to polymerise; purification of sensitive products, (**3b** and **3d**), being accomplished by chromatography rather than distillation. While the yields were generally modest (18–24%), h.p.l.c. analysis showed that the




(1-5) a ; R=CH=CHMe
b ; R=CMe=CH$_2$
c ; R=CH=CHPh
d ; R=CH=CH$_2$

residue was mostly unreacted amide; there is therefore no evidence for a competing addition of ClCOSCl to the double bond of the alkene.[8]

The α-alkenyloxathiazolones have $^1$H and $^{13}$C nmr spectra consistent with their structures,[5] with characteristic peaks at $\delta_C$ 172–174 and 156–158 ppm due to carbons at the 2- and 5-positions of the heterocyclic ring (Table 1). Their mass spectra show the expected[5] peaks at $(M\text{-}44)^+$, attributable to loss of $CO_2$ leaving $RCNS^+$.

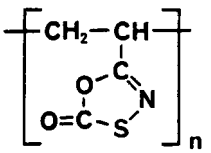
Attempted purification by vacuum distillation of the vinyl oxathiazolone (**3d**) afforded an oily solid resulting from partial polymerisation. The $^{13}$C nmr spectrum

TABLE 1

Nmr data (ppm from $Me_4Si$; $CDCl_3$ solvent) of α-alkenyl-1,3,4-oxathiazol-2-ones

| | $\delta_C$ | $\delta_H$ |
|---|---|---|
| (**3a**) | 173.2 (C-2); 156.8 (C-5); 141.4, 117.3 (=CH); 18.6 ($CH_3$) | 6.75 (dq, 1 H, $J_{BA}$ 17 Hz, $J_{BC}$ 7 Hz, $H^A$C=C$\underline{H}^B$C$H_3^C$); 6.02 (dq, 1 H, $J_{AB}$ 17 Hz, $J_{AC}$ 2 Hz, $H^A$); 1.94 (dd, 3 H, $J_{CB}$ 7 Hz, $J_{CA}$ 2 Hz, $CH_3^C$) |
| (**3b**) | 173.1 (C-2); 158.1 (C-5); 130.7 (=C); 123.8 (=$CH_2$); 17.2 ($CH_3$) | 5.95 (s, 1 H, =CH); 5.66 (q, 1 H, J 2 Hz, =CH); 2.05 (d, 3 H, J 2 Hz, $CH_3$) |
| (**3c**) | 172.7 (C-2); 157.1 (C-5); 133.7 (PhC); 141.3, 112.4 (=CH); 130.1 128.6, 127.9 (5 PhCH) | 7.6–7.2 (m, 5 H, PhH); 7.44 (d, 1 H, J 16 Hz, =CH); 6.58 (d, 1 H, J 16 Hz, =CH) |
| (**3d**) | 172.6 (C-2); 156.7 (C-5); 122.6 (=CH); 127.4 (=$CH_2$) | 6.26 (d, 1 H, $J_{BC}$ 17.5 Hz, $H^A\underline{H}^B$C=C$H^C$); 6.22 (d, 1 H, $J_{AC}$ 7 Hz, $H^A$); 5.88 (dd, 1 H, $J_{CA}$ 7 Hz, $J_{CB}$ 17.5 Hz, $H^C$) |

of the mixture contained peaks in addition to those at 172.6, 156.7, 127.4 and 122.6 ppm attributable to (**3d**); absorptions were also evident at 173.7 (C), 162.0 (C), 36.7 (CH) and 33.9 ($CH_2$). The similarity of these values to those of typical saturated alkyl oxathiazolones such as (**3**, R = $Pr^i$), for which $\delta_C$ = 174.0 (C-2), 165.3 (C-5), 30.6 (CH) and 18.6 ($2CH_3$),[9] strongly suggests that the additional peaks are due to the polymeric oxathiazolone (**6**). Furthermore, the $^1H$ nmr spectrum of the heated sample showed absorptions in the range 1–3δ, also consistent with the structure (**6**). This facile polymerisation precluded the generation of acrylonitrile sulphide (**2d**) and the study of its cycloaddition reactions. The isopropenyl oxathiazolone (**3b**) also showed a tendency to polymerise on prolonged heating, but in this case the formation of methacrylonitrile sulphide (**2b**) was not prevented.



