Chemical Reviews

Volume 89, Number 4 June 1989

The Chemistry of Sulfenamides

LESLIE CRAINE

Department of Chemistry, Trinity College, Hartford, Connecticut 06106

MORTON RABAN*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

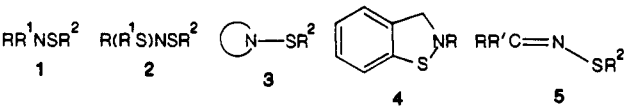
Received September 25, 1987 (Revised Manuscript Received December 5, 1988)

Contents

I. Introduction

Sulfenamides are compounds containing trivalent nitrogen bonded to divalent sulfur. They are derived formally from sulfenic acids, RSOH, just as sulfinamides are derived from sulfinic acids, RSO_2H, and sulfonamides are derived from sulfonic acids, RSO_3H. They have been of interest to the chemical community over the years because of their industrial applications, their utility as synthetic reagents, and their interesting stereochemical properties.

Sulfenamides and their derivatives exist in a variety of structures. The nomenclature for these compounds is not thoroughly systematized. Compounds of type 1–3

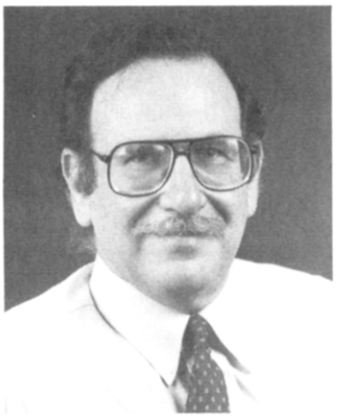


1 2 3 4 5

are referred to in *Chemical Abstracts* as sulfenamides. These compounds have also been termed thiohydroxylamines, although this nomenclature is less common. In sulfenamides of type 1, R and R^1 can be H, alkyl, aryl, acyl, or X, where X is a heteroatom, and R^2 can be alkyl, aryl, acyl, or X. Cyclic sulfenamides 3, where nitrogen is part of an aliphatic or aromatic ring, are also known. Sulfenamides in which R^2 is a halide are classified as sulfenyl halides. Sulfenamides of type 1 in which R^2 is OR or NR_2 can be considered as *S*-amino derivatives of sulfenate esters and sulfenamides, respectively. Sulfenamides in which R^2 is NR_2, SNR_2,

0009-2665/89/0789-0689$06.50/0

Leslie H. Craine was born in Bellefonte, PA, in 1943. In 1986, she received her Ph.D. in organic chemistry from Wayne State University, where she investigated the synthesis and torsional barriers of sulfenamides of heterocyclic amines under the direction of Professor Morton Raban. After a brief postdoctoral stint at the Michigan Cancer Foundation, she joined the faculty at Trinity College (Hartford, CT) in 1987 as Assistant Professor of Chemistry. Her current research interests include the synthesis of novel ionophores and examination of their properties.



Morton Raban was born in St. Louis, MO, in 1940. He received his B.A. degree from Harvard College in 1962. He carried out his graduate work under the direction of Professor Kurt Mislow at Princeton University and received his Ph.D. degree in 1967. Following a year on the faculty at Princeton, he joined the Department of Chemistry at Wayne State University, where he is now Professor of Chemistry. His research interests include the stereochemistry of organosulfur compounds and of novel ionophores.

or $SSNR_2$ have been termed bisamine sulfides, bisamine disulfides, and bisamine trisulfides, respectively.

Compounds of type **2** are called disulfenamides, bis(arylsulfen)imides, *N,N*-disulfenylamines, and occasionally *N*-(alkyl- or arylthio)sulfenamides. In this review the term disulfenylamines will be used.

A number of sulfenamides are known as derivatives of other classes of compounds. In compounds **1**, where R and R^1 are both acyl as well as **3** where the ring bears two acyl groups attached to nitrogen, the compounds are *N*-(alkylthio)imides or *N*-(arylthio)imides. Thus the sulfenamides of phthalimide and succinimide are *N*-thiophthalimides and *N*-thiosuccinimides. Cyclic sulfenamides of type **4** are correctly named as benzisothiazole derivatives.

Finally, compounds of type **5** are most commonly referred to as sulfenimines. They can also be considered *N*-alkylidenesulfenamides. They have incorrectly been referred to as thiooximes. A more accurate term for the known compounds of this type would be thiooxime

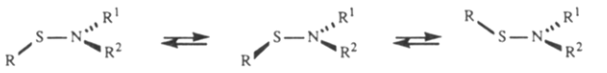


Figure 1. Axial chirality in sulfenamides.

ethers. The parent thiooximes (R^2 = H) are not very stable and are seldom isolated. In this review, the term sulfenylimine will be used.

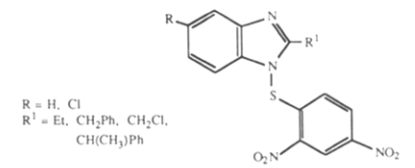
The literature contains a number of reviews on sulfenic acid chemistry, the synthesis and reactions of sulfenamide derivatives,[1-5] the stereochemistry,[6-8] and the industrial applications[1,9-11] of sulfenamides. This review focuses on the properties, synthesis, and reactions of sulfenamides and sulfenylimines and on their industrial applications. The literature from 1978 through 1986 is emphasized, although some overlap with previous reviews is essential for completeness.

II. Properties of Sulfenamides

A. Stereochemistry of Sulfenamides

Stereochemical interest in sulfenamides arises from the fact that the S–N bond is a chiral axis (Figure 1). The work of Raban and co-workers has established that a significant barrier to torsion around the S–N bond in sulfenamides can exist.[12] Sulfenamides with chiral and prochiral substituents on nitrogen give rise respectively to diastereomeric and diastereotopic groups whose NMR resonances allow the determination of S–N torsional barriers by dynamic NMR techniques. The highest barriers to date are found for sulfenamides with the 2,4-dinitrophenyl substituent on sulfur and large substituents on nitrogen.[13-15] Recent comprehensive reviews of sulfenamide stereochemistry have been published by Raban[6,8] and Yamamoto.[7]

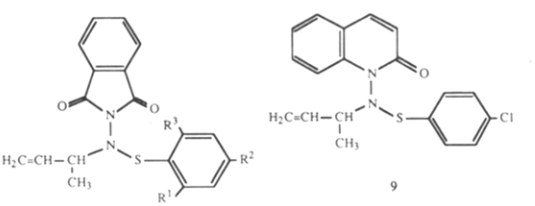
Raban and co-workers have recently reported substantial S–N torsional barriers (18.8–19.6 kcal/mol) in the 2,4-dinitrobenzenesulfenamides of 2-substituted benzimidazoles (**6**).[16,17] These high barriers are attributed in part to steric hindrance in the transition state by the peri hydrogen and minimization of steric hindrance in the ground state.



R = H, Cl
R^1 = Et, CH_2Ph, CH_2Cl, $CH(CH_3)Ph$

6

Atkinson[18] has reported S–N torsional barriers of 14.6 and 16.8 kcal/mol for compounds **7** and **8**. However, in sulfenamide **9**, the high torsional barrier (26.1 kcal/mol) is attributed to restricted rotation around the N–N bond, which is in this case a chiral axis.[18,19]



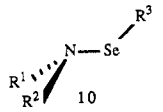
7 $R^1 = NO_2$, $R^2 = R^3 = H$

8 $R^1 = R^2 = NO_2$, $R^3 = H$

9

The N–Se torsional barriers in selenamides **10** are found to be 0.4–1.5 kcal/mol lower than the N–S bar-

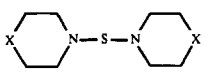
riers in identically substituted sulfenamides.[20] This difference is attributed to the longer N–Se bond, which lessens steric hindrance in the transition state as well as the overlap of the lone electron pairs on nitrogen and selenium.



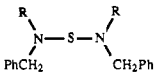
10

B. Mass Spectra of Sulfenamides

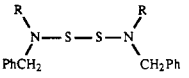
The mass spectral fragmentation of a number of sulfenamides has been examined. Field and Heimer found that the predominant EI fragmentations for sulfenamides $R^1S-NR^2R^3$ were C–S and N–S cleavage, with or without hydrogen rearrangement, depending on the nature of the substituents R^1, R^2, and R^3.[21] Harpp found that S–N cleavage dominates the fragmentation in sulfenamides **11**.[22] Raban also found the S–N cleavage to be dominant in sulfenamides **12–14**, with the formation of stable nitrogen-containing cations being common.[23]



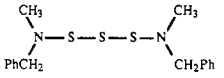
11 X = CH_2, O



12



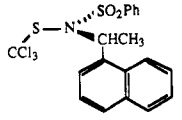
13



14

C. X-ray Crystal Structure

The X-ray crystal structure of sulfenamide **15** reveals a nearly planar configuration around nitrogen (the sum of the bond angles at nitrogen is 356.5°), with the C–S–N plane perpendicular to the plane of the two nitrogen substituents.[24] The X-ray structure of sulfenamide **9**, however, indicates a pyramidal sulfenamide nitrogen.[18]



15

D. Chiroptical Properties

The ORD spectra of *N*-(arylsulfonyl)-2,4-dinitrobenzenesulfenamides of optically active primary amines are found to exhibit a long-wavelength transition near 350 nm. The sign of this Cotton effect dominates the sign of rotation at the sodium D line.[25] Since asymmetric induction by the chiral amine on the stereolabile sulfenamide bond produces an excess of one sulfenamide diastereomer over the other, the sign of rotation at the sodium D line is directly related to the absolute configuration of the chiral amine.[26] Other large short-wavelength transitions are present in the ORD and CD spectra of these sulfenamides and in sulfenamides derived from other sulfenyl chlorides. However, these transitions involve coupling between the aromatic and sulfenamide systems. They are affected by substituent changes at the asymmetric center and are therefore not reliable indicators of the configuration at the sulfenamide chiral axis. The 2,4-dinitrophenyl chromophore, however, remains relatively unperturbed electronically by the substituents at the asymmetric center but does give rise to a long-wavelength transition, reflecting the effect of asymmetric induction on the chiral sulfenamide axis.

E. ^{13}C and ^{15}N NMR

Although sulfenamides are well-known, very little NMR chemical shift data on nuclei other than ^1H have been published. Hakkinen and Ruostesuo report that the ^{15}N NMR chemical shift of *N,N*-diethylbenzenesulfenamide is −334.4 ppm in chloroform (with respect to CH_3NO_2 doped with $Cr(acac)_3$).[27] This is upfield of sulfinamide N (−305.1 ppm neat) and sulfonamide N (−298.9 ppm in chloroform), corresponding to greater shielding of the sulfenamide nitrogen. The aromatic carbon attached to sulfur in the same sulfenamide has a chemical shift of 141.5 ppm (in chloroform), which is consistent with the inductive deshielding effect of sulfur. The other aromatic carbons are close to the normal values, with C_2 and C_4 being shifted slightly upfield. This is consistent with the electron-donating capacity of sulfur through the π system.

III. Synthesis of Sulfenamides

A large number of synthetic routes to sulfenamides have been developed over the years. There are several good reviews of these synthetic methods prior to 1979.[1-4,28,29] Most of these methods can be categorized according to the oxidation state of sulfur in the sulfur-containing reagent: (1) use of sulfur reagents RSX (X = Cl, Br, OR, NR_2, SO_2Ar, SCN); (2) use of disulfides RSSR, in which the oxidation state of sulfur is lower by one unit; and (3) use of thiols RSH, in which the oxidation state of sulfur is lower by two units.

A. From RSX

1. Sulfenyl Halides

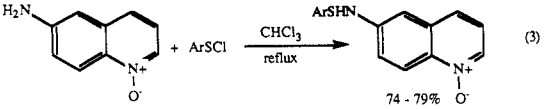
By far the most common method employed in the synthesis of sulfenamides is the condensation of amines with sulfenyl halides.[4,17,30-36] The reaction proceeds via nucleophilic attack of the amine on the sulfenyl halide (eq 1). The acid formed in the reaction is neutralized

$$R^1R^2NH + RSX \rightarrow R^1R^2NSR + HX \quad (1)$$

$$R^1R^2NH + HX \rightarrow R^1R^2N^+H_2 + X^- \quad (2)$$

by excess amine or by another acid acceptor, such as triethylamine, alkali-metal hydroxide, sodium hydride, and others (eq 2). Yields for the reaction of arenesulfenyl halides with aliphatic amines are usually high, especially with amines of lower basicity and a higher degree of substitution.[21]

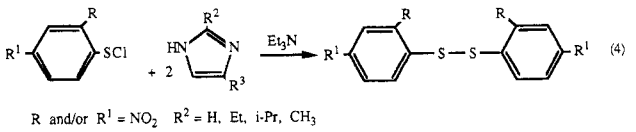
The 2-nitro- and 2,4-dinitrobenzenesulfenamides of 6-aminoquinoline *N*-oxide are formed in 74–79% yield from the quinoline *N*-oxide and the appropriate arenesulfenyl chloride (eq 3).[37]



(3)

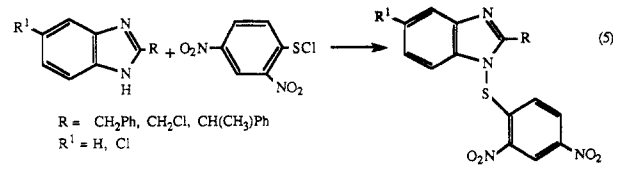
The reaction of nitrobenzenesulfenyl chlorides with indoles yields only 3-(arylthio)indoles under the usual reaction conditions.[38] In selected cases these can be thermally rearranged to the sulfenamides in small yield.[39] Somewhat better yields of the sulfenamides are obtained at low reaction temperatures with the sodium salt of the indole.[40]

The reaction of nitrobenzenesulfenyl chlorides with imidazoles alone or in the presence of 1 equiv of triethylamine yields exclusively disulfides (eq 4).[41] However, benzimidazoles react in the usual manner with 2,4-dinitrobenzenesulfenyl chloride in the presence of triethylamine to produce sulfenamides (eq 5).[16,17]



(4)

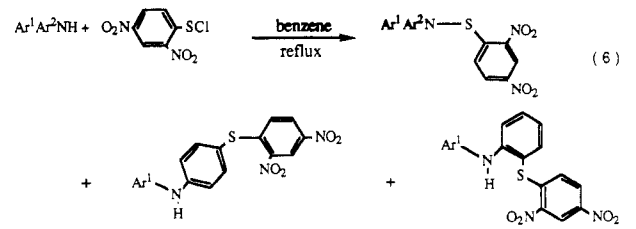
R and/or $R^1 = NO_2$ R^2 = H, Et, i-Pr, CH_3
R^3 = H, NO_2, CH_3



(5)

R = CH_2Ph, CH_2Cl, $CH(CH_3)Ph$
R^1 = H, Cl

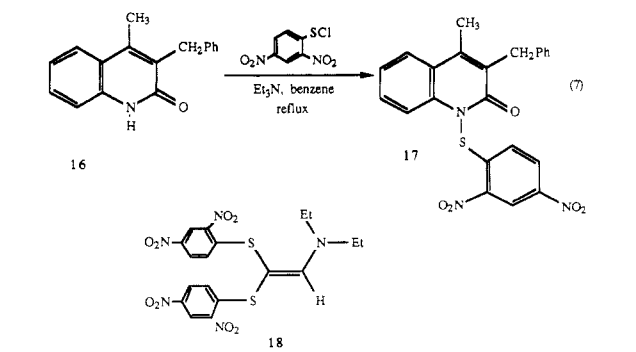
The reaction of 2,4-dinitrobenzenesulfenyl chloride with diarylamines in the absence of base yields several products, with the product distribution dependent on the aryl substituents (eq 6). The sulfenamide is the



(6)

major product for diphenylamine, but diaryl sulfides resulting from electrophilic aromatic substitution are the exclusive products when *N*-phenyl-α-naphthylamine is used.[42]

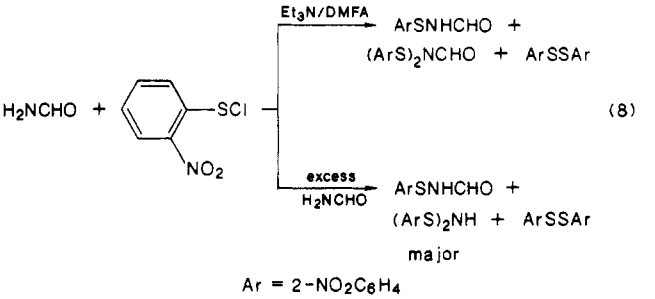
3-Benzyl-4-methylcarbostyril (**16**) reacts with 2,4-dinitrobenzenesulfenyl chloride and triethylamine to form the sulfenamide **17** (eq 7). However, under the



(7)

same reaction conditions 8-ethyl-4-methylcarbostyril does not react, and the enamine **18** is formed in small quantities. Similar results have been noted by Senning and Traynelis.[43]

Parfenov et al. report that equimolar amounts of 2-nitrobenzenesulfenyl chloride and formamide in the presence of triethylamine produce *N*-formyl-2-nitrobenzenesulfenamide and formylbis((2-nitrophenyl)sulfenyl)amine in roughly equal amounts, but excess formamide results in production of bis((2-nitrophenyl)sulfenyl)amine as the major product (eq 8).[44]



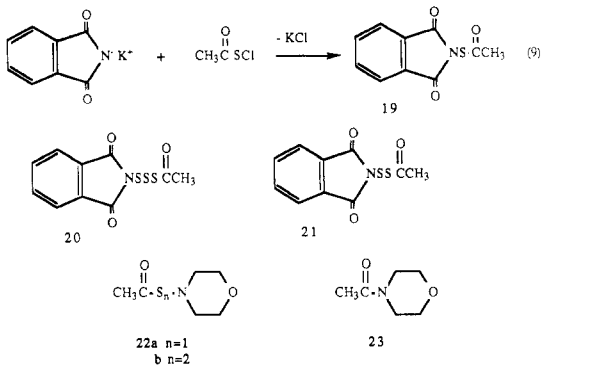
(8)

Ar = $2\text{-}NO_2C_6H_4$

The disulfide product is assumed to arise from a redox reaction. Both the sulfenyl chloride and the sulfenylated derivatives can act as electron acceptors, and the latter can also act as donor in electron-transfer reactions.

The reaction of methanesulfenyl chloride with amines in excess produces *gem*-diamines $CH_2(NR_2)_2$, methyl disulfide, and methyl trisulfide as well as sulfenamides.[45] Use of ethanesulfenyl chloride produces similar results, but no *gem*-diamine is formed.

Acyl sulfenyl chlorides have also been employed (eq 9). Senning reports that sulfenamide **19** is not stable

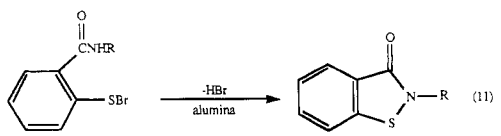


(9)

and is converted upon standing for 6–8 weeks to trisulfide **20**. Sulfenamide **21**, in contrast, is stable for months.[46] Similar relative stabilities have been reported for sulfenamides **22** (also synthesized from acyl sulfenyl chlorides), which decompose with loss of sulfur to give amide **23**.[47]

Sulfenyl bromides, although less commonly used, can also be condensed with amines to produce sulfenamides.[33,48,49] Michalski has reported the synthesis of organophosphorus sulfenamides via (*O,O*-dialkylthiophosphono)sulfenyl bromides (eq 10).[48] An intramolecular cyclization of N-substituted 2-carbamoylbenzenesulfenyl bromides to produce the corresponding 2-substituted 1,2-benzisothiazol-3(2*H*)-ones (eq 11) was recently reported by Kamigata.[49]

$$RR^1P(S)SBr + R^2_2NH \rightarrow RR^1P(S)SNR^2_2 \quad (10)$$



(11)

Sulfenyl halides react with hydroxyl groups, active methylene groups, and multiple bonds. Thus sulfenamides containing these functionalities cannot be syn-

thesized by this method unless protecting groups are employed.

2. Arenesulfenate Esters, Sulfenyl Thiocyanates, and Thiolsulfonates

Arenesulfenate esters react with amines in the same manner but more slowly than arenesulfenyl halides (eq 12).[50] For primary amines, the amine must be present

$$ArSOR + HNR^1_2 \rightarrow ArSNR^1_2 + ROH \quad (12)$$

in excess to prevent the formation of diaryl sulfenamides $(ArS)_2NR$. The *N*-trimethylsilyl derivatives of secondary amines may be used in place of the amines with equal success.

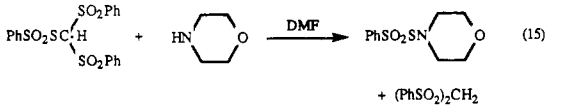
Moderate yields of *N,N'*-dialkylalkanesulfenamides have been reported from the addition of alkanesulfenyl thiocyanates to dialkylamines (eq 13).[51]

$$RSSCN + 2R^1_2NH \rightarrow RSNR^1_2 + R^1_2NH{\cdot}HSCN \quad (13)$$

Sulfenamides have been prepared from primary and secondary aliphatic amines and thiolsulfonates (eq 14).[52] For aromatic amines, only the 2-nitrophenyl benzenethiolsulfonate has been used successfully.

$$R^1SSO_2Ar + R_2NH \rightarrow R^1SNR_2 + ArSO_2H{\cdot}HNR_2 \quad (14)$$

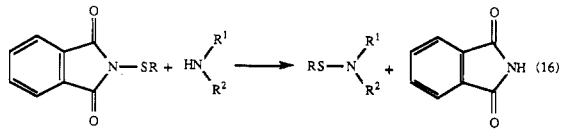
An unusual reaction of a thiolsulfonate with an amine to form a sulfenamide has been reported in which the S(II)–C bond is cleaved in preference to the S(II)–S(VI) bond (eq 15).[53] In this case, the doubly stabilized carbanion is the better leaving group.



