Methyl β-(2,2,3-trimethylcyclopropyl)acrylate (11) and 1-methoxycarbonyl-2,2-dimethyl-3-(1-propenyl)cyclopropane (12) were prepared from methyl *trans,trans*-sorbate (**10**) according to the procedures described above. The isomers were separated by glpc using a 20 ft × 0.25 in. column of 10% SE-30 at 160° (R_T of **10**, 7.8 min; **11**, 16.4 min; **12**, 11.8 min.

Methyl β-(2,2,3-trimethylcyclopropyl)acrylate (11): uv λ_{max} 242 nm; ir ν_{max} 1725 cm^{-1}; nmr δ 1.2 (9 H's, $C<^{CH_3}_{CH_3}$ and CH_3CH), 3.65 (s, $COOCH_3$), 5.85 (d, J = 15 Hz, $C{=}CH{-}COOCH_3$), 6.4 (m, $C{=}CHCH$); mass spectrum m/e 168 (M^+).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5. Found: C, 71.4; H, 9.7.

1-Methoxycarbonyl-2,2-dimethyl-3-(1-propenyl)cyclopropane (12): uv λ_{max} 200–210 nm; ir ν_{max} 1725 cm^{-1}; nmr δ 1.2 (6 H's, $C<^{CH_3}_{CH_3}$), 1.7 (d, J = 5 Hz, $CH_3CH{=}C$), 1.41 (d, J = 5 Hz, cyclopropane CH), 1.9 (m, cyclopropane CH), 3.65 (s, $COOCH_3$), 4.7 ($CH_3CH{=}CH$), 5.35 (m, $CH_3CH{=}CH$); mass spectrum m/e 168 (M^+).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5. Found: C, 71.6; H, 9.4.

n-Propyldiphenylsulfonium Triflate (13b) and n-Butyldiphenylsulfonium Triflate (13c).—To a solution of 3 g (10.6 mmol) of trifluoromethanesulfonic anhydride[12] was added 10.6 mmol of the *n*-alkyl alcohol and 1.1 g (11 mmol) of triethylamine in 10 ml of CH_2Cl_2 at 0°. The mixture was stirred for 1 hr at 0°, the CH_2Cl_2 was evaporated, and the residue was chromatographed on silica eluting with *n*-pentane to give a 16% yield of the *n*-alkyl triflate.

***n*-Propyl triflate (13b)**: nmr δ 1.1 (t, CH_3CH_2), 1.83 (m, CH_3CH_2), 4.5 (t, $CH_2CH_2OSO_2CF_3$).

***n*-Butyl triflate (13c)**: nmr δ 1.0 (br d, CH_3CH_2), 1.65 (m, $CH_3CH_2CH_2CH_2$), 4.5 (t, $CH_2CH_2OSO_2CF_3$).

To a solution of 1.5 mmol of *n*-alkyl triffate was added a tenfold excess of diphenyl sulfide at −35°. With stirring, the mixture was allowed to rise to room temperature, remained at room temperature for 24 hr, and was heated to 45° for 0.5 hr. The oil that was formed was separated, washed with CCl_4, and dried *in vacuo* to give ~10% yields of sulfonium triflates **13b** and **13c**.

***n*-Propyldiphenylsulfonium triflate (13b)**: nmr (DMSO-d_6) δ 1.09 (t, CH_2CH_3), 1.85 (m, CH_2CH_3), 4.4 (t, $<S^+{-}CH_2CH_2$), 7.8 (m, Ar H's).

***n*-Butyldiphenylsulfonium triflate (13c)**: nmr (DMSO-d_6) δ 1.0 (br d, CH_2CH_3), 1.7 (m, $CH_2CH_2CH_2CH_3$), 4.4 (br t, $>S^+{-}CH_2CH_2$), 7.9 (Ar H's).

Registry No.—**2d**, 16601-43-7; **7**, 3725-40-4; **8**, 40464-16-2; **9**, 40464-17-3; **10**, 689-89-4; **11**, 40447-54-9; **12**, 40447-55-0; **13b** triflate, 40447-56-1; **13c** triflate, 40447-57-2; isopropyldiphenylsulfonium tetrafluoroborate, 40447-58-3; trifluoromethylsulfonic anhydride, 358-23-6.

