67049-15-4; **18**, 67048-80-0; **19**, 67048-74-2; **20**, 67048-78-6; benzamide, 55-21-0; *o*-fluorobenzamide, 445-28-3; *o*-toluamide, 527-85-5; α,α,α-trifluoro-*o*-toluamide, 360-64-5; 2,6-dichlorobenzamide, 2008-58-4; *m*-toluamide, 618-47-3; *m*-chlorobenzamide, 618-48-4; *m*-nitrobenzamide, 645-09-0; *p*-toluamide, 619-55-6; *p*-chlorobenzamide, 619-56-7; *p*-nitrobenzamide, 619-80-7; 3,4-dimethoxybenzamide, 1521-41-1; 3,4-methylenedioxybenzamide, 4847-94-3; 3,4-dichlorobenzmaide, 2670-38-4; 3,5-bis(trifluoromethyl)benzamide, 22227-26-5; acetamide, 60-35-5; 2,2-dimethylpropanamide, 754-10-9; cyclohexanecarboxamide, 1122-56-1; 2-chloroacetamide, 79-07-2; ethyl oxamate, 617-36-7; α,α,α-trifluoro-*m*-toluamide, 1801-10-1; *p*-cyanobenzamide, 3034-34-2; 3,5-dimethoxybenzamide, 17213-58-0; ClCl(O)5CL, 2757-23-5; dimethyl acetylenedicarboxylate, 762-42-5; ethyl phenylpropiolate, 2216-94-6.

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Cycloaddition Reactions of Nitrile Sulfides with Olefins

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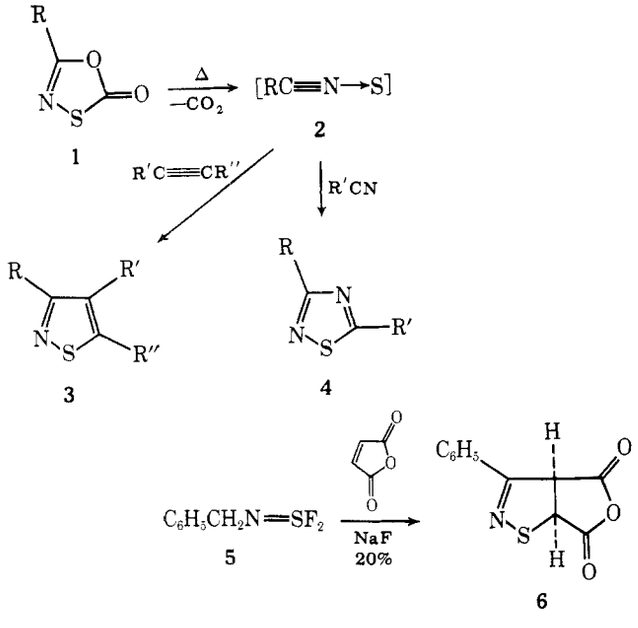
Dipolar cycloadditions of arenecarbonitrile sulfides to various olefins are described. Isothiazolines were obtained in fair to good yields from diethyl fumarate, phenyl acrylate, a norbornene derivative, and maleimides. Isothiazolecarboxylates were formed (via intermediate isothiazolines) from ethyl 2-chloroacrylate and ethyl β-pyrrolidinylacrylate. Significant amounts of adducts were not obtained from tetraethyl ethenetetracarboxylate, β-nitrostyrene, and 3-nitrostyrene.

We have reported previously cycloaddition reactions of nitrile sulfides (**2**), generated by thermolysis of 5-substituted-1,3,4-oxthiazol-2-ones (**1**), with acetylenic esters to give isothiazoles[1-3] (**3**) and with nitriles to give 1,2,4-thiadiazoles[4-6] (**4**) (Scheme I). We report here our studies of cycloadditions of nitrile sulfides with olefins. Subsequent to the completion of our work but prior to this account, Grunwell and Dye[7] reported cycloaddition of benzonitrile sulfide, generated from *N*-benzyliminosulfur difluoride (**5**), to maleic anhydride to give 3-phenyl-2-isothiazoline-*cis*-4,5-dicarboxylic acid anhydride (**6**) in 20% yield.