(15)

3. Sulfenamides

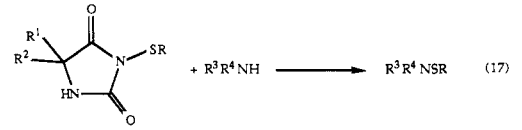
Some sulfenamides function as sulfenyl-transfer reagents and can be used to prepare other sulfenamides. The thiophthalimides are the best known of these reagents (eq 16).[54-56]



(16)

R = alkyl, phenyl, benzyl

Recently, Sosnovsky reported the effective use of 3-(alkylthio)-, 3-(arylthio)-, and 3-((trichloromethyl)thio)hydantoins as sulfenyl-transfer reagents (eq 17).[41] The transfer reaction appears to be facilitated by a polar solvent, since yields in chloroform are 55–61% while yields from benzene are only 34–37%. Also, *N,N'*-thiobisamines RSR, where R = piperidyl or morpholinyl, were prepared with *N,N'*-thiodicaprolactam and *N,N'*-thiobis(5,5-dimethylhydantoin) as sulfenylating reagents.



(17)

$R^1 = R^2 = CH_3$ R = C_6H_5, CCl_3
R^3 = H, -$(CH_2)_5$-, C_6H_5 R^4 = $C_6H_4CH_3$, -$(CH_2)_5$-, H

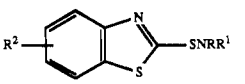
B. From RSH

Aromatic thiols and amines react to form sulfenamides in the presence of oxidizing reagents (eq 18).

$$ArSH + HNR_2 \xrightarrow{[O]} ArSNR_2 + H_2O \quad (18)$$

Formation of disulfides is the primary competing reaction. Hydrogen peroxide, hypochlorites, halogens, potassium persulfate, and potassium ferrocyanide are reported to be useful oxidants. Chloramine has been employed successfully to make sulfenamide derivatives of mercaptopyridines under conditions where the products were insoluble in the reaction medium.[57]

Sterically hindered 2-benzothiazolesulfenamides **24** have been synthesized from the 2-mercaptobenzothiazole sodium, potassium, or calcium salts and the corresponding amine with NaOCl as the oxidant.[58]



24

R, R^1 = sec-alkyl, cycloalkyl R^2 = H, C_{1-6} alkyl

Oxygen and a cobalt phthalocyanine catalyst have also been employed to produce 2-benzothiazolesulfenamides from the corresponding mercaptans and amines.[59] Oxidation of the mercaptan to the disulfide is believed to be the first step in this process.[60]

tert-Butyl azidoacetate and *tert*-butyl azidoformate react with *tert*-butyl and benzyl mercaptans in the presence of copper(I) to give sulfenamides in moderate yield (eq 19).[61]

$$RSH + R^1N_3 \xrightarrow{Cu(I)} RSNHR^1 \quad (19)$$

C. From Disulfides

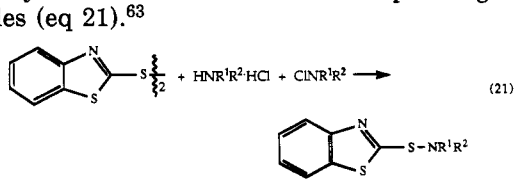
Davis and co-workers have developed an effective one-step synthesis of sulfenamides from disulfides and amines in the presence of silver or mercuric salts (eq 20).[62]

$$RSSR + MX + 2R^1_2NH \rightarrow RSNR^1_2 + RSM + R^1_2NH_2X \quad (20)$$

$$MX = AgNO_3, AgOAc, HgCl_2$$

The mechanism is believed to involve the complexation of the metal ion with one of the disulfide sulfurs, followed by nucleophilic attack on the other sulfur by the amine. The reaction gives the best results with aromatic disulfides and works well with hindered amines. Unlike sulfenyl halides, the disulfide reaction can be used with amines containing hydroxyl groups and C–C double bonds. The resulting sulfenamides have a longer shelf life than the same sulfenamides prepared with sulfenyl chlorides, since the latter cannot be entirely freed of traces of HCl, to which sulfenamides are not stable.

A mixture of *N,N*-dialkylchloramine and the corresponding amine hydrochloride will react with 2-benzothiazolyl disulfides to form the corresponding sulfenamides (eq 21).[63]



(21)

The stoichiometric reaction of diaryl disulfides with benzoic acid *N*-chloramide is reported to yield sulfenamides and sulfenyl chlorides as the cleavage products of the disulfides (eq 22). Excess chloramide produces $BzNH_2$, $ArS^+(NHBz)_2Cl^-$, and/or sulfinamidine ArS(NHBz)=NBz.[64]

$$Ar_2S_2 + BzNHCl \rightarrow ArSNHBz + ArSCl \quad (22)$$

Lithium amides have also been employed successfully to cleave disulfides and form sulfenamides (eq 23).[65]

$$RSSR + LiNR^1R^2 \rightarrow \underset{62\text{–}96\%}{RSNR^1R^2} \quad (23)$$

R = Pr, Ph; $R^1 = R^2$ = Et, Pr, *i*-Pr, *i*-Bu; R^1 = H, R^2 = Bu

Bis(dialkoxyphosphoryl) disulfides react with primary and secondary amines to give the corresponding sulfenamides (eq 24).[66] Anilines undergo an analogous reaction with bis(diisopropxythiophosphoryl) and (diphenylthiophosphoryl) disulfides.[67]

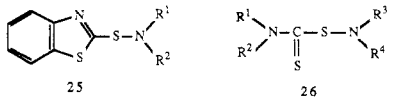
$$[(RO)_2P(O)S]_2 + R^1R^2NH \rightarrow (RO)_2P(O)SNR^1R^2 + (RO)_2P(O)SH\cdot NHR^1R^2 \quad (24)$$

R = Et, $CH(CH_3)_2$

D. Miscellaneous Methods

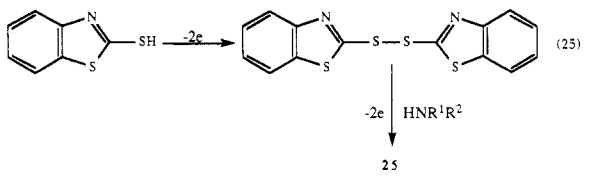
1. Electrochemical Syntheses

An electrochemical synthesis of sulfenamides **25** and **26** that proceeds cleanly and with high yields (70–98%) has been reported by Torii and co-workers.[68] The synthesis of **25** involves the electrolytic cross coupling of 2-mercaptobenzothiazole or bis(2-benzothiazolyl) disulfide with various aliphatic amines (eq 25). Sul-



25

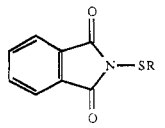
26



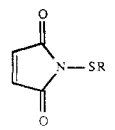
(25)

fenamides **26** are produced from direct electrolysis of CS_2 in the presence of amines or from electrolysis of the intermediate disulfides and amines. The reaction is run in DMF in the presence of tetraethylammonium perchlorate with platinum or stainless steel electrodes. The mechanism is believed to involve nucleophilic attack on the disulfide by the amine. Evidence that lends support to this mechanism is the failure of disulfides that do not possess electron-withdrawing groups (diphenyl disulfide, di-*tert*-butyl disulfide, dibenzyl disulfide) to produce sulfenamides when electrolyzed under the same conditions.

An extension of the electrolytic cross-coupling reaction to phthalimide or succinimide and disulfides to afford sulfenamides **27** and **28** requires the presence of



27



28

a catalytic amount of NaBr in acetonitrile solvent.[69] The mechanism differs from that for the formation of sulfenamides **25** and **26** in that a key step is the nucleophilic attack of the disulfide on an *N*-bromo imide intermediate. Hence, the reaction of the electron-poor bis(*o*-nitrophenyl) disulfide with phthalimide produces only a 3% yield of sulfenimide. The salt apparently serves as a redox catalyst, Br^- being anodically oxidized to Br_2, which subsequently serves as an oxidant.

2. Thiocarbamyl Sulfenamides from CS_2

Another method of preparing thiocarbamyl sulfenamides involves the reaction of CS_2, an amine, and a monochloroamine in the presence of base (eq 26).[70]

$$Me_2NH + Me_2NCl + CS_2 \xrightarrow{NaOH} \underset{72\%}{Me_2NC(S)SNMe_2} \quad (26)$$

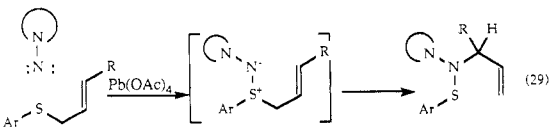
Polythiocarbamyl sulfenamides have recently been prepared for use as vulcanization accelerators in the two-step procedure outlined in eq 27 and 28,[71] using iodine as an oxidant. It is believed that polymerization occurs by a radical mechanism.

$$H_2NCH_2(CH_2)_4CH_2NH_2 + CS_2 \xrightarrow[H_2O]{NaOH} Na^+{}^-SC(S)NH(CH_2)_6NHC(S)S^-Na^+ \quad (27)$$

$$Na^+{}^-SC(S)NH(CH_2)_6NHC(S)S^-Na^+ \xrightarrow[I_2,\ EtOH]{H_2N(CH_2)_6NH_2} \underset{85\%}{-(NH(CH_2)_6NHC(S)S)_n^-} \quad (28)$$

3. Rearrangements

Another reaction that generates sulfenamides is the allylic sulfilimine rearrangement. Atkinson and coworkers have synthesized *N*-(*N*-heteroaryl)arenesulfenamides by the addition of *N*-aminonitrenes to substituted allyl aryl sulfides (eq 29).[18,72,73] The nitrene is generated in situ from the *N*-amino compound with lead tetraacetate, and the intermediate sulfilimine undergoes a 2,3-sigmatropic rearrangement to yield the sulfenamide.

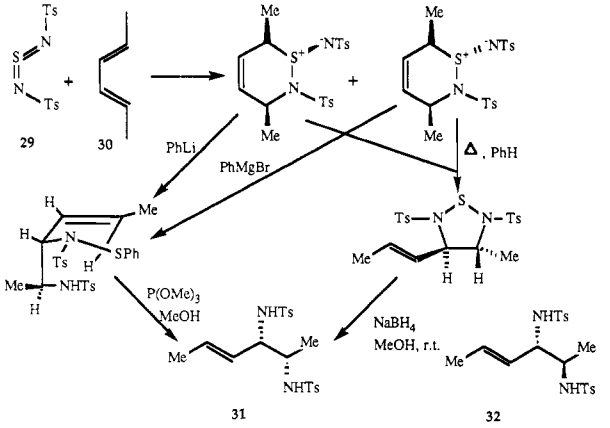


(29)

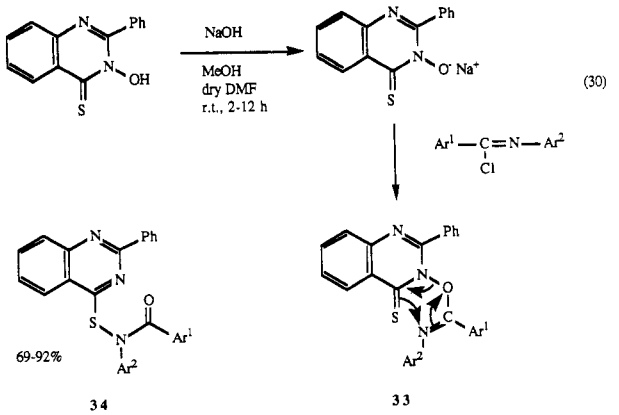
The allylic sulfilimine rearrangement has recently been used by Weinreb and co-workers as a significant step in the stereocontrolled synthesis of unsaturated vicinal diamines.[74] The Diels–Alder adducts of sulfur diimides **29** and diene **30** are the epimeric cyclic sulfimides. When organometallic nucleophiles are introduced, these sulfimides form acyclic sulfimides that undergo rearrangement to the sulfenamides. Alternatively, thermolysis of the sulfimides produces cyclic bisamine sulfides. Trimethyl phosphite or sodium borohydride reduction gives exclusively the (*E*)-threo vicinal diamine **31** (Scheme I). Use of (*E*,*Z*)-hexadiene in the same sequence yields the (*E*)-erythro vicinal diamine **32**. Cyclic dienes can also be used in this sequence.

Molina reports the synthesis of heteroaryl sulfenamides through [3,3]-sigmatropic rearrangement of the

SCHEME I



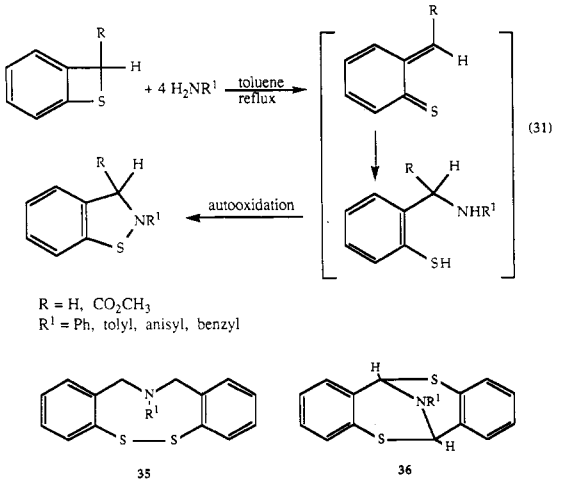
products of the reaction of 2-phenyl-3-hydroxy-4-thioxo-3,4-dihydroquinazoline sodium salt with diaryl imidoyl chlorides (eq 30).[75] It is believed that initial S-alkylation of the sodium salt is followed by S to O migration to give the intermediate **33**, which undergoes [3,3]-sigmatropic rearrangement to give **34**.



(30)

4. Ring Expansion

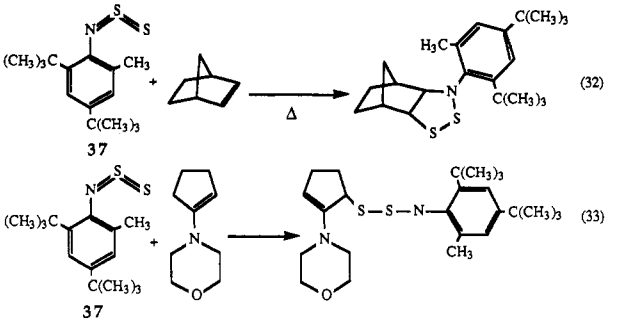
A new route to 2,3-dihydrobenz[*d*]isothiazoles has been reported.[76] Reaction of benzothietes with primary amines in a ratio of 1:4 affords the ring-expanded benzisothiazoles (eq 31). A stoichiometry of 1:1 yields adducts **35** and **36**.



(31)

5. Additional Methods

The thermal cycloaddition of thionitroso *S*-sulfide **37** to cyclic alkenes yields cyclic sulfenamides (1,2,3-dithiazolidines, eq 32). Acyclic sulfenamides are formed by the addition of **37** to enamines (eq 33).[77]

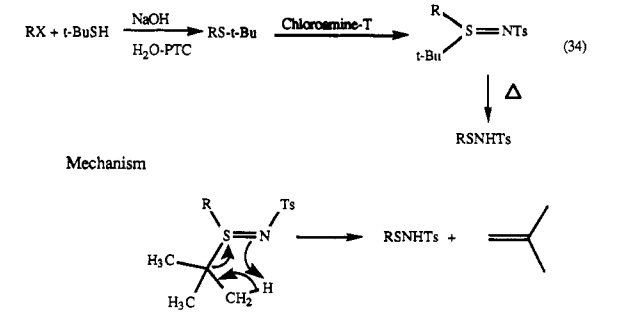


(32)

(33)

Addition of organometallic reagents to sulfenylimines is reported to give sulfenamides.[4] Treatment of bromoethyl *p*-tolyl sulfoxide with piperidine, diethylamine, or morpholine is reported to give the corresponding *p*-toluenesulfenamide in excellent yield.[78]

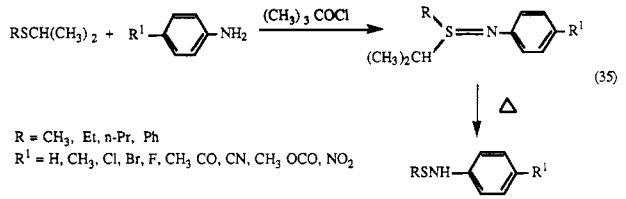
S-Alkyl sulfenamides have been prepared via the selective elimination of the *tert*-butyl group as isobutylene in the thermolysis of *S*-alkyl-*S*-*tert*-butyl sulfimides (eq 34).[79]



(34)

Mechanism

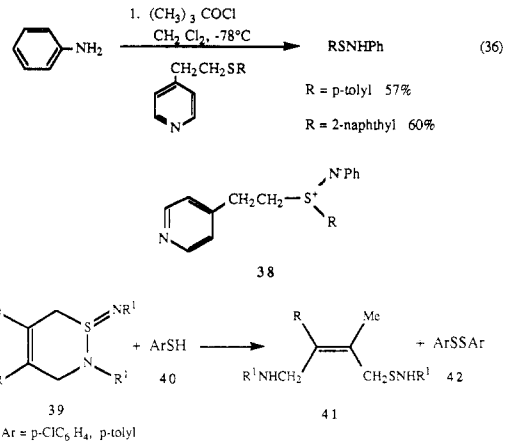
This reaction, which is analogous to the sulfoxide and selenoxide eliminations, is known for arenesulfenamides, which are side products in a preparative route to olefins.[80] The thermolysis reaction is characterized by mild conditions and excellent yields. In the case where R = isopropyl, the isopropyl group was eliminated competitively with the *tert*-butyl group in a ratio of 17:83. Another recent example of the preparation of *S*-alkyl and *S*-aryl sulfenanilides by thermal elimination of propene from *S*-isopropyl sulfimides is given in eq 35.[81] The intermediate sulfimides have been isolated as picrates. However, the cycloelimination occurs readily at room temperature when R = C_6H_5.



(35)

Katritzky and co-workers report that aryl 2-(4-pyridyl)ethyl sulfides (R = *p*-tolyl, 2-naphthyl) react with aniline in the presence of *tert*-butyl hypochlorite to form sulfenanilides (eq 36).[82] The reaction was expected to proceed through formation of an intermediate sulfimide, **38**, but this intermediate was not detected.

Reductive cleavage of the imidodihydrothiazines **39** with thiophenols **40** yields the corresponding aminobutenesulfenamides **41** and disulfides **42** in 65–95%



yield and quantitative yield, respectively (eq 37).[83]

IV. Reactions of Sulfenamides

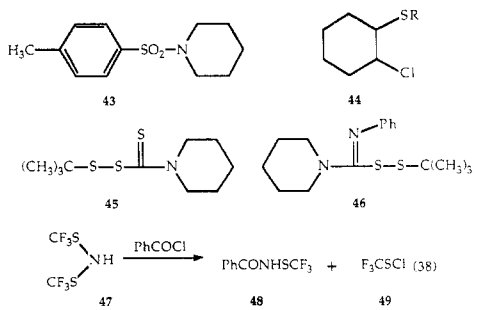
Many useful and interesting reactions of sulfenamides are known. Because of the polarization of the S–N bond, sulfenamides are subject to attack by nucleophiles at sulfur and electrophiles at nitrogen. They can be oxidized at sulfur or nitrogen, and they can be reductively cleaved. Some interesting thermal and photochemical reactions are also known.

A. Reactions with Electrophiles

The reaction of sulfenamides with electrophiles involves the coordination of the electrophile with nitrogen and subsequent nucleophilic attack on sulfur. An investigation by Epshtein et al. of the electron-donor properties of sulfenamides by infrared spectroscopy indicates clearly that the nitrogen atom is the coordination center in sulfenamides.[84]

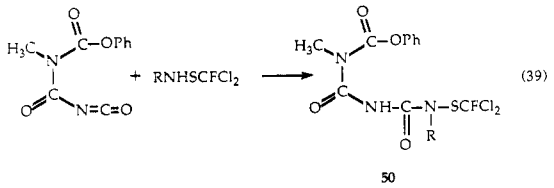
Cleavage of the S–N bond with HCl to produce a sulfenyl chloride and an amine is a procedure commonly used in peptide synthesis for the removal of sulfenyl protecting groups.[85]

N-(Alkylthio)piperidines react with *p*-toluenesulfonyl chloride in the presence of cyclohexene to give **43** and **44**.[21] *N*-(*tert*-Butylthio)piperidine reacts with carbon disulfide and phenyl thioisocyanate to give **45** and **46**, respectively.[21] Disulfenylamine **47** reacts with benzoyl chloride to give sulfenamide **48** and sulfenyl chloride **49** (eq 38).[86]

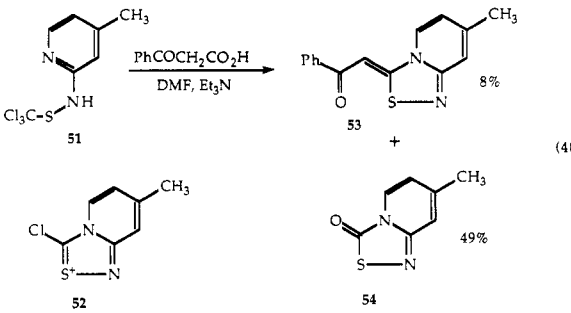


Acyl isocyanates are also electrophiles for sulfenamides (eq 39).[87] The resulting sulfenamides **50** are fungicides.

