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Nitrile Sulfides. Synthesis of 1,2,4-Thiadiazoles

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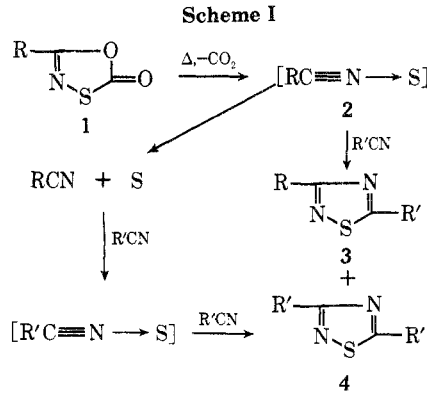
Received November 12, 1973

Reaction of nitriles with nitrile sulfide intermediates, generated by thermolysis of 1,3,4-oxathiazol-2-ones, resulted in 1,2,4-thiadiazoles. The scope of this new synthesis of thiadiazoles was explored; highest yields are obtained with electrophilic nitriles and with aromatic nitrile sulfides.

1,3-Dipolar cycloaddition reactions of nitrile oxides have been employed repeatedly in syntheses of heterocyclic compounds.[1,2] Until recently,[3,4] nitrile sulfides have been unavailable for syntheses of N–S heterocycles *via* cycloadditions. We have provided evidence that nitrile sulfides may be generated as reactive intermediates by thermolysis of 1,3,4-oxathiazol-2-ones and may be trapped in 1,3-dipolar cycloaddition reactions with acetylenes such as dimethyl acetylenedicarboxylate and ethyl propiolate.[3,4] We report here a new synthesis of 1,2,4-thiadiazoles *via* cycloaddition of nitrile sulfides to nitriles.

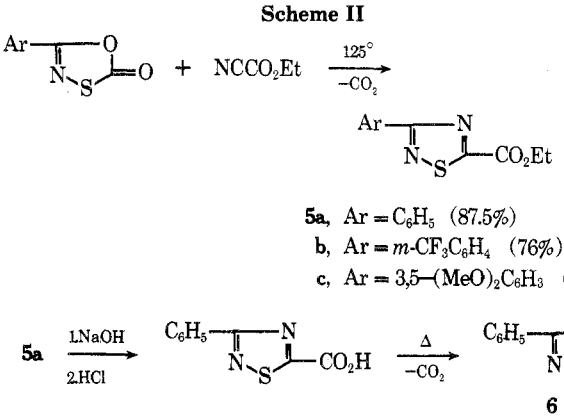
Thermolysis of 5-substituted 1,3,4-oxathiazol-2-ones (**1**) in excess nitrile led to thiadiazoles **3** and, in several cases, to lesser amounts of by-products **4** (Scheme I, Table I). Competitive decomposition of the intermediate nitrile sulfides produced sulfur and the nitrile derived from the oxathiazolone. Although the thiadiazole reaction proceeds less readily than the analogous 1,3-dipolar cycloaddition of nitrile oxides to nitriles to give 1,2,4-oxadiazoles,[5,6] under certain conditions reasonable yields of thiadiazoles may be obtained (Tables I and II). Thus, decarboxylation of 5-phenyl-1,3,4-oxathiazol-2-one in 35 equiv of benzonitrile at 190° gave 3,5-diphenyl-1,2,4-thiadiazole in 50% yield. The product and authentic material, prepared by iodine oxidation of thiobenzamide,[7] gave identical ir spectra and gave an undepressed mixture melting point. Products **3** and **4** were further characterized by mass spectrometry; the major fragmentation routes result in loss of RCN and R′CN (see Experimental Section), as found previously[8] for 3,5-disubstituted 1,2,4-thiadiazoles.

Scheme I



The cycloadditions of aromatic nitrile sulfides to ethyl cyanoformate proceeded especially well to give the ethyl 3-aryl-1,2,4-thiadiazole-5-carboxylates **5a**, **5b**, and **5c** (Scheme II; the indicated yields are for isolated pure products). Hydrolysis of **5a** and decarboxylation of the resultant acid gave the known[9] 3-phenyl-1,2,4-thiadiazole (**6**) in 99% yield.

