The Synthesis and Some Reactions of 1,2,4-Thiadiazolylsulfenyl Chlorides

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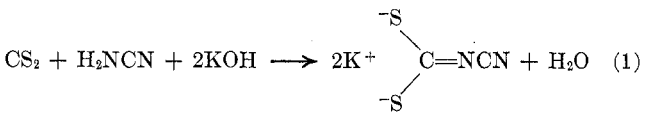
Cyanodithioimidocarbonate anion undergoes a novel reaction with halogens to produce 3-halo-1,2,4-thiodiazol-5-yl sulfenyl halides or the corresponding disulfides. Although chlorination produced 3-chloro-1,2,4-thiadiazol-5-yl sulfenyl chloride (**2**) directly, bromination gave the bis(3-bromo-1,2,4-thiadiazol-5-yl) disulfide (**6**) which was converted to the 3-bromo-1,2,4-thiadiazol-5-yl sulfenyl chloride (**7**) by subsequent chlorination. Treatment of cyanodithioimidocarbonate ion with sulfur and subsequent chlorination provided a convenient route to the 1,2,4-thiadiazol-3,5-yl bis(sulfenyl chloride) (**11**). The preparations and some reactions of 1,2,4-thiadiazolylsulfenyl chlorides are described

Hantzsch and Wolvekamp[1] established the structure of dipotassium cyanodithioimidocarbonate (**1**) in 1934 by means of a convenient synthesis from cyanamide and carbon disulfide (eq 1). The chemistry of

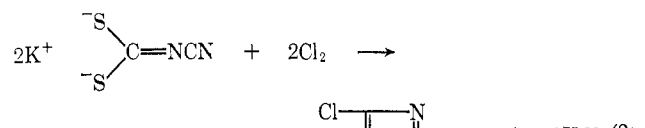


(1)

1

this salt has received comparatively little attention until quite recently when several publications appeared concerning alkyl,[2,3] acyl,[3] and organotin[4] derivatives. The dithiolate anion has also proved useful for the preparation of metal complexes.[5,6] The halogenation reactions of the cyanodithioimidocarbonate anion had not been investigated, and it was felt that they might provide an interesting route to either geminal bis(sulfenyl halides) or to heterocyclic sulfenyl halides.

Halogenation of Cyanodithioimidocarbonate Anion.—Chlorination of a slurry of **1** in methylene chloride conveniently provided an 85–100% yield of 3-chloro-1,2,4-thiadiazol-5-yl sulfenyl chloride, after filtering off the KCl precipitate and evaporating the solvent (eq 2).



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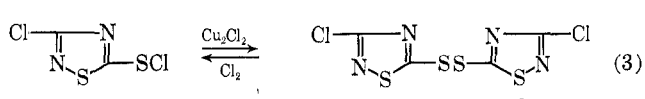
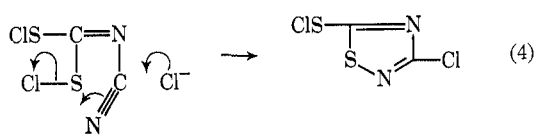


(3)

3, mp 118–120°

The product is a stable yellow solid which can be kept at room temperature for a prolonged period without any noticeable decomposition. On heating above 40°, it melted with decomposition but was recovered unchanged after refluxing with sulfuryl chloride in CCl_4 solution for 3 days. The ultraviolet spectra (run in cyclohexane) showed an absorption maximum at 225 mμ (log ε 3.73). The parent compound, 1,2,4-thiadiazole,[7,8] has a maximum at 229 mμ (log ε 3.7). The sulfenyl chloride was readily reduced to the corresponding disulfide **3** by treatment with cuprous chloride while chlorination of the disulfide regenerated compound **2** (eq 3). The disulfide exhibited five absorption bands in the infrared which were almost identical with that of its sulfenyl halide precursor. During chlorination, the formation of a cyclized thiadiazole ring could occur either by an attack of a sulfenyl chloride upon the nitrile group *via* an episulfonium type ion[9,10] (**4**), by an acyl type ion[11] (**5**), or by an attack of a chloride ion upon the nitrile carbon with concommittant nucleophilic attack of nitrogen on sulfur (eq 4). The

4 **5**



(4)

latter mechanism has been postulated by Hatchard[12] and by Timmons and Wittenbrook[3] for cyclizations also presumably involving transient sulfenyl chloride intermediates.