In sulfenamide **51**, the nucleophile is not the sulfenamide nitrogen but the pyridine nitrogen, which is in conjugation with the sulfenamide nitrogen anion formed under base catalysis. Attack on the internal trichloromethyl electrophile leads to cyclization. It is believed

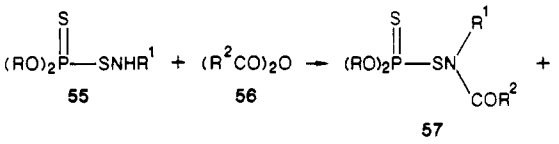


to form the intermediate pyrido[2,1-*c*][1,2,4]thiadiazolylium salt **52**, which then condenses with benzoylacetic acid to form **53**, or is hydrolyzed to form **54** (eq 40).[88]



Acylation of alkene- and arenesulfenamides with acetic anhydride yields disulfenylamines and acetamides (eq 41).[89] However, *S*-(dialkoxyphosphinothioyl)sulfenamides **55** react readily with various anhydrides **56** to form the N-acylated sulfenamides **57** (eq 42).[89]

$$2RSNHR^1 + (CH_3CO)_2O \rightarrow (RS)_2NR^1 + CH_3C(O)NHR^1 + CH_3COOH \quad (41)$$

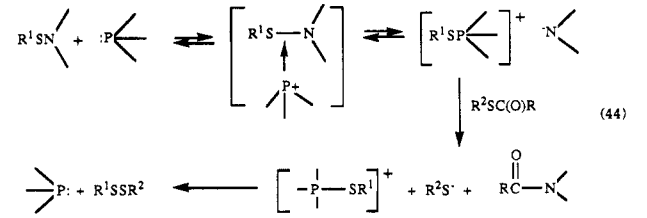


$$R^2COOH \quad (42)$$

R = alkyl, phenyl, R^1 = H, Me,
R^2 = Me, Ph, CH=CHCOOH

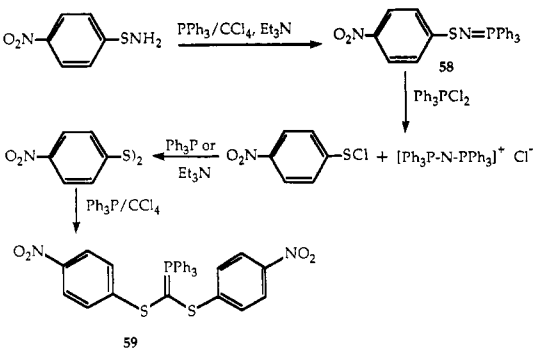
Parfenov and Fomin report that the base-catalyzed exchange reaction of *S*-arenesulfenamides with *S*-esters of thiocarboxylic acids yields amides and disulfides (eq 43).[33] The reaction does not proceed in the absence of a catalytic amount of a trivalent phosphorus compound. The authors suggest the following mechanism for this reaction (eq 44):

Mechanism:



Similar phosphorus(III)-catalyzed reactions of sulfenamides with linear anhydrides (eq 45) and carboxylic acid chlorides (eq 46) yield the indicated amides.[90] In the case of the linear anhydrides, the trivalent phosphorus compound functions both as a catalyst in the

SCHEME II

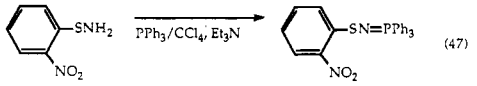


exchange reaction and as a stoichiometric reducing agent.

$$2ArSNR^1R^2 + (R^3CO)_2O + PX_3 \rightarrow ArSSAr + O{=}PX_3 + 2R^3CONR^1R^2 \quad (45)$$

$$ArSNR^1R^2 + RCOCl \xrightarrow{PX_3} R^3CONR^1R^2 + ArSCl \quad (46)$$

Zhmurova and co-workers report an unusual variant of the Appel reaction of sulfenamides with the binary system PPh_3–CCl_4.[91] *o*-Nitrobenzenesulfenamide reacts in the usual nucleophilic manner with PPh_3–CCl_4 to produce *o*-nitro-*N*-(triphenylphosphoranylidene)-benzenesulfenamide (eq 47). The reaction of *p*-nitro-

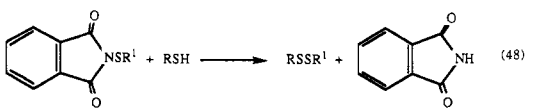


(47)

benzenesulfenamide with PPh_3–CCl_4, however, produces not the expected *p*-nitro-*N*-(triphenylphosphoranylidene)benzenesulfenamide, but the methylide **59**. It is believed that *p*-nitro-*N*-(triphenylphosphoranylidene)benzenesulfenamide is formed initially but reacts further by cleavage of the S–N bond by dichlorotriphenylphosphorane and conversion of the sulfenyl chloride to bis(*p*-nitrophenyl) disulfide. The disulfide then reacts with the binary system to form the methylide (Scheme II). The probability of this route is supported by the fact that both phosphoranylidene **58** and bis(*p*-nitrophenyl) disulfide react in the presence of PPh_3–CCl_4 and Et_3N to form **59**.

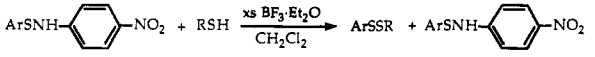
B. Reactions with Nucleophiles

In reactions with nucleophiles, the sulfenamide bond is usually attacked at the more electropositive sulfur. Thus *N*-alkylthiophthalimides react with thiols to form unsymmetrical disulfides and phthalimide (eq 48).[92]



(48)

4′-Nitroarenesulfenanilides are also reported to be useful intermediates for the synthesis of unsymmetrical disulfides (eq 49).[93] The sulfenamide precursors are

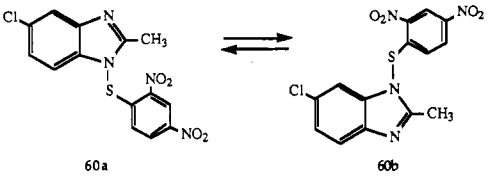


(49)

Ar = Ph, *p*-tolyl, *p*-ClC_6H_4
R = Et, *t*-Bu, $PhCH_2$, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$, *n*-Pr, Ph

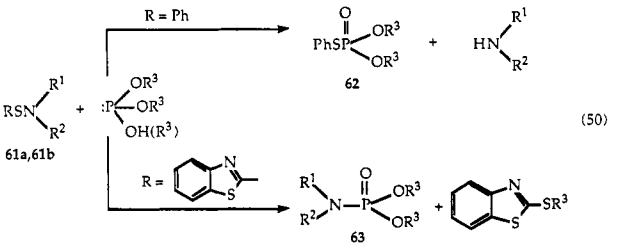
stable, crystalline materials. Yields for this acid-catalyzed reaction range from 51% to 99%; lower yields are obtained for disulfides derived from arenethiols. Higher yields for diaryl disulfides were obtained when arenethiols with electron-withdrawing substituents were used.

Transfer of the arylsulfenyl group was considered as one mechanistic possibility in the equilibration of isomeric *N*-(arylsulfenyl)benzimidazoles (**60a** ⇌ **60b**).[17]



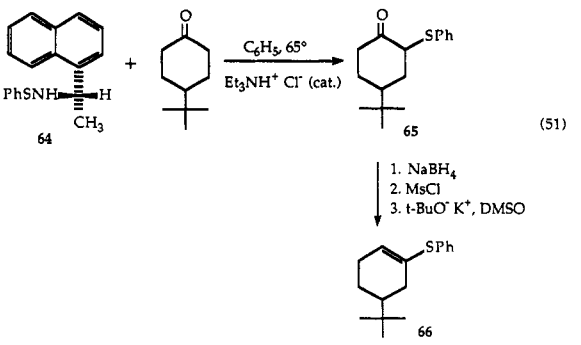
Three mechanistic possibilities were considered: (a) homolysis of the S–N bond and radical recombination, (b) 1,3-sigmatropic rearrangement, and (c) nucleophilic attack by imidazole nitrogen on the sulfenyl sulfur atom of another sulfenamide molecule. The observation of kinetics that were second order in sulfenamide and catalysis by added benzimidazoles provided evidence that the exchange took place by the third mechanistic route, namely, nucleophilic attack at sulfenyl sulfur.

In a similar manner, phenyl sulfenamides **61a** are attacked at sulfur by dialkyl and trialkyl phosphites to form phosphorothiolates **62** (eq 50). However, (2-benzothiazolyl) sulfenamides **61b** appear to be attacked at nitrogen, and phosphoramidates **63** are produced in excellent yield.[94]



(50)

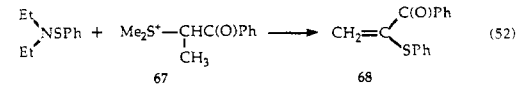
Sulfenamides react with active methylene compounds such as malononitrile, acetylacetone, ethyl acetoacetate, enamines, and ketones to give sulfides.[95] Asymmetric sulfenylation of 4-alkylcyclohexanones with chiral sulfenamides has been reported.[96] Thus (*S*)-(−)-*N*-(phenylthio)-α-naphthylethylamine (**64**) reacted with 4-*tert*-butylcyclohexanone in the presence of a catalytic amount of triethylamine hydrochloride to produce a 62% yield of a diastereomeric mixture of **65**. Reduction of the ketone with $NaBH_4$ followed by mesylation and elimination gave the alkene **66**, in which the *S* absolute configuration was dominant. The optical yield was 64% (eq 51).



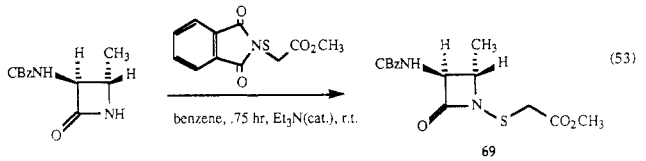
(51)

N,*N*-Diethylbenzenesulfenamide reacts with sulfonium salt **67** to give ketone **68** (eq 52).[97]

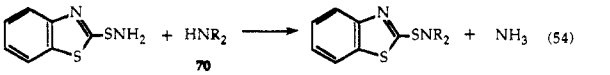
Transamination of sulfenamides by alkyl- and arylamines occurs.[3] A recent example is Miller's use of a



variety of S-substituted thiophthalimides to sulfenylate 2-azetidinones (eq 53).[98] (A low N–S torsional barrier was observed by NMR for sulfenamide **69**.)

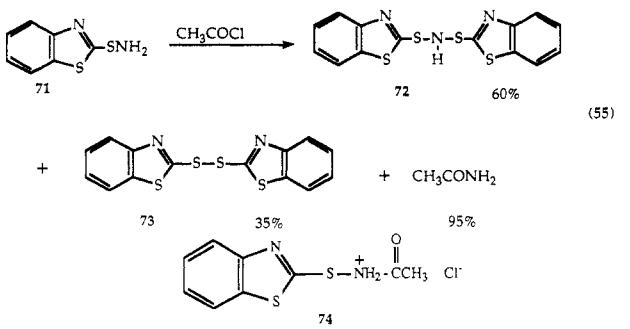


In the transamination reactions of 2-benzothiazolesulfenamide, Ignatov et al. have found that the reaction time is increased with increasing basicity of the amine **70** (eq 54).[99] The presence of water and other basic



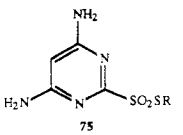
additives also increases the reaction time. Reaction rates of *N*-alkyl-2-benzothiazolesulfenamides with nucleophiles were increased by acids in the order aromatic thiol < HOAc < HCl, indicating that protonation of the amide nitrogen increases the electrophilicity of the exocyclic sulfur atom.[100]

It is known that disulfenylamines and disulfides are formed from the reaction of monosulfenamides with carboxylic acids, acid chlorides, and anhydrides. For example, 2-benzothiazolesulfenamide **71** reacts with itself in the presence of acetyl chloride (1 equiv) to yield disulfenylamine **72** and disulfide **73** (eq 55).[101] The



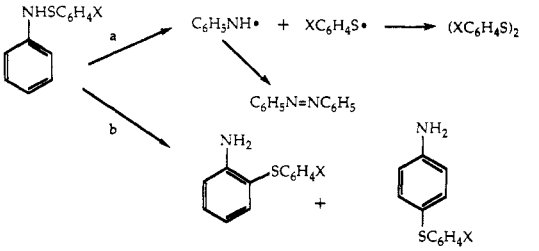
mechanism involves the formation of the (arylthio)ammonium compound **74**, which either can be directly attacked by the free sulfenamide or can dissociate to the sulfenyl chloride and amide. The sulfenyl chloride reacts with free sulfenamide to form the disulfenylamine or can be reduced to disulfide via a radical mechanism.

Alkyl esters **75** of 4,6-diaminopyridine-2-thiosulfonic acid have been synthesized in 38.5–56.4% yield by treatment of the sulfinic acid with $RSNEt_2$ (R = Me, Et, *n*-Pr, *n*-Bu).[102]

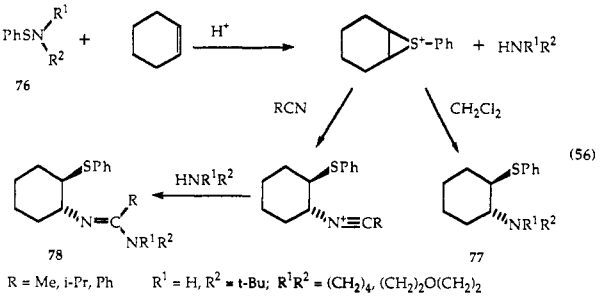


Sulfenamides will add to alkenes with acid catalysis. Brownbridge reports that while sulfenamides **76** add to cyclohexene in chloroform to give the expected **77**, the same reaction run in the presence of a nitrile gives amidines **78** (eq 56) via a Ritter-type mechanism.[103] The

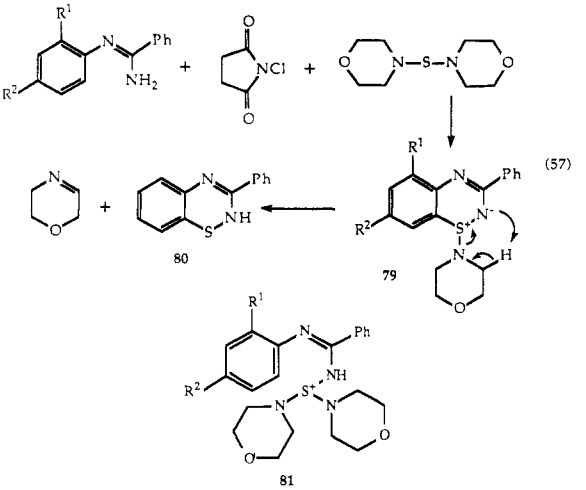
SCHEME III



regiochemistry of the addition in unsymmetric alkenes is exclusively Markovnikov.



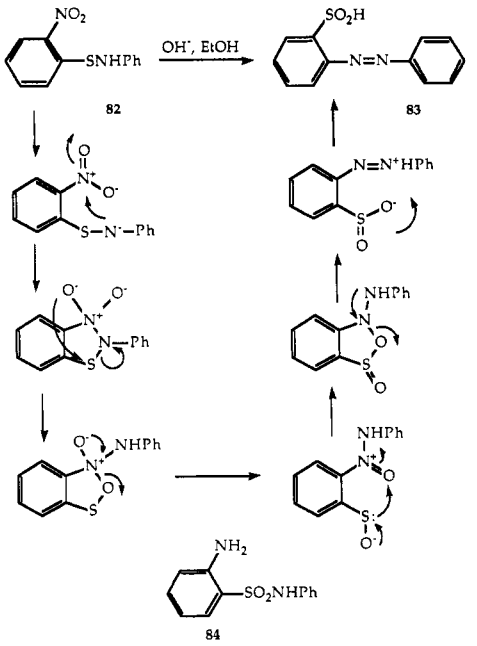
Gilchrist and co-workers have reported the reaction of *N*-arylbenzamidines with *N*-chlorosuccinimide and 4,4′-thiobis(morpholine) to give after basic workup the 1λ⁴,2,4-benzothiadiazine ylides **79** (eq 57).[104] Ylides **79** have been converted, presumably by cycloelimination, to the 2*H*-1,2,4-benzothiadiazines **80**. The mechanism for formation of the ylide has not been clearly established. It is probable that *N*-chlorosuccinimide chlorinates either the amidine or the sulfenamide and that azasulfonium salts **81** are formed, which may then cyclize, but the role of these salts is not certain.



C. Thermal and Photochemical Reactions

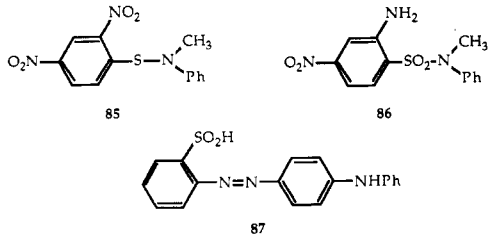
The thermal reactions of arenesulfenanilides have been extensively examined by Davis and co-workers.[105-107] They have concluded that two types of reactions are characteristic of these compounds: (a) homolytic cleavage of the S–N bond to give amino and sulfenyl radicals and the products thereof and (b) rearrangement to produce *o*- and *p*-aminodiphenyl sulfides (Scheme III). Solvents, substituents, and the method of preparation of the sulfenamides all affect the ratio of products. The rearrangement of sulfides is acid catalyzed,[105,106] and the high ortho/para ratio of products suggests an intramolecular mechanism. A π complex and a caged radical ($ArS{\cdot}NH_2Ar'$) have been suggested as possible intermediates.[107]

SCHEME IV

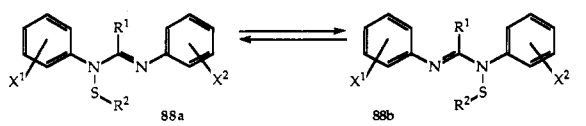


The thermal reactions of 2-nitrobenzenesulfenanilides are also well-known. These reactions are characterized by the transfer of oxygens from the nitro group to the adjacent sulfur in an internal oxidation–reduction reaction. When sulfenanilide **82** was heated with sodium hydroxide in ethanol, the product was 2-azobenzenesulfinic acid (**83**) (Scheme IV).[108] When **82** was heated in aniline at 95 °C for 15 h, the *o*- and *p*-aminodiphenyl sulfides and phenothiazine (from a Smiles rearrangement of the *o*-aminodiphenyl sulfide) were minor products, and the major product was 2-aminobenzenesulfonanilide **84**.[109] Davis and Johnston proposed a radical mechanism involving homolytic cleavage of the sulfenamide bond.[106]

Photolysis of 2-nitrobenzenesulfenanilides yields the same types of products generated by thermolysis. Thus sulfenamides **85**[110] and **82**[111] yield **86** and **87**, respectively.



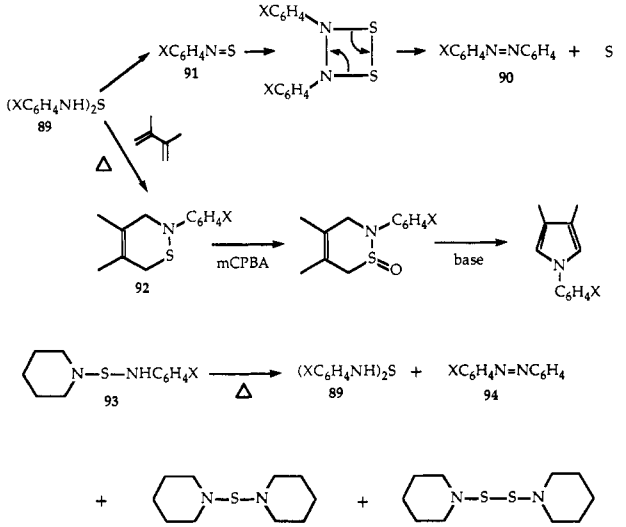
Although the nitrogen-to-nitrogen rearrangement of the arylsulfenyl group in *N*-(arylsulfenyl)benzimidazoles (**60a** ⇌ **60b**) discussed above was shown to take place via a nucleophilic displacement mechanism, the similar rearrangements of arylsulfenyl moieties in a series of acyclic *N*-arenesulfenamidines (**88a** ⇌ **88b**) that were



$X^1 = X^2$ = o-Me, p-Me, o-OMe, p-OMe
R^1 = H, Ph, p-C_6H_4OMe, p-C_6H_4Cl, p-C_6H_4Br, p-$C_6H_4NO_2$
R^2 = 2,4-$C_6H_3(NO_2)_2$, 2-$C_6H_4NO_2$, CCl_3

studied by variable-temperature NMR spectroscopy were assigned mechanisms involving unimolecular nitrogen-to-nitrogen rearrangement via acyclic structure.[112,113]

SCHEME V



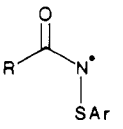
The thermal decomposition of *N,N'*-thiodiamines **89** (synthesized from piperidine-1-sulfenyl chloride and 2 equiv of aryl amine) yields azobenzenes **90**, aryl amines, and sulfur (eq 58).[114] The proposed mechanism in-

$$(XC_6H_4NH)_2S \xrightarrow[50\ °C,\ 72\ h]{\text{benzene}} XC_6H_4N{=}NC_6H_4 + XC_6H_4NH_2 \quad (58)$$

X = 4-OMe, H, 4-Br, 4-Cl, 3-NO_2

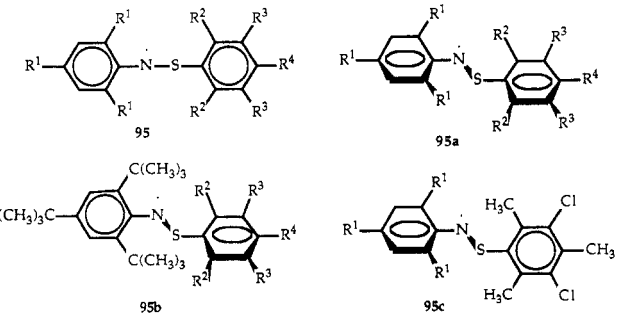
volves initial formation of thionitrosobenzene (Scheme V). The existence of thionitrosobenzene **91** was demonstrated by trapping the product of thermal decomposition of **89** with 2,3-dimethyl-1,3-butadiene to give 1,2-thiazine **92**. Thermal decomposition of *N*-((arylamino)thio)piperidines **93**, believed to be an intermediate in the formation of *N,N'*-thiodiamines **89**, yielded, in addition to **90**, the *N,N'*-thiodiamines **89**, *N,N'*-piperidinyl disulfide, and *N,N'*-piperidinyl sulfide. These products were attributed to the recombination of radical intermediates formed from homolytic cleavage of the S–N bond.