Scheme II



By-product **4** (Scheme I) probably occurs *via* cycloaddition of R′CNS to R′CN. The R′CNS could form from reaction of atomic sulfur with R′CN[10] (Scheme I) or from direct sulfur atom transfer between RCNS and R′CN. Yields of **3** were found to increase with greater excesses of nitrile, as expected, and with higher temperatures (Tables I and II). Evidently, the rate of cycloaddition reaction to form thiadiazole increases more rapidly with temperature than the competing decomposition of nitrile sulfide to nitrile and sulfur. The data of Table I reveal that the yields of thiadiazoles increase with more electrophilic nitriles and decrease with less electrophilic nitriles.[11] Substituent effects in the oxathiazolones are similar. Because the yield of cycloaddition product **3** depends on the relative rates of cycloaddition and decomposition of the substituted nitrile sulfide, the absolute effects of substituents in the oxathiazolones on the cycloaddition rate are not readily determined. Thermolysis of 5-phenyl-1,3,4-oxathiazol-2-one at 125° in chlorobenzene in the presence of 1 equiv of boron trifluoride etherate showed an eightfold rate enhancement, but the presence of boron trifluoride etherate resulted in lower yields of thiadiazole (Table II) in the cycloaddition reaction.[12]

Our new synthesis of 1,2,4-thiadiazoles allows ready preparation of 3,5-unsymmetrically substituted derivatives with no uncertainty about the position of the substituents. Thus, both 3-phenyl-5-*p*-tolyl-1,2,4-thiadiazole, mp 115–116°, and 5-phenyl-3-*p*-tolyl-1,2,4-thiadiazole, mp 77.5–79°, were prepared unambiguously. A previous report[13] of the preparation of 3- (or 5-) phenyl-5- (or 3-) *p*-tolyl-1,2,4-thiadiazole, mp 56°, did not allow an exact

Table I
Thiadiazole Preparations *via* Nitrile Sulfides[a] at 190°

R	R′	Mole ratio,[b] 1:2	Yield[c] of 3, %	Yield[c] of 4, %
C_6H_5	C_6H_5	0.0287	50 (41)	
C_6H_5	p-$CH_3C_6H_4$	0.0287	33	2.3
C_6H_5	p-$CH_3C_6H_4$	0.0324	30 (10)	1.7
C_6H_5	p-ClC_6H_4	0.0287	56	8.6
p-$CH_3C_6H_4$	C_6H_5	0.0287	30 (8)	4.8
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	0.0287	28 (12)	
p-ClC_6H_4	C_6H_5	0.0287	57 (36)	7
p-ClC_6H_4	p-ClC_6H_4	0.0287	73	
p-ClC_6H_4	p-ClC_6H_4	0.0383	71 (62)	
CH_3	C_6H_5	0.0500[d]	6.9 (2.7)	3.7
p-ClC_6H_4	EtO_2CCH_2	0.0287	15.7 (6)	

[a] See Scheme I. [b] Unless otherwise indicated, **1** was added in three equal portions at 5-min intervals to **2** stirred at 190°. [c] Yields determined by gc analysis. Yields in parentheses are yields of isolated pure products. [d] The liquid oxathiazolone was added dropwise during 35 min to the nitrile.

structural assignment and very probably led to a mixture, based on the reported melting point.

Experimental Section

Melting points were taken in open capillaries in a Mel-Temp apparatus and are corrected. All nitriles were redistilled and checked for purity by gc prior to use, as impurities present in the commercial nitriles resulted in lower product yields. The 1,3,4-oxathiazol-2-ones were prepared by reaction of acid amides with chlorocarbonylsulfenyl chloride according to reported procedures.[14]

General Procedure for 3,5-Diaryl-1,2,4-thiadiazoles. To 1.0 mol of aromatic nitrile stirred at 190° was added in three equal portions at 5-min intervals a total of 0.0287 mol of 5-aryl-1,3,4-oxathiazol-2-one. The solution was stirred for another 10 min at 190°, cooled, analyzed by gc on a 2-ft column of 10% SE-30 programmed from 70 to 250°, and concentrated under vacuum to remove excess nitrile. The residue was boiled with methanol or ethanol, undissolved sulfur was removed by filtration, and the filtrate was concentrated somewhat and cooled to give solid product, which then was recrystallized from an appropriate solvent.