Chemistry of the Sulfur–Nitrogen Bond. VI.[1] A Convenient One-Step Synthesis of Sulfenimines (*S*-Aryl Thiooximes)[2]

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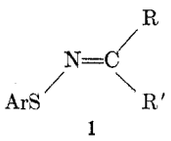
The scope and limitations of a convenient one-step synthesis of sulfenimines (*S*-aryl thiooximes) from aromatic disulfides, silver nitrate, ammonia, and aldehydes or ketones is described. The procedure fails with aliphatic disulfides and diaryl ketones. The structure, properties, and mechanism of formation of sulfenimines are discussed.

The carbon–nitrogen double bond in imines ($RN{=}CR_2$) has been extensively studied[4] and is an important intermediate in organic syntheses and biological transformations. The mechanism of syn–anti isomerization or stereomutation at the C–N double bond has been the subject of considerable interest.[2,5]

Compounds that contain the sulfur–nitrogen bond are important both from practical as well as theoretical points of view. They have found applications in synthesis, as pesticides, and as accelerators in the vulcanization of rubber. Knowledge of the various types of interactions possible between adjacent sulfur and nitrogen are essential to understanding lone-pair interactions, bond polarization effects, and p–d π bonding.[6]

A study of sulfenimines (*S*-aryl thiooximes) **1**, which



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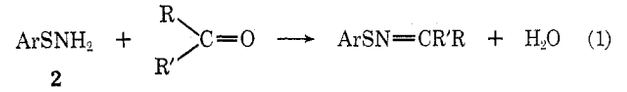
contains both the imine and sulfur–nitrogen functional groups, is therefore of considerable interest. Although a few sulfenimines have been known for some time, their chemistry is relatively unexplored. Undoubtedly this is due to the lack of a convenient synthetic route to these compounds.

The method generally used for the preparation of sulfenimines is condensation of a sulfenamide, **2**, with



$$\underset{\mathbf{2}}{ArSNH_2} + \begin{matrix} R \\ \diagdown \\ \quad C{=}O \\ \diagup \\ R' \end{matrix} \longrightarrow ArSN{=}CR'R + H_2O \quad (1)$$

R′ = alkyl, aryl, H

an aldehyde or ketone (eq 1).[7–11] Quinoline sulfenimines have been prepared by oxidation of the cor-

(1) Part V: F. A. Davis, C. J. Horner, E. R. Fretz, and J. F. Stackhouse, *J. Org. Chem.*, **38**, 695 (1973).

(2) For a preliminary communication see F. A. Davis, W. A. R. Slegeir, and J. M. Kaminski, *Chem. Commun.*, 634 (1972).

(3) Undergraduate Research Participant.

(4) (a) P. Y. Sollenberger and R. B. Martin in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 7; (b) S. Patai, Ed., "The Chemistry of the Carbon–Nitrogen Bond," Interscience Publishers, New York, N. Y., 1970; (c) R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).

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(6) For a recent review see F. A. Davis, *Int. J. Sulfur Chem., B*, in press.

(7) T. Zincke and J. Baeumer, *Justus Liebigs Ann. Chem.*, **416**, 86 (1918).

(8) N. V. Khromov-Broisoc and M. B. Kolesova, *J. Gen. Chem. USSR*, **25**, 361 (1955).

(9) J. A. Barltrop and K. J. Morgan, *J. Chem. Soc.*, 3072 (1957).

(10) J. J. D'Amico, *J. Org. Chem.*, **26**, 3436 (1961).

(11) D. Kaminsky, J. Shavel, Jr., and R. I. Meltzer, *Tetrahedron Lett.*, 859 (1967).

