THE SULFENIC ACIDS AND THEIR DERIVATIVES

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Received March 13, 1946

CONTENTS

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I. Introduction

The sulfenic acids are generally designated as organic compounds of bivalent sulfur which correspond to the formula RSOH.[2] Although there is but one instance of the isolation of an acid of this type,—namely, 1-anthraquinonesulfenic acid,—substances which may be conveniently classified as derivatives of these acids are well known. The first section of this review will concern itself chiefly with the sulfenic acids as such. Subsequent sections will consider the sulfenyl halides (RSX), the sulfenyl thiocyanates (RSSCN), the sulfenamides ($RSNR_2$), the alkyl and aryl sulfenates (RSOR'), and the sulfenic anhydrides (RSOSR). A concise discussion of this subject has been presented previously by Connor (21). From a geometric viewpoint, it is possible to regard certain other substances, for example, the organic thiocyanates or the isothiazoles, as derivatives of sulfenic acids. Compounds such as the latter, however, will be included in this review only insofar as they may occur as products in the reactions of substances under primary consideration.

Of the inorganic oxygen acids of sulfur, only those in which the sulfur atom displays its maximum valence of six can be isolated in the free state. In contrast to sulfuric acid, sulfurous acid and sulfoxylic acid (HOSOH) have not as yet been isolated (27, 36). In considering the organic oxygen acids of sulfur, a similar relation between the oxidation state of the sulfur atom and the ability of the corresponding acids to exist as such is to be found among sulfonic, sulfinic, and sulfenic acids. It is generally recognized that the sulfinic acids are decidedly more subject to decomposition than are the corresponding sulfonic acids (2, 35, 78). The still lesser tendency of the sulfenic acids to remain structurally intact is implied by the circumstance that only one such acid has been reported, and is emphasized by the fact that the hydrolytic reactions of various sulfenic acid derivatives cannot be correctly formulated by a simple metathetical exchange as shown in equation 1.

$$RSX + HOH \rightarrow RSOH + HX \qquad (1)$$

[2] English authors have used the term "sulphoxylic acids" (55, 82); the German designation is "Sulfensäure."

Such reactions are reported, instead, to give rise to a variety of products, including sulfinic acids, disulfides, sulfenic anhydrides, and thiolsulfonic esters.[3] Specific examples of such changes will be considered in appropriate places throughout this paper.

II. The Sulfenic Acids

A. Early Work of Fries

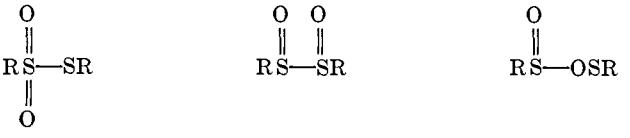
In 1912, Fries (30) reported the synthesis of 1-anthraquinonesulfenic acid (IV) by the steps shown below (R = 1-anthraquinonyl).

$$\mathrm{RCl} \xrightarrow{Na_2S_2} \underset{A}{\mathrm{RSSR}} \xrightarrow{Br_2} \underset{B}{\mathrm{RSBr}} \xrightarrow{CH_3OH} \underset{C}{\mathrm{RSOCH_3}}$$

$$\mathrm{C} \xrightarrow{KOH} \underset{D}{\mathrm{RSOK}} \rightarrow \underset{IV}{\text{1-anthraquinonesulfenic acid}} \qquad (2)$$

Although it would seem that 1-anthraquinonesulfenic acid could be obtained directly from the sulfenyl bromide (B), this was not found to be the case. If the latter was treated with aqueous sodium hydroxide, instead of the expected salt there was obtained 1-anthraquinonyl disulfide (A), and by acidification of the hydrolysate, 1-anthraquinonesulfinic acid. With alcoholic solutions of sodium or potassium hydroxide, the formation of the disulfide (A) and of the sulfinate salt occurred more rapidly, and, simultaneously, the characteristic color associated with the salts of 1-anthraquinonesulfenic acid was observed. In the reaction of 1-anthraquinonesulfenyl bromide with sulfuric acid, there was also obtained a mixture of products wihich consisted principally of the disulfide (A) and 1-anthraquinonesulfenic acid. 1-Anthraquinonesulfenyl bromide, how-

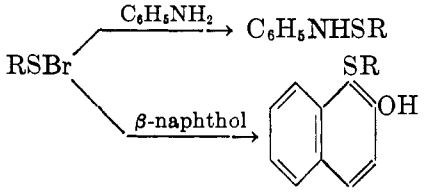
[3] There is some question in the literature as to whether the products obtained are thiolsulfonic esters (I), disulfoxides (II), or possibly mixed anhydrides of sulfinic and sulfenic acids (III).