3,5-Diphenyl-1,2,4-thiadiazole. Pure product, mp 86–88° (lit.[7] mp 90°), was obtained from ethanol: uv max (CH_3CN) 219 nm (log ϵ 4.20), 255 (4.59); mass spectrum m/e (rel intensity, fragment) 238 (2, M^+), 135 (100, $M^+ - C_6H_5CN$), 103 (22, $C_6H_5CN^+$), 77 (23, $C_6H_5^+$).

5-*p*-Chlorophenyl-3-phenyl-1,2,4-thiadiazole. The product mixture was crystallized from ethanol and from acetonitrile to give a 90:10 mixture (gc assay), mp 145–147°, of 5-*p*-chlorophenyl-3-phenyl-1,2,4-thiadiazole and 3,5-bis(*p*-chlorophenyl)-1,2,4-thiadiazole (identified by gc retention time and gc–mass spectral data). A pure sample of product, mp 152°, was obtained by gas chromatographic purification, mass spectrum m/e (rel intensity, fragment) 272 (17, M^+), 169 (6, $M^+ - C_6H_5CN$), 135 (100, $M^+ - ClC_6H_4CN$), 111 (2, $C_6H_4Cl^+$), 103 (18, $C_6H_5CN^+$), 77 (18, $C_6H_5^+$). This isomer is distinguished from 3-*p*-chlorophenyl-5-phenyl-1,2,4-thiadiazole by ir absorptions ($CHCl_3$ solvent) at 11.96 (s) and 12.18 μ (w, shoulder) whereas the 5-phenyl isomer has absorption at 11.88 μ (s), with no shoulder at 12.18 μ.

Anal. Calcd for $C_{14}H_9ClN_2S$: C, 61.65; H, 3.33. Found: C, 61.80; H, 3.44.

3-*p*-Chlorophenyl-5-phenyl-1,2,4-thiadiazole. The product was recrystallized from acetonitrile to give 100% pure (gc assay) product, mp 118–119°. This isomer has weak ir absorptions ($CHCl_3$ solvent) at 7.40, 10.00, and 10.88 μ that are not present in the 3-phenyl isomer.

Anal. Calcd for $C_{14}H_9ClN_2S$: C, 61.65; H, 3.33. Found: C, 61.45; H, 3.33.

3,5-Bis(*p*-chlorophenyl)-1,2,4-thiadiazole. Pure product, mp 163–164° (lit.[15] mp 161–162°), was obtained from ethanol: mass spectrum m/e (rel intensity, fragment) 306 (18, M^+), 169 (100, $M^+ - ClC_6H_4CN$), 137 (30, $ClC_6H_4CN^+$), 111 (10, $C_6H_4Cl^+$), 102 (15, $C_6H_4CN^+$).

3-Phenyl-5-*p*-tolyl-1,2,4-thiadiazole. Gc and gc–mass spectral analyses of the reaction mixture revealed that 0.3% 3,5-diphenyl-1,2,4-thiadiazole, 33.2% 3-phenyl-5-*p*-tolyl-1,2,4-thiadiazole, and 2.3% 3,5-di-*p*-tolyl-1,2,4-thiadiazole had formed. Crystallization of the product mixture from methanol and then methylcyclohexane gave pure 3-phenyl-5-*p*-tolyl-1,2,4-thiadiazole: mp 115–116°; mass spectrum m/e (rel intensity, fragment) 252 (25, M^+), 149 (34, $M^+ - C_6H_5CN$), 135 (100, $M^+ - CH_3C_6H_4CN$), 117 (5, $CH_3C_6H_4CN^+$), 103 (24, $C_6H_5CN^+$), 91 (11, $C_7H_7^+$), 77 (29, $C_6H_5^+$); nmr ($CDCl_3$) δ 7.2–8.5 (m, 9, ArH), 2.40 (s, 3, CH_3). This isomer has a strong ir absorption ($CHCl_3$ solvent) at 12.20 μ that is absent in the isomeric 5-phenyl-3-*p*-tolyl-1,2,4-thiadiazole.