Although sulfenyl halides do not commonly react with nitriles, the addition of sulfur chlorides to aminonitriles and cyanogen[13] and of trifluoromethanesulfenyl chloride to a nitrile group of tetracyanoethylene[14] has been reported. Here again, the mechanism is not certain, although in the case of the tetracyanoethylene–F_3CSCl reaction, chloride ion serves as a catalyst. With four powerful electron-withdrawing groups on ethylene, it appears likely that initial attack by chloride is on the carbon–carbon double bond rather than upon the nitrile group. Possibly cyclization to aromatic ring systems provides the driving force for the sulfenyl chloride addition to the nitrile group of cyanogen and cyanoimidiocarbonate molecules. No analogous addi-

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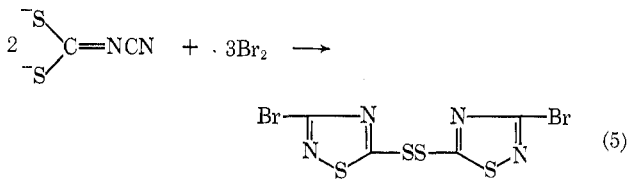
(1) A. Hantzsch and M. Wolvekamp, *Justus Liebigs Ann. Chem.*, **331**, 265 (1904).
(2) J. J. D'Amico and R. H. Campbell, *J. Org. Chem.*, **32**, 2537 (1967).
(3) R. J. Timmons and L. S. Wittenbrook, *ibid.*, **32**, 1566 (1967).
(4) R. Seltzer, *ibid.*, **33**, 3896 (1968).
(5) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **6**, 229 (1967).
(6) J. P. Fackler, Jr., and D. Coucouranis, *J. Amer. Chem. Soc.*, **88**, 3913 (1966).
(7) J. Goerdeler, J. Ohm, and O. Tegtmeyer, *Chem. Ber.*, **89**, 1534 (1956).
(8) J. Goerdeler and O. Tegtmeyer, *Angew. Chem.*, **67**, 302 (1955).
(9) W. A. Thaler, W. H. Mueller, and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2069 (1968).
(10) W. H. Mueller and P. E. Butler, *ibid.*, **90**, 2075 (1968).
(11) W. A. Thaler, *Chem. Commun.*, 527 (1968).
(12) W. R. Hatchard, *J. Org. Chem.*, **29**, 660 (1964).
(13) L. M. Weinstock, P. Davis, B. Handelsman, and R. Tull, *Tetrahedron Lett.*, 1263 (1966); (b) L. M. Weinstock, P. Davis, B. Handelsm, and R. Tull, *J. Org. Chem.*, **32**, 2823 (1967).
(14) H. D. Hartzler, *ibid.*, **29**, 1194 (1964).

tions to nitriles resulting in acyclic structures have to our knowledge been observed.

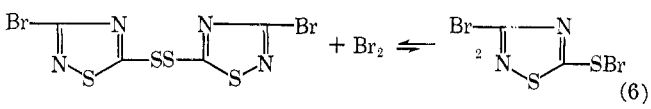
The bromination of cyanodithioimidocarbonate ion, in contrast to the chlorination, does not produce a sulfenyl chloride but gives instead bis(3-bromo-1,2,4-thiadiazol-5-yl) disulfide (**6**) in excellent yield (eq 5).