I II III

From the studies concerned with these substances (21, 35, 43, 44, 51, 52, 71, 80, 81), it may be concluded that the thiolsulfonic ester structure is in best agreement with the experimental evidence. When these products are referred to in a general sense, in this paper, they will be designated as thiolsulfonic esters. In specific instances, however, the name used by the author whose work is cited will be employed.

ever, was found to resemble other aromatic sulfenyl halides in its reactions with ammonia, amines, and phenols. Thus, with aniline (32) and with β-naphthol (30), the products shown in equations 3 and 4 were obtained (R = 1-anthraquinonyl).



(3)

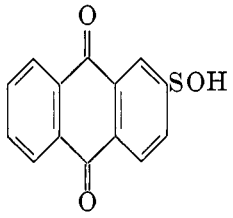
(4)

1-Anthraquinonesulfenyl bromide was converted to methyl 1-anthraquinonesulfenate (C) by reaction with boiling methanol. When the methylsulfenate was heated with 33 per cent potassium hydroxide solution for a few minutes, the potassium salt (D) was precipitated. By acidification, free 1-anthraquinonesulfenic acid (IV) was obtained in the form of bright red crystals, which could be recrystallized from benzene if certain precautions were taken. When subjected to heat, the free acid began to lose water at 100°C., but the sample did not melt completely even at 300°C. The main product of thermal decomposition was the sulfenic anhydride (see table 5), with some accompanying disulfide and "disulfoxide." By reaction with hydrogen chloride and hydrogen bromide, the sulfenic acid was reconverted to the known 1-anthraquinonesulfenyl chloride and the original sulfenyl bromide (B). In contrast to these results with hydrogen chloride and hydrogen bromide, it was later reported that the action of hydrogen iodide on 1-anthraquinonesulfenic acid resulted in the formation of the disulfide (A) rather than of 1-anthraquinonesulfenyl iodide (31). Reaction of the free acid with sodium sulfide gave 1-mercaptoanthraquinone, whereas with β-naphthol, the sulfide shown in equation 4 was obtained. Free 1-anthraquinonesulfenic acid displayed distinctly acid properties. It dissolved in aqueous or alcoholic solutions of sodium or potassium hydroxide, sodium carbonate, or ammonia to form solutions of characteristic color. When isolated, the salt crystals appeared black, with a metallic green surface luster. The sodium and potassium salts dissolved in absolute alcohol with development of a brilliant green color, while aqueous solutions were of pure blue tint. These salts were easily soluble in water, but were extensively hydrolyzed. The lead and barium salts, however, were only slightly soluble in water. If air was excluded, solutions of the acid (IV) in alcoholic potassium hydroxide remained unaltered; but if air was admitted, or more quickly with potassium ferricyanide, oxidation to the sulfinate occurred. An interesting difference between the salts and the free sulfenic acid was noted. In reactions of the free acid with methyl sulfate or methyl alcohol, methyl 1-anthraquinonesulfenate (C) was obtained. By treatment of the sodium or potassium salts of IV with methyl sulfate, however, the distinctly different methyl 1-anthraquinonyl sulfoxide was obtained exclusively. This difference between 1-anthraquinonesulfenic acid and its salts was also observed in the reactions of these substances with ethyl sulfate and ethyl alcohol (32). In this behavior, the salts of 1-anthraquinonesulfenic acid resemble those

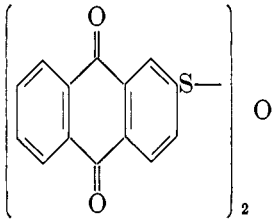
of sulfinic acids, for the latter also give sulfones, rather than sulfinic esters, when treated with alkyl halides and alkyl sulfates (79, 86), as well as with certain heterocyclic halogen derivatives, such as 5-amino-8-chloroquinoline (4). Probably on the basis of this contrasting behavior of 1-anthraquinonesulfenic acid and its salts, as well as to facilitate his understanding of the various products obtained by hydrolysis of 1-anthraquinonesulfenyl bromide, Fries suggested that the acid may exist in a "pseudo" structure, RSO. Similar considerations, with less experimental basis, were also made some years earlier by Gutmann in a discussion of the probable structure of ethanesulfenic acid (46).

B. LATER WORK OF FRIES AND COWORKERS

A portion of the experimental work of Fries was described above to show that this investigator had reasonable basis for reporting the isolation of 1-anthraquinonesulfenic acid. In 1919, Fries and Schürmann (32) reported their attempts to isolate 2-anthraquinonesulfenic acid. The conversion of 2-anthraquinonesulfenyl chloride to the free sulfenic acid (V) could not be effected. Instead, there was obtained its anhydride (VI). The latter dissolved in alcoholic



