methylene chloride gave **3**, 0.14 g, as an oil: *m/e* 191; IR 1765 cm^{-1}; NMR δ 1.40 (s, 9), 7.0–8.0 (m, 4).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.1; H, 6.8; N, 7.3. Found: C, 68.9; H, 6.8; N, 7.4.

***N-tert*-Butylanthranilic Acid Anhydride (4).** A solution of 5.2 g (0.027 mol) of **2** in 100 mL of benzene was refluxed for 18 h using a Dean-Stark water trap. The solution was then evaporated to dryness and the residue crystallized from ether/pentane to give 3.7 g of **4** (75%): mp 92–94 °C; IR 3390, 1735, and 1680 cm^{-1}; NMR δ 1.48 (s, 18), 6.4–8.1 (m, 8), 8.20 (broad s, 2); *m/e* 368.

Anal. Calcd for $C_{22}H_{28}N_2O_3$: C, 71.7; H, 7.7; N, 7.6. Found: C, 71.5; H, 7.9; N, 7.8.

Methyl *N-tert*-Butylanthranilate (6). To a suspension of 26.3 g (0.10 mol) of **1** in 250 mL of benzene was added a solution of 6 g (0.11 mol) of sodium methoxide in 25 mL of methanol. After stirring the mixture at room temperature for 30 min, 50 mL of water was added and the benzene layer was separated. It was washed once with 50 mL of water and then dried (Na_2SO_4) and evaporated. The residue, 21 g (100%), was a yellow oil which was shown by NMR analysis to contain 1-*tert*-butyl-3-methoxy-2,1-benzisoxazoline (**5**) and **6** in a ratio of 5:1.

For **5**: NMR δ 1.32 (s, 9), 3.48 (s, 3), 6.18 (s, 1) 6.90–7.4 (m, 4).

This crude mixture was maintained under nitrogen at 200 °C for 6 h and then distilled under high vacuum to give 17.6 g of **6** (84%): bp 75–78 °C (0.1 mm); mp 32–34 °C; NMR δ 1.46 (s, 9), 3.82 (s, 3), 6.4–8.0 (m, 5).

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.5; H, 8.3; N, 6.8. Found: C, 69.6; H, 8.3; N, 6.9.

***N-tert*-Butylanthranilic Acid (7).** To a solution of 15.5 g (0.075 mol) of **6** in 100 mL of methanol was added a solution of 4 g (0.1 mol) of sodium hydroxide in 10 mL of water. After refluxing for 4 h the solution was evaporated under reduced pressure and the residue was dissolved in 100 mL of water. The aqueous solution was washed with 50 mL of ether and then made neutral with 2 N hydrochloric acid. It was extracted with three 50-mL volumes of ether and the combined ether extracts were dried (Na_2SO_4) and concentrated. The residue crystallized to yield 12.2 g (84%) of **7**: mp 151–153 °C; NMR (Me_2SO) δ 1.38 (s, 9), 6.4–8.0 (m, 4).

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.4; H, 7.8; N, 7.3. Found: C, 68.4; H, 8.1; N, 6.9.

***N-tert*-Butyl-2*H*-3,1-benzoxazine-2,4(1*H*)-dione (8).** To a solution of 8 g (0.04 mol) of **7** in 100 mL of water containing 3.2 g (0.08 mol) of sodium hydroxide and some solid carbon dioxide was added, with vigorous stirring, 50 mL of a 12.5% solution (0.06 mol) of phosgene in benzene. The stirring was continued for 4 h when the benzene was removed under reduced pressure and the precipitate was filtered off. The solid was dissolved in methylene chloride and the solution dried (Na_2SO_4). Concentration of the solution and addition of ether gave 4.3 g (52%) of **8**: mp 110–112 °C; IR 1790 and 1750 cm^{-1}; NMR δ 1.76 (s, 9), 7.0–8.2 (m, 4).

Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.7; H, 6.0; N, 6.4. Found: C, 66.0; H, 6.2; N, 6.3.

Registry No.—**1**, 24766-87-8; **2**, 61752-02-1; **3**, 61752-03-2; **4**, 61752-04-3; **5**, 61752-05-4; **6**, 61752-06-5; **7**, 61752-07-6; **8**, 61752-08-7; anthranil, 271-58-9; *tert*-butyl alcohol, 75-65-0.