TABLE I

SULFENIMINES PREPARED FROM BIS(3-NITROPHENYL) DISULFIDE AND ALDEHYDES AND KETONES IN METHANOL

Entry	Sulfenimine[a]	Aldehyde or ketone	Yield, %	E/Z ratio[b]	Mp or bp, °C (mm)	Nmr[c]
1	3	Acetaldehyde	97	56:44	63	2.1 (q, 3, J = 5 Hz), 7.6 (m, 3), 8.4 (m, 2)
2	4	Isobutyraldehyde	60	97:3	160 (0.1)	1.2 (d, 5.8), 1.4 (d, 2), 2.7 (m, 1), 7.3–8.3 (m, 5)
3	5	Benzaldehyde	64		94–95	7.7 (m, 7), 8.6 (m, 2), 8.8 (s, 1, CH=)
4	6	4-Nitrobenzaldehyde	94		187	7.6–8.5 (m, 8), 8.9 (s, 1, CH=)
5	7	4-Methoxybenzaldehyde	87		114	4.0 (s, 3, OCH_3), 7.0–8.2 (m, 8), 8.7 (s, 1, CH=)[d]
6	8	Furfural	88		109	6.5–8.6 (m, 8)
7	9	Acetone	92		50–51	2.2 (d, 6), 7.8–8.6 (m, 3), 8.9 (m, 1)
8	10	2-Butanone	60	73:27	139 (0.7)	1.2 (t, 2.2, CH_3), 1.5 (t, 0.8, CH_3), 2.1 (s, 2.2, CH_3), 2.2 (s, 0.8), 2.4 (q, 2), 7.4–8.1 (m, 3), 8.5 (m, 1)
9	11	Methyl *tert*-butyl ketone	30		138 (0.45)	1.2 (s, 9), 2.1 (s, 3), 7.3–8.1 (m, 3), 8.4 (m, 1)
10	12	Acetophenone	60		58–60	2.5 (s, CH_3), 7.3–8.7 (m, 9)
11	13	Cyclohexanone	61		143–144	1.7(br s, 6), 2.4 (br s , 4), 7.2–8.0 (m, 3), 8.4 (m, 1)
12		Benzophenone	*e*			
13		Camphor	*e*			
14		Acetylacetone	Polymer			
15		Crotonaldehyde	Polymer			

[a] Satisfactory elemental analyses, ±0.3%, were obtained for all new compounds unless otherwise noted. [b] Measured from the nmr spectra. [c] Solvent $CDCl_3$ unless otherwise noted. [d] DMSO solvent. [e] No reaction.

responding sulfenamides[12] and by reaction of aromatic thiols with *N*-chloro-*p*-quinone imine.[13] Only a relatively few sulfenimines have been reported, since there is difficulty in preparing the necessary precursors.

In this paper we wish to report on the scope and limitations of a convenient one-step synthesis of sulfenimines. In addition, their structure and properties, as well as the probable mechanism of formation, will be discussed.

Synthesis.—Sulfenimines, **1**, are prepared in one step from aryl disulfides, silver nitrate, ammonia, and aldehydes or ketones (eq 2). One equivalent each of di-

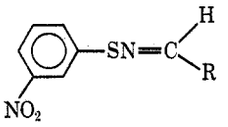
$$(ArS)_2 + AgNO_3 + \begin{matrix} R' \\ \diagdown \\ \quad C{=}O \\ \diagup \\ R \end{matrix} \xrightarrow{NH_3} \underset{\mathbf{1}}{ArSN{=}CR'R} + AgSR + NH_4NO_3 + H_2O \quad (2)$$

sulfide and silver nitrate are dissolved in methanol; ammonia is passed through the solution and an excess of the aldehyde or ketone is added. After stirring for 12 hr the precipitated silver mercaptide is removed by filtration to give the sulfenimine.

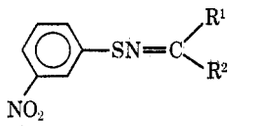
Occasional difficulty was encountered in separating the sulfenimine from imine polymers that were always formed. The imine polymers result from the reaction of ammonia with aldehydes and ketones to give unstable imines which polymerize.[14] In the majority of cases the sulfenimine was separated from these polymers by extraction into ether, washing with water, and distillation.

This synthetic procedure (eq 2) works well with aldehydes (compounds **3–8**), less well with ketones (compounds **9–13**), and fails with diaryl ketones. Sterically hindered ketones such as methyl *tert*-butyl ketone gave only 30% yield of the sulfenimine **11**, and camphor failed. These results are summarized in Table I.

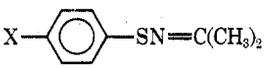
This procedure also works well with a variety of substituted aromatic disulfides. Sulfenimines **14–21** were



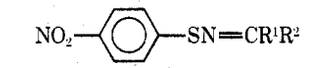
3, R = CH_3
4, R = $CH(CH_3)_2$
5, R = C_6H_5
6, R = 4-$NO_2C_6H_4$
7, R = 4 $CH_3OC_6H_4$
8, R = 2-C_4H_3O



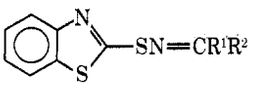
9, $R^1 = R^2 = CH_3$
10, $R^1 = CH_3$; $R^2 = C_2H_5$
11, $R^1 = CH_3$; $R^2 = C(CH_3)_3$
12, $R^1 = CH_3$; $R^2 = C_6H_5$
13, R^1, $R^2 = C_5H_{10}$



14, X = H
15, X = Cl
16, X = Br
17, X = NO_2



18, R^1, $R^2 = C_5H_{10}$
19, R^1 = H; R^2 = 4-$(CH_3)_2NC_6H_4$



20, $R^1 = R^2 = CH_3$
21, R^1 = H; $R^2 = C_6H_5$
22, R^1, $R^2 = C_5H_{10}$

prepared using this method (Table II). Not only is this procedure more convenient than those previously reported, but the yields, in many cases, are also higher (entries 4–6, Table II).