(5)

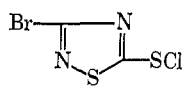
6, mp 142–144°

The disulfide appeared inert to excess bromine and, despite the fact that aromatic disulfides such as phenyl disulfide are readily cleaved by bromine, the thiadiazole disulfide displayed no such tendency. Possibly thermodynamic considerations are important here, and what is observed is an equilibrium very strongly favoring the disulfide, rather than any intrinsic inertness of this disulfide bond (eq 6). The disulfide is however



(6)

readily cleaved by chlorine, thereby providing the 3-bromo-1,2,4-thiadiazol-5-yl sulfenyl chloride (**7**). Here again the sulfenyl chloride **7** exhibited an infrared spec-



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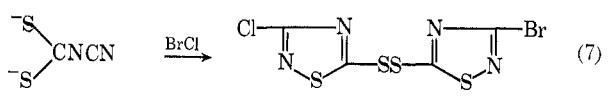
trum with absorptions nearly identical with those of the disulfide precursor **6**. The 3-bromo compounds, however, showed significant shifting of absorptions compared to the 3-chloro compounds (see Experimental Section) permitting convenient distinction between the two systems.

The reaction of bromine chloride with **1** gives a 92% yield of a disulfide which after one recrystallization (69%) melts at 118–120° (eq 7). Elemental

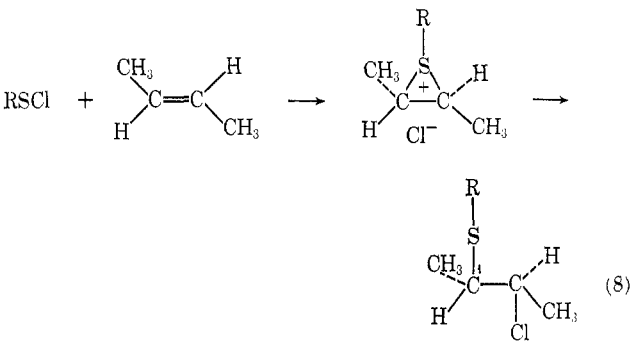


(7)

8, mp 118–120°

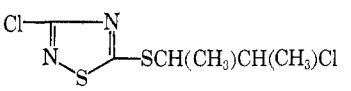
analysis indicated that the product was either a disulfide with a chlorine and a bromine in the 3 and 3′ positions (**8**) or else an exactly equal mixture of the dichloro and dibromo disulfides (**3** and **6**). The infrared spectrum was the same as the combined spectrum of **3** and **6**, a fact which is inconclusive since either the unsymmetrical disulfide or a mixture of the two disulfides could be expected to show similar infrared characteristics. The sharp melting point suggested that the product was a single compound **8**. In support of this, a 1:1 mixture of **3** and **6** had a broad melting point range (120–135°) which did not change even after recrystallization of the mixture. Furthermore, mixture melting points of **8** and **3** and of **8** and **6** also exhibited a broad range. Since it would have been quite fortuitous to have obtained an equal mixture of **3** and **6** directly from the reaction, and such a mixture exhibited different melting point characteristics, it was concluded that the reaction product was indeed the unsymmetrical disulfide **8**.

Reactions of 3-Halo-1,2,4-thiadiazol-5-yl Sulfenyl Chloride with Olefins.—The reaction of **2** or **7** with olefins at −40° in methylene chloride solution is a very rapid exothermic process wherein the olefin is consumed almost as rapidly as it is introduced. The addition to *trans*-butene produces a single diasteriomer which according to nmr analysis is different from the single diasteriomer obtained from reaction with *cis*-butene. Such stereospecific additions of sulfenyl chlorides have been attributed to an episulfonium ion reaction mechanism resulting in exclusively trans addition[15,16] (eq 8).



(8)

It would appear, therefore, that *trans*-butene gives rise to the erythro adduct and *cis*-butene to the threo adduct. Infrared and uv analyses demonstrate that the heterocyclic ring system is not itself involved in the reaction with olefins. Mass spectroscopic analysis of the *cis*-butene adduct shows parent and cracking peaks consistent with an adduct of structure **9**.