Scheme I



Thermolysis of 5-phenyl-1,3,4-oxathiazol-2-one (**1a**) at 190 °C in 4 equiv of dimethyl fumarate under nitrogen gave dimethyl 3-phenyl-2-isothiazoline-*trans*-4,5-dicarboxylate (**7**) in 55% yield (GC analysis) (Scheme II); the pure product was isolated in 45% yield. The coupling constant J = 4 Hz between H_4 and H_5 in the proton NMR spectrum of **7** reveals that H_4 and H_5 are trans. The corresponding coupling constant in dimethyl 3-phenyl-2-isoxazolin-*trans*-4,5-dicarboxylate is 4.9 Hz and in dimethyl 3-phenyl-2-isoxazolin-*cis*-4,5-dicarboxylate is 11.5 Hz.[8] Dehydrogenation of **7** with dichlorodicyanobenzoquinone (DDQ) gave dimethyl 3-phenyl-4,5-isothiazoledicarboxylate (**3a**), which we had prepared earlier[1-3] from **1a** and dimethyl acetylenedicarboxylate.

Thermolysis of **1a** in 4 equiv of tetraethyl ethenetetracarboxylate at 190 °C gave benzonitrile (from decomposition of benzonitrile sulfide)[1,2] in 91% yield and an unidentified high-boiling material (~6%, GC analysis). Because of steric

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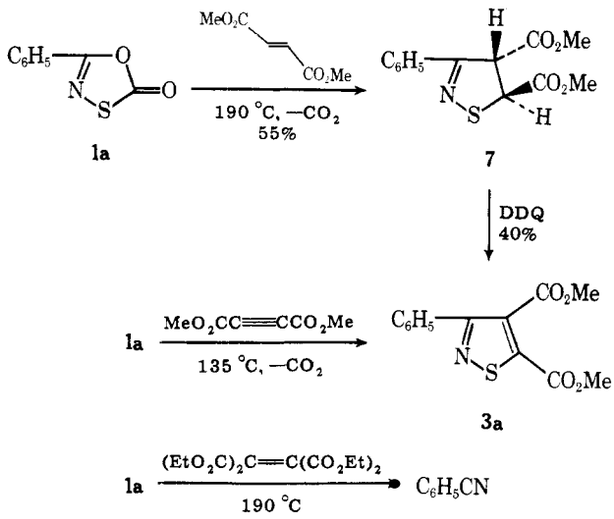
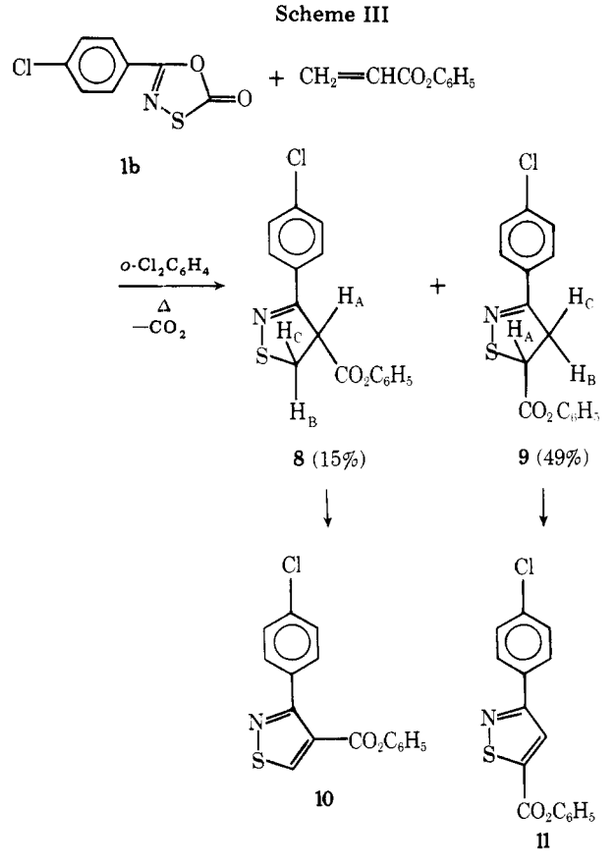
Scheme II