Anal. Calcd for $C_{15}H_{12}N_2S$: C, 71.40; H, 4.79. Found: C, 71.63; H, 4.84.

5-Phenyl-3-*p*-tolyl-1,2,4-thiadiazole. The product was recrystallized from hexane to give 100% pure material, mp 77.5–79°, which has a medium-intensity ir absorption ($CHCl_3$ solvent) at 6.65 μ that is absent in the 3-phenyl isomer.

Anal. Calcd for $C_{15}H_{12}N_2S$: C, 71.40; H, 4.79. Found: C, 71.32; H, 4.79.

3,5-Di-*p*-tolyl-1,2,4-thiadiazole. Pure product, mp 127–129° (lit.[13] mp 129°), was obtained from aqueous ethanol: mass spectrum m/e (rel intensity, fragment) 266 (22, M^+), 149 (100, $M^+ - CH_3C_6H_4CN$), 117 (23, $CH_3C_6H_4CN^+$), 91 (16, $C_7H_7^+$); nmr ($CDCl_3$) δ 8.27 (d, 2, ArH), 7.93 (d, 2, ArH), 7.27 (d, 4, ArH), 2.40 (s, 6, CH_3).

3-Methyl-5-phenyl-1,2,4-thiadiazole. To 86.8 g (0.842 mol) of redistilled benzonitrile at reflux was added dropwise 4.92 g (0.0421 mol) of 5-methyl-1,3,4-oxathiazol-2-one[14] during 35 min. The solution was held at reflux for another 10 min, cooled, analyzed by gc (see Table I), and concentrated under vacuum to remove excess benzonitrile. The residue was triturated with 30 ml of methanol, and the mixture was filtered free of sulfur. The filtrate was cooled in Dry Ice to give 0.24 g of 97% pure (gc assay) 3,5-diphenyl-1,2,4-thiadiazole, mp 82–87°. Recrystallization of this solid from methanol gave 0.12 g of solid, mp 87–89° (mmp 87–89° with authentic material), that gave the same ir spectrum as authentic 3,5-diphenyl-1,2,4-thiadiazole.

The filtrate from the first crystallization was distilled under vacuum; 86% pure product, 0.32 g of oil that solidified, was collected at bp 100–125° (2 mm). This solid was recrystallized from cold aqueous methanol to give 0.20 g of 100% pure 3-methyl-5-phenyl-1,2,4-thiadiazole (2.7% yield): mp 54–55.5° (lit.[16] mp 50°); nmr ($CDCl_3$) δ 8.00 (m, 2, ArH), 7.53 (m, 3, ArH), 2.73 (s, 3, CH_3).

3-(*p*-Chlorophenyl)-1,2,4-thiadiazole-5-acetic Acid Ethyl Ester. The general procedure was employed. The product was crystallized from aqueous ethanol and from hexane to give pure product: mp 127.5–129°; ir ($CHCl_3$) 5.78 μ; nmr ($CDCl_3$) δ 8.23 (m, 2, ArH), 7.43 (m, 2, ArH), 4.33 (q, 2, J = 7 Hz, OCH_2CH_3), 4.27 (s, 2, CH_2CO), 1.35 (t, 3, J = 7 Hz, OCH_2CH_3).

Anal. Calcd for $C_{12}H_{11}ClN_2O_2S$: C, 50.98; H, 3.92. Found: C, 50.98; H, 3.87.