(6)

The generation of the α-alkenylnitrile sulphides on thermolysis of the oxathiazolones, (**3a**)–(**3c**), was demonstrated by trapping experiments using dimethyl acetylenedicarboxylate (DMAD) and ethyl cyanoformate (ECF) as representative activated dipolarophiles. (**3a**) was heated in dry xylene under reflux in the presence of DMAD [5 mol per mol of (**3a**)] until t.l.c. or h.p.l.c. analysis indicated complete consumption of the oxathiazolone. Removal of the solvent and most of the excess dipolarophile was performed under vacuum, keeping the temperature below 50°C, and the isothiazole (**4a**) (68%) isolated by chromatography. Similarly (**4b**) and (**4c**) were produced from (**3b**) and (**3c**) in 34 and 50% yields respectively. Thermolysis with ECF afforded the 1,2,4-thiadiazoles (**5a**, 64%), (**5b**, 23%) and (**5c**, 64%). The significantly lower yields of cycloadducts derived from methacrylonitrile sulphide may be due to polymerisation occurring, either of (**3b**) prior to the generation of (**2b**), or of the cycloadducts, (**4b**) and (**5b**). In all cases the identities of the products were determined by analytical and spectroscopic methods. Their mass spectra show the expected fragmentation patterns.[10,11] The thiadiazoles have characteristic peaks corresponding to RCNS and RCN, while for the isothiazoles cleavage at the methoxycarbonyl substituents predominates. In the $^{13}C$ nmr spectra the $\delta_C$ values (Table 2) for the carbons at the 3-positions of these isothiazoles (163–165 ppm) and 1,2,4-thiadiazoles (174–175 ppm) are shifted by 10 ppm from those observed[9] for (**4**, R = $Pr^i$) (174.5 ppm) and (**5**, R = $Pr^i$) (183.5 ppm), consistent with the change of substituent from alkyl to α-alkenyl.

## EXPERIMENTAL

The analytical methods for monitoring the reactions and the instrumentation used for recording i.r., $^1H$ nmr, and mass spectra were as previously described.[5] $^{13}C$ nmr spectra were measured with Varian CFT20 and XL100 spectrometers.

TABLE 2

Nmr data (ppm from $Me_4Si$; $CDCl_3$ solvent) of α-alkenylisothiazoles (**4**) and 1,2,4-thiadiazoles (**5**)