N-Acyl-*N*-(arylthio)aminyls have been generated by thermolysis and by photolysis.[32] These captodative radicals are relatively stable and insensitive to oxygen. ESR spectra of **94** generated by these procedures indicate that these radicals exist in a π-electronic ground state and that the unpaired electron is located predominantly on the nitrogen atom and the arylthio group.



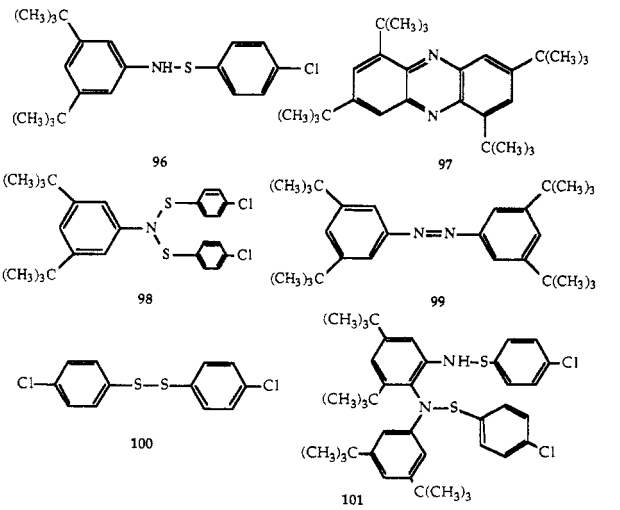
94, R = aryl, *tert*-butyl

Polysubstituted *N*-aryl-*N*-(arylthio)aminyls **95** have been generated by photolysis (di-*tert*-butyl peroxide in benzene) and by oxidation (PbO_2, K_2CO_3).[115] These



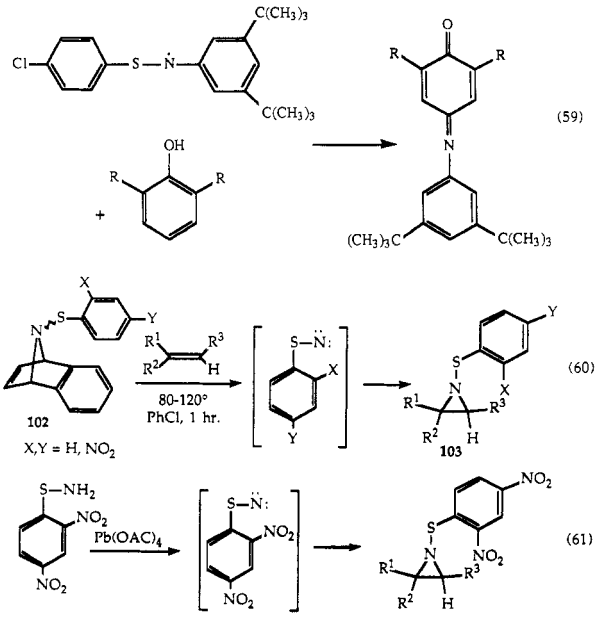
radicals are persistent compared to other aminyl radicals. The sterically protected aminyl **95**, in which R^1 = *tert*-butyl and $R^4 = NO_2$, has been isolated as pure crystals and is a stable solid in the presence of oxygen.[116] From ESR spectral data it appears that the conformations of these radicals are affected by the nature of the ortho substituents on the *N*-aryl and *S*-aryl rings. Thus **95a** (R^1 = H, CH_3, OCH_3, *i*-C_3H_7; $R^2 = R^3$ = H; R^4 = H, Cl, NO_2) has the geometry shown, whereas in **95b** (R^1 = *tert*-butyl; $R^2 = R^3$ = H; $R^4 = NO_2$, Cl) the plane of the *N*-aryl ring is twisted out of conjugation, with the nitrogen p orbital containing the unpaired electron for steric reasons. In **95c** ($R^1 = OCH_3$, H; $R^2 = R^4 = CH_3$; R^3 = Cl), the plane of the *S*-aryl ring is perpendicular to the plane of the *N*-aryl ring, also for steric reasons.

N-((4-Chlorophenyl)thio)-3,5-di-*tert*-butylphenylaminyl radicals, which are in stable equilibrium with their hydrazine dimers at room temperature in benzene,[117] decompose over time to form the sulfenamide **96**, 1,3,5,7-tetra-*tert*-butylphenazine (**97**), *N*,*N*-bis((4-



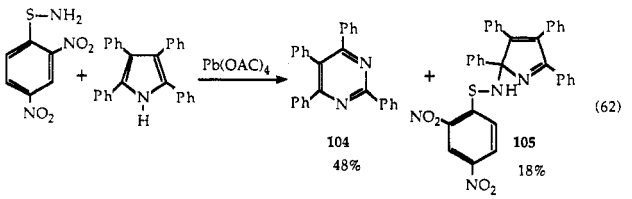
chlorophenyl)thio)-3,5-di-*tert*-butylaniline (**98**), and 3,3′,5,5′-tetra-*tert*-butylazobenzene (**99**) as major products. Minor amounts of **100** and **101** were also found. From the stoichiometry of the products, it is deduced that the azobenzene is the product of the dimer, whereas the other major products come from hydrogen extraction and radical coupling via the monomer.[118] The same aminyl radicals react with phenols to give as major products *p*-benzoquinone 3,5-di-*tert*-butylphenylimines (eq 59)[119] via the phenoxide radical.

Atkinson and Malpass report that (arylsulfenyl)nitrenes are efficiently generated thermally from sulfenamides **102** and trapped by alkenes to give the corresponding aziridines **103** in quantitative yield (eq 60).[120] Nitrenes can also be generated by oxidation of

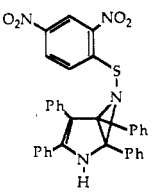


arylsulfenamides with lead tetraacetate (eq 61),[121] but they are not as efficiently trapped by alkenes as are the nitrenes generated under the milder conditions of cheleotropic extrusion. Only the ((2,4-dinitrophenyl)sulfenyl)nitrene can be trapped.

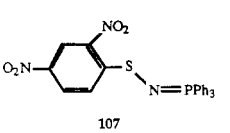
When ((2,4-dinitrophenyl)sulfenyl)nitrene is generated by lead tetraacetate oxidation in the presence of 2,3,4,5-tetraphenylpyrrole, 2,4,5,6-tetraphenylpyrimidine (**104**) and 2-(((2,4-dinitrophenyl)thio)amino)-2,3,4,5-tetraphenyl-2*H*-pyrrole (**105**) are isolated as the major products (eq 62).[122] Both products are



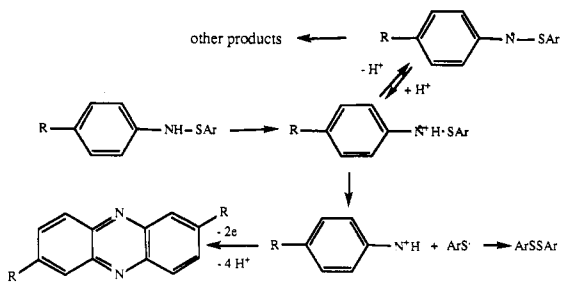
believed to arise from an aziridine intermediate, **106**. Disrotatory ring opening accompanied by loss of the sulfide anion yields the pyrimidine, while competing acid-catalyzed (by acetic acid) ring opening of the aziridine produces the sulfenamide.



Kemmitt et al. report that ((2,4-dinitrophenyl)sulfenyl)nitrene, generated thermally from sulfenamide **102**, reacts with *trans*-[IrCl(CO)(PPh_3)$_2$] in refluxing toluene to produce (((2,4-dinitrophenyl)sulfenyl)imino)triphenylphosphorane (**107**).[123] The structure of **107** was confirmed by X-ray diffraction, which indicated the presence of an S–N single bond and a P=N double bond.



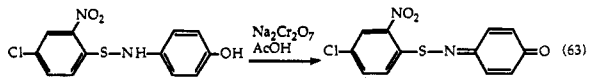
SCHEME VI



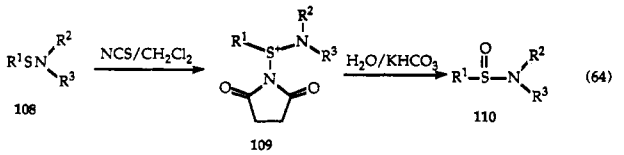
Less is known about the thermal reactions of alkylsulfenamides, but there is general agreement that alkylsulfenamides show less thermal stability than arylsulfenamides.[3]

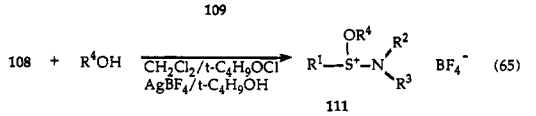
D. Oxidation and Reduction Reactions

Oxidation of sulfenamides can occur at nitrogen or at sulfur. 4- or 2-hydroxy sulfenanilides are oxidized to sulfenylquinone imines with sodium dichromate (eq 63).[1]



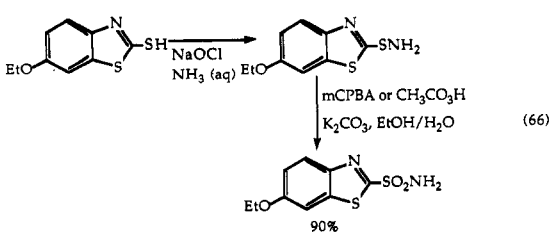
Haake and co-workers report that *N,N*-dialkylsulfenamides **108** are readily oxidized to sulfinamides **110** via their succinimidosulfonium salts **109** (eq 64).[124]



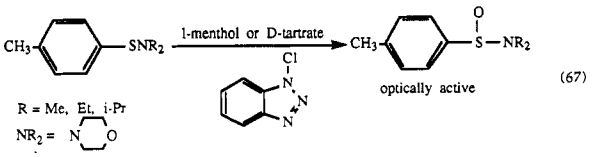


The same authors report that the derivatives **111** of sulfinamides **108** are obtained when sulfenamides are oxidized with *tert*-butyl hypochlorite in the presence of alcohols and silver tetrafluoroborate (eq 65).[125] Salts **111** are fairly stable at room tempertaure for primary and secondary alcohols, and this route to their preparation is more general than direct alkylation of sulfinamides with Meerwein type reagents.

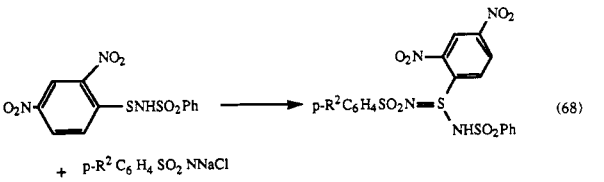
The efficient synthesis of 6-ethoxy-2-benzothiazolesulfonamide by oxidation of the corresponding sulfenamide with *m*-CPBA or peracetic acid has been reported (eq 66).[126] No competing oxidation of the heterocyclic ring was observed. Hydrogen peroxide and *tert*-butyl hydroperoxide did not oxidize the sulfenamide.



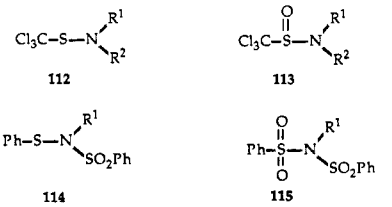
Optically active sulfinamides have been synthesized by the oxidation of sulfenamides with *N*-chlorobenzotriazole in the presence of *l*-menthol or D-tartrate (eq 67).[127]



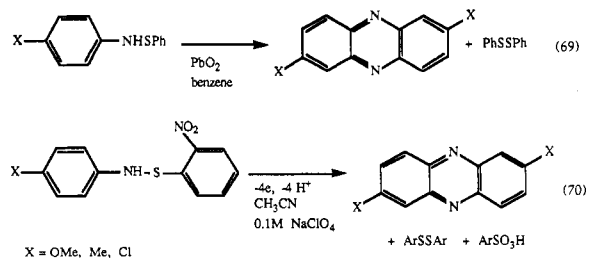
The sulfenamide sulfur has also been oxidized by arylsulfonylimination (eq 68).[128-131] The ease of imination depends on the nucleophilicity of the sulfenamide sulfur and therefore on the acidity characteristics of the sulfenamides.[132] Sulfenamides with $pK_a > 11$, in which the *S*-aryl substituent is electron donating, are readily iminated by sodiochloramides of sulfonic acids in acetone. Sulfenamides with pK_a's of 8–11 are iminated in strongly basic solvents with high dielectric constants or as the sodium salts in acetone. More acidic sulfenamides are iminated in acetone by the sodiochloramides of sulfonic acids. Two equivalents of sodioamide is required in this case, since 1 equiv is consumed in initial formation of the sodiosulfenamide.



Trichloromethanesulfonamides **113** have been prepared from trichloromethanesulfenamides **112** by oxidation with *m*-chloroperoxybenzoic acid.[35] *N*-Alkyl-*N*-(phenylsulfonyl)benzenesulfonamides **115** have been prepared in the same manner from *N*-alkyl(phenylsulfenyl)benzenesulfonamides **114**.[35]

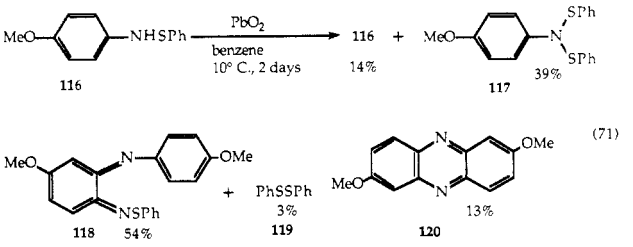


4′-Substituted benzenesulfenanilides and 4′-substituted 2-nitrobenzenesulfenanilides have been oxidized by lead dioxide (eq 69) or by controlled-potential electrolysis (eq 70) to produce phenazines as major products.[133-139] Sayo et al. initially proposed a mechanism involving the formation of benzenesulfenanilidyl radicals in protic equilibrium with radical cations. Homolytic cleavage of the radical cations (Scheme VI) is presumed to produce arylthio radicals, which couple to form the disulfide, and arylamino cations (nitrenium ions), from which the phenazines are believed to form by dimerization of intermediate nitrenes, resulting from the cations by proton loss. In the case of anodic oxi-



dation with $NaClO_4$ as the supporting electrolyte, immediate two-electron oxidation of the sulfenanilide to the dication and subsequent homolytic cleavage are proposed to explain the products formed.

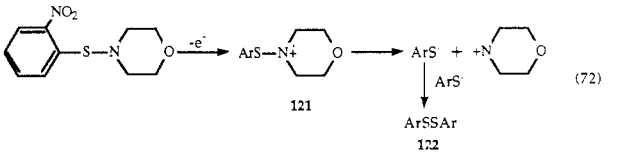
Spagnolo et al. carried out further work on the oxidation of substituted sulfenanilides by lead dioxide and by *tert*-butoxide radical. On the basis of their results they were able to conclude that Sayo's proposed mechanism is incorrect and have proposed an alternative mechanism for the lead dioxide oxidation of 4′-methoxy- and 4′-methoxy-2-nitrobenzenesulfenanilides in benzene.[140,141] When the reaction was run at 10 °C, the product distribution was as shown in eq 71. At 30



(71)

°C, **117** and **118** disappeared over time with a corresponding augmentation in **119** and **120**. It is suggested that the initial arylaminyl radicals undergo C_{ortho}–N coupling (a well-known reaction for these radicals) and that the subsequent product **118** is the intermediate to the phenazine. The fact that Sayo and co-workers used an acid wash to isolate the phenazines from the reaction mixture explains why they did not observe intermediates **117** and **118**. These intermediates are destroyed by HCl, as was demonstrated in a control experiment by Spagnolo and co-workers. The observation of **118** rules out the intermediacy of nitrenium ions in the formation of phenazines under these conditions.

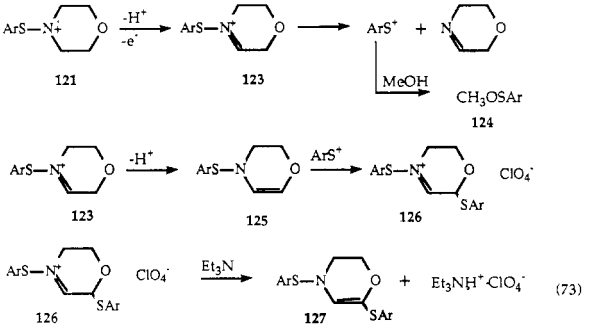
Anodic oxidation of the 2-nitrobenzenesulfenamide of morpholine yields diaryl disulfide **122** in acetonitrile with 0.1 M $NaClO_4$ (eq 72). The major products in



(72)

methanol are methyl 2-nitrobenzenesulfenate (**124**) and 2,4-bis((*o*-nitrophenyl)thio)-5,6-dihydro-2*H*-1,4-oxazinium perchlorate (**126**). The oxazinium perchlorate reacts with triethylamine in acetonitrile to give 2,4-bis((*o*-nitrophenyl)thio)-5,6-dihydro-1,4-oxazine (**127**) (eq 73).[142] Sayo has proposed that in acetonitrile, one-electron oxidation of the sulfenamide produces radical cation **121**. The S–N bond of the cation cleaves homolytically to give the arylthio radicals, which couple to form the disulfide. In methanol, the initially formed radical cation is further oxidized to iminium ion **123** (Scheme VII). This ion can cleave heterolytically (or undergo nucleophilic attack at sulfur by methanol) to yield the sulfenate ester, or it can form enamine **125** through proton loss. Attack by the enamine on **123** would produce oxazinium perchlorate **126**. The stepwise oxidations in Scheme VII are supported experimentally by coulometric *n* values. Data from cyclic voltammetric and ESR studies support the formation of radical cation **121** as the first step in anodic oxidation of the sulfenamide.[143]

SCHEME VII



(73)

Radical cations generated from sulfenamides and diamino sulfides have been obtained by one-electron oxidation (eq 74 and 75).[144] The resulting radicals are

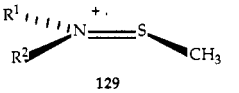
$$MeSNR_2 \xrightarrow[MeNO_2]{AlCl_3 \text{ or } TiCl_4} [MeSNR_2]^{\bullet+} \quad \textbf{128a} \qquad (74)$$

R = Me, Et

$$R_2NSNR_2 \xrightarrow[MeNO_2]{AlCl_3} [R_2NSNR_2]^{\bullet+} \quad \textbf{128b} \qquad (75)$$

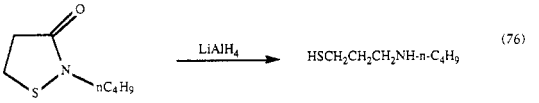
R = Me, Et

not influenced by oxygen and are stable for 20 h at room temperature. Nonequivalence of R^1 and R^2 in **128a** is attributed to restricted rotation around the S–N bond, and conformation **129** is proposed to account for the nonequivalence. This geometry is also supported by ESR data for radical cations electrochemically generated from *N*-((*o*-nitrophenyl)thio) alicyclic amines.[145]



129

Cyclic N-acylated sulfenamides are reductively cleaved by lithium aluminum hydride (eq 76).[146]

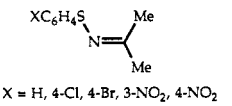


(76)

V. Properties of Sulfenylimines

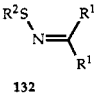
In comparison to the sulfenamides, much less is known about the properties of sulfenylimines. However, there have been several studies of the barriers to stereomutation in sulfenylimines, which are low compared to the inversion barriers in imines, which do not have strong conjugating substituents at nitrogen or at the iminyl carbon.

Davis and co-workers found that the barriers to stereomutation in sulfenylimines **130** are all between 20 and 20.6 kcal/mol.[147] The barriers were found to

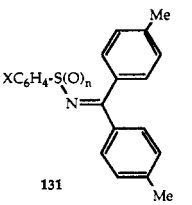


X = H, 4-Cl, 4-Br, 3-NO_2, 4-NO_2

130



132



131

n = 0, 1, 2
X = H, 4-NO_2

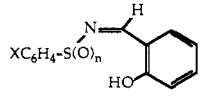
be relatively insensitive to changes in the *S*-aryl sub-

stituent. The UV spectra of these compounds suggested that there is delocalization of the nitrogen lone pair into the aromatic π system. A planar nitrogen inversion mechanism for stereomutation, in which donation of electrons from nitrogen to sulfur stabilizes both the ground state and the transition state, was considered to be consistent with these data.

An NMR study of barriers to planar inversion in *N*-(4,4′-dimethylbenzophenylidene)arenesulfenamides **131** and their sulfinyl and sulfonyl analogues revealed a decrease in the barrier (18 to 13 kcal/mol) as the oxidation state of sulfur increased.[148] This trend was attributed to (p–d) π conjugation between nitrogen and sulfur for sulfur in the higher oxidation states, resulting in greater stabilization of the planar transition state. Steric factors and electronegativity of sulfur were found to be unimportant in determining the barriers in these compounds.

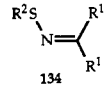
An NMR study of symmetrical *N*-sulfenylimines **132** corroborated the finding that substitution on an *S*-aryl group has little effect on the free energy barrier to stereomutation.[149] However, it was found that substitution at the iminyl carbon and at sulfur did affect the barriers, which are significantly lower when $R^1 = CF_3$ (15.7 kcal/mol) or $R^2 = CCl_3$ (14.8 kcal/mol) than when R^1 or $R^2 = CH_3$ or XC_6H_4 (18–20 kcal/mol). These results were interpreted within the framework of a planar nitrogen inversion mechanism, using an extended-Hückel perturbational approach. According to this model, changes in the free energy of isomerization are produced mainly by overlap of the nitrogen lone pair with filled orbitals in the σ framework of the substituents on the iminyl carbon and on the sulfur in a linear transition state (four-electron interactions). These repulsive interactions are stronger for alkyl substituents.