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The products from the reaction of **2** or **7** with several olefins were examined by nmr (Table I). Yield, and analyses for these adducts are presented in Table II. The direction of the addition (Markovnikoff or anti-Markovnikoff) of sulfenyl halides to terminal olefins, is usually easily determined by nmr analysis[16] because of the marked downfield shift of methylene or methine protons on carbons bonded to chlorine, relative to those on carbons bonded to sulfur. (Sulfenyl chlorides are polarized with the positive charge on sulfur, $RS^{\delta+}$–$Cl^{\delta-}$. Therefore, adducts with the chlorine bonded to the more highly substituted position of the hydrocarbon skeleton are designated Markovnikoff addition products.) However, the difference in chemical shift due to a chlorine substituent is very close to that of the strongly electron-withdrawing 3-chloro-1,2,4-thiodiazol-5-yl sulfenyl substituent, and it is difficult to make unequivocal structural assignments based on chemical shifts. Chemical shifts of adducts from symmetrical olefins were assigned by attributing the larger downfield shift to protons on the chlorine-bearing carbon. These values were utilized to assign

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(16) W. H. Mueller and P. E. Butler, *ibid.*, **88**, 2866 (1966).

TABLE I

NMR PARAMETERS OF 3-CHLORO-1,2,4-THIADIAZOLE-5-SULFENYL CHLORIDE–OLEFIN ADDUCTS

Olefin	Registry no.	Group assignments 1	2	3	4	5	6	Chemical shifts,[a] ppm 1	2	3	4	5	6	Coupling constants, cps
Ethylene	26542-82-5	$RSCH_2$		CH_2Cl				3.67[b] m		3.89[b] m				
				$ClCH_2$	RSCH		CH_3			3.95[b] dd	4.17[c] q dd		1.59 d	$J_{3,3'} = 10.8$, $J_{3,4} = 4.1$, $J_{3',4} = 7.4$, $J_{4,6} = 6.8$
										3.76[c] dd				
Propylene[f]	26542-83-6 26542-84-7	$RSCH_2$				CHCl	CH_3	3.66 d				4.34 qt	1.66 d	$J_{1,5} = 6.5$, $J_{5,6} = 6.8$
Isobutylene	26542-85-8	$RSCH_2$					$C(Cl)(CH_3)_2$	3.79 s					1.69 s	
3,3-Dimethyl-1-butene	26542-86-9			$ClCH_2$	RSCH		$C(CH_3)_3$			4.09[c] dd	3.70[c] dd		1.13 s	$J_{3,3'} = 4.0$, $J_{3,4} = 8.5$, $J_{3',4} = 12.5$
										4.04[c] dd				
trans-2-Butene	26542-87-0		CH_3		RSCH	CHCl	CH_3		1.55 d		4.20[d] dq	4.48[d] dq	1.61 d	$J_{2,4} = 6.8$, $J_{4,5} = 3.8$, $J_{5,6} = 6.8$
cis-2-Butene			CH_3		RSCH	CHCl	CH_3		1.59 d		4.36[d] dq	4.45[d] dq	1.61 d	$J_{2,4} = 6.8$, $J_{4,5} = 3.0$, $J_{5,6} = 6.8$
2-Methyl-2-butene	26542-88-1		CH_3		RSCH		$C(Cl)(CH_3)_2$		1.66 d		4.28 q		1.73 s	$J_{2,4} = 7.0$
1,4-Butadiene	26542-89-2	$RSCH_2$				CHCl	H H′ C=C H″	3.73 d				4.73[e] dtt	5.96[e] ddd	$J_{1,5} = 6.5$, $J_{5,6} = 8.0$, $J_{5,6} = 1.0$, $J_{5,6} = 1.0$
													5.29[e] dt	
													5.41[e] dt	$J_{6,6'} = 10.0$, $J_{6,6''} = 17.0$, $J_{6,6''} = 1.0$

[a] Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; dq, double quartet; qt, quartet of triplets; ddd, double doublet of doublets; dt, double triplet; dtt double triplet of triplets; m, multiplet. [b] Protons form an AA′BB′ type system; chemical shifts evaluated by comparison to calculated spectrum 5-4 "Interpretation of NMR Spectra," Wiberg and Nost, W. A. Benjamin, New York, N. Y., 1962. [c] Protons 3, 3′, and 4 form ABC type systems; chemical shifts are approximated from a first-order analysis. [d] Protons 4 and 5 form AB part of ABX_3Y_3 system; chemical shifts for A and B are calculated from decoupled AB quartet. [e] Protons 5, 6, 6′, and 6″ form an ABCX system; chemical shifts are approximated from a first-order analysis. Chemical shift values are listed in the order, 6, 6′, 6″. Protons 6 and 6″ are trans. [f] Addition to propylene produced an anti-Markovnikoff product (60%) and a Markovnikoff product (40%); the mixture was not separated.