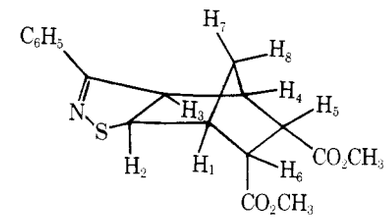
effects,[9,10] cycloaddition of benzonitrile sulfide to the ethenetetracarboxylate is less facile than addition to the fumarate ester. Earlier we found that nitrile sulfides add to the cyano group of tetracyanoethylene and not to the carbon–carbon double bond.[5]

A mixture of **1b** and 26 equiv of phenyl acrylate in *o*-dichlorobenzene heated at reflux gave isothiazolines **8** and **9** in 15 and 49% yields, respectively (GC and GC–MS analyses), and a trace (~0.8% yield) of isothiazole **10** (GC, GC–MS) (Scheme III). Pure samples of **8** (4% isolated yield) and of **9** (30% isolated yield) were obtained by fractional crystallization. Both **8** and **9** are somewhat unstable in solution and aromatize to significant extents within a few days (GC, GC–MS analyses). After 5 days at room temperature in acetone solution, **8** gave 6% of **10** and **9** produced 13% of **11**. Both **8** and **9** give ABC NMR spectra for the H_A, H_B, and H_C protons. Computer-assisted analysis of these spectra, with use of the LAOCOON III program, allowed extraction of the shifts and coupling constants for **8** and **9**. Most significantly, **8** has $J_{BC} = -11.5$ Hz, corresponding to $J_{BC} = -8.57$ Hz for the related methyl 3-phenyl-2-isoxazolin-3-ylcarboxylate,[11] and **9** has $J_{BC} = -17.7$ Hz, corresponding to -17.1 Hz for the related methyl 3-phenyl-2-isoxazolin-5-ylcarboxylate.[11] This NMR analysis secures the structural assignments for the isomers **8** and **9**.

Scheme III



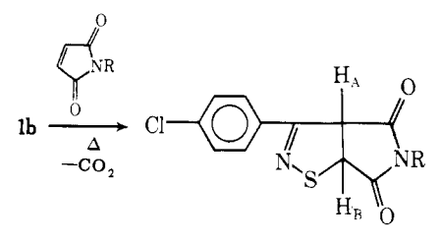
Addition of benzonitrile sulfide to dimethyl 5-norbornene-*cis,endo*-2,3-dicarboxylate gave **12** in 28% yield (pure isolated product). The stereochemistry of **12** was determined through analysis of the NMR spectrum of **12** in degassed



12

benzene-d_6 solvent.[12] The aromatic solvent induced shifts, $\delta(CDCl_3) - \delta(C_6D_6)$ (taken as positive when a resonance moves upfield attending the change in solvent from $CDCl_3$ to C_6D_6), were employed to aid assignments of the various protons. Selective benzene solvation of **12** about the carbonyl groups results in greater shielding of protons near the carbonyl groups. Thus, H_8 undergoes a +0.69 ppm solvent shift compared to +0.15 ppm for H_7, and protons H_5 and H_6 exhibit +0.68 and +0.48 ppm solvent shifts, respectively, compared to 0.00 and +0.07 ppm, respectively, for protons H_2 and H_3. The stereochemistry is revealed from the following data: protons H_2 and H_3 are coupled to H_8 ($J = 1.4$ Hz, $J = 1.8$ Hz), are not coupled to H_1 and H_4, and are coupled to each other with $J_{23} = 10.8$ Hz, so protons H_2 and H_3 are cis to each other and are endo; protons H_5 and H_6 are not coupled to H_7, are coupled to each other with $J_{56} = 12.0$ Hz, and H_5 couples with H_4 ($J_{45} = 4.0$ Hz) and H_6 couples with H_1 ($J_{16} = 4.4$ Hz), so H_5 and H_6 are cis,exo.[13]