V



VI

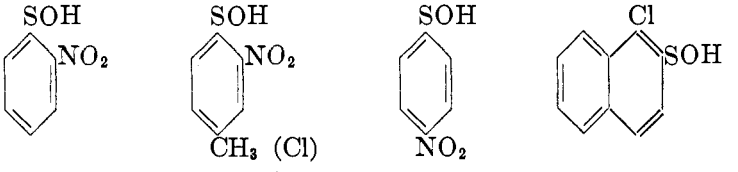
sodium hydroxide to form a red solution, from which the original anhydride (VI) was reprecipitated by acidification. The development of a characteristic color during solution of VI in alcoholic sodium or potassium hydroxide was in accord with experiments of Zincke concerning sulfenic anhydrides, such as those corresponding to the acids VII, VIII, and IX shown below (106, 108, 109, 113, 114). Following the suggestion of Zincke, it was considered that the formation of the salts of 2-anthraquinonesulfenic acid was the cause of the color. However, all attempts to isolate 2-anthraquinonesulfenic acid (V), by the same methods as were effective for 1-anthraquinonesulfenic acid, were not successful.

Additional investigations were carried out by Fries and Schürmann (32, 33) with the intent to obtain other sulfenic acids in the anthraquinone series. By methods similar to those described above, they sought to prepare 4-hydroxy-1-anthraquinonesulfenic acid, 4-ethoxy-1-anthraquinonesulfenic acid, and 4-amino-1-anthraquinonesulfenic acid. In the attempted syntheses of these compounds, difficulties were encountered in preparing the sulfenyl halides required as starting materials. In the reactions of the 4-hydroxy- and 4-methoxy-1-anthraquinonyl disulfides with chlorine, under conditions similar to those previously used to prepare 1-anthraquinonesulfenyl chloride, the products obtained were the 1-anthraquinonesulfonyl chlorides, rather than the desired sulfenyl chlorides.

With 4-amino-1-anthraquinonyl disulfide, there was formed 3-chloro-4-amino-1-anthraquinonesulfonyl chloride. The preparation of the sulfenyl bromides from the 4-hydroxy- and 4-ethoxy-1-anthraquinonyl disulfides could not be achieved, because bromine failed to effect the cleavage of the disulfide linkage in these compounds. By reaction of 4-amino-1-anthraquinonyl disulfide with bromine, however, there was obtained the hydrobromide of 4-amino-1-anthraquinonesulfenyl bromide (33). The identity of the latter was established by analysis and the nature of its typical reactions. It dissolved in alcoholic solutions of sodium or potassium hydroxide to give deep green solutions of the sodium or potassium salts of 4-amino-1-anthraquinonesulfenic acid. These salts behaved in the same manner as those of 1-anthraquinonesulfenic acid: with hydrogen bromide, in acetic acid solution, they yielded the original sulfenyl bromide; by oxidation with air, and acidification, the corresponding sulfinic acid was obtained; and by the action of methyl sulfate, methyl 4-amino-1-anthraquinonyl sulfoxide was formed. Free 4-amino-1-anthraquinonesulfenic acid, however, could not be obtained in a condition suitable for analysis. By hydrolysis of the salts in acid solution there was formed a red precipitate which, "after short standing," could not be reconverted to the original salts of the sulfenic acid. The analysis of the hydrolysate showed it to consist mainly of the sulfinic acid and the disulfide. These changes had also been observed with 1-anthraquinonesulfenic acid. With the latter compound, however, they occurred only when a glacial acetic acid solution of the sulfenic acid was boiled, whereas with the product presumed to be 4-amino-1-anthraquinonesulfenic acid, the decomposition took place instantaneously.

C. OTHER ATTEMPTS TO ISOLATE SULFENIC ACIDS

Attempts to isolate free sulfenic acids in other series have been attended with even less success than in the anthraquinone series. Those of Zincke and coworkers (106, 108, 109, 113, 114) to obtain free sulfenic acids, such as VII, VIII, IX, and X, from the corresponding sulfenyl chlorides, led invariably to the forma-



VII VIII IX X

tion of products such as the corresponding sulfinic acids, disulfides, sulfenic anhydrides, "disulfoxides," and sulfonyl chlorides, but the free sulfenic acids or their salts could not be isolated. Such repeated failures seem to have discouraged other investigators from pursuing studies whose central aim would be the isolation of free sulfenic acids. There are, however, the records of a number of investigators who were not primarily interested in the isolation of sulfenic acids, but who found it convenient to assume the formation of these acids as intermediates in various reactions (34, 35, 45, 46, 50, 55, 64, 71, 82, 89). As a single

example of several similar postulations, Lecher (64) proposed that benzenesulfenic acid (C_6H_5SOH) was the first product of the hydrolysis of benzenesulfenyl chloride to benzenesulfinic acid and phenyl disulfide (compare the hydrolysis of benzeneselenenyl bromide, page 278). Hinsberg (50, 51) and Fromm (35) postulated sulfenic acids as primary products in the decomposition of sulfinic acids:

$$2RSO_2H \rightarrow RSOH + RSO_3H \tag{5}$$

On the basis of the sulfenic acids as intermediates, these authors accounted for the formation of the products found in the decomposition mixtures of sulfinic acids, as well as for such products as amino sulfides or hydroxy sulfides which are obtained in the reactions of the sulfinic acids with aromatic amines or phenols (see equations 11). Additional examples of the postulation of sulfenic acids as intermediates, which may be briefly mentioned, are those of Prescott and Smiles (82) and of Schöberl (89), who considered that sulfenic acids and mercaptans were obtained in the hydrolytic scissions of disulfides.