An NMR and UV study of the transmission of electronic effects through the S–N bond in *N*-alkylidenearenesulfenamides has been reported.[150] Hammett ρ values for the chemical shifts of OH, N=CH, and NH protons were used as the measure of transmission of substituent electronic effects through the S–N bond in compounds **133–135**. The UV spectra of these com-



133 n = 0, 1, 2

X = 4-N(Me)$_2$, 4-OMe, 4-CH$_3$, H, 4-Cl, 3-NO$_2$, 4-NO$_2$, 2-NO$_2$



134

XC_6H_4-S–NHPh

135

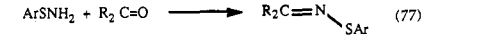
pounds were measured in nonpolar solvents (cyclohexane, acetonitrile, ethanol). Effects of substituents X on the ^1H NMR chemical shifts of the imidyl and hydroxyl protons in **133** pointed to conjugation of the two aryl groups resulting from transmission of electronic effects through the S–N bond. The mechanism has been rationalized in terms of p–π, d–π bonding involving both the sulfur p and d orbitals. Although conjugation is destroyed upon oxidation of sulfur, UV bathochromic shifts in ethanol for sulfinylimines and sulfonylimines **133** (n = 1 and 2) have been attributed to a shift in the tautomeric equilibrium toward the quinone amine form. The lack of such a shift in **133** (n = 0) was attributed to stabilization of the phenolimine form by conjugation of the two aryl groups.

VI. Synthesis of Sulfenylimines

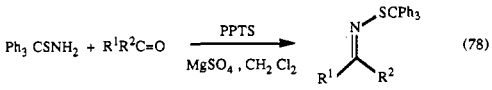
Sulfenylimines can be formed from sulfenamides, disulfides, sulfenyl halides, and sulfenamide enolate equivalents.[4]

A. From Sulfenamides

The arenesulfenamides of ammonia condense with ketones and aldehydes to form the corresponding sulfenylimines (eq 77). This reaction can be acid or base



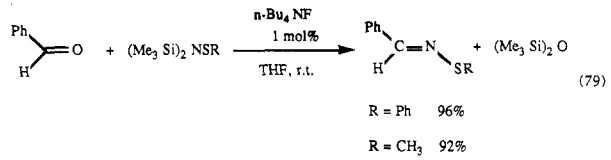
(77)



(78)

catalyzed but does not work with diaryl ketones.[4] Branchaud[151] reports that triphenylmethanesulfenamide also undergoes condensation with ketones and aldehydes to form sulfenylimines when pyridinium *p*-toluenesulfonate (PPTS) is used as a catalyst (eq 78). Again, aromatic and α,β-unsaturated ketones do not react efficiently with this sulfenamide. Thus acetophenone and 3-methyl-2-cyclohexenone gave 59% and 44% yields, respectively, of sulfenylimine when CaH_2 was used as a catalyst and a Soxhlet extractor or Dean–Stark trap was employed.[152]

Morimoto reports a convenient general synthesis of sulfenylimines by the reaction of aldehydes and ketones with *N*,*N*-bis(trimethylsilyl) sulfenamides in the presence of tetrabutylammonium fluoride catalyst (eq 79).[153]



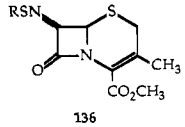
(79)

R = Ph 96%

R = CH_3 92%

The bis(trimethylsilyl) sulfenamides are stable N-unsubstituted sulfenamide synthons, providing easy access to *S*-alkyl sulfenylimines as well as *S*-aryl sulfenylimines. Diaryl ketones also react under these conditions to give sulfenylimines in good yield.

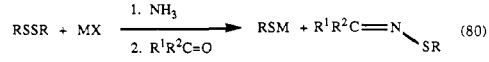
Quinone sulfenylimines have been prepared by oxidation of the corresponding sulfenamides with sodium dichromate in acetic acid.[1] Cephalosporin sulfenamides **136** have been prepared by oxidation of the corresponding sulfenamides with manganese dioxide, *tert*-butyl hypochlorite/triethylamine, *N*-chlorosuccinimide, and other reagents, manganese dioxide being the most effective.[154]



136

B. From Disulfides

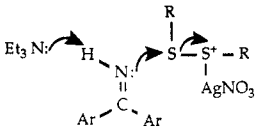
Davis and co-workers have developed a one-step synthesis of sulfenylimines from disulfides, metal salts, ammonia, and aldehydes or ketones (eq 80). The



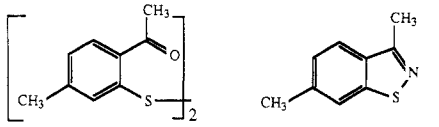
(80)

mechanism is thought to involve the formation of an intermediate sulfenamide, which then condenses with

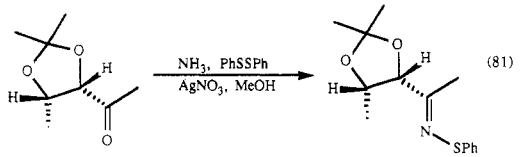
SCHEME VIII



the aldehyde or ketone. An interesting intramolecular application of this method is the formation of the 1,2-benzisothiazole **138** from bis(2-acyl-4-methylphenyl) disulfide (**137**).[155] This method was employed by Fronza et al. to produce intermediate **139** (eq 81) in the synthesis of the *N*-benzoyl derivatives of L-*arabino*-, L-*xylo*-, and L-*lyxo*-2,3,6-trideoxy-3-*C*-methyl-3-amino-hexose.[156]



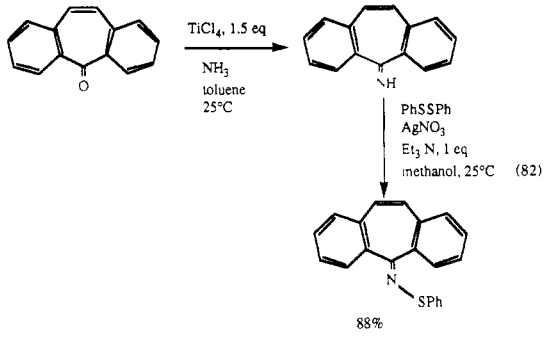
137 138



(81)

139

One limitation of this method is its failure to work with diaryl ketones. In a modification of this method developed by Shepard and co-workers,[157] the ketimines of diaryl ketones react with disulfides in the presence of silver nitrate and 1 equiv of triethylamine to form sulfenylimines in good yield (eq 82). It is believed that

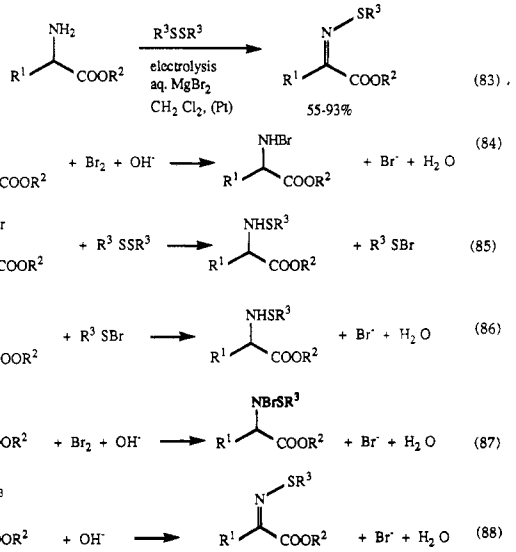


(82)

88%

triethylamine acts as a proton acceptor, in lieu of a second molecule of the ketimine (Scheme VIII). The ketimines are produced under mild conditions from the ketones by addition of ammonia in the presence of titanium tetrachloride.

Torii and co-workers report that sulfenylimines can be synthesized in high yields from the electrolysis of α-amino alkanoates and diaryl or dialkyl disulfides in the presence of $MgBr_2$ (eq 83).[158] Both Mg^{2+} and Br^- are necessary components of the two-phase electrolysis system. It is believed that bromine generated at the anode oxidizes the amine, which then reacts with the disulfide to form a sulfenamide. The sulfenyl bromide thus produced also reacts with the initial amine to form the sulfenamide. The sulfenamide is further oxidized by bromine and dehydrobrominated by $Mg(OH)_2$, formed at the cathode. This base is also responsible for the other proton abstractions in the proposed mechanism (eq 84–88). Separate experiments, in which the proposed sulfenamide intermediates are converted to sulfenylimines under the electrolysis conditions used for coupling of the amines and disulfides, support the proposed mechanism. The *S*-phenyl sulfenylimines of penicillin (72%) and cephalosporin (60%) have been successfully synthesized by this method.



(83)

(84)

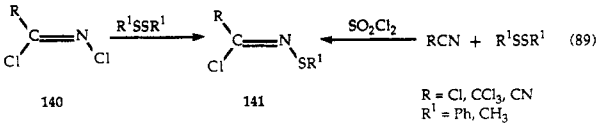
(85)

(86)

(87)

(88)

Diphenyl or dimethyl disulfide will react at room temperature with *N*-chloroformimidoyl chloride **140** to form sulfenylimines **141** in good yield (eq 89). The same disulfides also react with nitriles in the presence of sulfuryl chloride and a catalytic amount of chloride ion to form the sulfenylimines.[159]



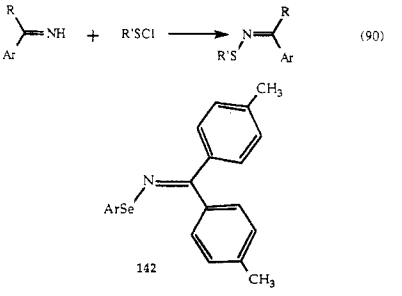
(89)

140 141

R = Cl, CCl_3, CN
R^1 = Ph, CH_3

C. From Sulfenyl Halides

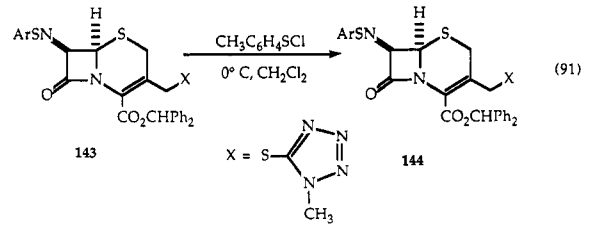
Sulfenyl halides condense with imines ($R_2C{=}NH$) in the presence of base to form sulfenylimines (eq 90). This method makes available the sulfenylimines of diaryl ketones. Selenimine **142** has also been prepared in this manner.[160]



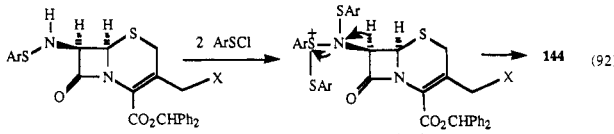
(90)

142

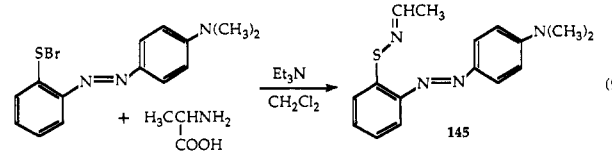
Gordon and co-workers[161] have reported the synthesis of cephalosporin sulfenylimines **144** in high yield from the reaction of cephalosporins **143** with 3 equiv of *p*-toluenesulfenyl chloride in the presence of acid scavengers (propylene oxide, molecular sieves, or sodium bicarbonate) (eq 91). The authors propose a mechanism involving addition of 2 equiv of sulfenyl chloride to the initially formed sulfenamide, followed by β elimination to form the sulfenylimine and an equimolar amount of disulfide (eq 92). An alternative mechanism could involve addition of 1 equivalent of ArSCl to the sulfenamide nitrogen followed by elimination of ArSH. The



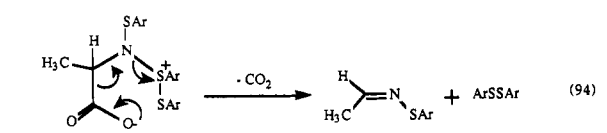
(91)



(92)



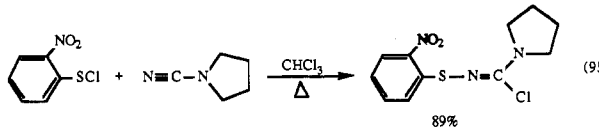
(93)



(94)

thiol could then react with the second equivalent of sulfenyl chloride to form the disulfide. Battacharjee and Dasgupta[162] propose the same mechanism as Gordon et al. for the formation of sulfenylimine **145** from the reaction of alanine and 4-(dimethylamino)azobenzene-2′-sulfenyl bromide in the presence of a catalytic amount of triethylamine (eq 93). In one proposed mechanism, decarboxylation is the key step in formation of the sulfenylimine (eq 94).

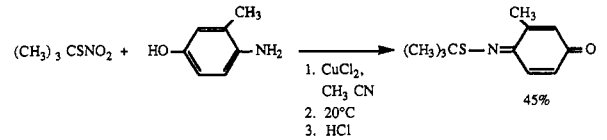
Sulfenyl halides also react with *N*-cyano amines to form sulfenylimines (eq 95).[163]



(95)

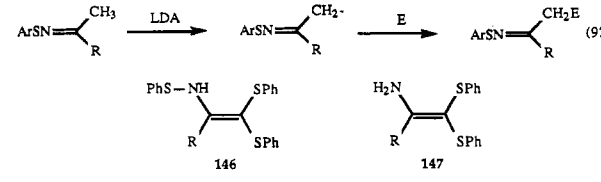
D. Additional Methods

Oae and others have obtained sulfenylimines from the condensation of alkyl thionitrates and *p*-hydroxyanilines in the presence of copper(II) in acetonitrile solvent (eq 96).[164,165] Oxidation of the initially formed sulfenamide by nitrous acid formed in the reaction yields the *p*-benzoquinone imine.

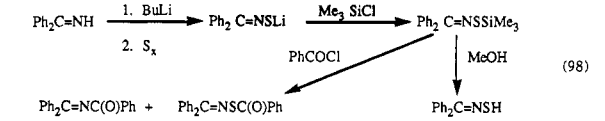


(96)

Davis and co-workers have synthesized α-substituted sulfenylimines from sulfenylimines through the intermediacy of sulfenamide enolate equivalents (SEE) (eq 97).[166a] The use of sulfenylating reagents as electrophiles produces α-(arylthio) sulfenylimines.[166b] α,α-Bis(arylthio) and α,α,α-tris(arylthio) sulfenylimines are also produced in good yield with the proper choice of reaction conditions. When phenyl disulfide is used, the enamino sulfide **147** is also produced via isomerization of the initially formed sulfenylimine to *N*-arylthio enamine **146**. This product can be avoided by using more reactive sulfenylating reagents.

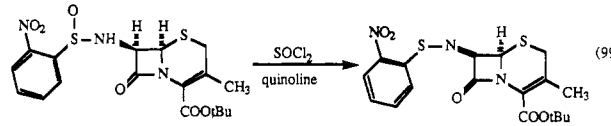


Lithium thiooximates have been generated from the cleavage of bisamine disulfides by *n*-butyllithium, or by lithium in the presence of triethylamine, and alkylated.[167,168] Pike and Walton report a more direct approach to the production of thiooximate ions that avoids the byproducts of disulfide cleavage.[169] Thus benzophenone imine was deprotonated with butyllithium and treated with sulfur to obtain the thiooximate anion (eq 98). The anion was quenched with trimethylsilyl chloride, producing the *S*-(trimethylsilyl)benzophenone thiooxime, stable at −25 °C. This sulfenylimine proved a useful precursor for other sulfenylimines, including the unstable free benzophenone thiooxime.



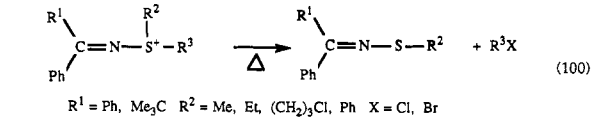
(98)

In his synthesis of cephamycins, Kobayashi has reported an unusual Pummerer-type rearrangement of a sulfinamide to a sulfenylimine (eq 99).[170]

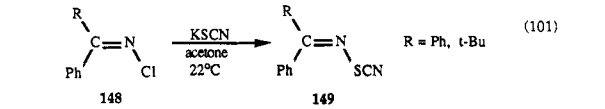


(99)

The thermal decomposition of alkylideneamino sulfonium salts is reported to yield thiooxime *S*-ethers (eq 100).[171] The salts are obtained from α-halogen isocyanates by reaction with sulfoxides, from the reaction of *N*-chloro imines with sulfides, or by alkylation of sulfenylimines with trimethyloxonium hexachloroantimonate. Reck and Jochims also report that treatment of *N*-chloro imines **148** with potassium thiocyanate yields the alkylideneamino thiocyanates **149** (eq 101).[171]

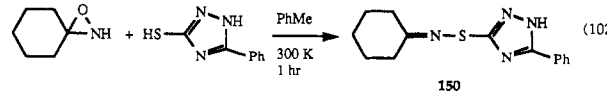


(100)



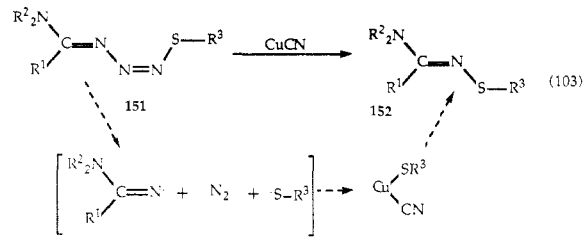
(101)

Andreae and Schmitz have reported the preparation of sulfenylimine **150** by reaction of 1-oxa-2-azaspiro[2.5]octane with the appropriate thiol (eq 102).[172]



(102)

Stansfield and co-workers have reported that triazines **151** extrude nitrogen to form *N*-sulfenamidines **152**.[173] The reaction is catalyzed by CuCN or copper powder and is thought by the authors to involve the coupling of an amidine radical with a copper-stabilized *S*-alkyl radical (eq 103).[174] It could also be explained by an oxidative addition–reductive elimination sequence.

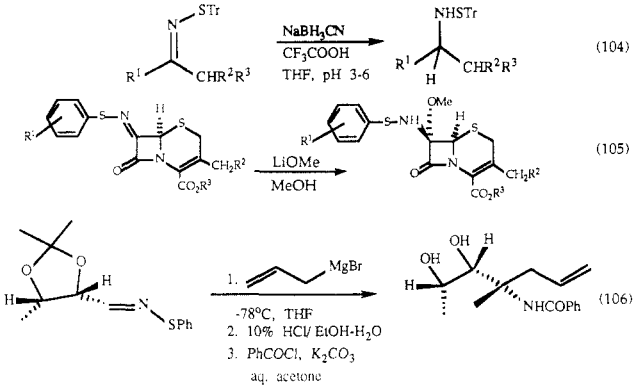


VII. Reactions of Sulfenylimines

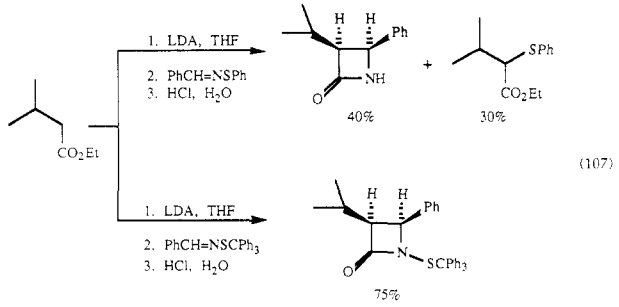
Sulfenylimines are useful intermediates on the route to other products. They undergo reduction at the imine bond and oxidation at sulfur. They undergo nucleophilic addition at the iminyl carbon, electrophilic addition at nitrogen, and alkylation at sulfur. Either the C=N or the N-S bond can be cleaved by hydrolysis. They can also function as sulfenamide enolate equivalents.

A. Reactions of *N*-Sulfenylimines with Nucleophiles

N-Sulfenylimines can serve as intermediates in the synthesis of sulfenamides. The latter may be obtained by reduction of the imines (eq 104)[151] or addition of various nucleophiles to the imine carbon, such as alkoxides (eq 105)[170] and Grignard reagents (eq 106).[156]

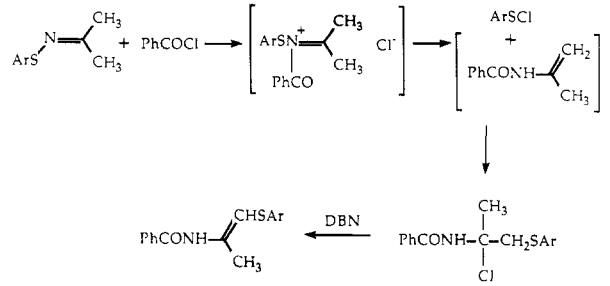


Nucleophilic attack at the iminyl carbon by ester enolates leads to the formation of β-lactams (eq 107).[175] Attack of the ester anion on sulfur is a competing reaction, which can be eliminated by the use of sterically hindered triphenylmethyl sulfenylimines. Enolizable trityl sulfenylimines can also be employed.

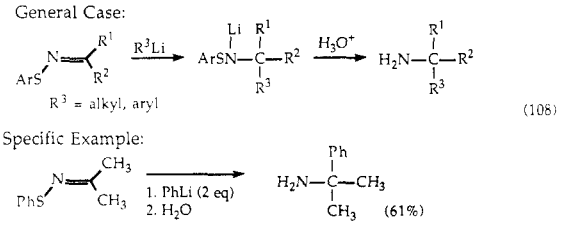


Secondary and tertiary carbinamines are formed by the nucleophilic addition of alkyl- or aryllithium reagents to *N*-alkylidenearenesulfenamides followed by hydrolysis (eq 108).[176] Reported yields range from 43% to 87%. Thus the sulfenylimine serves as a masked imine derivative of ammonia. It is more resistant to hydrolysis than imines derived from ammonia and

SCHEME IX

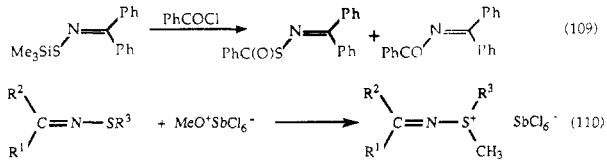


provides, therefore, an excellent starting material for this one-step synthesis of primary amines.