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Nitrile Sulfides. Synthesis of 5-Aryl-1,2,4-thiadiazole-3-carboxylates

Robert K. Howe,* Terry A. Gruner, and John E. Franz

Research Department, Monsanto Agricultural Products Company, St. Louis, Missouri 63166

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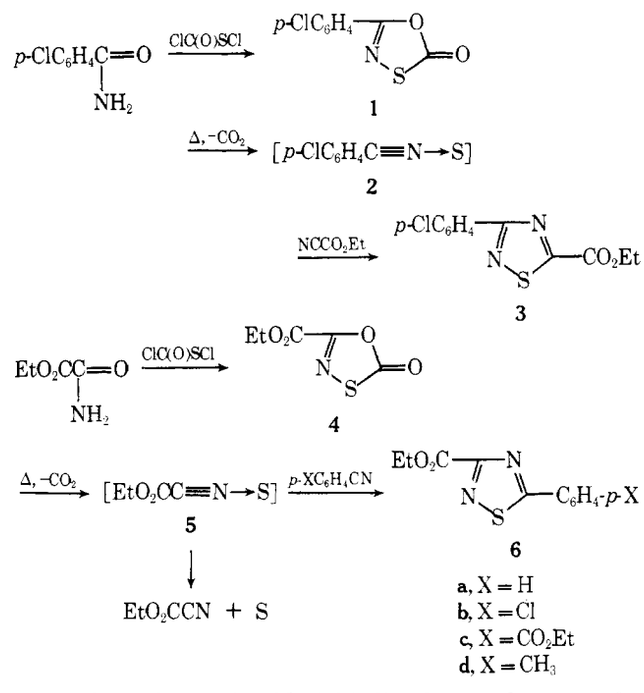
We reported recently[1] preparation of 3-aryl-1,2,4-thiadiazole-5-carboxylates in excellent yields by 1,3-dipolar cycloaddition reactions of aryl nitrile sulfides with ethyl cyanoformate, as exemplified by the synthesis of **3**, a new compound. Synthesis of the heretofore unknown, isomeric 5-aryl-1,2,4-thiadiazole-3-carboxylates now has been accomplished by cycloaddition of ethoxycarbonylnitrile sulfide (**5**) to aryl nitriles. Nitrile sulfide **5** was generated and trapped in situ by thermolysis of oxathiazolone **4** in excess aryl nitrile.

Table I. Thiadiazole-3-carboxylates 6 from Thermolysis of 4 in Aromatic Nitriles at 190 °C

Mol ratio, *p*-XC_6H_4-CN/4	Registry no.	Product	Registry no.	% yield of 6 GC	% yield of 6 Isolated
10	100-40-0	**6a**	61689-35-8	26	
35		**6a**		62	33
10	623-03-0	**6b**	61689-36-9	69	61
10	7153-22-2	**6c**	61689-37-0	53	23.5
10	104-85-8	**6d**	61689-38-1	16	7



The dependence of yield of thiadiazole **6** on the para substituent (Table I) is in general agreement with qualitative predictions based on the generalized perturbation theory,[2] with the assumption that the reaction is dipole–HOMO controlled. Electropositive substituents will raise the dipolarophile LUMO level, decreasing the rate of the cycloaddition reaction, and electronegative substituents will lower the dipolarophile LUMO level, increasing the rate of the cycloaddition reaction.[2,3] Coulombic effects will reinforce these frontier orbital effects.[2,3] The yield of thiadiazole depends on the relative rates of cycloaddition of **5** and decomposition of **5** to ethyl cyanoformate and sulfur. Thermolysis of neat oxathiazolone **4** at 235–290 °C (bath temperature) gave ethyl cyanoformate (48% distilled yield), carbon dioxide (94%), and sulfur (96%). Ethyl cyanoformate is both relatively volatile (bp 115–116 °C) and thermally unstable[4] and was found to disappear completely within 86 h from benzonitrile solution heated at reflux. Thus, the measured yields (GC analysis) of ethyl cyanoformate in the cycloaddition reactions did not account fully for the balance of oxathiazolone that was thermolyzed but not converted to thiadiazole.

Experimental Section

Melting points were determined in open capillaries with a Mel-Temp apparatus and are corrected. Infrared spectra were obtained

on a Perkin-Elmer Model 137 spectrophotometer. Chlorocarbonylsulfenyl chloride[5] and 5-*p*-chlorophenyl-1,3,4-oxathiazol-2-one (1), mp 129–131 °C (lit.[5a] mp 127.5 °C; lit.[6] mp 127–130 °C) were prepared by literature methods. GC yields were determined with internal standards (usually chlorobenzene) and calibration mixtures.