$$RSSR + HOH \leftrightarrows RSH + RSOH \tag{6}$$

Davis and Smiles (23) and Marsden and Smiles (68) considered that there was no satisfactory alternative to the assumption of the intermediate formation of sulfenic acids in the preparation of thioxanthone and substituted thioxanthones, as shown in equations 7, 8, and 9.

$$HOOCC_6H_4SH + H_2SO_4 \rightarrow HOOCC_6H_4SOH + H_2SO_3 \tag{7}$$

$$HOOCC_6H_4SOH + HSC_6H_4COOH \leftrightarrows (HOOCC_6H_4S)_2 + H_2O \tag{8}$$

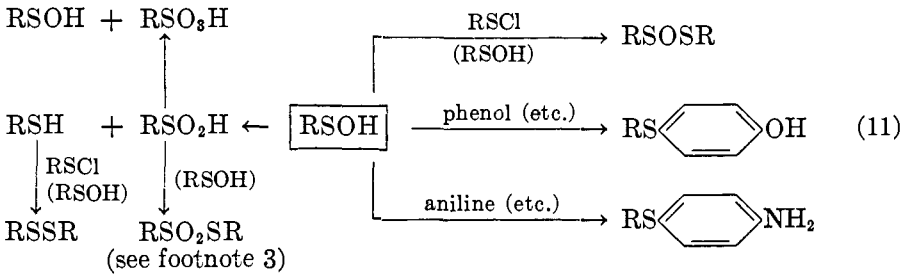
$$HOOCC_6H_4SOH + C_6H_6 \rightarrow C_6H_4\begin{<}\begin{matrix}CO\\S\end{matrix}\begin{>}C_6H_4 + 2H_2O \tag{9}$$

These authors have presented evidence for the reversibility of the hydrolytic scissions of the disulfides (equations 6 and 8). Another interesting example of the postulation of intermediate sulfenic acids is found in the interpretation of the formation of thianthrenes from disulfides (55).

$$ArSSAr \rightarrow 2ArSOH \rightarrow Ar\begin{<}\begin{matrix}S\\S\end{matrix}\begin{>}Ar + 2H_2O \tag{10}$$

Gutmann (45, 46) considered that ethanesulfenic acid (C_2H_5SOH) was formed as an intermediate product when sodium ethyl thiosulfate was hydrolyzed in alkaline solutions of sodium arsenite, and that the reduction of the sulfenic acid by the arsenite then led to the formation of ethyl mercaptan, the product actually isolated. While additional examples of sulfenic acids as postulated intermediates could be enumerated, it will suffice to state that such reports have in

common the facts (*a*) that free sulfenic acids were never isolated, and (*b*) that the ability to predict correctly the products obtained in various reactions in which such intermediates have been postulated lends credence to the consideration that these products may stem from a common type of intermediate. The general relationships are indicated below:

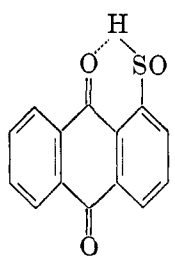


(11)

D. CONCLUSION

In view of the non-isolation of free sulfenic acids, except in the one instance, there seems at present to be inadequate basis for conclusions as to their correct structures. For the purpose of classifying compounds as sulfenyl halides, sulfenamides, etc., the structure RSOH suggests itself as a suitable one. Similarly, it seems justifiable to assume, as an aid to exposition, that structures such as RSOH result as intermediates in certain reactions. However, this does not exclude the possibility that the structure RSOH may be convertible to the "pseudo" form, $RS\overset{H}{O}$. Since the actual structures of the sulfenic acids are not known with certainty, the mechanisms whereby various sulfenic acid derivatives are converted into products such as the disulfides, sulfinic acids, thiolsulfonic esters, etc., necessarily have only hypothetical status, and will probably warrant deeper consideration than has previously been given to them in the literature. In this regard, the clarification of the analogous problems in the study of selenenic acid derivatives (see page 278) should be of assistance.