TABLE II

REACTION OF 1,2,4-THIADIAZOLYLSULFENYL, CHLORIDES WITH SOME UNSATURATED HYDROCARBONS[a]

A. 3-Halo-1,2,4-thiadiazol-5-yl Sulfenyl Chlorides

Reagent	Olefin	Yield, % Crude	Yield, % Purified
2	Ethylene	97	80
2	Propylene	100	79
2	Isobutylene	91	71
7	Isobutylene	100	95
2	*cis*-Butene-2	91	85
2	*trans*-Butene-2	94	81
2	3,3-Dimethylbutene-1	88	74
2	Butadiene	96	
2	2-Methylbutene-2	98	76

B. 1,2,4-Thiadiazol-3,5-yl Bis(sulfenyl chloride)

Reagent	Olefin	Yield, %[b]
11	Ethylene	100
11	Propylene	97
11	*cis*-Butene-2	104
11	Isobutylene	94
11	Allyl chloride	102
11	Butadiene	92

[a] Satisfactory analytical values (±0.35%) for C, H, N were obtained on all adducts. [b] All diadducts with the exception of the ethylene adduct were nondistillable oils and were analyzed without further purification.

analogous methylene and methine signals from adducts of unsymmetrical olefins. The chemical shifts assigned in this fashion appear to be internally consistent (Table I).

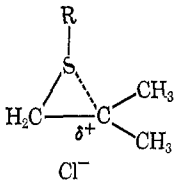
The reactions of 3-halo-1,2,4-thiadiazol-5-yl sulfenyl chlorides with terminal olefins were remarkably specific. With the exception of unbranched olefins such as propylene where similar quantities of the two positional isomers were obtained, reactions with substituted olefins such as isobutylene and 3,3-dimethyl-1-butene gave single products. The Markovnikoff or anti-Markovnikoff structure of these products assigned tentatively by analogy with other sulfenyl halide–terminal olefin adductions was completely consistent with assignments based on nmr analysis.

In general, increased electron-withdrawing character of R decreases the anti-Markovnikoff and increases the Markovnikoff adducts from the reaction of RSCl with terminal olefins.[10,17] Thus the adducts derived from isobutylene were reported to contain 80, 32, and 19% anti-Markovnikoff product when R was the CH_3, $CH_3C(O)S$, or $(CH_3O)_2P(O)$ substituent, respectively. Furthermore, with an electron-withdrawing substitute such as the $CH_3C(O)S$ group, the tendency toward Markovnikoff product increased in going from propylene to isobutylene (40% Markovnikoff product from propylene, 68% Markovnikoff product from isobutylene). This behavior has been attributed to increased positive charge on carbon when R tends to destabilize the positive charge on the sulfur atom in the episulfonium ion. Thus the direction of episulfonium ring opening *via* chloride ion attack is controlled by steric factors which favor attack at the terminal carbon, and opposing electronic factors which favor attack at the more highly substituted carbon. Electron-withdrawing R groups destabilize the positive charge on sulfur and therefore increase the importance

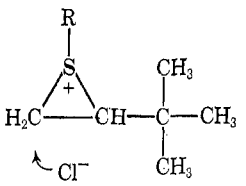
(17) W. H. Mueller and P. E. Butler, *J. Org. Chem.*, **32**, 2925 (1967).

of electronic factors, thus bringing about enhanced chloride attack at a more highly substituted internal carbon atom.

The powerful electron-withdrawing character of the 3-halo-1,2,4-thiadiazol-5-yl (R) group is attested by the large downfield shift of adjacent protons and the proximity of chemical shifts to those of analogous protons on chlorine-bearing carbons. Thus, a strong tendency toward Markovnikoff product formation would be expected and would explain the formation of single products from olefins such as isobutylene which are well suited for charge stabilization on carbon.