This synthetic procedure may also be used to prepare benzisothiazoles from the corresponding disulfide. For example, 2-acetyl-4-methylphenyl disulfide (**23**)[15] gave a greater than 30% yield of 3,5-dimethylbenzisothiazole (**24**).

All attempts to prepare *S*-alkyl thiooximines by this

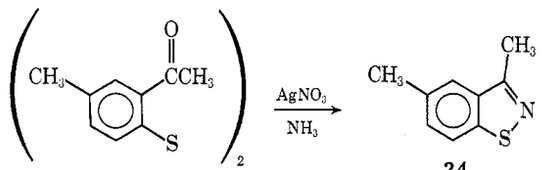
(12) E. Gebauer-Felnegg and H. A. Beatty, *J. Amer. Chem. Soc.*, **49**, 1361 (1927).
(13) D. N. Kramer and R. M. Gamson, *J. Org. Chem.*, **24**, 1154 (1959).
(14) R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 1822 (1961).
(15) D. Walker and J. Leib, *J. Org. Chem.*, **28**, 3077 (1963).

TABLE II

SULFENIMINE FROM AROMATIC DISULFIDE AND ALDEHYDES AND KETONES

Entry	Sulfenimine	Disulfide	Ketone or aldehyde	Yield, %	Mp or bp, °C (mm)	Nmr (CDCl3)
1	14	Phenyldisulfide	Acetone	60	66 (0.5)	2.0 (d, 6), 7.0–7.5 (m, 5)
2	15	4-Chlorophenyl disulfide	Acetone	65	39–40	2.1 (d, 6), 7.4 (m, 4)
3	16	4-Bromophenyl disulfide	Acetone	60	48–49	2.1 (d, 6), 7.4–7.9 (m, 4)
4	17	Bis(4-nitrophenyl) disulfide	Acetone	94 (75)[a]		2.1 (d, 6), 7.5–8.3 (ab q, 4)
5	18	Bis(4-nitrophenyl) disulfide	Cyclohexanone	98 (90)[b]		1.8 (br s, 6), 2.5 (br s, 4), 8.0 (ab q, 4)
6	19	Bis(4-nitrophenyl) disulfide	4-*N*,*N*-Dimethylaminobenzaldehyde	55 (51)[a]		3.0 (s, 6, CH_3), 6.6 (d, 2, J = 9 Hz), 7.5 (d, 4, J = 9 Hz), 8.1 (d, 2, J = 9 Hz), 8.5 (s, 1, CH=)
7	20	2-Benzothiazolyl disulfide	Acetone	49 (89)[c]		2.3 (d, 6), 7.4–7.9 (m, 4)
8	21	2-Benzothiazolyl disulfide	Cyclohexanone	Polymer (72)[c]		1.7 (br s, 6), 2.4 (m, 4), 7.25 (m, 2), 7.8 (m, 2)
9	22	2-Benzothiazolyl disulfide	Benzaldehyde	60 (69)[c]		8.2–8.0 (m, 9), 8.6 (s, 1, CH=)
10	24	2-Acetyl-4-methyl phenyl disulfide		30	50–55 (0.7)	2.5 (s, 3, imine CH_3), 2.7 (s, 3), 7.0–8.0 (m, 3)
11		Ethyl disulfide	Acetone	*d*		
12		Benzyl disulfide	Acetone	*d*, *e*		

[a] Reference 8. [b] Reference 11. [c] Reference 10. [d] No reaction. [e] Less than 1% of the sulfenimine may have formed as indicated by nmr.



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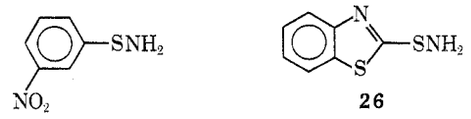
method failed. Starting material was recovered from both ethyl and benzyl disulfide (Table II, entries 11 and 12).

The crotonaldehyde and acetylacetone 3-nitrobenzenesulfenimines as well as the cyclohexanone 2-benzothiazolesulfenimines (**18**) could not be prepared using this method (eq 2). In these examples the sulfenimine could not be separated from the imine polymers.