The isolation of 1-anthraquinonesulfenic acid by Fries (30) enhances the interest in the inability of Fries and Schürmann to isolate 2-anthraquinonesulfenic acid (32) and 4-substituted 1-anthraquinonesulfenic acids (33). This also indicates that some special structural feature in 1-anthraquinonesulfenic acid renders this compound less subject to conversion into the disulfide, sulfinic acid, and other products. A structure involving hydrogen bonding, such as XI, may be



XI

suggested, but there is no concrete evidence for such an assumption, nor does it explain why 4-amino-1-anthraquinonesulfenic acid is not similarly stabilized, although salt formation with the amino group may be a conflicting factor in this instance. Clearly, more experimental evidence is desirable.

E. NOTATIONS CONCERNING SELENENIC ACIDS AND THEIR DERIVATIVES

The study of sulfenic acids and their derivatives gains added interest in view of the existence of corresponding compounds of selenium.[4] The following notations are intended to point out some of the similarities and contrasts between these two classes of substances.

(*1*) The most extensive recorded studies of selenenic acids and their derivatives are those of Behaghel and coworkers (9, 10, 11, 12, 13). References to earlier investigations are cited in these papers.

(*2*) In contrast to the repeated failures of Zincke and coworkers to isolate substances such as *o*-nitrobenzenesulfenic acid, it was found that *o*-nitrobenzeneselenenic acid and 2,4-dinitrobenzeneselenenic acid could be readily isolated by hydrolysis of the corresponding selenenyl bromides (ArSeBr) or of the acetates ($ArSeOCOCH_3$).

(*3*) Corresponding to the work of Fries (30), 1-anthraquinoneselenenic acid was also prepared (11). The preparation of this acid could not be effected by hydrolysis of 1-anthraquinoneselenenyl bromide, but it was obtained from 1-anthraquinoneselenenyl acetate (compare the isolation of 1-anthraquinonesulfenic acid, page 271).

(*4*) It may be pointed out that the only selenenic acids reported are those which have a nitro group or a quinone oxygen group so situated in the molecule as to suggest a possible stabilization by means of hydrogen bridging, as in the postulated structure (XI) for 1-anthraquinonesulfenic acid. One might be tempted to consider this as indirect evidence for the correctness of such structures. This reasoning, however, has rather obvious pitfalls. For example, it might be expected on this basis that *o*-nitrobenzenesulfenic acid should be isolable, but this is contrary to the known facts (109). Nevertheless, it may be justifiable to follow such a line of thought. It suggests, for example, that it would be interesting to ascertain whether 2-anthraquinoneselenenic acid and *m*- and *p*-nitrobenzeneselenenic acids can be isolated. Apparently, the two latter compounds are not sufficiently stable to permit isolation (11).

(*5*) A very interesting property of the selenenic acids is their definitely amphoteric character. Salt formation was found to take place when these substances were treated either with bases or with a mineral acid. In his studies of sulfenic acids, Zincke (109) implied a similar amphoterism for *o*-nitrobenzenesulfenic acid (see page 328).

(*6*) In addition to the selenenyl halides, and the selenenic acids and their salts, other related compounds, including selenenamides ($RSeNR_2$), acetates ($RSeOCOCH_3$), and cyanides (ArSeCN), have also been adequately charac-

[4] Tellurium analogs of the sulfenic acid derivatives have also been claimed (69), but the information regarding such compounds seems to be very scant.

terized and their properties have been investigated. However, in contrast to the ease of preparation of aryl and alkyl sulfenates, reactions which might be expected to lead to the analogous selenenates (RSeOR') have not been effective in the preparation of these substances. Thus, ethyl *o*-nitrobenzenesulfenate (*o*-$NO_2C_6H_4SOC_2H_5$) was easily formed from the sulfenyl halide and sodium ethoxide (see page 325), but the reaction of *o*-nitrobenzeneselenenyl bromide with sodium ethoxide resulted in a mixture of products containing the corresponding diselenide, the selenenic acid, and probably some of the selenophenol (11).

(*7*) Definite resemblances between the type reactions of selenenic acid derivatives and those of the sulfenic acids are clearly apparent from a comparative study of examples of each of the two classes of substances. It seems, however, that as a class the selenium derivatives are the more stable group. For example, the selenenyl halides are less readily hydrolyzed than the corresponding sulfenyl halides (12), and another illustration of this tendency toward greater stability is seen in the isolation of a larger number of selenenic acids than of sulfenic acids. As already noted in paragraph 4, however, it may be that the isolation of the selenenic acids, as in the case of 1-anthraquinonesulfenic acid, depends on structural features which are peculiar to those selenenic acids which permit of isolation.