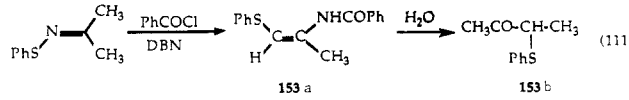


B. Reactions of *N*-Sulfenylimines with Electrophiles

N-Sulfenylimines react with electrophiles at sulfur, resulting in substitution (eq 109)[170] or addition, depending on the nature of the substituent at sulfur. Alkylation on sulfur converts sulfenylimines to alkylideneamino sulfonium salts (eq 110).[171]



The nitrogen, as well, in sulfenylimines can act as a nucleophile. In an attempted Fischer-indole type synthesis of benzo[*b*]thiophenes, Davis and Skibo have reported that *S*-aryl sulfenylimines that are treated with benzoyl chloride in the presence of DBN rearrange to form enamides **153a**, which are readily hydrolyzed to β-keto sulfides **153b** (eq 111).[177]



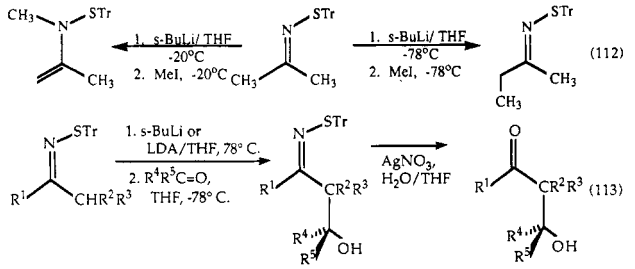
It is believed that a sulfenyl halide is the intermediate in the rearrangement of sulfenylimines to enamides (Scheme IX). The sulfenyl halide results from cleavage of the S-N bond following the electrophilic addition of the benzoyl group to nitrogen.

C. *N*-Sulfenylimines as Sulfenamide Enolate Equivalents

The generation of enolate equivalents by treatment of *N*-sulfenylimines with LDA and their subsequent reaction with electrophiles has been reported by Davis and co-workers (eq 58; vide supra).[166] Sulfenamide enolate equivalents were found to be more reactive than carbonyl enolates but less reactive than enolates derived from *N*,*N*-dimethylhydrazones.

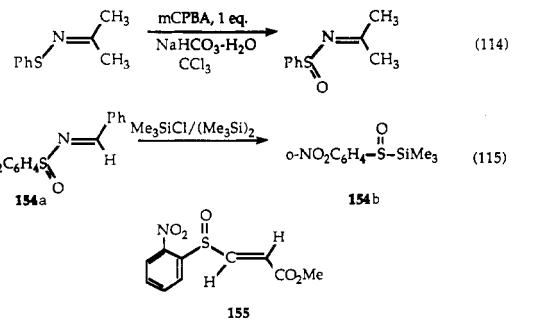
Recently, Branchaud[151,152] has developed *S*-trityl sulfenylimines into very versatile intermediates. Either

end of the imine bond can be alkylated under appropriate conditions (eq 112). The sulfenylimine is also a masked ketone and provides an alternative route to "directed" aldol products (eq 113).



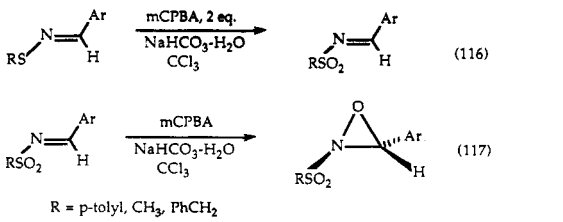
D. Oxidation of *N*-Sulfenylimines

Oxidation of *N*-sulfenylimines affords *N*-sulfinylimines (eq 114).[178,179] *N*-Sulfinylimines derived from



aldehydes (i.e., RS(O)N=CHAr) upon heating are important mild sources of sulfenic acids (RSOH). Thus when *N*-sulfinylimine **154a** was heated in the presence of trimethylsilyl chloride/hexamethyldisilazane (2:1), compound **154b** was obtained (eq 115).[180] Treatment of **154b** with 4 equiv of ethanol in the presence of methyl propynoate yielded compound **155**, confirming the generation of the arenesulfenic acid. Sulfenic acids have been proposed as key intermediates in a number of important biological transformations of organosulfur compounds.

The oxidation of *N*-sulfenylimines to *N*-sulfonylimines has also been reported (eq 116).[181] A two-phase system was found to be a necessary condition for obtaining high yields and clean products. *N*-Sulfenylimines have been further oxidized to form 2-(arylsulfonyl)-3-aryloxaziridines having the *E* configuration (eq 117).[182]

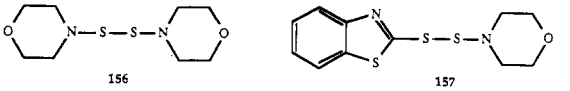


VIII. Applications of Sulfenamides

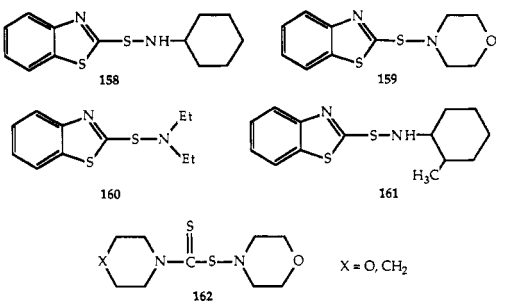
A number of practical applications for sulfenamides have been developed over the years. For many years, sulfenamides have been used as additives in the rubber industry. They have been used in the agrochemical industry as insecticides, fungicides, and ovicides and have been used in materials protection. They have recently been found potentially useful as growth regulators in plants, and some have potential medicinal value. Sulfenamides have also been used as protective groups in peptide and alkaloid synthesis.[1]

A. Sulfenamides in the Rubber Industry

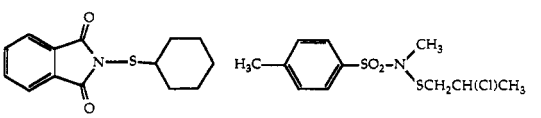
Sulfenamides as a source of sulfur are found to be superior to elemental sulfur as cross-linking agents in the vulcanization of natural and synthetic rubber.[182-199] Their use provides greater operational safety and higher cross-linkage yields. In addition, vulcanizates using these sulfur sources display improved heat resistance and less tendency toward revulcanization. *N,N'*-Dithiobis(morpholine) (**156**) and 2-morpholinodithiobenzo-1,3-thiazole (**157**) are typical of these vulcanizing agents.



Benzo-1,3-thiazole-2-sulfenamides are commonly used as vulcanization accelerators.[1,9-11,200-285] These accelerators display a strongly retarded onset of vulcanization, which increases the safety of the operation. They also promote rapid vulcanization and result in products with strong resistance to aging and good elasticity and tensile strength. Typical accelerators are **158**, **159**, **160**,[203] and **161**.[215] More recently, thiocarbamyl sulfenamides such as **162** used in conjunction with benzothiazole sulfenamides are reported to be more efficient accelerators than benzothiazole sulfenamides used alone.[286,287]



Sulfenamides are also used as vulcanization retarders,[288-291] i.e., compounds that prolong the prevulcanization period in rubber mixtures, thus conferring operational safety and allowing adequate flow time for the filling of molds. *N*-Acylated sulfenamides such as *N*-(cyclohexylthio)phthalimide (**163**) are commonly used as vulcanization retarders.[1] *N*-Sulfenyl sulfonamides such as **164**[292] are also effective vulcanization retarders.

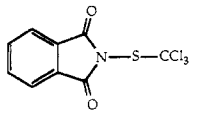


These sulfenamide reagents are often used in varied combinations to meet the requirements of particular vulcanization systems.

B. Sulfenamides in Agriculture

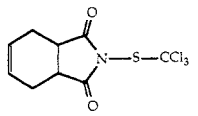
The first two sulfenamide fungicides developed were the trichloromethanesulfenamide of phthalimide (**165**) and tetrahydrophthalimide (**166**). The first is used as a downy-mildew agent in grapes and hop-growing and

as an anti-scab agent in fruit orchards. The second is a foliar fungicide widely used in fruit orchards and as a soil treatment agent.



165

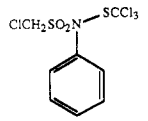
Folpet (Phaltan R)



166

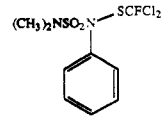
Captan (Orthocid R)

The trichloromethanesulfenamides of alkanesulfonanilides (e.g., **167**) are also effective foliar fungicides. The most effective fungicide of the same type is the *N*-cyclohexyl sulfonamide **169**.[292] Other recently de-



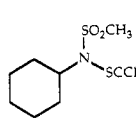
167

Chlorosulfan R

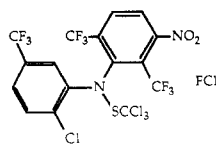


168

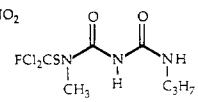
Dichlofluanid



169

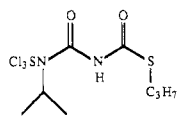


170

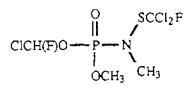


171

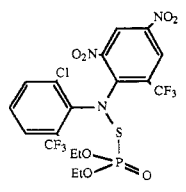
veloped fungicides are the sulfenamides of substituted diphenylamines (**170**),[30,293,294] sulfenamides derived from substituted ureas (**171**, **172**),[295,296] and phosphorus-containing sulfenamides (**173–175**).[297-299] Many of these sulfenamides also display miticidal (acaricidal), ovicidal, and pesticidal activity. The benzoylphenylurea derivative **176** has insecticidal activity against mosquitos.[300] Finally, sulfenamides such as **177** are plant growth regulators.[301] This sulfenamide selectively inhibits lettuce growth without affecting oats. Other variants inhibit stem growth or stimulate root growth in various plants.



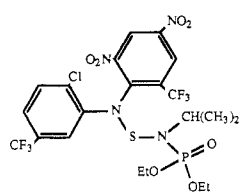
172



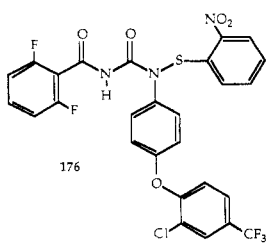
173



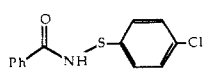
174



175



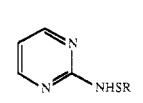
176



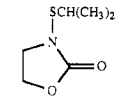
177

C. Medicinal Applications of Sulfenamides

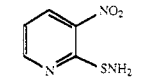
Within the past few years, several sulfenamides have been developed that have potential medicinal applications. The pyrimidinamine sulfenamides **178** (R = Ph, *i*-Pr) are inhibitors of platelet lipoxygenase and of leu-



178

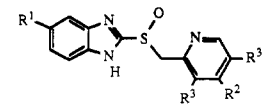


179

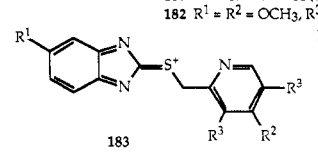


180

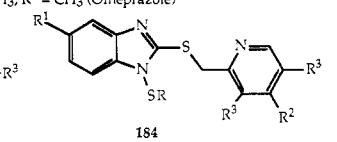
kocyte migration.[302,303] Oxazolidinone sulfenamide **179** displays the same activity as **178** and is an antiasthmatic agent.[304] The pyridyl sulfenamide **180** and other analogues exhibit antitumor activity against Ehrlich tumor cells in ICR female mice.[305] The drug omeprazole (**182**), used to treat gastric ulcers, owes its biological activity to the inhibition of the gastric (H^+/K^+)-ATPase present in the acidic compartments of the parietal cells.[306-308] It is accepted that omeprazole and a num-



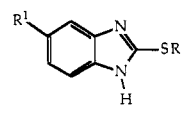
181 $R^1 = R^2 = R^3 = H$ (Timoprazole)
182 $R^1 = R^2 = OCH_3$, $R^3 = CH_3$ (Omeprazole)



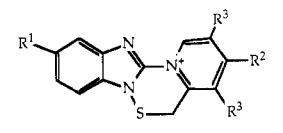
183



184



185



186

ber of related compounds are not active enzyme inhibitors but are transformed in acidic media into the active form. There has been considerable debate concerning the chemical structure of the active form. Several mechanisms have been advanced to account for the inhibition. In part the evidence adduced for these various mechanistic possibilities has derived from reactions of omeprazole and analogues such as timoprazole (**181**) carried out under acidic conditions and/or in the presence of thiols. Small differences in conditions have led to different products isolated by the three groups.

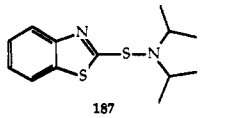
Two of the groups have isolated sulfoxides that they suggest are intermediates (or analogues of intermediates) in the biological reactions of these compounds. The American[306] and German[307] groups have postulated that initial reaction of omeprazole with acid leads to a sulfenium ion **183** via a Pummerer-like reaction. This sulfenium ion was thought to suffer attack by a sulfhydryl group in the enzyme (or from an added mercaptan) either at one of the imidazole nitrogen atoms to form a sulfenamide[306] **184** or at C-2 of the imidazole ring to form a thioketal that could lose either of the two mercapto groups to form a sulfide[307] **185**. Alternatively, the German group postulated that in the absence of added nucleophile the sulfonium salt could be attacked by the pyridine nitrogen to form a spirocyclic intermediate that led to a purple solid whose structure was suggested to be a tetracyclic aromatic mercaptyl radical. The Swedish group[308] also postulated a spirocyclic intermediate, but one derived by attack by the pyridine nitrogen on C-2 of the sulfoxide itself rather than an intermediate sulfonium ion. The spirocyclic sulfoxide was thought to open to a sulfenic acid that could recyclize to form a cyclic sulfenamide **186**. This cyclic

sulfenamide, which could be isolated, was postulated to act as sulfenylating group that would react with a sulfhydryl group in the enzyme to form a disulfide. Thus the three groups have postulated enzymatic deactivation by conversion of an enzymic sulfhydryl group to a sulfide, a sulfenamide, or a disulfide.

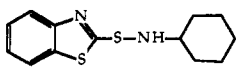
Although further investigations will be required before the mode of action of these interesting compounds is definitively established, it is worth noting that much of the chemistry reported or postulated in these papers has relatively little precedent. For example, the vinylogous Pummerer reaction to form sulfenium ion **183**, while reasonable, has not previously been observed. Similarly, the formation of sulfenamides by reaction of sulfenic acids with amines has not previously been described, although the formation of an S–N bond by reaction of a postulated sulfenic acid form of the enzyme glyceraldehyde-3-phosphate dehydrogenase with phenylhydrazine had been suggested.[309]

D. Miscellaneous Applications

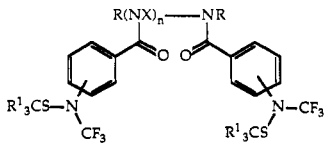
Sulfenamides are also used as load-capacity improvers in lubricants (**187**),[310,311] as wood preservatives (**188**),[312,313] as fungicides in paints,[314] as antimicrobial finishes for textiles,[315] and as an additive to a wood-free thermal recording material (**189**).[316]



187



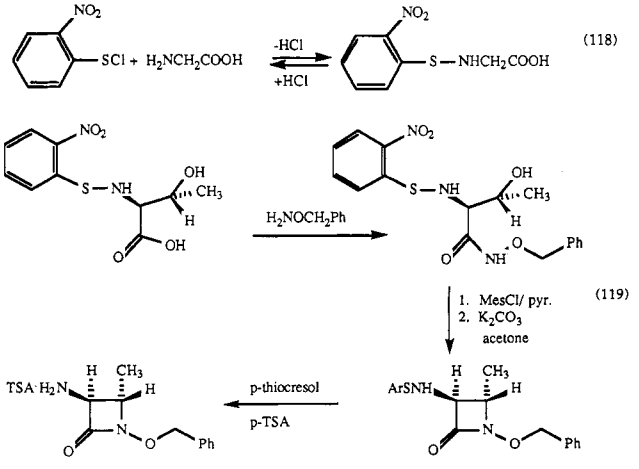
189



188

E. Sulfenamides as Protecting Groups in Synthesis

For over 20 years, the (2-nitrophenyl)sulfenyl group has been used as a protecting group in peptide synthesis. The amino acid sulfenamides of 2-nitrobenzenesulfenyl chloride are generally crystalline compounds and are readily cleaved by anhydrous HCl (eq 118).[317] More recently, this protective group has been used by Gordon et al. in the synthesis of monocyclic β-lactam antibiotics from L-threonine (eq 119).[318]



Sulfenylimines have been used as intermediates in the synthesis of cephalosporins,[161] cephamycins,[154] and carbohydrate derivatives.[156] These intermediates have permitted stereoselective nucleophilic additions to the imine carbon.

Finally, the (triphenylmethyl)sulfenyl group, while not as useful in peptide synthesis as the (*o*-nitrophenyl)sulfenyl group, has proved to be an excellent protecting group in the synthesis of other organic compounds such as the alkaloid δ-coniceine.[152]

IX. References

(1) Kuehle, E. *The Chemistry of the Sulfenic Acids*; Georg Thieme: Stuttgart, 1973.
(2) Brown, C.; Grayson, B. T. *Mech. React. Sulfur Compd.* **1970**, 93.
(3) Davis, F. A. *Int. J. Sulfur Chem.* **1973**, *8*(1), 71.
(4) Davis, F. A.; Nadir, U. K. *Org. Prep. Proced. Int.* **1979**, *11*(1), 33.
(5) Schubart, R. In *Houben Weyl*, Band E11, Par 1, 4th Suppl., 1985, pp 107–122.
(6) Raban, M. In *Organic Sulfur Chemistry*; Friedlina, R. Kh., Skorova, A. G., Eds.; Pergamon: Oxford, 1981; p 141.
(7) Yamamoto, G. *Kagaku no Ryoiki* **1978**, *32*(3), 207.
(8) Raban, M.; Kost, D. *Tetrahedron* **1984**, *40*, 3345.
(9) Rayner, G. H.; Hill, P. *Rubbercon 81, Int. Rubber Conf.* **1981**, *1*, C3.1–C3.13.
(10) Morita, E. *Nippon Gommu Kyokaishi* **1978**, *51*(11), 842.
(11) Kempermann, T. *Bayer-Mitt. Gummi-Ind.* **1980**, *52*, 13.
(12) Raban, M.; Jones, F. B., Jr.; Kenney, G. W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 6677.
(13) Raban, M.; Yamamoto, G. *J. Am. Chem. Soc.* **1979**, *101*, 5890.
(14) Raban, M.; Yamamoto, G. *J. Am. Chem. Soc.* **1977**, *99*, 4160.
(15) Kost, D.; Zeichner, A.; Sprecher, M. A. *J. Chem. Soc., Perkin Trans. 2* **1980**, 317.
(16) Raban, M.; Hu, C.; Craine, L. H. *Tetrahedron Lett.* **1984**, *25*(13), 1337.
(17) Raban, M.; Hu, C.; Craine, L.; Hortelano, E. *J. Org. Chem.* **1985**, *50*, 2205.
(18) Atkinson, R. S.; Judkins, B. D.; Patwardhan, B. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1490.
(19) Atkinson, R. S.; Judkins, B. D. *J. Chem. Soc., Perkin Trans. 2* **1981**, 509.
(20) Meese, C. O.; Walter, W.; Muller, H.-W. *Tetrahedron Lett.* **1977**, 19.
(21) Heimer, N. E.; Field, L. *J. Org. Chem.* **1970**, *35*, 3012.
(22) Harpp, D. N.; Back, T. G.; Snyder, J. P. *Phosphorus Sulfur* **1976**, *1*(2–3), 143.
(23) Raban, M.; Noyd, D.; Bermann, L. *Phosphorus Sulfur* **1976**, *1*(2–3), 153.
(24) Kay, J.; Glick, M.; Raban, M. *J. Am. Chem. Soc.* **1971**, *93*, 5224.
(25) Raban, M.; Lauderback, S. K. *J. Org. Chem.* **1980**, *45*, 2636.
(26) Raban, M.; Moulin, C. P.; Lauderback, S. K.; Swilley, B. *Tetrahedron Lett.* **1984**, *25*(32), 3419.
(27) Hakkinen, Am-M.; Ruostesuo, P. *Magn. Reson. Chem.* **1985** *23*(6), 424.
(28) Kharasch, N.; Potempa, S. J.; Whermeister, L. *Chem. Rev.* **1946**, *39*, 269.
(29) Riez, E. *Bull. Soc. Chim. Fr.* **1966**, 1449.
(30) Grantham, D. D. U.S. Patent 4,323,580, 1982; *Chem. Abstr.* **1982**, *97*, 5979*p*.
(31) Oka, K.; Hara, S. *Tetrahedron Lett.* **1977**, 695.
(32) Miura, Y.; Katsura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*(10), 3004.
(33) Parfenov, E. A.; Fomin, V. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1981**, *51*, 947; *Zh. Obshch. Khim.* **1981**, *51*, 1129.
(34) Phillips, W. G. U.S. Patent 3,988,321, 1976; *Chem. Abstr.* **1977**, *86*, 72168*j*.
(35) Glass, R. S.; Swedo, R. J. *Synthesis* **1977**, 798.
(36) Furukawa, M.; Suda, T.; Hayashi, S. *Chem. Lett.* **1974**, 881.
(37) Senczuk, L.; Sobolewski, H.; Rzemykowska, Z. *Acta Pol. Pharm.* **1979**, *36*(5), 557; *Chem. Abstr.* **1980**, *93*, 204413*s*.
(38) Raban, M.; Chern, L.-J. *J. Org. Chem.* **1980**, *45*, 1688.
(39) Dmitrienko, G. L.; Friesen, R. W.; Carson, L.; Vice, S. F. *Tetrahedron Lett.* **1982**, *23*, 821.
(40) Huynh-Dinh, T.; Namane, A.; Babin, F.; Igolen, J.; Rousselle, J. C.; Fillion, M. P.; Fillion, G. *Tetrahedron Lett.* **1985**, *26*(37), 4443.
(41) Sosnovsky, G.; Krogh, J. A. *Liebigs Ann. Chem.* **1982**, 121.
(42) Raban, M.; Craine, L. H.; King, N., unpublished work.
(43) (a) Raban, M.; Craine, L. H., unpublished work. (b) Senning, A.; Kelly, J. *Acta Chem. Scand.* **1972**, *26*, 2877. (c) Traynelis, V. J.; Rieck, J. N. *J. Org. Chem.* **1973**, *38*, 4339.
(44) Parfenov, E. A.; Fomin, V. A.; Maksimova, A. A. *Zh. Obshch. Khim.* **1981**, *51*(5), 1137; *J. Gen. Chem. USSR (Engl. Transl.)* **1981**, *51*, 954.