An alternate procedure, which avoids the presence of excess ammonia, is to condense the sulfenamide **2** with aldehydes and ketones (eq 1).[7-10] The major difficulty of using this method involves the preparation of the required sulfenamides (**2**). Our recent report of the synthesis of sulfenamides from aryl disulfides, silver nitrate, and amines[16] is applicable to the synthesis of the required sulfenamides (**2**). Sulfenamides **25** and **26** were prepared using this method in 72 and 90% yields, respectively.



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Using procedure 1, ammonium chloride as a catalyst, and 3-nitrobenzenesulfenamide (**25**), the crotonaldehyde sulfenimine **27** was prepared in good yield.

Sulfenamide **25** with acetylacetone, however, gave **28**. Sulfenamides are well known to react with compounds containing activated methylene groups to give the mono- and disulfenylated products[6,17] (Table III). D'Amico has reported similar products in the base-catalyzed reaction of **26** with acetylacetone.[10]

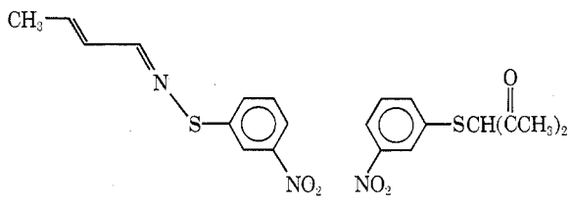

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TABLE III

SULFENIMINES PREPARED FROM SULFENAMIDES IN ETHANOL

Entry	Sulfenamide	Ketone or aldehyde	Catalyst[a]	Products[b] (yield, %)
1	**25**	Acetone		**9** (13), **25** (87)
2		Acetone	NH_4NO_3	**9** (25)
3		Acetone	NH_4Cl	**9** (96)
4		Acetone	NaCl	**9** (17), **25** (83)
5		Acetone	$NaNO_3$	**9** (15), **25** (85)
6		Acetone	HCl[c]	**9** (95)
7		Acetone	KOH[d]	**25** (86)
8		Crotonaldehyde	NH_4Cl	**27** (60)
9		Acetylacetone	NH_4Cl	**28** (63)
10		Acetophenone	NH_4Cl	**12** (46), **25** (54)
11	**26**	Acetone	NH_4Cl	**20** (83)
12		Cyclohexanone	NH_4Cl	Polymer
13		Cyclohexanone	KOH[d]	**20** (80)

[a] 0.019 mol of catalyst added unless otherwise noted. [b] Determined by isolation and nmr. [c] 3 drops of 10% HCl added. [d] 0.0007 mol of potassium hydroxide added.

(16) M. D. Bentley, I. B. Douglass, J. A. Lacadie, D. C. Weaver, F. A. Davis, and S. J. Eitelman, *Chem. Commun.*, 1625 (1971).

(17) T. Kumamoto, S. Kobayashi, and Y. Mukaiyama, *Bull. Chem. Soc. Jap.*, **45**, 866 (1972).

Similar yields of sulfenimines were obtained using either procedure 1 or 2 (compare entries 7 and 10, Table I, with entries 2 and 10, Table III). The exception was with 2-benzothiazolyl disulfide. Using procedure 1, 2-benzothiazolyl disulfide with acetone gave a 49% yield of **20** and with cyclohexanone polymer was isolated (entries 7 and 8, Table II). Sulfenamide **26** with ammonium chloride and acetone gave an 83% yield of **20**, but with cyclohexanone polymer was still the only product isolated (entries 11 and 12, Table III). A good yield of **21** was obtained using a basic catalyst as previously reported by D'Amico.[10]

Properties and Structure of Sulfenimines.—The majority of sulfenimines were considerably more resistant to hydrolysis than the corresponding imines. They could be stored at 10–20° almost indefinately with little decomposition. Aqueous acid gave the disulfide, ammonia, and the aldehyde or ketone.

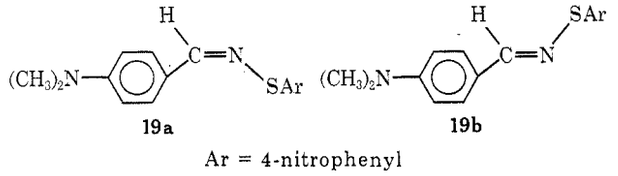
Satisfactory elemental analyses were not obtained for sulfenimines **4**, **10**, and **11** despite repeated crystallization and purification by preparative gas chromatography. On standing at room temperature for several days the odor of ammonia was detected. The mass spectra, however, were consistent with the proposed structures. Gas chromatographic analysis indicated the presence of bis(3-nitrophenyl) disulfide. All these sulfenimines contain bulky groups, which may contribute to their instability.