(*8*) The selenenic acids display a characteristic property, associated also with sulfenic acids, in that they tend to undergo disproportionation reactions. In the hydrolysis of benzeneselenenyl bromide, for example, the products obtained are benzeneseleninic acid and phenyl diselenide. It is important to note that the proportions of products actually isolated in this instance corresponded quantitatively to those to be expected if the change occurred as indicated by the equations below (13):

$$C_6H_5SeBr + HOH \rightarrow C_6H_5SeOH + HBr \quad (12)$$

$$2C_6H_5SeOH \rightarrow C_6H_5Se(O)OH + C_6H_5SeH \quad (13)$$

$$C_6H_5SeH + HOSeC_6H_5 \rightarrow C_6H_5SeSeC_6H_5 + H_2O \quad (14)$$

This correlates well with the postulation of the intermediate occurrence of sulfenic acids in similar reactions of sulfenyl halides (see, for example, reference 64).

The above-mentioned contrasts and similarities between selenenic acids and their derivatives, on the one hand, and corresponding sulfenic acid derivatives, on the other, are amplified by additional examples in the papers of Behaghel and coworkers. It is to be seen that the simultaneous development of the studies of these two classes of sulfur and selenium compounds will enhance the interest associated with each group separately, for work in the one suggests possible extensions of experimental studies in the other.

III. The Sulfenyl Halides

A. Tabulation of sulfenyl halides

As has been pointed out by Connor (21), the sulfenyl halides are generally precursors of the other derivatives of sulfenic acids. It therefore seems advisable to consider the methods of preparation and properties of these substances before discussing the other derivatives in detail. Table 1 lists some pertinent informa-

TABLE 1

*Sulfenyl halides**

p-Acetamidobenzenesulfenyl bromide, C_8H_8ONSBr	Not isolated; used in synthesis. From *p*-acetamidophenyl disulfide and bromine in carbon tetrachloride (19).
4-Acetamido-1-naphthalenesulfenyl bromide, $C_{12}H_{10}ONSBr$	Isolated only as the hydrobromide. Pale yellow powder. From 4-acetamido-1-mercaptonaphthalene and bromine in carbon disulfide (116).
4-Acetamido-1-naphthalenesulfenyl chloride, $C_{12}H_{10}ONSCl$	Pale yellow powder. From the mercaptan and chlorine in carbon disulfide or carbon tetrachloride (116).
4-Amino-1-anthraquinonesulfenyl bromide, $C_{14}H_8O_2NSBr$	Isolated only as the hydrobromide. From the disulfide and bromine, or in purer form from the sulfinic acid and hydrogen bromide in glacial acetic acid (33).
1-Anthraquinonesulfenyl bromide, $C_{14}H_7O_2SBr$	Orange needles. M.p. 214°C. From equivalent amounts of 1-anthraquinonyl disulfide and bromine, in chloroform, at boiling point of the reaction mixture. Practically theoretical yield (30). Also from 1-anthraquinonesulfenic acid and hydrogen bromide (30); and by reduction of the sulfinic acid with hydrogen bromide (31).
1-Anthraquinonesulfenyl chloride, $C_{14}H_7O_2SCl$	Orange needles. M.p. 224°C. From the disulfide and chlorine in same manner as the corresponding bromide above (30).
2-Anthraquinonesulfenyl chloride, $C_{14}H_7O_2SCl$	Yellow prisms. M.p. 136°C. From 2-mercaptoanthraquinone or 2-anthraquinonyl disulfide and chlorine, in chloroform, at room temperature (32).
Benzenesulfenyl bromide, C_6H_5SBr	Known only in solution. From thiophenol and bromine (about 20 per cent yield, based on conversion to benzenesulfenodiethylamide). Scission of this sulfenamide with hydrogen bromide gave only phenyl disulfide (64).
Benzenesulfenyl chloride, C_6H_5SCl	Deep red oil. B.p. 58°C./3 mm., 51–54°C./2.5 mm., 73–75°C./9 mm. (corr.). From benzenesulfenodiethylamide and hydrogen chloride in dry ether (42 per cent yield). Also from thiophenol and chlorine in carbon tetrachloride (nearly quantitative yield), and from phenyl disulfide (lower yield) (63, 64).
2-Benzothiazolesulfenyl bromide, $C_7H_4NS_2Br$	Decomposes 80–100°C. From 2-benzothiazolyl disulfide and bromine in carbon tetrachloride (69).