| | $\delta_C$ | $\delta_H$ |
|---|---|---|
| **(4a)** | 163.9,[a] 159.3 (C=O); 163.6[a] (C-3); 154.1 (C-5); 130.6 (C-4); 134.7, 122.3 (=CH); 52.7 (2 $OCH_3$); 18.2 ($CH_3$) | 6.81 (dq, 1 H, $J_{BA}$ 15 Hz, $J_{BC}$ 6 Hz, $H^AC{=}CH^BCH_3^C$); 6.51 (dq, 1 H, $J_{AB}$ 15 Hz, $J_{AC}$ 2 Hz, $H^A$); 3.91 (s, 3 H, $CH_3$); 3.87 (s, 3 H, $CH_3$); 1.91 (dd, 3 H, $J_{CB}$ 6 Hz, $J_{CA}$ 2 Hz, $CH_3^C$) |
| **(4b)** | 166.4 (C-3); 164.9, 159.0 (C=O); 154.5 (C-5); 132.4 (C-4); 138.3 (=C); 117.6 ($=CH_2$); 52.9, 52.7 ($OCH_3$); 21.1 ($CH_3$) | 5.42 (dq, 1 H, $J_{AB} = J_{AC} = 0.5$ Hz, $H^AH^B{=}CCH_3^C$); 5.36 (dq, 1 H, $J_{BC}$ 1.5 Hz, $J_{BA}$ 0.5 Hz, $H^B$); 3.91 (s, 3 H, $CH_3$); 3.88 (s, 3 H, $CH_3$); 3.18 (dd, 3 H, $J_{CB}$ 1.5 Hz, $J_{CA}$ 0.5 Hz, $CH_3^C$) |
| **(4c)** | 164.0, 159.6 (C=O); 163.6 (C-3); 156.9 (C-5); 131.2 (C-4); 136.5, 118.8 (=CH); 135.9 (PhC); 129.0, 128.7, 127.3 (5 PhCH); 53.0, 52.9 ($OCH_3$) | 7.69 (d, 1 H, J 16 Hz, =CH); 7.6–7.2 (m, 5 H, PhH); 7.23 (d, 1 H, J 16 Hz, =CH); 3.97 (s, 3 H, $CH_3$); 3.92 (s, 3 H, $CH_3$) |
| **(5a)** | 178.0 (C-5); 174.1 (C-3); 159.2 (C=O); 138.5, 123.3 (=CH); 63.0 ($OCH_2$); 18.1, 13.9 ($CH_3$) | 7.24 (dq, 1 H, $J_{BA}$ 15 Hz, $J_{BC}$ 7 Hz, $H^AC{=}CH^BCH_3^C$); 6.62 (dq, 1 H, $J_{AB}$ 15 Hz, $J_{AC}$ 2 Hz, $H^A$); 4.51 (q, 2 H, $CH_2$); 1.96 (dd, 3 H, $J_{CB}$ 7 Hz, $J_{CA}$ 2 Hz, $CH_3^C$) |
| **(5b)** | 177.5 (C-5); 175.2 (C-3); 157.8 (C=O); 136.2 (=C); 121.0 ($=CH_2$); 62.5 ($OCH_2$); 13.6, 13.4 ($CH_3$) | 6.41 (s, 1 H, =CH); 5.20 (q, 1 H, J 1 Hz, =CH); 4.51 (q, 2 H, $CH_2$); 2.27 (d, 3 H, J 1 Hz, $CH_3$); 1.44 (t, 3 H, $CH_3$) |
| **(5c)** | 177.9 (C-5); 173.8 (C-3); 158.0 (C=O); 139.1, 127.1 (=CH); 135.1 (PhC); 128.9, 128.7, 128.4 (5 PhCH); 62.8 ($OCH_2$); 13.7 ($CH_3$) | 7.94 (d, 1 H, J 16 Hz, =CH); 7.7–7.3 (m, 5 H, PhH); 7.27 (d, 1 H, J 16 Hz, =CH); 4.52 (q, 2 H, $CH_2$); 1.44 (t, 3 H, $CH_3$) |

[a]Alternative assignments.



*Preparation of the α-Alkenyl-1,3,4-oxathiazol-2-ones* (**3**).

These were prepared by reaction of chlorocarbonylsulphenyl chloride with the appropriate amide following the general approach described in the literature,[7] but modified to take account of the lower thermal stability of the products. Their $^1H$ and $^{13}C$ nmr spectra are presented in Table 1.

*5-(Prop-1-enyl)-1,3,4-oxathiazol-2-one (**3a**).* This compound was prepared as a white crystalline solid (22%) by the above method from an equimolar mixture of crotonamide and ClCOSCl in $CHCl_3$. It was purified by chromatography (silica, petrol–$CH_2Cl_2$/4 : 1) followed by recrystallisation from ethanol, m.p. 45–47°C (lit.[10] b.p. 82°C at 10 mmHg) (Found: m/e 143.001619. $C_5H_5NO_2S$ requires *M*, 143.004098); $\nu_{max}$ (Nujol) 1775 (C=O), 1650 $cm^{-1}$ (C=C); m/e 143 ($M^+$), 115 ([*M*—CO]$^+$), 99 (MeCH=CHCNS$^+$), 69 (MeCH=CHCO$^+$), 41(MeCH=$\overset{+}{C}$H). H.p.l.c. analysis (ODS, MeOH—$H_2O$/4 : 1) of the reaction mixture indicated the presence of unreacted crotonamide (75%).

*5-Isopropenyl-1,3,4-oxathiazol-2-one (**3b**).* A mixture of α-methylacrylamide (80 g, 0.94 mol) and ClCOSCl (122.5 g, 0.94 mol) dissolved in dry chloroform (800 ml) was heated under reflux for 18 h. Evaporation of the solvent and distillation under reduced pressure (80°C, 10 mmHg) yielded 5-isopropenyl-1,3,4-oxathiazol-2-one (23.8 g, 0.17 mol, 18%) as a colourless oil which crystallised on cooling, m.p. 28–29°C (Found: m/e 143.003191. $C_5H_5NO_2S$ requires *M*, 143.004098); $\nu_{max}$ (Nujol) 1770 (C=O), 1635 $cm^{-1}$ (C=C); m/e 143 ($M^+$), 115 ([*M*—CO]$^+$), 99 ($CH_2$=CMeCNS$^+$), 69 ($CH_2$=CMeCO$^+$), 41 ($CH_2=\overset{+}{C}Me$).