Ethyl 3-Phenyl-1,2,4-thiadiazole-5-carboxylate (5a). A solution of 14.0 g (0.0783 mol) of 5-phenyl-1,3,4-oxathiazol-2-one and 31.0 g (0.313 mol) of ethyl cyanoformate in 150 ml of dodecane was held at reflux under N_2 (pot temperature was 138° at start) for 12.75 hr, at which time gc analysis revealed that the reaction was complete and that the product had formed in 89% yield. Removal of the solvent and crystallization of the residue from ethanol gave 15.97 g (87.5%) of white needles: mp 70–71°; ir ($CHCl_3$) 5.72, 5.81 μ; uv max (CH_3CN) 242 nm (log ϵ 4.24), 293 (3.44);

Table II
Effect of Mole Ratio, Temperature, and Boron Trifluoride Etherate on Yield of 3,5-Diphenyl-1,2,4-thiadiazole[a]

Mole ratio,[b] 1:2	Equiv of $BF_3 \cdot Et_2O$	Temp, °C	Yield of 3,[c] %
0.100	0	190	74
0.0287	0	190	39
0.10	0	190	14
0.0287	0	160	35
0.0287	0	130	25
0.0287	2[d]	190	10
0.0287	1	130	0

[a] See Scheme I. [b] All the **1** was added in one portion to **2** at the indicated temperature. [c] Determined by gc analysis. [d] Some of the boron trifluoride etherate was lost through the air-cooled condenser.

mass spectrum m/e (rel intensity, fragment) 234 (46, M^+), 189 (4, (M^+ − OEt), 161 (3, M^+ − CO_2Et), 135 (100, $C_6H_5CNS^+$), 103 (32, $C_6H_5CN^+$), 77 (16, $C_6H_5^+$).

Anal. Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.40; H, 4.30. Found: C, 56.21; H, 4.45.

Ethyl 3-(α,α,α-Trifluoro-m-tolyl)-1,2,4-thiadiazole-5-carboxylate (5b). Use of a similar procedure to that above (92.5-hr reaction time) gave product thiadiazole in 76% yield (isolated product) as a white solid, mp 79–80.5° (from heptane), ir ($CHCl_3$) 5.72, 5.80 μ.

Anal. Calcd for $C_{12}H_9F_3N_2O_2S$: C, 47.68; H, 3.00. Found: C, 47.86; H, 2.84.

Ethyl 3-(3,5-Dimethoxyphenyl)-1,2,4-thiadiazole-5-carboxylate (5c). Use of a similar procedure to that above (92.5-hr reaction time) gave product thiadiazole in 94% yield (isolated) as a white solid, mp 125–126.5° (from dodecane), ir ($CHCl_3$) 5.72, 5.80 μ.

Anal. Calcd for $C_{13}H_{14}N_2O_4S$: C, 53.05; H, 4.79. Found: C, 53.19; H, 4.90.

3-Phenyl-1,2,4-thiadiazole (6). A mixture of 8 g (0.034 mol) of ethyl 3-phenyl-1,2,4-thiadiazole-5-carboxylate, 1.5 g (0.037 mol) of sodium hydroxide, 10 ml of ethanol, and 60 ml of water was heated with stirring on a steam bath for 1 hr. The resultant solution was allowed to cool and was acidified with 3.5 ml (0.042 mol) of concentrated hydrochloric acid. The resultant mixture, containing granular solid carboxylic acid, was heated on a steam bath until decarboxylation was complete. The mixture was cooled and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated under vacuum to give 5.5 g (99%) of colorless oil. Distillation of this material gave a single fraction, bp 76.5° (0.5 mm) [lit.[9] bp 78–80° (0.3 mm)], nmr ($CDCl_3$) δ 9.90 (s, 1, 5-H), 8.37 (m, 2, ArH), 7.48 (m, 3, ArH).

Anal. Calcd for $C_8H_6N_2S$: C, 59.23; H, 3.74; N, 17.27; S, 19.76. Found: C, 59.03; H, 3.84; N, 17.23; S, 19.91.