TABLE 1—*Continued*

2-Benzothiazolesulfenyl chloride, $C_7H_4NS_2Cl$	Melts with decomposition at 132–135°C. From 2-benzothiazolyl disulfide or 2-mercaptobenzothiazole and chlorine, in various solvents under anhydrous conditions (26, 69).
2-Benzothiazolesulfenyl iodide, $C_7H_4NS_2I$	Decomposes at 105–125°C. (69).
4,4′-Biphenyldisulfenyl chloride, $C_{12}H_8S_2Cl_2$	Yellow needles or prisms. M.p. 115°C.; decomposes at 140°C. From 4,4′-dimercaptobiphenyl (or the corresponding disulfide or dibenzyl thioether) and chlorine, in carbon tetrachloride or benzene (104, 107).
p-Chlorobenzenesulfenyl chloride, $C_6H_4SCl_2$	B.p. 94°C./6 mm. From thiophenol and chlorine in carbon tetrachloride at 0°C. (37).
1-Chloro-2-naphthalenesulfenyl chloride, $C_{10}H_6SCl_2$	M.p. 74–75°C. From 2-mercaptonaphthalene and chlorine, in chloroform (108; see also reference 64).
4-Chloro-2-nitrobenzenesulfenyl bromide, $C_6H_3O_2NSBrCl$	Yellow-brown needles. M.p. 111°C. From the disulfide and bromine in chloroform (106); also by reduction of 4-chloro-2-nitrobenzenesulfinic acid with hydrogen bromide (31).
4-Chloro-2-nitrobenzenesulfenyl chloride, $C_6H_3O_2NSCl_2$	Golden yellow needles. M.p. 98°C. From the disulfide and chlorine in chloroform in 90 per cent yield (106).
4-Chlorosulfonebenzenesulfenyl chloride, $ClSC_6H_4SO_2Cl$	From the disulfide and chlorine in carbon tetrachloride; product precipitates from reaction mixture. Not isolated, but used in synthesis (101).
2,5-Dibromobenzenesulfenyl bromide, $C_6H_3SBr_3$	Yellow crystals. From the disulfide and bromine. Too unstable to isolate, but used in synthesis (71).
2,5-Dibromobenzenesulfenyl chloride, $C_6H_3SBr_2Cl$	Not isolated, but used in solution for synthetic purposes. From disulfide and chlorine (96).
2,5-Dichlorobenzenesulfenyl chloride, $C_6H_3SCl_3$	Yellow oil. B.p. 92°C./3 mm. From 2,5-dichlorothiophenol and chlorine in carbon tetrachloride at 0°C. (37). Also from the disulfide as golden yellow needles, m.p. 32–33°C. (71).
4,6-Dichloro-1,3-benzenedisulfenyl chloride, $C_6H_2S_2Cl_4$	Yellow needles. M.p. 103°C. From thioresorcinol or from the corresponding dibenzyl thioether, $C_6H_4(SCH_2C_6H_5)_2$, and chlorine in chloroform (104).

TABLE 1—*Continued*

2,5-Dichloro-3-methyl-6-hydroxybenzenesulfenyl chloride, $C_7H_5OSCl_3$	Could not be obtained by various methods (105).
2,4-Dinitrobenzenesulfenyl chloride, $C_6H_3O_4N_2SCl$	M.p. 94–96°C. From the disulfide and chlorine in nitrobenzene (14) or ethylene bromide (59).
4-Hydroxy-1-anthraquinonesulfenyl chloride or bromide, $C_{14}H_6O_3SCl$ (Br)	Could not be prepared from the corresponding disulfide (33).
2-Hydroxy-5-methylbenzenesulfenyl bromide, C_7H_7OSBr	Could not be prepared from the corresponding sulfinic acid and hydrogen bromide. Protection of the phenolic hydroxyl group by forming the carbethoxy ester also did not allow formation of the sulfenyl bromide from the disulfide (104).
Methanesulfenyl iodide, CH_3SI	Postulated as intermediate (see page 300).
4-Methoxy-1-anthraquinonesulfenyl bromide or chloride, $C_{15}H_9O_2SCl$ (Br)	Could not be prepared from the corresponding disulfide (33).
4-Methyl-2-nitrobenzenesulfenyl bromide, $C_7H_6O_2NSBr$	Orange needles. M.p. 95°C. From the disulfide and bromine in carbon tetrachloride. Good yield (114).
4-Methyl-2-nitrobenzenesulfenyl chloride, $C_7H_6O_2NSCl$	Yellow needles. M.p. 90°C. From the disulfide and chlorine in carbon tetrachloride. Yield, about 90 per cent (114, 115).
2-Naphthalenesulfenyl chloride, $C_{10}H_7SCl$	Yellow-red crystalline powder. M.p. 50–60°C. Not obtained pure. From 2-mercaptonaphthalene and one equivalent of bromine. Very unstable (108).
2-Nitrobenzenesulfenyl bromide, $C_6H_4O_2NSBr$	Orange needles. M.p. 85°C. From the disulfide and bromine in carbon tetrachloride (108), or from 2-nitrobenzenesulfinic acid (31).
2-Nitrobenzenesulfenyl chloride, $C_6H_4O_2NSCl$	Yellow needles. M.p. 75°C. From the disulfide and chlorine in carbon tetrachloride at 50–60° C. in 96–97 per cent yield (54, 104).
3-Nitrobenzenesulfenyl chloride, $C_6H_4O_2NSCl$	From the disulfide and chlorine. Properties not described. Used in synthesis (29).
4-Nitrobenzenesulfenyl chloride, $C_6H_4O_2NSCl$	Bright yellow scales. M.p. 52°C. Prepared in same manner as the *o*-isomer above (113).
p-Toluenesulfenyl chloride, C_7H_7SCl	Red oil. B.p. 77.5–78.5°C./2.5 mm. From *p*-thiocresol and chlorine at low temperature in carbon tetrachloride. Light must be avoided, and strictly anhydrous conditions insured. Yield, about 85 per cent. Odor like sulfur dichloride (64).