Thermolysis of **1b** in the presence of 4 equiv of *N*-ethylmaleimide at 180 °C gave **13a** in 82% yield (61% isolated) and *p*-chlorobenzonitrile in 18% yield. Thermolysis of **1b** in the presence of 4 equiv of *N*-phenylmaleimide gave **13b** in 64%

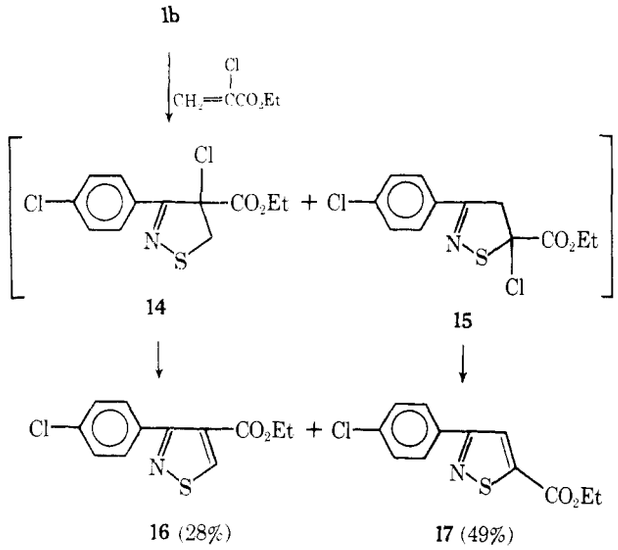


13a, R = Et
b, R = C_6H_5

yield and *p*-chlorobenzonitrile in 21% yield; the other 15% was not accounted for. Both **13a** and **13b** are cis isomers based on the observed $J_{AB} = 11$ Hz coupling in their NMR spectra. The corresponding J_{AB} in the cis anhydride **6** was reported to be 11 Hz.[7]

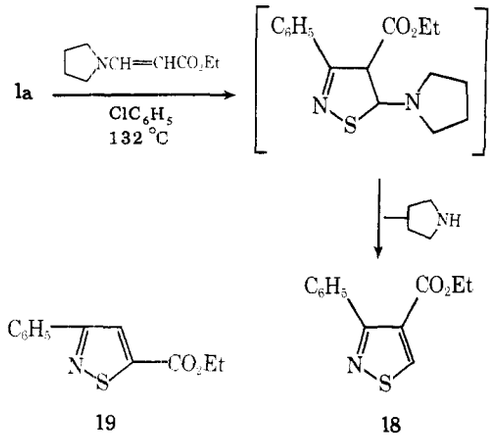
Oxathiazolone **1b** was heated in 30 equiv of ethyl 2-chloroacrylate in dodecane solvent at 165–175 °C for 55 min, resulting in ~70% reaction of **1b** (Scheme IV); **16** and **17** formed in 28 and 49% yields and were isolated in 16 and 17% yields, respectively (based on 70% reaction). No ethyl propiolate was detected in either the starting reaction mixture or in the final reaction mixture. Evidently, the reaction proceeds by cycloaddition of the nitrile sulfide to the chloroacrylate, followed

Scheme IV



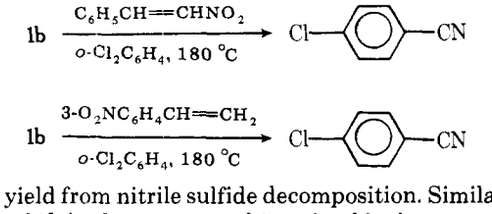
by loss of hydrogen chloride from the intermediate isothiazolines **14** and **15**. The isolated, pure samples of **16** and **17** were identical with authentic materials prepared by addition of *p*-chlorobenzonitrile sulfide to ethyl propiolate.[3]

Thermolysis to completion of **1a** in the presence of 10 equiv of ethyl β-pyrrolidinylacrylate in chlorobenzene solution at 132 °C gave ethyl 3-phenyl-4-isothiazolecarboxylate (**18**) in 8% yield. GC analysis revealed that the amount of ethyl 3-phenyl-5-isothiazolecarboxylate (**19**) present amounted to



≤2% of the amount of **18** present. Nitrile oxides have been reported to add regiospecifically to β-aminoacrylates to give exclusively 3-substituted-4-isoxazolecarboxylates.[14]

A mixture of **1b** and 4 equiv of β-nitrostyrene heated in *o*-dichlorobenzene at 180 °C gave *p*-chlorobenzonitrile in



98.5% yield from nitrile sulfide decomposition. Similarly, reaction of **1b** in the presence of 4 equiv of 3-nitrostyrene gave no significant amount of cycloadduct.