Ethyl 2-Oxo-1,3,4-oxathiazole-5-carboxylate (4). A mixture of 99.7 g (0.85 mol) of ethyl oxamate and 552 g (4.23 mol) of chlorocarbonylsulfenyl chloride in toluene was held at reflux for 5.25 h and then was concentrated under vacuum. Benzene was added to the residue, and the solution was extracted twice with water, twice with 5% $NaHCO_3$, again with water, and was dried ($CaSO_4$) and concentrated under vacuum. The residual oil was filtered to remove sulfur and was crystallized twice from methylcyclohexane to give 95.61 g (64%) of white solid, mp 49–50.5 °C.

Anal. Calcd for $C_5H_5NO_4S$: C, 34.29; H, 2.88. Found: C, 34.28; H, 2.81.

Ethyl 3-(*p*-Chlorophenyl)-1,2,4-thiadiazole-5-carboxylate (3). A solution of 4.27 g (0.020 mol) of 5-(*p*-chlorophenyl)-1,3,4-oxathiazol-2-one and 7.93 g (0.080 mol) of ethyl cyanoformate in 40 mL of dodecane was held at reflux (145–160 °C) for 21 h, cooled, and filtered to give 3.32 g of needles, mp 82–84 °C. Another 0.75 g of product, mp 82–84 °C, was obtained from the filtrate (total yield 76%).

Anal. Calcd for $C_{11}H_9ClN_2O_2S$: C, 49.17; H, 3.38; N, 10.42. Found: C, 48.94; H, 3.19; N, 10.43.

Ethyl 5-Phenyl-1,2,4-thiadiazole-3-carboxylate (6a). A solution of 8.76 g (0.050 mol) of ethyl 2-oxo-1,3,4-oxathiazole-5-carboxylate (4) in 180 g (35 equiv, 1.75 mol) of redistilled benzonitrile was held at reflux for 72 h (after 25 h, most of 4 was gone, and ethyl cyanoformate was present in ca. 7% yield). The solution, which contained the product in 62% yield (GC assay), was concentrated under vacuum to 90 °C (0.5 Torr). The residue was heated with 200 mL of hexane at reflux; the supernatant was decanted, treated with charcoal, filtered, and concentrated under vacuum to 6.1 g of oil and solid. The mixture was chromatographed on 200 g of silica gel (Woelm, for dry column chromatography) with benzene. The first 500 mL of eluate contained 0.8 g of product and impurities. The next 1200 mL of eluate gave 3.82 g (33%) of pure liquid product (GC assay), which crystallized after several months: mp 32–35 °C; $n^{25}D$ 1.5937; mass spectrum *m/e* (rel intensity, fragment) 234 (18, M^+), 206 (3, $M^+ - C_2H_4$), 189 (10, $M^+ - OEt$), 135 (100, $M^+ - EtO_2CCN$), 103 (14, $C_6H_5CN^+$). The infrared spectrum of this material showed considerable differences from that of the isomeric ethyl 3-phenyl-1,2,4-thiadiazole-5-carboxylate:[1] IR (film) 5.75 (s), 8.17 (m), 8.40 (s), 8.62 μ (m); only very weak absorptions were present at 8.94; 9.00, and 14.05 μ where the 5-carboxylate absorbs strongly.

Anal. Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.40; H, 4.30. Found: C, 56.38; H, 4.40.

Ethyl 5-(*p*-Chlorophenyl)-1,2,4-thiadiazole-3-carboxylate (6b). A sample of *p*-chlorobenzonitrile (Eastman) was distilled and then crystallized twice from methylcyclohexane to remove impurities that interfered in the following reaction.

A solution of 8.76 g (0.050 mol) of ethyl 2-oxo-1,3,4-oxathiazole-5-carboxylate and 68.8 g (0.50 mol, 10 equiv) of purified *p*-chlorobenzonitrile was held at 190 °C for 72 h. The solution, which contained the product in 69% yield, was concentrated under vacuum to 150 °C (ca. 2 Torr). The residue was crystallized from heptane (charcoal) to give 8.25 g (61%) of gold crystals, mp 98–99.5 °C. A small sample was crystallized twice from heptane (charcoal) to give a white solid, mp 98–99.5 °C.

Anal. Calcd for $C_{11}H_9ClN_2O_2S$: C, 49.17; H, 3.38. Found: C, 49.21; H, 3.29.