Structural proofs of **3**–**22**, **24**, and **27** were based on elemental analysis, infrared and nmr spectra and in some cases mass spectra. The infrared spectra of **3**–**22** and **27** showed weak to medium absorption at 1600–1620 cm^{-1}. We attribute this absorption to C=N stretching, since absorption in this area was absent in the corresponding disulfides. Benzisothiazole, **24**, showed weak absorption at 1610 cm^{-1} and absorption in the ultraviolet (ethanol) at λ_{max} 233 nm (ϵ 15,200) and 312 (3300).

The proton nmr spectra of **3**–**22**, **24**, and **27** were also in agreement with the proposed structures. The R and R′ groups in **1** are diastereotopic and occupy magnetically nonequivalent sites. If the barriers to syn–anti isomerization or stereomutation are sufficiently high a separate signal in the nmr will be observed for R and R′ at ambient temperatures when R = R′.

The barriers to stereomutation in diaryl and dialkyl ketone sulfenimines have been reported to be 18.5[18] and 20.1[2] kcal/mol. The two methyl groups in the nmr spectra of sulfenimines **9**, **14**–**17**, and **20**, therefore, appear as doublets separated by about 9 Hz.

Unsymmetrical sulfenimines like oximes are capable of forming geometric isomers. Two isomers, **19a**,



19a **19b**

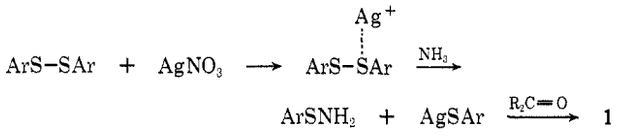
Ar = 4-nitrophenyl

and **19b**, were reported isolated in the preparation of **19**.[8] The unstable isomer, presumably **19a**, was converted on heating to the more stable isomer **19b**. Using procedure 2 for the synthesis of **19**, however, gave only one isomer, presumably **19b**.

The presence of two isomers was detected by nmr for several of the unsymmetrical sulfenimines. The methyl group in the nmr spectrum of sulfenimine **3** appears as two doublets almost equally populated. Assuming that the *E* isomer[19] is the more stable and therefore more abundant, then the *E*:*Z* ratio is 56:44. As one of the groups in the sulfenimine became large only one isomer was detected (Table I).

Mechanism of Formation.—The mechanism of formation of sulfenimines by procedure 2 most likely involves formation of the sulfenamide **2**. Silver ion complexes with one of the lone pairs of electrons in the disulfide bond followed by nucleophilic attack by ammonia on the activated disulfide bond. The resulting sulfenamide condenses with the aldehyde or ketone, giving the sulfenimine (Scheme I).

SCHEME I



Cooperative assistance to nucleophilic displacement by an electrophile at the disulfide bond has been discussed by Kice,[20] and silver ion is well known to form complexes with disulfides.[21] Thiosulfonate esters[22] and sulfenamides[16] have been prepared under similar conditions.

Additional evidence for the proposed scheme is the isolation of sulfenamide **25** in good yield when bis(3-nitrophenyl) disulfide is treated according to procedure 2 without adding the aldehyde or ketone. Sulfenamide **25** condenses separately with acetone in the presence of ammonium nitrate to give a high yield of sulfenimine **9** (Table III). Ammonium nitrate is a by-product in the sulfenimine synthesis (eq 2). The inability to prepare sulfenimines from ethyl and benzyl disulfides probably results from the known instability of alkyl sulfenamides.[6,16]

The condensation of sulfenamides with aldehydes and ketones is acid catalyzed. Ammonium salts and aqueous hydrochloric acid with sulfenamide **25** and acetone gave greater than 96% yield of the sulfenamide **9**. In the absence of these catalysts only 13–15% yield of the sulfenamide was isolated. Basic catalysts such as potassium hydroxide have been used in the preparation of 2-benzothiazole sulfenimines from **26**.[9,10] With sulfenamide **2** base catalyst failed to give any sulfenimine (entry 7, Table III).

Two additional mechanism must also be considered. Ammonia reacts with aldehydes and ketones to give unstable imines.[14] The sulfenamide **2** may condense with this unstable imine to give the sulfenimine. For example, *N*-benzylidenemethylamine reacts quantitatively with **25** to give **5**. A second possibility is that

(18) C. Brown, G. T. Grayson, and R. F. Hudson, *Tetrahedron Lett.*, 4925 (1970).