From the reactions reported here, it appears that nitrile sulfides react best with very electron-deficient olefins. This result is consistent with dipole–HOMO control[15] of these cycloadditions, similar to the cycloadditions of nitrile sulfides with acetylenes[3] and nitriles.[3,4]

Experimental Section

Dimethyl 3-Phenyl-2-isothiazoline-4,5-dicarboxylate (7). Technical grade dimethyl fumarate (Pfizer) was recrystallized twice (with filtration) from methylcyclohexane to give solid, mp 101–103 °C.

To 23.0 g (0.16 mol) of dimethyl fumarate stirred at 190 °C under nitrogen was added 7.16 g (0.040 mol) of 5-phenyl-1,3,4-oxthiazol-2-one. The solution was stirred at 190 °C for 10 min, and then the light amber solution was cooled and dissolved in 60 mL of warm THF. Chlorobenzene, 6.0 g, was added as an internal GC standard. An aliquot of the solution was diluted with more THF and was analyzed by GC; this analysis revealed that 6.17 g (55% yield) of product had formed.

The reaction mixture was concentrated under vacuum to remove the THF, and 60 mL of *o*-dichlorobenzene was added. The solution was concentrated under vacuum to remove the *o*-dichlorobenzene and dimethyl fumarate. The addition of *o*-dichlorobenzene and the concentration was repeated twice. The residue was triturated with 20 mL of methanol, the insoluble sulfur was removed by filtration, and the filtrate was concentrated under vacuum to 6.5 g of oil. The oil was chromatographed on 350 g of silicic acid (Mallinckrodt SilicAR CC-7). After elution with 1 L of 50:50 hexane–benzene, the column was eluted with benzene. The first 1300 mL of benzene eluate gave no material. The next 100 mL of benzene eluate gave 0.33 g of 98% pure product; the next 660 mL of benzene eluate gave 3.1 g (28% yield) of 100% pure (GC assay) product as a viscous oil of mp ~6 °C. The next 1350 mL of benzene eluate gave 1.6 g of 98% pure product. The total amount of product was 5.03 g (45% yield); IR (mineral oil mull) 5.8 μm; NMR ($CDCl_3$) δ 7.96 (m, 2, ArH), 7.61 (m, 3, ArH), 5.22 (d, 1, J = 4 Hz, SCH), 4.81 (d, 1, J = 4 Hz, SCCH), 3.79 (s, 3, OCH_3), 3.69 (s, 3, OCH_3); mass spectrum *m/e* 279, 247, 220, 188, 176, 161, 135, 103; UV (CH_3CN) max (log ε) 222 (4.00), 313 nm (4.05). Anal. Calcd for $C_{13}H_{13}NO_4S$: C, 55.90; H, 4.69. Found: C, 56.05; H, 4.80.

Dehydrogenation of 7. A mixture of 1.93 g (0.00692 mol) of dimethyl 3-phenyl-2-isothiazoline-4,5-dicarboxylate, 2.36 g (0.014 mol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 40 mL of chlorobenzene was held at reflux for 5 h. The mixture was allowed to cool and was filtered. The insoluble gray solid, after washing with chlorobenzene and hexane, weighed 1.5 g and appeared to be 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (IR identification). The filtrate and washings were combined and concentrated under vacuum to 2.65 g of dark oil. This oil was extracted with 150 mL of hexane and then with three 40-mL portions of hot hexane to give 0.6 g of insoluble solid that appeared to be slightly impure DDQ. The hexane extracts were combined, concentrated, and cooled in ice to give 0.95 g of solid, mp 68–70 °C. This solid was dissolved in hexane, the mixture was filtered to remove a few milligrams of insoluble solid, and the filtrate was concentrated and cooled in ice to give 0.77 g (40% yield) of white solid dimethyl 3-phenyl-4,5-isothiazoledicarboxylate, mp 71–72 °C (lit.[1] mp 71–73 °C); the IR spectra of this and of authentic material were identical.