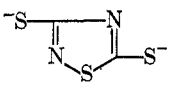


In contrast, the product from 3,3-dimethyl-1-butene has been assigned the anti-Markovnikoff orientation. Since unhindered terminal olefins which have a single alkyl group bonded to ethylene (*e.g.*, propylene) give similar quantities of isomeric adducts, it would be anticipated that more hindered analogs would enhance chloride attack at the terminal carbon. Indeed, the strong tendency to form anti-Markovnikoff products from 3,3-dimethyl-1-butene[10,17,18] is well documented even with sulfenyl chlorides containing strongly electron-withdrawing R groups.



The reaction of **2** with butadiene is noteworthy. To avoid multiple additions, the sulfenyl chloride was added to an excess of diene (18.5 mol diene/mol RSCl). Under these conditions, the product contained 29% isobutylene adduct in conjunction with the simple 1,2-addition product from butadiene ($RSCH_2CHClCH{=}CH_2$). Analysis of the butadiene reagent revealed 1.84% isobutylene impurity. The product composition corresponds to complete removal of the isobutylene from the butadiene. On this basis, the isobutylene is at the very least 21.8 times more reactive than butadiene. This number only represents a minimum value since isobutylene may have been consumed during the initial stages of reaction. It is significant, however, that even this minimal value for the relative reactivity indicates that **2** is a more selective reagent than methanesulfenyl chloride which shows a relative reactivity of 4.85[19] [k(isobutylene)/k(butadiene)]. The increased selectivity toward more nucleophilic double bonds is consistent with the greater electron-withdrawing power of the thiadiazole ring. The thiadiazolylsulfenyl chloride in comparison to methanesulfenyl chloride, should exhibit even more preference for *cis* olefins since it is even more important for the bulky substituents on sulfur to be oriented away from the ethylenic substituents in transition state for this first reaction step.[19] A similar tetravalent sulfur structure has been proposed as an actual intermediate rather than a contributing transition state structure in reactions involving cyclooctene.[20]

1,2,4-Thiadiazol-3,5-yl Bis(sulfenyl chloride) (11).—The dipotassium salt of 3,5-dimercapto-1,2,4-thiadiazole (perthiocyanic acid) and its salts have been obtained by a number of routes,[21] but the dianion **10** is most conveniently prepared by refluxing a methanol solution of **1** with sulfur. The salt is readily chlorinated to give the bis(sulfenyl chloride) **11** which is a stable yellow solid.



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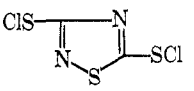

11

The bis(sulfenyl chloride) rapidly consumed 2 mols of an olefin giving fairly pure 1:2 adducts in high yield (Table II). With the exception of the ethylene adduct which was a solid, the products were all nondistillable liquids. Theoretically, the products from unsymmetrical olefins can be comprised of four different adducts (excluding geometrical isomers). Four different types of olefin incorporation could be verified with products giving relatively simple nmr spectra. The reaction of **11** with isobutylene showed four different methyl and methylene signals: two from Markovnikoff addition (in equal quantities) comprising 78% of the mixture (δ_{CH_3} 1.652, 1.672; δ_{CH_2} 3.730, 3.760), and two from anti-Markovnikoff addition (in equal quantities) comprising 22% of the mixture (δ_{CH_3} 1.715, 1.578; δ_{CH_2} 4.115, 3.870). The observed increase in anti-Markovnikoff product from the bis(sulfenyl chloride) **11** in contrast to the reaction of isobutylene with the monosulfenyl chloride (**2** or **7**) is consistent with the decrease in electron-withdrawing ability of R when the chlorine substituent is no longer bonded directly to the 1,2,4-thiadiazole ring.

Experimental Section

Infrared analyses were determined on Beckman IR-5 and IR-20 spectrophotometers. Gas chromatographic analyses were determined on an F & M Model 810 gas chromatograph using a 5 ft × 1/8 in. Dowfax column at 165°. Nuclear magnetic resonance spectra were obtained on Varian A-60 and HA-100 spectrometers. Extinction coefficients were determined on a Beckman DK-2 spectrophotometer. All melting points were taken upon a Fisher–Johns block and are uncorrected.