(45) Armitage, D. A.; Clark, M. J. *J. Chem. Soc. C* **1971**, 2840.
(46) Senning, A.; Jensen, B. *Sulfur Lett.* **1984**, *2*, 11.
(47) Senning, A.; Jensen, B. *Sulfur Lett.* **1983**, *1*(5), 147.
(48) Michalski, J.; Potrzebowdki, M.; Lopusinski, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*(2), 135.
(49) Kamigata, N.; Hashimoto, S.; Kobayashi, M. *Org. Prep. Proc. Int.* **1983**, *15*(5), 315.
(50) Armitage, D. A.; Clark, M. J.; Kinsey, A. C. *J. Chem. Soc. C* **1971**, 3867.
(51) Major, R. T.; Peterson, L. H. *J. Am. Chem. Soc.* **1956**, *78*, 6181.
(52) Dunbar, J. E.; Rogers, J. H. *J. Org. Chem.* **1966**, *31*, 2842.
(53) Senning, A. *Sulfur Lett.* **1982**, *1*(1), 33.
(54) Harpp, D. N.; Back, T. G. *Tetrahedron Lett.* **1971**, 4953.
(55) Boustany, K. *Chimia* **1970**, *24*, 396.
(56) Boustany, K.; Vander Kooi, J. P. *Tetrahedron Lett.* **1970**, 4983.
(57) See ref 4 and references therein.
(58) Koenigshofen, H.; Nierth, A.; Finzenhagen, M. Ger. Offen. DE 3233395 C1, 1984; *Chem. Abstr.* **1984**, *100*, 209801*q*.
(59) Cobb, A. S.; Williams, D. J. Eur. Pat. Appl. EP 29718, 1981; *Chem. Abstr.* **1981**, *95*, 150644*p*.
(60) Lazovenko, A. N.; Ignatov, V. A.; Maizlish, V. E.; Borodkin, V. F. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1981**, *24*(6), 685; *Chem. Abstr.* **1981**, *95*, 219547*d*.
(61) Saegusa, T.; Ito, Y.; Shimizu, T. *J. Org. Chem.* **1970**, *35*, 2979.
(62) Davis, F. A.; Friedman, A. J.; Kluger, E. W.; Skibo, E. B.; Fretz, E. R.; Milicia, A. P.; LeMasters, W. C. *J. Org. Chem.* **1977**, *42*, 967.
(63) Alicot, M. J. C.; Ciccotto, L.; Tignol, A. P. N. Eur. Pat. Appl. EP 10477, 1980; *Chem. Abstr.* **1980**, *93*, 220730*y*.
(64) Levchenko, E. S.; Bubinina, T. N.; Budnik, L. V. *Zh. Org. Khim.* **1983**, *19*(10), 2158.
(65) Ikehira, H.; Tanimoto, S. *Synthesis* **1983**, 716.
(66) Mel'nikov, N. N.; Khaskin, B. A.; Torgasheva, N. A. *Zh. Obshch. Khim.* **1975**, *45*, 1005; *Chem. Abstr.* **1975**, *83*, 58008*p*.
(67) Khaskin, B. A.; Torgasheva, N. A.; Negrebetskii, V. V. *Zh. Obshch. Khim.* **1983**, *53*(8), 1775.
(68) Torii, S.; Tanaka, H.; Ukida, M. *J. Org. Chem.* **1978**, *43*(16), 3223.
(69) Torii, S.; Tanaka, H.; Ukida, M. *J. Org. Chem.* **1979**, *44*(9), 1554.
(70) Taylor, R. D. U.S. Patent 3,985,743, 1976; *Chem. Abstr.* **1977**, *86*, P30837*w*.
(71) Khamrai, A. K.; Adhikari, B.; Maiti, M. M.; Maiti, S. *Angew. Makromol. Chem.* **1986**, *143*, 39.
(72) Atkinson, R. S.; Awad, S. B. *J. Chem. Soc., Perkin Trans. 1* **1977**, 346.
(73) Atkinson, R. S.; Awad, S. B.; Barlow, J. M.; Russell, D. R. *J. Chem. Res.* **1978**, 331.
(74) Natsugari, H.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7867.
(75) Molina, P.; Arques, A.; Cartagena, I.; Valcarcel, M. V. *Synth. Commun.* **1985**, *15*(7), 643.
(76) Kanakarajan, K.; Meier, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 244.
(77) Huisgen, R.; Peng, X. *Tetrahedron Lett.* **1986**, *27*(50), 6063.
(78) Numeta, J.; Oae, S. *Int. J. Sulfur Chem.* **1971**, 215.
(79) Yamamoto, T.; Kakimoto, M.; Maijima, T.; Okawara, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1249.
(80) Oae, S.; Tsujihara, K.; Furukawa, N. *Tetrahedron Lett.* **1970**, 2663.
(81) Claus, P. K.; Silbernagel, W.; Franek, W.; Rieder, W. *Monatsh. Chem.* **1985**, *116*(6–7), 841.
(82) Katritzky, A. R.; Takahashi, I.; Marson, C. M. *J. Org. Chem.* **1986**, *51*, 4914.
(83) Levchenko, E. S.; Pel'kis, N. P. *Zh. Org. Khim.* **1984**, *20*(3), 672.
(84) Epshtein, L. M.; Zhdanova, A. N.; Dolyopyat, N. S.; Bochvar, D. A.; Gambaryan, N. P.; Kozitsyna, L. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2487; *J. Natl. Acad. Sci. USSR, Chem. Ser. (Engl. Transl.)* **1980**, 2302.
(85) Fontana, A.; Scoffone, E. *Mech. React. Sulfur Compd.* **1969**, *4*, 14.
(86) Haas, A.; Lorenz, R. *Z. Anorg. Allg. Chem.* **1971**, *385*, 33.
(87) Kuehle, E.; Hagemann, H.; Oehlmann, L.; Wendisch, D. *Synthesis* **1982**, 949.
(88) Mitchell, J. A.; Reid, D. H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 499.
(89) Khaskin, B. A.; Torgasheva, N. A.; Mel'nikov, N. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1979**, *49*(6), 1250.
(90) Parfenov, E. A.; Fomin, V. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1981**, *51*, 961; *Zh. Obshch. Khim.* **1981**, *51*, 1144.
(91) Zhmurova, I. N.; Yurchenko, V. G.; Pinchuk, A. M. *J. Gen. Chem. USSR (Engl. Transl.)* **1985**, *55*, 281; *Zh. Obshch. Khim.* **1985**, *55*(2), 321.
(92) See ref 3 and references therein.
(93) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *Tetrahedron Lett.* **1986**, *27*(15), 1739.
(94) Torii, S.; Sayo, N.; Tanaka, H. *Chem. Lett.* **1980**, 695.
(95) Kumamoto, T.; Kobayashi, S.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 866.
(96) Hiroi, K.; Nishida, M.; Nakayama, A.; Nakazwa, K. *Chem. Lett.* **1979**, 969.
(97) Mukaiyama, T.; Hosoi, K.; Inokuma, S.; Kumamoto, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2453.
(98) Woulfe, S. R.; Iwagami, H.; Miller, M. J. *Tetrahedron Lett.* **1985**, *26*, 3891.
(99) Ignatov, V. A.; Akchurina, R. A.; Pirogov, P. A.; Bairakova, R. S. *Zh. Obshch. Khim.* **1981**, *51*(3), 609; *J. Gen. Chem. USSR (Engl. Transl.)* **1981**, *51*, 483.
(100) Ignatov, V. A.; Degtyarev, L. S.; Razgovorov, B. A. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1981**, *24*(9), 1074; *Chem. Abstr.* **1981**, *95*, 219514*r*.
(101) Ignatov, V. A.; Akchurina, R. A.; Volkov, I. V.; Pirogov, P. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1977**, *47*(5), 1004; *Zh. Obshch. Khim.* **1977**, *47*(5), 1096.
(102) Bilozor, T. K.; Yarish, M. E. *Visn. L'viv. Politekh. Inst.* **1983**, *171*, 40; *Chem. Abstr.* **1983**, *99*, 158370*z*.
(103) Brownbridge, P. *Tetrahedron Lett.* **1984**, *25*(34), 3759.
(104) Gilchrist, T. L.; Rees, C. W.; Vaughan, D. *J. Chem. Soc., Chem. Commun.* **1978**, 1049.
(105) Davis, F. A.; Fretz, E. R.; Horner, C. J. *J. Org. Chem.* **1973**, *38*, 690.
(106) Davis, F. A.; Johnston, R. P., II. *J. Org. Chem.* **1972**, *37*, 859.
(107) Davis, F. A.; Horner, C. J.; Fretz, E. R.; Stackhouse, J. F. *J. Org. Chem.* **1973**, *38*, 695.
(108) Cava, M. P.; Blake, C. E. *J. Am. Chem. Soc.* **1956**, *78*, 5444.
(109) Davis, F. A.; Wetzel, R. B.; Devon, T. J.; Stackhouse, J. F. *J. Org. Chem.* **1971**, *36*, 799.
(110) Barton, D. H. R.; Nakano, T.; Sammes, P. G. *J. Chem. Soc. C* **1968**, 322.
(111) Goudie, R. S.; Preston, P. N. *J. Chem. Soc. C* **1971**, 3081.
(112) Olekhnovich, L. P.; Minkin, V. I.; Mikhailov, I. E.; Ivanchenko, N. M.; Zhdanov, Yu. A. *Dokl. Aka. Nauk SSSR* **1977**, *233*, 874; *Chem. Abstr.* **1977**, *87* 52497*h*.
(113) Olekhnovich, L. P.; Mikhailov, I. E.; Ivanchenko, N. M.; Zhdanov, Yu. A.; Minkin, V. I. *Zh. Org. Khim.* **1979**, *15*, 1355 (Engl. p 1121); *Chem. Abstr.* **1979**, *91*, 210648*x*.
(114) Davis, F. A.; Skibo, E. B. *J. Org. Chem.* **1976**, *41*(8), 1333.
(115) Miura, Y.; Katsura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*(4), 1121.
(116) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Chem. Soc., Chem. Commun.* **1980**, 37.
(117) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Org. Chem.* **1980**, *45*, 3875.
(118) Miura, Y.; Yamamoto, A.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3215.
(119) Miura, Y.; Yamamoto, A.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1476.
(120) Atkinson, R. S.; Lee, M.; Malpass, J. R. *J. Chem. Soc., Chem. Commun.* **1984**, 919.
(121) Atkinson, R. S.; Judkins, B. D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2615.
(122) Atkinson, R. S.; Judkins, B. D.; Russell, D. R.; Sherry, L. J. S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1967.
(123) Chiu, K. W.; Fawcett, J.; Kemmitt, R. D. W.; Russell, D. R. *J. Chem. Soc., Dalton Trans. 2* **1986**, 457.
(124) Haake, M.; Gebbing, H.; Benack, H. *Synthesis* **1979**, 97.
(125) Haake, M.; Gebbing, H. *Synthesis* **1979**, 98.
(126) Larsen, R. D.; Roberts, F. E. *Synth. Commun.* **1986**, *18*(8), 899.
(127) Okuma, K.; Doikawa, T.; Ohta, H.; Kobayashi, M. *Fukuoka Daigaku Rigaku Shuho* **1982**, *12*(2), 105; *Chem. Abstr.* **1983**, *98*, 197702*h*.
(128) Koval, I. V.; Oleinik, T. G.; Kremlev, M. M. *Zh. Org. Khim.* **1981**, *17*(3), 565; *Chem. Abstr.* **1981**, *95*, 61668*g*.
(129) Koval, I. V.; Tarasenko, A. I.; Kremlev, M. M.; Molchanova, N. P. *Zh. Org. Khim.* **1981**, *17*(3), 533; *Chem. Abstr.* **1981**, *95*, 80365*x*.
(130) Koval, I. V.; Oleinik, T. G.; Kremlev, M. M. *Zh. Org. Khim.* **1980**, *16*(3), 633; *Chem. Abstr.* **1980**, *93*, 71232*h*.
(131) Koval, I. V.; Oleinik, T. G.; Kremlev, M. M. *Zh. Org. Khim.* **1979**, *15*(11), 2319; *Chem. Abstr.* **1980**, *92*, 180765*j*.
(132) Koval, I. V.; Oleinik, T. G.; Tarasenko, A. I.; Kremlev, M. M. *J. Org. Chem. USSR (Engl. Transl.)* **1986**, *22*, 2358; *Zh. Org. Khim.* **1985**, *21*(12), 2578.
(133) Sayo, H.; Mori, K.; Ueda, A.; Michida, T. *Chem. Pharm. Bull.* **1978**, *26*, 1682.
(134) Sayo, H.; Mori, K.; Michida, T. *Chem. Pharm. Bull.* **1979**, *27*, 351.
(135) Sayo, H.; Mori, K.; Michida, T. *Chem. Pharm. Bull.* **1979**, *27*, 2093.
(136) Sayo, H.; Mori, K.; Michida, T. *Chem. Pharm. Bull.* **1979**, *27*, 2316.
(137) Sayo, H.; Mori, K.; Michida, T. *Chem. Pharm. Bull.* **1980**, *28*, 3707.
(138) Sayo, H.; Mori, K.; Michida, T. *Chem. Pharm. Bull.* **1981**, *29*, 2598.

(139) Sayo, H.; Mori, K.; Michida, T. *Chem. Pharm. Bull.* **1982**, *30*, 3782.
(140) Benati, L.; Montevecci, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1982**, 3049.
(141) Balboni, C.; Benati, L.; Montevecci, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2111.
(142) Sayo, H.; Yamada, Y.; Michida, T. *Chem. Pharm. Bull.* **1983**, *31*, 4530.
(143) Sayo, H.; Michida, T. *Chem. Pharm. Bull.* **1985**, *33*(6), 2541.
(144) Izuoka, A.; Kobayashi, M. *Chem. Lett.* **1981**, 1603.
(145) Sayo, H.; Michida, T. *Chem. Pharm. Bull.* **1985**, *33*(8), 3271.
(146) Luttringhaus, A.; Schneider, R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 67.
(147) Davis, F. A.; Slegeir, W. A.; Kaminski, J. M. *J. Chem. Soc., Chem. Commun.* **1972**, 634.
(148) Davis, F. A.; Kluger, E. W. *J. Am. Chem. Soc.* **1976**, *98*, 302.
(149) Brown, C. ; Grayson, B. T.; Hudson, R. F. *J. Chem. Soc., Perkin Trans. 2* **1979**, 427.
(150) Davis, F. A.; Kaminski, J. M.; Kluger, E. W.; Freilich, H. S. *J. Am. Chem. Soc.* **1975**, *97*, 7085.
(151) Branchaud, B. P. *J. Org. Chem.* **1983**, *48*(20), 3531.
(152) Branchaud, B. P. *J. Org. Chem.* **1983**, *48*(20), 3538.
(153) Morimoto, T.; Nezu, Y.; Achiwa, K.; Sekiya, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1584.
(154) Kobayashi, T.; Iino, K.; Hiraoka, T. *J. Am. Chem. Soc.* **1977**, *99*, 5505.
(155) Davis, F. A.; Slegeir, W. A. R.; Evans, S.; Schwartz, A.; Goff, D. L.; Palmer, R. *J. Org. Chem.* **1973**, *38*, 2809.
(156) Fronza, G.; Fuganti, C.; Grasselli, P.; Pedrocci-Fantoni, G. *Tetrahedron Lett.* **1981**, *22*(50), 5073.
(157) Brenner, D. G.; Cavolowsky, K. M.; Shepard, K. L. *J. Heterocycl. Chem.* **1985**, *22*(3), 805.
(158) Torii, S.; Tanaka, H.; Hamano, S.; Tada, N.; Nokami, J.; Sasaoka, M. *Chem. Lett.* **1984**, 1823.
(159) Brumistrov, S. I.; Glazkow, V. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1952**, *22*, 1901.
(160) Davis, F. A.; Kluger, E. W. *J. Am. Chem. Soc.* **1976**, *98*, 302.
(161) Gordon, E. M.; Chang, H. W.; Cimarusti, C. M. *J. Am. Chem. Soc.* **1977**, *99*, 5504.
(162) Bhattacharjee, S. K.; Dasgupta, S. K. *Curr. Sci.* **1981**, *50*(18), 813.
(163) Ried, W.; Dietschmann, H.; Erle, H. E. *Synthesis* **1980**, 619.
(164) Oae, S.; Shinhama, K.; Kim, Y. H. *Chem. Lett.* **1979**, 1077.
(165) Wako Pure Chemical Industries, Ltd. Jpn. 81 65,866, 1981; *Chem. Abstr.* **1981**, *95*, 168784*u*.
(166) (a) Davis, F. A.; Mancinelli, P. A. *J. Org. Chem.* **1978**, *43*, 1797. (b) Davis, F. A.; Mancinelli, P. A. *J. Org. Chem.* **1980**, *45*, 2597.
(167) Barton, D. H. R.; Magnus, P. D.; Pennanen, S. I. *J. Chem. Soc., Chem. Commun.* **1974**, 1007.
(168) Brown, C.; Gregson, B. T.; Hudson, R. F. *J. Chem. Soc., Chem. Commun.* **1974**, 1007.
(169) Pike, S.; Walton, D. R. M. *Tetrahedron Lett.* **1980**, *21*(51), 4989.
(170) Kobayashi, T.; Iino, K.; Hiraoka, T. *Chem. Pharm. Bull.* **1979**, *27*(11), 2727.
(171) Reck, R.; Jochims, J. C. *Chem. Ber.* **1982**, *115*, 1494.
(172) Andreae, S.; Schmitz, E. East Ger. DD 210685 A1, 1984; *Chem. Abstr.* **1985**, *102*, 6497*p*.
(173) Beddoes, R. L.; Cernik, R. J.; Mills, O. S.; Stansfield, F. *J. Chem. Soc., Chem. Commun.* **1983**, 390.
(174) Stansfield, F. *J. Chem. Soc., Perkin Trans. 1* **1984**, *51*, 2933.
(175) Burnett, D. A.; Hart, D. J.; Jun Liu *J. Org. Chem.* **1986**, *51*, 1929.
(176) Davis, F. A.; Mancinelli, P. A. *J. Org. Chem.* **1977**, *42*, 398.
(177) Davis, F. A.; Skibo, E. B. *J. Org. Chem.* **1974**, *39*, 807.
(178) Davis, F. A.; Friedman, A. J.; Kluger, E. W. *J. Am. Chem. Soc.* **1974**, *96*, 5000.
(179) Davis, F. A.; Friedman, A. J.; Nadir, U. K. *J. Am. Chem. Soc.* **1978**, *100*, 2844.
(180) Davis, F. A.; Friedman, A. J. *J. Org. Chem.* **1976**, *41*, 897.
(181) Davis, F. A.; Lamendola, J., Jr.; Nadir, U. K.; Kluger, E. W.; Sedergran, T. C.; Panunto, T. W.; Billmers, R.; Jenkins, R., Jr.; Turchi, I. J.; Watson, W. J.; Chen, J. S.; Kimura, M. *J. Am. Chem. Soc.* **1980**, *102*, 2000.
(182) Dontsova, A. A.; Novitskaya, S. P.; Kuzin, V. S.; Stepanova, L. N. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1977**, *20*(3), 432; *Chem. Abstr.* **1977**, *86*, 191078*q*.
(183) Esaulova, A. V.; Kykin, A. S.; Sapronov, V. A.; Alekseeva, I. K.; Katsobashvili, V. Ya.; Sal'nikova, G. A.; Kulikova, T. N.; Klenova, N. I. USSR 681,073, 1979; *Chem. Abstr.* **1979**, *91*, P176495*h*.
(184) Verveloet, C.; Deaville, W. D. Brit. 1,589,570, 1981; *Chem. Abstr.* **1981**, *95*, P188083*t*.
(185) Zinchenko, A. V.; Frenkel, R. Sh.; Tikhonov, S. I. USSR 1,639,902, 1978; *Chem. Abstr.* **1979**, *90*, P105382*n*.
(186) Anisimova, E. G.; Pasternak, V. Sh.; Galata, L. A.; Kofman, L. S. *Kauch. Rezina* **1979**, (11), 12.
(187) Barnes, C.; Sylvest, R. T. *GAK, Gummi, Asbest., Kunstst.* **1983**, *36*(4), 150.
(188) Dunn, J. R. Eur. Pat. Appl. EP 122109 A1, 1984; *Chem. Abstr.* **1984**, *101*, 132245*x*.
(189) Japan Synthetic Rubber Co., Ltd. JP 55/139439 [80/139439], 1980; *Chem. Abstr.* **1981**, *94*, 104709*v*.
(190) Meilakhs, L. A.; Gorelik, R. A.; Popov, I. T.; Shmuilovich, L. V.; Lepeshenkova, I. E. USSR SU 1070142 A1, 1984; *Chem. Abstr.* **1984**, *100*, 2121447*x*.
(191) Osaka Soda Co., Ltd. JP 57/151634 A2 [82/151634], 1982; *Chem. Abstr.* **1983**, *98*, 108681*k*.
(192) Osaka Soda Co., Ltd. JP 59/142239 A2 [84/142239], 1984; *Chem. Abstr.* **1985**, *102*, 114936*q*.
(193) Polyak, M. A.; Babyuk, D. N.; Kostrykina, G. I.; Turov, B. S.; Zakharov, N. D.; Golitsyn, A. N. USSR SU 802316, 1981; *Chem. Abstr.* **1981**, *94*, 193516*v*.
(194) Prokhorovskii, Yu. F.; Shikhirev, N. E.; Pukhov, A. P. *Kauch. Rezina* **1980**, (6), 34.
(195) Shevchenko, Yu. G.; Oleinik, G. E.; Dzyura, E. A.; Panasyuk, M. V.; Panchuk, F. D.; Kolobenin, V. N. USSR SU 891706 A1, 1981; *Chem. Abstr.* **1982**, *96*, 201110*s*.
(196) Sinel'nichenko, G. B.; Petrova, L. F.; Blokh, G. A. *Izv. Vyssh. Uchebn. Zaved., Tekhnol. Legk. Prom-sti.* **1983**, *26*(6), 57.
(197) Stenberg, B.; Jansson, J. F. *J. Macromol. Sci., Phys.* **1981**, *B19*(1), 143.
(198) Titarenko, S. A.; Bukhina, M. F.; Klyuchinikova, L. F.; Kozlova, T. A. *Kauch. Rezina* **1980**, (5), 18.
(199) Yuzhakova, N. A.; Anfimova, E. A.; Lykin, A. S.; Shumanov, L. A. *Kauch. Rezina* **1984**, (7), 12.
(200) Paste, J. *Rev. Gen. Caoutch. Plast.* **1980**, *606*, 133.
(201) Chakravarty, S. N.; Pandit, R. R. *Indian J. Technol.* **1976**, *14*, 180.
(202) Franz, C. A. Ger. Offen. 2,827,933, 1979; *Chem. Abstr.* **1979**, *90*, P122845*h*.
(203) Kleemann, W.; Beger, R.; Waschkowiak, J.; Seelig, H.; Meister, A. East Ger. 142,544, 1980; *Chem. Abstr.* **1981**, *94*, P141007*k*.
(204) Ricordeau, Y.; Katzanevas, F. *Rev. Gen. Caoutch. Plast.* **1983**, *633*, 75.
(205) Schubart, R.; Eholzer, U.; Kempermann, T.; Roos, E. Ger. Offen. 2,918,469, 1980; *Chem. Abstr.* **1981**, *94*, P67058*j*.
(206) Severina, N. C.; Gal'perina, N. M.; Bukhina, M. F. *Kauch. Rezina* **1984**, (5), 8.
(207) Soos, I.; Nagy, K. *GAK, Gummi, Asbest., Kunstst.* **1980**, *33*(9), 608–10, 612.
(208) Torii, S.; Tanaka, H.; Ukita, M. Jpn. Kokai Tokyo Koho 79,115,323, 1979; *Chem. Abstr.* **1980**, *92*, P84927*t*.
(209) Acetta, A.; Vergnaud, J. M. *Rubber Chem. Technol.* **1981**, *54*(2), 302.
(210) Adhikari, B.; Pal, D.; Basu, D. K.; Chaudhuri, A. K. *Rubber Chem. Technol.* **1983**, *56*(2), 327.
(211) Aisin Kako Co., Ltd. JP 58/189246 A2 [83/189246], 1983; *Chem. Abstr.* **1984**, *100*, 104921*a*.
(212) Ashida, M.; Nakatani, M.; Takemoto, Y. *Kenkyu Hokoku-Asahi Garasu Kogyu Gijutsu Shoreikai* **1982**, *41*, 97; *Chem. Abstr.* **1983**, *99*, 71975*b*.
(213) Banerjee, B.; Chakravarty, S. N. *J. Indian Chem. Soc.* **1982**, *59*(3), 403.
(214) Basu, K. K.; Adhikari, B.; Pal, D.; Chaudhuri, A. K. *Talanta* **1980**, *27*(8), 671.
(215) Hofmann, W. *Kautsch. Gummi, Kunstst.* **1983**, *36*(12), 1044.
(216) Orlik, I.; Argalas, P.; Jezova, E.; Karvas, M. Czech. 176,039, 1979; *Chem. Abstr.* **1979**, *91*, P40741*e*.
(217) Bavbel, M. A. *Khim. Khim. Tekhnol. (Minsk)* **1983**, *16*, 93.
(218) Beniska, J.; Staudner, E.; Kysela, G.; Fuzy, S.; Rezacova, J.; Bednarcikova, M. *Plasty Kauch.* **1981**, *18*(11), 326.
(219) Bhomick, A. K.; De, S. K. *Rubber Chem. Technol.* **1980**, *53*(5), 1015.
(220) Bridgestone Tire Co., Ltd. JP 59/47239 A2 [84/47239], 1984; *Chem. Abstr.* **1984**, *101*, 74144*a*.
(221) Chakraborty, S. K. *Kautsch. Gummi, Kunstst.* **1983**, *36*(6), 461.
(222) Chakravarti, S. N.; Rajamani, A.; Kapur, A. L.; Mithal, M. *Kautsch. Gummi, Kunstst.* **1981**, *34*(2), 122.
(223) Collins, W.; Brooks, H. L. U.S. Patent 4,463,120 A, 1984; *Chem. Abstr.* **1984**, *101*, 132272*d*.
(224) Das, C. K.; Millns, W. *Kautsch. Gummi, Kunstst.* **1982**, *35*(5), 402.
(225) Das, M. M.; Basu, D. K.; Chaudhuri, A. K. *Kautsch. Gummi, Kunstst.* **1983**, *36*(7), 569.
(226) Das, M. M.; Datta, R. N.; Basu, D. K.; Chaudhuri, A. K. *Kautsch. Gummi, Kunstst.* **1985**, *38*(2), 113.
(227) Datta, R. N.; Das, M. M.; Basu, D. K.; Chaudhuri, A. K. *Rubber Chem. Technol.* **1984**, *57*(5), 879.
(228) Davies, K. M.; Lionnet, R. In *Rubbercon 81, Int. Rubber Conf.* **1982**, *2*, G4.1–G.4.11.
(229) Debnath, K. K.; Munje, I. L.; Ganguli, K. K. *Rubber News* **1983**, *22*(4), 36.
(230) DeFilippo, D.; Rossi, A.; Spezziga, M. A. *Corros. Sci.* **1985**, *25*(3), 217.