*5-Styryl-1,3,4-oxathiazol-2-one (**3c**).* This compound was prepared (42%) from cinnamamide and ClCOSCl by the same method and recrystallised from cyclohexane, m.p. 83°C (Found: C, 58.5; H, 3.6; N, 6.9. $C_{10}H_7NO_2S$ requires C, 58.6; H, 3.4; N, 6.8%); $\nu_{max}$ (Nujol) 1775 (C=O, 1635 $cm^{-1}$ (C=C); m/e 204 ($M^+$), 161 (PhCH=CHCNS$^+$), 131 (PhCH=CHCO$^+$), 129 (PhCH=CHCN$^+$), 103 (PhCH=CH$^+$), 77 (Ph$^+$).

*5-Vinyl-1,3,4-oxathiazol-2-one (**3d**).* ClCOSCl (18.3 g, 0.14 mol) was added dropwise to a solution of acrylamide (10.0, 0.14 mol) in dry chloroform (100 ml) and the mixture heated under reflux for 8 h. The solvent and unreacted ClCOSCl were removed by evaporation under reduced pressure and precipitated acrylamide separated by filtration. The residue was chromatographed (silica, petrol–$CH_2Cl_2$/9 : 1) to yield 5-vinyl-1,3,4-oxthiazol-2-one (4.0 g, 0.031 mol, 22%) as a yellow oil (Found: m/e 128.98925. $C_4H_3NO_2S$ requires *M*, 128.988449); $\nu_{max}$ 1770 (C=O), 1640 $cm^{-1}$ (C=C); m/e 129 ($M^+$), 101 ($[M-CO]^+$), 85 ($CH_2$=CHCNS$^+$), 55 ($CH_2$=CHCO$^+$), 27 ($CH_2$=$\overset{+}{C}$H).

An attempt to purify the product by vacuum distillation resulted in partial polymerisation; $\delta_C$ (DMSO-$d_6$, $Me_4Si$) 174.7, 173.2 (C-2), 162.0, 156.8 (C-5), 128.4 (=$CH_2$), 122.9 (=CH), 36.7 (CH), 33.9 ($CH_2$); $\delta_H$ 1–3 m, CH and $CH_2$ in structure (**6**).

*Synthesis of Isothiazoles and 1,2,4-Thiadiazoles from 5-(α-Alkenyl)-1,3,4-oxathiazol-2-ones.* The general method was to heat under reflux a solution of the oxathiazolone and the alkyne or nitrile in dry xylene as described below for dimethyl 3-(prop-1-enyl)isothiazole-4,5-dicarboxylate, the reaction being monitored by t.l.c. or h.p.l.c. After removal of the solvent and excess dipolarophile by evaporation under reduced pressure the product was purified by chromatography and distillation or recrystallisation. Their $^1H$ and $^{13}C$ nmr spectra are presented in Table 2.

*Dimethyl 3-(prop-1-enyl)isothiazole-4,5-dicarboxylate (**4a**).* A solution of 5-(prop-1-enyl)-1,3,4-oxathiazol-2-one (1.41 g, 9.9 mol) and dimethyl acetylenedicarboxylate (DMAD) (7.10 g, 50 mmol) in dry xylene (25 ml) was heated under reflux for 20 h. The solvent and most of the excess dipolarophile were removed by evaporation under reduced pressure (65°C, 0.05 mmHg) and the residual oil chromatographed on silica (petrol–$CH_2Cl_2$/1 : 4). Distillation of the product (100°C, 0.05 mmHg) yielded dimethyl 3-(prop-1-enyl)isothiazole-4,5-dicarboxylate (1.62 g, 6.7 mmol, 68%) as a colourless oil (Found: C, 49.6; H, 4.4; N, 6.0. $C_{10}H_{11}NO_4S$ requires C, 49.8; H, 4.6; N, 5.8%); $\nu_{max}$ (film) 1740 (C=O), 1655 $cm^{-1}$ (C=C); m/e 241 ($M^+$), 226 ($[M-Me]^+$), 210 ($[M-OMe]^+$), 209, 201, 198, 182, 151, 150, 123, 110, 59.