Dipotassium Cyanodithioimidocarbonate (1).—To a stirred solution of 100 g (2.38 mol) of cyanamide (Eastman) in 250 ml of absolute alcohol 199 g (2.62 mol) carbon disulfide was added. The mixture was maintained below 20° while a solution of 314 g of 85% potassium hydroxide in 600 ml of absolute alcohol was added over the period of 30 min. The mixture was stirred for an additional 45 min and then suction filtered, washed with tetrahydrofuran, and dried in a vacuum oven at 50° yielding 416 g (90%) of product, mp 225°.

3-Chloro-1,2,4-thiadiazol-5-yl Sulfenyl Chloride (2).—A slurry of 103 g (0.53 mol) of potassium cyanodithioimidocarbonate (1) in 750 ml of methylene chloride was cooled to −40° and 75.3 g (1.06 mol) of chlorine was slowly added to the stirred mixture. The reaction mixture was then stirred at 0° for 1 hr and suction

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filtered under dry nitrogen, and the methylene chloride evaporated under reduced pressure yielding 85 g (86%) of the yellow solid.

Anal. Calcd for $C_2S_2N_2Cl_2$: C, 12.84; N, 14.98; Cl, 37.90. Found: C, 12.86; N, 15.63; Cl, 37.69.

The uv spectrum in cyclohexane showed maximum at 261 mμ (log ε 3.78) and 225 (3.73). [The parent compound 1,2,4-thiadiazole has an absorption maximum at 229 mμ (log ε 3.7).] Infrared analysis (CCl_4) shows a five-peak pattern with maxima at 6.97, 8.20, 9.38, 10.91, and 14.3 μ.

Bis(3-chloro-1,2,4-thiadiazol-5-yl) Disulfide (3).—A solution of 9.35 g (0.05 mol) of **2** in 100 ml of dry tetrahydrofuran was stirred with 4.9 g (0.025 mol) Cu_2Cl_2 for 1 hr at room temperature, during which time the green cuprous chloride changed to the brown cupric chloride. The solid was filtered off, and the solution evaporated, redissolved in methylene chloride, and filtered again. Evaporation of the methylene chloride yielded 7.6 g (100%) of the disulfide product which was recrystallized from CH_2Cl_2–methanol giving 5.0 g of a pale yellow solid, mp 118–120°.

Anal. Calcd for $C_4N_4S_4Cl_2$: C, 15.84; N, 18.48; S, 42.30. Found: C, 15.47; N, 18.46; S, 41.90.

The infrared spectrum (CCl_4) was very similar to that of the corresponding sulfenyl chloride **2** showing five maxima at 6.97, 8.23, 9.46, 10.97, and 14.2 μ.

Bis(3-bromo-1,2,4-thiadiazol-5-yl) Disulfide (6).—A slurry of 9.7 g (0.05 mol) of **1** in 75 ml of CH_2Cl_2 was stirred at −40° while 16 g (0.1 mol) of Br_2 was added dropwise. The mixture was then stirred at 10° for an additional 2 hr, after which excess bromine and some solvent were removed at reduced pressure. The solid was filtered and the solvent was removed *in vacuo* yielding 8.5 g (87%) of a yellow solid product. The product (8.0 g) was recrystallized from CH_2Cl_2–*tert*-butylethylene to give 7.5 g of a white solid, mp 142–144.

Anal. Calcd for $C_4N_4S_4Br_2$: C, 12.25; N, 14.29; S, 32.71; Br, 40.76. Found: C, 12.62; N, 14.13; S, 32.67; Br, 40.90.

The infrared spectrum (CCl_4) was very similar to the analogous disulfide **3** with small shifts in the corresponding peaks. Absorptions were observed at 7.01, 8.39, 9.46, 11.21, and 15.0 μ.

3-Bromo-1,2,4-thiadiazol-5-yl Sulfenyl Chloride (7).—A solution of 8.0 g (0.020 mol) of **4** in 150 ml of CH_2Cl_2 was stirred at −40° while 1.5 g (0.020 mol) of Cl_2 was added slowly. The reaction mixture remained at ambient for 3 hr before the solvent was evaporated *in vacuo* yielding 9.5 g (100%) of product. Satisfactory elemental analysis could not be obtained on the crude product which analyzed correctly for nitrogen and chlorine but was approximately 1% high in carbon and bromine. Infrared analysis showed similar absorptions to that of the disulfide with peaks at 7.01, 8.29, and 8.37 (doublet), 9.37, 11.18, and 15.0 μ.