(19) J. E. Blackwood, C. L. Gladys, K. L. Leoning, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

(20) J. L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968).

(21) R. Cecil and J. R. McPhee, *Biochem. J.*, **66**, 538 (1957).

(22) M. D. Bentley, I. B. Douglass, and J. A. Lacadie, *J. Org. Chem.*, **37**, 333 (1972).

the unstable imine attacks the silver disulfide complex to give the sulfenimine. However, attempts to form a sulfenimine by addition of phenylethylketimine[23] to a silver nitrate disulfide solution failed.

Experimental Section

Disulfides were prepared and purified according to literature procedures. Melting points were obtained on a Fisher-Johns apparatus. Proton nmr spectra were measured on a Varian A-60A instrument. Infrared spectra were measured on a Perkin-Elmer 457 spectrometer. Mass spectra were obtained on a Hitachi RMU-6 instrument. Gas chromatographic analyses were performed on a Perkin-Elmer 900 gas chromatograph using a 3% OV-17 on 80/100 Chromosorb W (regular) column.

General Procedure for the Synthesis of Sulfenimines (Procedure 2).—In a 100-ml, three-necked flask equipped with mechanical stirrer and ammonia inlet was dissolved 4.5 g (0.027 mol) of silver nitrate in 300 ml of methanol. The solution was cooled in an ice bath, an equivalent amount of disulfide was added, and ammonia was passed through the solution for about 15 min. The aldehyde or ketone was added in excess (usually 5 equiv) and the reaction was allowed to stir overnight at room temperature. The precipitated silver mercaptide was removed by filtration; solvent was removed to give a residue which was redissolved in ether and filtered. The ether solution was washed (4 × 100 ml) with water and dried over $MgSO_4$. Removal of the solvent gave the sulfenimine. At this point it was occasionally necessary to distill off the imine polymer. The sulfenimine was either distilled or crystallized from ether–pentane or ethanol.

3,5-Dimethylbenzisothiazole (24).—In a 100-ml, three-necked flask equipped with magnetic stir bar and ammonia inlet was dissolved 0.24 g (0.0017 mol) of silver nitrate and 0.5 g (0.0017 mol) of 2-acetyl-4-methylphenyl disulfide[15] in 35 ml of methanol. The solution was warmed to about 50° for 5 min and allowed to cool to room temperature. Ammonia was passed through the solution for 4 min, and the reaction mixture was stirred overnight. The precipitated silver mercaptide was removed by filtration, solvent was removed under vacuum (water pump), and the resulting residue was dissolved in ether. The ether solution was washed with water (3 × 50 ml) and dried over $MgSO_4$. Removal of the ether solvent gave an oil which was distilled, bp 50–55° (0.7 mm), to give 0.08 g (30%) of a pale yellow oil which solidified on cooling below ambient temperature: ir (thin film) 1610 cm^{-1} (w, C=N); uv (absolute ethanol) λ_{max} 233 nm (ϵ 15,500) and 312 (3300); nmr see Table II.

Anal. Calcd for C_9H_9NS: C, 66.20; H, 5.52. Found: C, 66.37; H, 5.63.

3-Nitrobenzenesulfenamide (15).—Sulfenamide **25** was prepared as described above (procedure 2), omitting the addition of aldehyde or ketone, from 2.8 g (0.0162 mol) of silver nitrate and 5.0 g (0.0162 mol) of bis(3-nitrophenyl) disulfide in 250 ml of methanol. After the dried ether solvent was removed the resulting residue was crystallized from ethanol to give 2.0 g (72%) of orange-yellow needles: mp 60–61°; ir (KBr) 3280 and 3380 cm^{-1} (m, NH_2); nmr ($CDCl_3$) δ 2.8 (br s, 2, NH_2) and 7.3–8.3 (m, 4).

Anal. Calcd for $C_6H_6N_2O_2S$: C, 42.35; H, 3.53. Found: C, 42.45; H, 3.75.

(23) C. Mourear and G. Mignonac, *C. R. Acad. Sci.*, **156**, 1801 (1913).

2-Benzothiazolesulfenamide (26).—Sulfenamide **26** was prepared as described above from 5.0 g (0.015 mol) of 2-benzothiazalyl disulfide and 2.6 g (0.015 mol) of silver nitrate. Crystallization from chloroform gave 2.5 g (90%) of white crystals: mp 123° (lit.[9] mp 122–124°); ir (KBr) 3160 and 3320 cm^{-1} (s, NH_2); nmr ($CDCl_3$) δ 3.3 (br s, 2, NH_2), 7.3 (m, 2), and 7.8 (m, 2).