Phenyl 3-(*p*-Chlorophenyl)-2-isothiazoline-4-carboxylate (8) and Phenyl 3-(*p*-Chlorophenyl)-2-isothiazoline-5-carboxylate (9). A solution of 0.20 g of hydroquinone, 35.7 g (0.241 mol) of redistilled phenyl acrylate (Monomer-Polymer Laboratories), 2.0 g (0.00935 mol) of 5-(*p*-chlorophenyl)-1,3,4-oxthiazol-2-one, and 45.0 g of *o*-dichlorobenzene was heated rapidly to reflux and was held at reflux under N_2 for 20 min. GC analysis of the reaction mixture revealed that the 4-carboxylate and the 5-carboxylate had formed in 15 and 49% yields, respectively. Further GC and GC–MS analyses revealed the presence of a trace (~0.8% yield) of **10** (m/e 315). The reaction mixture was concentrated under vacuum to 5.3 g of grape colored gum. The gum was extracted with two 125-mL portions of hot heptane. Upon cooling, the heptane deposited 1.35 g (45%) of 98% pure 5-carboxylate **9**. Recrystallization of the solid from ethanol gave 0.89 g (30% yield) of white crystals, mp 127.5–129 °C, that was 100% pure 5-carboxylate (GC assay): IR ($CHCl_3$) 5.70 μm; NMR ($CDCl_3$) δ 7.73 (m, 2, one-half of an AA'BB' multiplet, Ar**H**), 7.53–7.07 (m, 7, Ar**H**), 4.82 (dd, 1, J_{AB} = 5.2, J_{AC} = 11.3 Hz, $CH_ACH_BH_C$), 4.10 (m, 1, J_{BC} = −17.7, J_{AB} = 5.2 Hz, $CH_ACH_BH_C$), 3.60 (m, 1, J_{AC} = 11.3, J_{BC} = −17.7 Hz, $CH_ACH_BH_C$). Anal. Calcd for $C_{16}H_{12}ClNO_2S$: C, 60.47; H, 3.81. Found: C, 60.22; H, 3.72.

Fractional crystallization from ethanol of the residue from the combined heptane filtrates gave 100% pure (GC assay) 4-carboxylate **8** in 4% yield as white needles: mp 123.5–125 °C; IR ($CHCl_3$) 5.70 μm; NMR ($CDCl_3$) δ 7.87 (m, 2, one-half of an AA'BB' multiplet, Ar**H**), 7.53–6.87 (m, 7, Ar**H**), 4.88 (dd, 1, J_{AB} = 6.3, J_{AC} = 10.2 Hz, $CH_ACH_BH_C$), 4.01 (m, 1, J_{AB} = 6.3, J_{BC} = −11.5 Hz, $CH_ACH_BH_C$), 3.93 (m, 1, J_{AC} = 10.2, J_{BC} = −11.5 Hz, $CH_ACH_BH_C$). Anal. Calcd for $C_{16}H_{12}ClNO_2S$: C, 60.47; H, 3.81. Found: C, 60.64; H, 3.76.

A dilute solution of **8** in acetone was allowed to stand 5 days at room temperature. After this time GC and GC–MS analysis revealed formation of ~6% of **10** (*m/e* 315). Similarly, after 5 days in acetone, **9**

produced ~13% of **11** (*m/e* 315). Retention times on a 2-ft long GC column packed with 10% SE-30 on Chromosorb W, 60 mL/min He flow, at 240 °C for **8**, **9**, **10**, and **11** were 4.2, 6.2, 3.3, and 4.7 min, respectively.