Registry No.—**1**, R = Me, 17452-74-3; **1**, R = Ph, 5852-49-3; **3**, R = R′ = Ph, 4115-15-5; **3**, R = Ph, R′ = p-ClC_6H_4, 50483-71-1; **3**, R = p-ClC_6H_4, R′ = Ph, 50483-72-2; **3**, R = R′ = p-ClC_6H_4, 4115-17-7; **3**, R = Ph, R′ = p-MeC_6H_4; 50483-74-4; **3**, R = p-MeC_6H_4, R′ = Ph, 50483-75-5; **3**, R = R′ = p-MeC_6H_4, 17590-34-0; **3**, R = Me, R′ = Ph, 50483-77-7; **4**, R = p-ClC_6H_4, R′ = CH_2CO_2Et, 50483-78-8; **5a**, 50483-79-9; **5b**, 50483-80-2; **5c**, 50483-81-3; **6**, 50483-82-4.

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Hypervalent Sulfur Chemistry. Evidence for Tetracoordinate Sulfur(IV) and Tricoordinate Sulfur(II) Intermediates in the Reaction of p-Tolyl Sulfoxide with p-Tolyllithium[1a]

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Received March 13, 1973

p-Tolyl sulfoxide (1) reacted with excess p-tolyllithium (2) to give p-tolyl sulfide (3, 66%), p,p′-bitolyl (4, 31%), and m,p′-bitolyl (5, 26%). The reaction of tri-p-tolysulfonium salt with 2, which gave 3 (87%), 4, (72%), and 5 (5%), is thought to proceed largely through a tetra-p-tolylsulfurane which collapses to product. A mechanism for the reaction of 1 with 2 is proposed which involves 4-toluyne formation from a tetracoodinate S(IV) precursor, tri-p-tolyloxysulfurane (7). The 4-toluyne adds 2 to give 4 and 5. *N*-p-toluenesulfonyl-*S*,*S*-di-p-tolylsulfimide and 2 gave 3 (80%), 4 (66%), 5 (1–2%), and p-toluenesulfonamide (60%), while methoxydi-p-tolylsulfonium salt and 2 gave 3, 4, and 5 in the ratio of 135:96:1. These two reactions are proposed to proceed largely through tetra-p-tolylsulfurane which collapses to 3 and 4; very little 4-toluyne is involved as an intermediate. Methyl p-toluenesulfinate and 2 gave 3 (77%), 4 (37%), and 5 (32%). The reaction is thought to proceed *via* formation of 1 which then reacts *via* 7. Mesityl sulfoxide and mesityllithium gave 2,4,4′,6,6′pentamethyl-2′-(2,4,6-trimethylphenylmethyl)diphenyl sulfide (16%) but no mesityl sulfide or bimesityl.

Hypervalent sulfur chemistry,[2] the chemistry of nonoctet sulfur compounds such as sulfonium ylides, sulfoxides, and sulfuranes in which the sulfur participates in the reaction, has been of great synthetic utility and theoretical interest and consequently much studied during the past decade. In nucleophilic substitution at tricoordinate sulfur(IV),[3] *e.g.*, sulfinyl sulfur, the presence or absence of tetracoordinate S(IV) intermediates, conveniently named sulfuranes, formed by bonding of the nucleophile to sulfur, has occupied the attention of many workers. In principle, these intermediates can exist, since stable sulfuranes, such as SF_4, are known. In practice, their detection has often proved difficult. Kinetic studies have not unequivocally demonstrated their presence even though efforts have been made to detect them in various reactions (eq 1[4] and 2[5]).

$$ArSOCH_3 + CD_3OH \longrightarrow ArS(=O)CD_3 + CH_3OH \quad (1)$$

$$ArS(=O)NHAr' + OH^- \longrightarrow ArSO_2^- + Ar'NH_2 \quad (2)$$

Stable sulfuranes usually have four electronegative atoms such as F, Cl, O, or N around sulfur, but recently examples having two carbon atoms as ligands have been synthesized.[6-8] The carbon atoms were shown in one case to be equatorial by X-ray analysis.[6] The two remaining