General Procedure for the Synthesis of Sulfenimines from Sulfenamides (Procedure 1).—In a 500-ml round-bottom flask equipped with magnetic stir bar was placed the appropriate sulfenamide (0.006 mol) and the appropriate catalyst in 250 ml of absolute ethanol. A 5 *M* excess of the aldehyde or ketone was added, and the reaction mixture was stirred overnight. The solvent was removed under vacuum to give a residue which was dissolved in ether. The ether solution was washed with water (3 × 50 ml), dried over $MgSO_4$, and removed to give the sulfenimine.

Crotonaldehyde-3-nitrobenzenesulfenimine (27).—Sulfenimine **27** was prepared as described above (procedure 1) from sulfenamide **25** and crotonaldehyde to give a clear yellow oil which was chromatographed on Florisil (elution with 20:80 ether–pentane). The resulting yellow solid was crystallized from pentane to give 0.67 g (50%) of yellow needles: mp 45–46°; ir (KBr) 1640 (w), 1525, and 1350 cm^{-1} (s, NO_2); nmr ($CDCl_3$) δ 2.0 (m, 3, CH_3), 6.3 (m, 2), and 7.2–8.4 (m, 5).

Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.05; H, 4.50. Found: C, 53.77; H, 4.30.

3-(3-Nitrophenylthio)-2,4-pentandione (28).—Sulfenamide **25** and acetylacetone were allowed to react as described above (procedure 1). The residue remaining after the ether solvent was removed was sublimed at 120° (0.25 mm) and crystallized from ether–pentane to give 1.0 g (64%) of cream-colored needles: mp 72–73°; ir (KBr) 1700–1600 cm^{-1} (br, C=O); nmr ($CDCl_3$) δ 2.4 (s, 7, CH_3 and SCH) and 7.2–8.0 (m, 4).

Anal. Calcd for $C_{11}H_{11}NO_4S$: C, 52.17; H, 4.35. Found: C, 52.05; H, 4.28.

Reaction of 3-Nitrobenzenesulfenamide (25) and *N*-Benzylidenemethylamine.—In a 250-ml round-bottom flask equipped with stir bar was placed 1.0 g (0.006 mol) of sulfenamide **25** and 0.7 g (0.006 mol) of *N*-benzylidenemethylamine (Aldrich) in 100 ml of methanol. After stirring overnight the solvent was removed to give 1.5 g (100%) of a yellow solid identified as sulfenimine **5** by comparison of its infrared and nmr spectra with those of an authentic sample.

Registry No.—**3**, 40576-71-4; **4**, 40576-72-5; **5**, 40576-73-6; **6**, 40576-74-7; **7**, 40576-75-8; **8**, 40576-76-9; **9**, 38205-95-7; **10**, 40576-78-1; **11**, 40576-79-2; **12**, 40576-80-5; **13**, 40576-81-6; **14**, 38206-14-3; **15**, 38205-93-5; **16**, 38205-94-6; **17**, 38205-96-8; **18**, 14006-46-3; **19**, 40576-87-2; **20**, 40576-88-3; **21**, 40576-89-4; **22**, 40576-90-7; **23**, 40576-91-8; **24**, 40576-92-9; **25**, 40576-93-0; **26**, 2801-21-0; **27**, 40576-95-2; **28**, 40576-96-3; bis(3-nitrophenyl) disulfide, 537-91-7; acetaldehyde, 75-07-0; isobutyraldehyde, 78-84-2; benzaldehyde, 100-52-7; 4-nitrobenzaldehyde, 555-16-8; 4-methoxybenzaldehyde, 123-11-5; furfural, 98-01-1; acetone, 67-64-1; 2-butanone, 78-93-3; methyl *tert*-butyl ketone, 75-97-8; acetophenone, 98-86-2; cyclohexanone, 108-94-1; phenyl disulfide, 882-33-7; 4-chlorophenyl disulfide, 1142-19-4; 4-bromophenyl disulfide, 5335-84-2; bis(4-nitrophenyl) disulfide, 100-32-3; 2-benzothiazolyl disulfide, 120-78-5; 4-*N*,*N*-dimethylaminobenzaldehyde, 100-10-7; crotonaldehyde, 4170-30-3; acetylacetone, 123-54-6; *N*-benzylidenemethylamine, 622-29-7.