Dimethyl *exo*-3a,4,5,6,7,7a-Hexahydro-3-phenyl-4,7-methano-1,2-benzisothiazole-*endo,cis*-5,6-dicarboxylate (12). A solution of 6.0 g (0.0335 mol) of 5-phenyl-1,3,4-oxthiazol-2-one and 100.0 g (0.476 mol) of dimethyl 5-norbornene-*endo,cis*-2,3-dicarboxylate[13b] (Frinton Laboratories) was stirred at 190 °C under N_2 for 10 min, allowed to cool, and concentrated under vacuum to 10.0 g of oil that contained ~45% of product. Crystallization of the oil from methanol gave 3.7 g of white solid, mp 149–153 °C. Recrystallization of the solid from methanol gave 3.2 g (28%) of pure product as a white solid: mp 155–156.5 °C; IR ($CHCl_3$) 5.77 μm; NMR (benzene-d_6) δ 8.33 (m, 3, ArH), 7.23 (m, 2, ArH), 4.70 (dd, 1, J = 1.4, 10.8 Hz, H_2), 4.27 (dd, 1, J = 1.8, 10.8 Hz, H_3), 3.47 (s, 3, OCH_3), 3.31 (s, 3, OCH_3), 2.77 (dd, 1, J = 4.4, 12.0 Hz, H_6 or H_5), 2.60 (bm, 1, H_4 or H_1), 2.35 (dd, 1, J = 4.0, 12.0 Hz, H_5 or H_6), 2.33 (bm, 1, H_1 or H_4), 1.77 (dt, 1, $J + J'$ = 3.2 Hz, J = 11.0 Hz, H_7), 0.68 (dp, 1, J_{78} = 11.0 Hz, H_8). Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; 5.54. Found: C, 62.41; H, 5.72.

3-(*p*-Chlorophenyl)-*N*-ethyl-2-isothiazoline-4,5-dicarboximide (13a). To a solution of 25.0 g (0.20 mol) of *N*-ethylmaleimide in 100 g of *o*-dichlorobenzene stirred at reflux (180 °C) under N_2 was added 10.68 g (0.050 mol) of 5-(*p*-chlorophenyl)-1,3,4-oxathiazol-2-one. The solution was stirred at reflux for 30 min and concentrated under vacuum at 90 °C (0.35 mm) to give 25.8 g of solid residue. Trituration of the solid with 125 mL of ethanol followed by cooling of the mixture gave 11.7 g (79%) of solid, mp 176–179 °C. Crystallization of the solid from ethanol (hot filtration) gave 9.02 g (61%) of white solid: mp 179–181 °C; IR ($CHCl_3$) 5.61 (w), 5.83 μm (s); NMR ($CDCl_3$) δ 7.67 (m, 4, $ClC_6\mathbf{H}_4$), 5.02 (s, 2, **CHCH**), 3.58 (q, 2, J = 7 Hz, $NC\mathbf{H}_2CH_3$), 1.17 (t, 3, J = 7 Hz, $NCH_2C\mathbf{H}_3$); NMR (50:50 $CDCl_3$–benzene-d_6) δ 7.57 (m, 4, $ClC_6\mathbf{H}_4$), 4.40 (d, 1, J = 11 Hz, $C\mathbf{H}_aCH_b$), 4.23 (d, 1, J = 11 Hz, $CH_aC\mathbf{H}_b$), 3.37 (q, 2, J = 7 Hz, $NC\mathbf{H}_2CH_3$), 1.00 (t, 3, J = 7 Hz, $NCH_2C\mathbf{H}_3$).