(231) Dunn, J. R. *Rubber World* **1984**, *190*(3), 16–8, 20–1, 24–7, 63.
(232) Eisenbrand, G.; Preussmann, R.; Spiegelhalder, B. Ger. Offen. DE 3243141 A1, 1984; *Chem. Abstr.* **1984**, *101*, 132259e.
(233) Ezrielev, A. I.; Kurlyand, V. D.; Marchenko, V. S.; Masagutova, L. V.; Nikolaeva, N. S.; Poluektova, L. E.; Sapronov, V. A.; Sakhnovskii, N. L.; Utkina, L. V. USSR SU 702041, 1979; *Chem. Abstr.* **1980**, *92*, 112058f.
(234) Fujikura Rubber Works, Ltd. JP 55/144037 [80/144037], 1980; *Chem. Abstr.* **1981**, *94*, 104712r.
(235) Ghatge, N. D.; Patil, D. R. *Indian J. Technol.* **1980**, *18*(2), 85.
(236) Gracheva, N. I.; Kornev, A. E.; Ginzburg, L. V.; Potapov, E. E. *Kauch. Rezina* **1984**, (1), 13.
(237) Graves, D. F. U.S. Patent 4,465,829 A, 1984; *Chem. Abstr.* **1984**, *101*, 153324n.
(238) Hepburn, C.; Hassan, A. A. *Int. J. Adhes.* **1981**, *1*(3), 141.
(239) Honskus, J. *Rubber Chem. Technol.* **1983**, *56*(4), 718.
(240) Ishikawa, Y. *Rubber Chem. Technol.* **1984**, *57*(5), 855.
(241) Kawaguchi Chemical Industry Co., Ltd. JP 58/167634 A2 [83/167634], 1983; *Chem. Abstr.* **1984**, *101*, 56332f.
(242) Kawasaki, H.; Kusano, F.; Kodama, S.; Nakatsuka, T.; Itadani, K. *Okayama-ken Kogyo Gijutso Senta Hokoku* **1983**, (9), 33; *Chem. Abstr.* **1985**, *102*, 168160a.
(243) Kharchevnikov, V. M.; Raskin, M. N.; Polivoda, E. N.; Uus, V. N.; Vinogradov, M. V.; Kazarnovskii, A. M.; Gapon, I. I. USSR SU 1106816 A1, 1984; *Chem. Abstr.* **1984**, *101*, 172851y.
(244) Kisela, T.; Beniska, I.; Staudner, E. *Kauch. Rezina* **1984**, (12), 18.
(245) Kitahara, S.; Fujii, T.; Sugi, N. Eur. Pat. Appl. EP 68468 A1, 1983; *Chem. Abstr.* **1983**, *98*, 162229g.
(246) Klucovsky, P.; Maseks, J.; Sudek, V.; Jozsa, L.; Kollar, J. Czech. CS 184052, 1980; *Chem. Abstr.* **1981**, *95*, 25046u.
(247) Komissarova, A. Yu.; Kharchevnikov, V. M.; Porfir'ev, V. I.; Karpova, N. V. *Khim. Tekhnol. Pererab. Elast.* L.54-8, (from *Ref. Zh. Khim.* **1984**, Abstr. No. 5T2060).
(248) Kuriakose, B.; Thomas, K. T.; Thomas, E. V. *Rubber India* **1983**, *35*(11), 9, 11, 13, 15–8.
(249) Lautenschlaeger, K. F.; Edwards, K.; Kirkham, M. C. *Rubber Chem. Technol.* **1979**, *52*(5), 1050.
(250) Leblanc, J. L. *Rheol. Acta* **1981**, *20*(1), 98.
(251) Li, M.-G.; Fu, G.-C.; Cao, H.-T.; Xie, H.-G. *Kao Feu Tzu T'ung Hsun* **1980**, (2), 65; *Chem. Abstr.* **1980**, *93*, 169403q.
(252) Litvinova, T. V.; Khodosh, T. S.; Shevchenko, A. R.; Dontsov, A. A. *Kauch. Rezina* **1981**, (8), 32.
(253) Loo, C. T.; Sin, S. W.; Chin, P. S. In *Proceedings of the Natural Rubber Technology Seminar, Meeting Date 1978*; Rubber Research Institute: Kuala Lumpur, Malaysia, 1979; p 42.
(254) Loo, C. T.; Sin, S. W.; Chin, P. S. In *Proceedings of the Natural Rubber Technology Seminar, Meeting Date 1978*; Rubber Research Institute: Kuala Lumpur, Malaysia, 1979; p 165.
(255) Luecken, J. J.; Sullivan, A. B. *Elastomerics* **1981**, *113*(8), 34–8, 44.
(256) Luecken, J. J.; Fath, M. A. *Kautsch. Gummi, Kunstst.* **1982**, *35*(6), 490.
(257) Lyapunova, V. D.; Khlebov, G. A. USSR SU 765310, 1980; *Chem. Abstr.* **1981**, *94*, 31922x.
(258) Lykin, A. S.; Anfimova, E. A.; Yuzhakova, N. A.; Shumanov, L. A. *Kauch. Rezina* **1982**, (7), 8.
(259) Mahovsky, J.; Chodura, J. Czech CS 187073, 1981; *Chem. Abstr.* **1981**, *95*, 188482x.
(260) Marchenko, V. S.; Kurlyand, V. D.; Utkina, L. V. *Kauch. Rezina* **1980**, (5), 16.
(261) Meilakhs, L. A.; Gorelik, R. A.; Popov, I. T.; Podalinskii, A. V.; Kholodnitskaya, G. A. *Prom-st. Sint. Kauch.* **1983**, (1), 11.
(262) Monsanto Co. JP 56/22337 [81/22337], 1981; *Chem. Abstr.* **1981**, *95*, 116856z.
(263) Mori, K.; Nakamura, Y. *J. Appl. Polym. Sci.* **1985**, *30*(3), 1049.
(264) Ouchi Shinko Chemical Industrial Co., Ltd. JP 59/100146 A2 [84/100146], 1984; *Chem. Abstr.* **1985**, *102*, 26136y.
(265) Pal, D.; Basu, D. K. *Kautsch. Gummi, Kunstst.* **1983**, *36*(5), 358.
(266) Pal, D.; Adhikari, B.; Basu, D. K.; Chaudhuri, A. K. *Kautsch. Gummi, Kunstst.* **1983**, *36*(10), 859.
(267) Plekhanova, A. L.; Chekanova, A. A.; Zakharov, N. D. *Pr-vo Shin, Rezinotekhnk.; Asbestotekhn. Izdelii Moskva* **1980**, (5), 8–10 (from *Ref. Zh. Khim.* **1980**, Abstr. No. 17T447; *Chem. Abstr.* **1981**, *94*, 4776w.
(268) Ramos-DeValle, L. F. *Rubber Chem. Technol.* **1981**, *54*(1), 24.
(269) Sharapova, L. N.; Chekanova, A. A.; Zakharov, N. D.; Lapshina, T. V. *Kauch. Rezina* **1981**, (3), 18.
(270) Smirnova, N. V.; Maksaeva, R. P.; Alekseenko, V. I. *Kozh.-Obuvn. Prom-st.* **1982**, *24*(9), 31.
(271) Solov'ev, M. E.; Zakharov, N. D. *Kauch. Rezina* **1984**, (8), 9.
(272) Soos, I.; Nagy, K. *Muanyag Gumi* **1980**, *17*(3), 89.
(273) Strelkov, E. D.; Vatozhina, V. I.; Panferova, A. I. *Sb. Tr.-Vses. Nauchno-Issled. Proektno-Konstr. Inst. Polim. Stroit. Mater.* **1982**, *57*, 91.
(274) Sudek, V.; Kacanik, S.; Holcik, J. Czech CS 209594 B, 1982; *Chem. Abstr.* **1983**, *98*, 107284w.
(275) Surkus, A.; Pipiraite, P.; Bolotin, A. B.; Simanenkova, L. B. *Teor. Eksp. Khim.* **1984**, *20*(5), 627.
(276) Toyo Rubber Chemical Industry Co., Ltd. JP 55/62941 [80/62941], 1980; *Chem. Abstr.* **1980**, *93*, 115729g.
(277) Van Ooij, W. J.; Weening, W. E.; Murray, P. F. *Rubber Chem. Technol.* **1981**, *54*(2), 227.
(278) Voronov, V. A.; Kostrykina, G. I.; Zakharov, N. D. *Kauch. Rezina* **1981**, (5), 21.
(279) Wheelans, M. A. *NR Technol.* **1980**, *11*, 11.
(280) Wilder, G. R. U.S. Patent 4,301,260 A, 1981; *Chem. Abstr.* **1982**, *96*, 53614s.
(281) Wolff, S. *Kautsch Gummi, Kunstst.* **1979**, *312*(10), 760.
(282) Yalovaya, L. I.; Kavun, S. M.; Sakhnovskii, N. L.; Lykin, A. S. *Kauch. Rezina* **1981**, (3), 12.
(283) Yulovskaya, V. D.; Shershnev, V. A.; Zainulina, N. M.; Kravtsov, E. I. *Kauch. Rezina* **1984**, (6), 8.
(284) Zengel, H.; Eisenhuth, L.; Bergfeld, M. Ger. Offen. DE 3325724 A1, 1985; *Chem. Abstr.* **1985**, *102*, 205251d.
(285) Zhang, H. *Hecheng Xiangjiao Gongye* **1984**, *7*(3), 223; *Chem. Abstr.* **1984**, *101*, 193418c.
(286) Layer, R. W. *Rubber Chem. Technol.* **1986**, *59*(2), 274.
(287) Datta, R. N.; Basu, D. K. *Rubber Chem. Technol.* **1986**, *59*(1), 27.
(288) Deubzer, B.; Brunner, E. E. Ger. Offen. 2,824,630, 1979; *Chem. Abstr.* **1980**, *92*, 95141h.
(289) Uhrhan, P.; Roos, E.; Abele, M. Ger. Offen. 2,551,504, 1977; *Chem. Abstr.* **1977**, *87*, 86217g.
(290) Anand, R.; Blackley, D. C.; Lee, K. S. *Plast. Rubber: Mater. Appl.* **1979**, *4*(1), 8.
(291) Jeblick, W.; Uhrhan, P.; Abele, M.; Klauke, E. Ger. Offen. DE 3002549 A1, 1981; *Chem. Abstr.* **1982**, *96*, 85247r.
(292) Kuehle, E.; Paulus, W.; Genth, H.; Klauke, E. Eur. Pat. Appl. EP27622, 1981; *Chem. Abstr.* **1981**, *95*, 132359v.
(293) Lepone, G. E. U.S. Patent 4,298,613 A, 1981; *Chem. Abstr.* **1982**, *96*, 68832k.
(294) Grantham, G. D. Eur. Pat. Appl. EP12036, 1980; *Chem. Abstr.* **1980**, *93*, 239032u.
(295) Kuehle, E.; Paul, V.; Brandes, W. Eur. Pat. Appl. EP55442 A2, 1982; *Chem. Abstr.* **1982**, *97*, 215593j.
(296) Kuehle, E.; Hagemann, H.; Paul, V.; Brandes, W. Eur. Pat. Appl. EP55429 A1, 1982; *Chem. Abstr.* **1982**, *97*, 162622j.
(297) Arlt, D.; Homeyer, B.; Hammann, I.; Paul, V. Eur. Pat. Appl. EP60474 A1, 1982; *Chem. Abstr.* **1983**, *98*, 143640t.
(298) Grantham, G. D. U.S. Patent 4,341,772 A, 1981; *Chem. Abstr.* **1983**, *98*, 16845p.
(299) Holyoke, C. W., Jr. U.S. Patent 4,302,451 A, 1981; *Chem. Abstr.* **1982**, *96*, 99434m.
(300) Anderson, M. Ger. Offen. DE 3314383 A1, 1983; *Chem. Abstr.* **1984**, *100*, 68028d.
(301) Pel'kis, N. P.; Karabanov, Yr. V.; Borisenkok, V. P.; Levchenko, E. S. *Fiziol. Akt. Veshch.* **1984**, *16*, 47.
(302) Busse, W. D.; Krauthause, E.; Mardin, M. Ger. Offen. DE 3118126 A1, 1982; *Chem. Abstr.* **1983**, *98*, 143447k.
(303) Busse, W. D.; Krauthause, E.; Mardin, M. Ger. Offen. DE 3118127 A1, 1982; *Chem. Abstr.* **1983**, *98*, 143446j.
(304) Busse, W. D.; Krauthause, E.; Mardin, M. Eur. Pat. Appl. EP64657 A1, 1982; *Chem. Abstr.* **1983**, *98*, 143405v.
(305) Matsueda, H.; Shinkai, K. JP 54/128578 [79/128578], 1979; *Chem. Abstr.* **1980**, *92*, 146617c.
(306) Im, W. B.; Sih, J. C.; Blakeman, D. P.; McGrath, J. P. *J. Biol. Chem.* **1985**, *260*, 4591.
(307) Rackur, G.; Bickel, M.; Fehlhabver, H.-W.; Herling, A.; Hitzer, B.; Lang, H.-J.; Rösner, M.; Weger, R. *Biochem. Biophys. Res. Commun.* **1985**, *128*, 477.
(308) Lindberg, P.; Nordberg, P.; Alminger, T.; Brändström, A.; Wallmark, B. *J. Med. Chem.* **1986**, *29*(8), 1327.
(309) Allison, W. S. *Acc. Chem. Res.* **1976**, *9*, 293.
(310) Steinmec, F.; Zajezierska, A.; Patzau, S.; Janik, M.; Kulesa, T. Pol. PL 118424 B1, 1983; *Chem. Abstr.* **1983**, *99*, 161256x.
(311) Steinmec, F.; Zajezierska, A.; Patzau, S.; Janik, M.; Kulesa, T. Pol. PL 121065 B, 1984; *Chem. Abstr.* **1984**, *101*, 113759b.
(312) Hiller, J. C.; Perrey, H.; Ritter, H. *Holzforsch. Holzverwert.* **1984**, *36*(4), 65.
(313) Ritter, H. *Forshungesber.-Bundesminist. Forsch. Technol., Technol. Forsch. Entwicl.* **1982**, BMFT-FB-T 82-200.
(314) Pauli, O. *Farben Lacke* **1971**, *77*, 888.
(315) Kuehle, E.; Klauke, E.; Hamburger, B.; Steinfatt, F. Ger. 1919180, 1969 (Farbenfabriken Bayer A. G.); *Chem. Abstr.* **1969**, *74*, 22563.
(316) Asahi Chemical Industry Co., Ltd. JP 59/135187 A2 [84/135187], 1984; *Chem. Abstr.* **1985**, *102*, 176585h.
(317) Goerdeler, J.; Holst, A. *Angew. Chem.* **1959**, *71*, 775.
(318) Gordon, E. M.; Ondetti, M. A.; Pluscek, J.; Cimarusti, C. M.; Bonner, D. P.; Sykes, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 6053.