*Dimethyl 3-isopropenylisothiazole-4,5-dicarboxylate (**4b**).* This compound was similarly prepared from 5-isopropenyl-1,3,4-oxathiazol-2-one (10.0 mmol) and DMAD (10.0 mmol) in 34% yield as a colourless oil (Found: C, 50.0; H, 4.8; N, 6.0. $C_{10}H_{11}NO_4S$ requires C, 49.8; H, 4.6; N, 5.8%); $\nu_{max}$ (film) 1735 (C=O), 1630 $cm^{-1}$ (C=C); m/e 241 ($M^+$), 226 ($[M-Me]^+$). 210 ($[M-OMe]^+$), 209, 151, 125, 84, 59.

*Dimethyl 3-styrylisothiazole-4,5-dicarboxylate (**4c**).* This compound was similarly prepared in 50% yield from (**3c**) and DMAD [5 mmol per mmol of (**3c**)] as white crystals, m.p. 85°C (from ethanol) (Found: C, 59.6; H, 4.5; N, 4.5. $C_{15}H_{13}NO_4S$ requires C, 59.4; H, 4.3; N, 4.6%); $\nu_{max}$ (Nujol) 1730 $cm^{-1}$ (C=O); m/e 303 ($M^+$), 302, 288 ($[M-Me]^+$), 272 ($[M-OMe]^+$), 240, 210, 192.

*Ethyl 3-(prop-1-enyl)-1,2,4-thiadiazole-5-carboxylate (**5a**).* This compound was prepared from (**3a**) and ethyl cyanoformate [3.5 mmol per mmol of (**3a**)] in 64% yield as a colourless oil (Found: C, 48.6; H, 5.1; N, 14.1. $C_8H_{10}N_2O_2S$ requires C, 48.5; H, 5.1; N, 14.1%); $\nu_{max}$ (film) 1760 (C=O), 1665 $cm^{-1}$ (C=C); m/e 198 ($M^+$), 183 ($[M-Me]^+$), 169 ($[M-Et]^+$), 153 ($[M-OEt]^+$), 125 ($[M-CO_2Et]^+$), 124, 99 (MeCH=CHCNS$^+$), 67 (MeCH=CHCN$^+$).

*Ethyl 3-isopropenyl-1,2,4-thiadiazole-5-carboxylate (**5b**).* This compound was prepared from (**3b**) and ethyl cyanoformate [4 mmol per mmol of (**3**)] in 23% yield as a colourless oil (Found: C, 48.3; H, 4.9; N, 14.1. $C_8H_{10}N_2O_2S$ requires C, 48.5; H, 5.1; N, 14.1%); $\nu_{max}$ (film) 1755 (C=O), 1630 $cm^{-1}$ (C=C); m/e 198 ($M^+$), 183 ($[M-Me]^+$), 170, 153 ($[M-OEt]^+$), 152, 125 ($[M-CO_2Et]^+$), 124, 99 ($CH_2$=CMeCNS$^+$), 67 ($CH_2$=CMeCN$^+$).

*Ethyl 3-styryl-1,2,4-thiadiazole-5-carboxylate (**5c**).* This compound was similarly prepared from (**3c**) in 64% yield as white crystals, m.p. 81°C (from ethanol) (Found: C, 60.4; H, 4.8; N, 10.8. $C_{13}H_{12}N_2O_2S$ requires C, 60.0; H, 4.6; N, 10.8%); $\nu_{max}$ (Nujol) 1745 (C=O), 1640 $cm^{-1}$ (C=C); m/e 260 ($M^+$), 259, 245 ($[M-Me]^+$), 231 ($[M-Et]^+$), 215 ($[M-OEt]^+$), 187 ($[M-CO_2Et]^+$), 161 (PhCH=CHCNS$^+$), 159, 129 (PhCH=CHCN$^+$), 128.

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