3-(*p*-Chlorophenyl)-*N*-phenyl-2-isothiazoline-4,5-dicarboximide (13b). A solution of 13.85 g (0.080 mol) of *N*-phenylmaleimide in 80 g of *o*-dichlorobenzene was heated rapidly to reflux (180 °C), and then 4.27 g (0.020 mol) of 5-(*p*-chlorophenyl)-1,3,4-oxthiazol-2-one was added. The solution was held at reflux under N_2 for 20 min. GC analysis indicated that 0.0448 mol of *N*-phenylmaleimide was left, that *p*-chlorobenzonitrile had formed in 21% yield, and that the dicarboximide had formed in 64% yield. The reaction mixture was concentrated under vacuum at 90 °C (0.2 mm). The residue was boiled with 375 mL of ethanol, and the mixture was filtered. The insoluble solid, 0.70 g, appeared from the IR spectrum to be polymeric *N*-phenylmaleimide. The filtrate was cooled to give 2.34 g of crude product, mp ~150–170 °C. Concentration of this filtrate gave a solid residue, which was stirred with 12 g of sodium metabisulfite in 70 mL of water–30 mL of ethanol for 25 min in order to convert the residual *N*-phenylmaleimide to the water-soluble sodium sulfonate derivative. The mixture was diluted with water and extracted three times with ether. The ether extracts were combined, washed with water, filtered, and concentrated under vacuum. The residue was crystallized from ethanol to give 1.0 g of crude product, mp 164–169 °C. Several crystallizations of the combined crude products, 3.34 g, from ethanol gave 2.41 g (35%) of solid, mp 173–175 °C, which gave 1.91 g (28%) of solid, mp 174–175 °C, upon recrystallization: IR (mineral oil mull) 5.61 (w), 5.84 μm (s); NMR ($CDCl_3$) δ 8.00 (m, 2, $ClC_6\mathbf{H}_a\mathbf{H}_a\mathbf{H}_b\mathbf{H}_b$), 7.40 (m, 7, $NC_6\mathbf{H}_5$, $ClC_6\mathbf{H}_a\mathbf{H}_a\mathbf{H}_b\mathbf{H}_b$), 5.20 (s, 2, $C\mathbf{H}_aC\mathbf{H}_b$). Addition of an equal volume of benzene to the $CDCl_3$ solution caused the δ 5.20 singlet to become an AB quartet, δ 4.37 (d, 1, J = 11 Hz, $C\mathbf{H}_aCH_b$), 4.27 (d, 1, J = 11 Hz, $CH_aC\mathbf{H}_b$). Anal. Calcd for $C_{17}H_{11}ClN_2O_2S$: C, 59.56; H, 3.23; S, 9.35. Found: C, 59.43; H, 3.16; S, 9.43.

Reaction of 1b with Ethyl 2-Chloroacrylate. A solution of 40.4 g (0.30 mol) of ethyl 2-chloroacrylate and 2.14 g (0.010 mol) of 5-(*p*-chlorophenyl)-1,3,4-oxathiazol-2-one (**1b**) in 75 g of dodecane was held at reflux (165–175 °C) for 55 min, at which time GC analysis indicated ~70% reaction of **1b**. The reaction mixture was allowed to cool, and the supernatant was decanted from polymeric ester and concentrated under vacuum. The residue was chromatographed on silicic acid (Mallinckrodt SilicAR CC-7). Elution with 25% benzene in hexane gave unreacted **1b**. Elution with 40% benzene in hexane gave the 5-carboxylate **17**. Elution with 75% benzene in hexane gave 0.46 g of the 4-carboxylate **16**. Crystallization of the **16** from aqueous ethanol gave 0.30 g (16%) of solid, mp 55.5–56.5 °C, that changed after several days to mp 69–70 °C (lit.[3] mp 70.5–71.5 °C). Crystallization of the **17** from ethanol gave 0.31 g (17%) of solid, mp 87–89 °C (lit[3] mp 87.5–89 °C). The IR and NMR spectra of these materials were identical with those of authentic materials.

Registry No.—**1a**, 5852-49-3; **1b**, 17452-79-8; **3a**, 27545-53-5; **7**, 67048-45-7; **8**, 67048-44-6; **9**, 67048-43-5; **10**, 67048-41-3; **11**, 67048-42-4; **12**, 67048-40-2; **13a**, 67048-39-9; **13b**, 67048-38-8; **16**, 67048-37-7; **17**, 67048-96-8; dimethyl fumarate, 624-49-7; dimethyl 5-norbornene-*endo,cis*-2,3-dicarboxylate, 39589-98-5; *N*-ethylmaleimide, 128-53-0; *N*-phenylmaleimide, 941-69-5; ethyl 2-chloroacrylate, 687-46-7.

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