3-Bromo-3′-chloro-1,2,4-thiadiazol-5-yl Disulfide (8).—To a slurry of 9.7 g (0.05 mol) of **1** in 150 ml of CH_2Cl_2 stirred at −40°, a cold solution of bromine chloride was added slowly. The bromine chloride solution, prepared by combining 8.0 g (0.05 mol) of Br_2 and 3.6 g (0.05 mol) of Cl_2 at −45° and adding cold CH_2Cl_2 after 0.5 hr, was maintained below −45° during the course of the reaction. The mixture was then allowed to come to room temperature and filtered, and the solvent was removed *in vacuo* yielding 8.0 g (92%) of crude yellow solid which melted at 118–120° after one recrystallization (69%) from methylene chloride–methanol.

Anal. Calcd for $C_4N_4S_4BrCl$: C, 13.81; N, 16.14; S, 36.88; Cl, 10.19; Br, 22.98. Found: C, 13.99; N, 16.18; S, 37.22; Cl, 10.04; Br, 23.00.

Infrared analysis provided a spectrum which resembled the superimposed spectra of combined **3** and **4**. Absorption maxima were observed at 6.97, 7.01, 8.23, 8.39, 9.48, 10.97, 11.21, 14.7, and 15.0 μ.

General Procedure for Sulfenyl Chloride–Olefin Adducts.—In a typical experiment 18.7 g (0.1 mol) of sulfenyl chloride was dissolved in 200 ml of CH_2Cl_2, 0.1 g of $CaCO_3$ was added, and the mixture cooled to −50°. *trans*-Butene-2, 5.6 g (0.1 mol), was slowly condensed into the solution at a rate such that the solution temperature remained below −20°. Almost immediately after the addition was completed, the solution temperature began to drop and cooling was discontinued. The solvent was then removed at reduced pressure leaving 23 g (94%) of an oil. Distillation, 98–99° (0.1 mm), provided an 81% overall yield of pure product. Both the undistilled and distilled products were analyzed by vpc and nmr. The distilled products were subject to elemental analyses.

1,2,4-Thiadiazol-3,5-yl Bis(sulfenyl chloride) (11).—A solution of 19.4 g (0.1 mol) of dipotassium cyanodithioimidocarbonate in 500 ml of methanol was refluxed with 3.2 g (0.1 g-atom) of sulfur for 15 min. The dipotassium salt of 3,5-dimercapto-1,2,4-thiadiazole (**10**) (perthiocyanic acid) was isolated by evaporation of solvent at reduced pressure and the product (22.6 g) was dried under vacuum at 80°.

A slurry of 113 g (0.5 mol) of **10** in 900 ml of CH_2Cl_2 was cooled to −50° and stirred while 71 g (0.1 mol) of chlorine was added slowly. The mixture was then allowed to come to ambient temperature, the KCl filtered off (under N_2), and the solvent removed by means of a rotary evaporator, yielding 82 g (74% yield) of the yellow solid bis(sulfenyl chloride) **11**.

Anal. Calcd for $C_2N_2S_3Cl_2$: C, 10.96; N, 12.78. Found: C, 11.29; N, 12.87.

General Procedure for 1,2,4-Thiadiazol-3,5-yl Bis(sulfenyl chloride)–Olefin Adducts.—In a typical experiment, 8.2 g (0.0375 mol) of the bis(sulfenyl chloride) **11** was dissolved in 75 ml of CH_2Cl_2, cooled to −50°, and stirred while propylene in slight excess was added. The solution was then stripped of solvent on a rotary evaporator. Traces of residual volatiles were removed by means of a high vacuum pump, yielding 11.0 g (97% yield) of product.

Registry No.—**1**, 13145-41-0; **2**, 26542-76-7; **3**, 26542-77-8; **6**, 26542-78-9; **7**, 26542-79-0; **8**, 26542-80-3; **11**, 2254-82-2.

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