Ethyl 5-(4-Ethoxycarbonylphenyl)-1,2,4-thiadiazole-3-carboxylate (6c). A solution of 1.75 g (0.010 mol) of oxathiazolone 4 and 17.5 g (0.10 mol) of ethyl *p*-cyanobenzoate was stirred at 190 °C for 72 h, cooled, and dissolved in acetone. GC analysis of the solution revealed that the product had formed in 53% yield. Concentration of the solution to 90 °C (0.1 Torr) and two crystallizations of the residue from ethanol (charcoal) at −20 °C gave 0.72 g (23.5%) of beige solid, mp 66–67.5 °C.

Anal. Calcd for $C_{14}H_{14}N_2O_4S$: C, 54.89; H, 4.61. Found: C, 54.89; H, 4.60.

Ethyl 5-*p*-Tolyl-1,2,4-thiadiazole-3-carboxylate (6d). A solution of 7.48 g (0.0427 mol) of oxathiazolone 4 and 50.0 g (0.427 mol) of *p*-tolunitrile (redistilled) was held at 190 °C for 72 h. The reaction mixture, which contained the product in 16% yield, was concentrated under vacuum to 90 °C (0.5 Torr) to give 4.4 g of black residue. Elution chromatography of this material on 200 g of silica gel (Woelm, for dry column chromatography) with benzene gave 1.7 g of product. Crystallization of this material from hexane (charcoal) gave 0.72 g (7%) of solid, mp 65–66.5 °C.

Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87; N, 11.28. Found: C, 58.32; H, 4.91; N, 11.29.

Thermolysis of Ethyl 2-Oxo-1,3,4-oxathiazole-5-carboxylate (4). A 2.00-g (0.01142 mol) sample of 4 was heated under a slow N_2 stream in a 25-mL flask, fitted with a distillation head, in an oil bath at 235–290 °C. The gas stream was bubbled through excess aqueous barium hydroxide. Barium carbonate formed in 94% yield. The liquid distillate consisted of 0.54 g (48%) of pure ethyl cyanoformate (IR, GC analyses). The pot residue, 0.35 g (96%), consisted solely of sulfur (blank IR spectrum).

Control Experiment. A solution of 0.21 g of ethyl cyanoformate in 18.0 g of distilled benzonitrile was held at reflux for 86 h. GC analyses of the solution before and after the heating revealed greater than 99% disappearance of the ethyl cyanoformate in the 86-h period.

Registry No.—1, 17452-79-8; 3, 61689-39-2; 4, 61689-40-5; ethyl oxamate, 617-36-7; chlorocarbonylsulfenyl chloride, 2757-23-5; ethyl cyanoformate, 623-49-4.

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A Convenient Preparation of Unsymmetrical Disulfides. Synthesis of 11,12-Dithiatetradecyl and 11,12-Dithiatridecyl Acetates[1a,b]

K. C. Mattes and O. L. Chapman*[1c]

Department of Chemistry, Iowa State University, Ames, Iowa 50010

J. A. Klun

Corn Borer Research Unit, Agricultural Research Service, Ankeny, Iowa 50021

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In conjunction with our studies regarding the stereochemical and electronic requirements of the sex pheromone receptors of the European corn borer (*Ostrinia nubilalis*, Hubner[2]) and the red-banded leaf-roller (*Argyrotaenia velutinana*, Walker[3]) moths[4] we required an efficient synthesis of 11,12-dithiatetradecyl acetate (1) and 11,12-dithiatridecyl acetate (2). Literature procedures[5] gave poor yields of 1 and 2 and large amounts of the corresponding symmetrical disulfides. We wish to report a convenient synthesis of unsymmetrical disulfides by a simple procedure that affords disulfides 1 and 2 in good yields.

$CH_3CO_2(CH_2)_{10}SSCH_2CH_3$ (1) $\quad$ $CH_3CO_2(CH_2)_{10}SSCH_3$ (2)

Unsymmetrical disulfides have been prepared by reaction of thiols with sulfenimides,[6] sulfenate esters,[7] sulfenylated thiocarbonates,[8] sulfoxides,[9] and sulfenyl halides[10] and by the reaction of sulfenyl halides with symmetrical disulfides.[11] All of these methods suffer from side reactions (eq 2–4)

$$RS^- + R'S{-}Y \rightleftarrows R{-}S{-}S{-}R' + Y^- \quad (1)$$

$$Y^- + R{-}S{-}S{-}R' \rightleftarrows R'S^- + R{-}S{-}Y \quad (2)$$

$$RS^- + R{-}S{-}S{-}R' \rightleftarrows R{-}S{-}S{-}R + R'S^- \quad (3)$$

$$R'S^- + R{-}S{-}S{-}R' \rightleftarrows R'{-}S{-}S{-}R' + RS^- \quad (4)$$

which have the effect of randomizing the products between