TABLE 1—*Concluded*

Trichloromethanesulfenyl chloride, Cl_3CSCl	Yellow oil. B.p. 73°C./50 mm., 149°C. at atmospheric pressure. Best prepared from carbon disulfide and chlorine with iodine as halogen carrier. Yield of 65 per cent is attainable. Can be steam distilled with little decomposition. Vapors are lachrymatory and toxic (3, 25, 49).
Trimethylmethanesulfenyl bromide, $(CH_3)_3CSBr$	Known only in solution, but used in synthesis. Prepared from $(CH_3)_3CSN(C_2H_5)_2$ and hydrogen bromide in ether, or from $(CH_3)_3CSHgSC(CH_3)_3$ and 2 moles of bromine. Reddish orange solution in ether. Completely decomposed by attempts to distill (85).
Trimethylmethanesulfenyl chloride, $(CH_3)_3CSCl$	From the diethylamide (see above) and hydrogen chloride at 0°C. Golden yellow solution in ether. Decomposes on distillation at reduced pressure. Could not be prepared from the *tert*-butyl mercaptide (see above) or from *tert*-butyl disulfide and chlorine, because extensive chlorination of the chain occurred in preference to scission of the S—S or S—Hg bonds (85).
Trimethylmethanesulfenyl iodide, $(CH_3)_3CSI$	From the silver or mercury *tert*-butyl mercaptide and iodine in ether solution. Reddish orange ethereal solution. Used in synthesis. Decomposed by distillation at reduced pressures (85).
Triphenylmethanesulfenyl chloride, $(C_6H_5)_3CSCl$	Pale yellow needles or prisms. M.p. 137°C. From triphenylmethyl mercaptan and *one* mole of sulfuryl chloride. Practically quantitative yield recorded (100).

* Yields and physical properties are stated unless these are not available in the references cited.

tion for the sulfenyl halides which were encountered in this literature survey. The list should include practically all of the examples for which indexed or cross-reference record has been made in the literature, but absolute completeness is not claimed. The total number of sulfenyl halides which have been adequately characterized and recorded in the literature is relatively small, but the preparation of this class of substances is surely capable of wide extension. The majority of the known sulfenyl halides are aromatic sulfenyl chlorides and bromides. The few aliphatic examples which are recorded in the literature have been included in table 1. While the preparation of at least two sulfenyl iodides has been reported (69, 87), there appear to be no records of the synthesis of sulfenyl fluorides. An attempt to convert trichloromethanesulfenyl chloride (CCl_3SCl) to the fluoride was not successful (49). The existence of polyfunctional sulfenyl chlorides has been established by the synthesis of 4,4′-biphenyldisulfenyl chloride and

4,6-dichloro-1,3-benzenedisulfenyl chloride (104). Several of the sulfenyl halides reported, such as the trimethylmethanesulfenyl halides, were not isolated, but were obtained in solution and used for synthetic purposes. The evidence for their existence is usually satisfactory.

Zincke, who was the first to prepare substances of this class, designated them as "arylsulfur halides." This name has persisted in many writings, although it seems less satisfactory than the name "sulfenyl halides." In the first place, it implies a parallelism to organometallic compounds, such as organomagnesium halides, which is not quite correct in view of the non-metallic character of sulfur; secondly, it fails to recognize the character of these substances as acid derivatives. Thus, the compound *o*-$NO_2C_6H_4SCl$ is listed in *Organic Syntheses* as *o*-nitrophenylsulfur chloride with the subtitle, *o*-nitrobenzenesulfenyl chloride (54). Other authors would refer to it as 2-nitrophenylchlorothiol (60), 2-nitrobenzenemercaptan chloride, or 2-nitrophenyl chloro sulfide (14). Another variation in nomenclature is the assignment of a special name, such as "thiocarbonyl perchloride" or "perchloromethyl mercaptan" to CCl_3SCl (25, 49), whereas the name "trichloromethanesulfenyl chloride" seems more expressive. The use of the term "sulfenyl halide," which is now preferred by *Chemical Abstracts*, agrees best with the accepted names for the related derivatives of sulfonic and sulfinic acids, and it would seem that its general acceptance should be encouraged.

B. PREPARATION OF SULFENYL HALIDES

In his earlier studies concerning sulfenyl halides, Zincke demonstrated that aromatic sulfenyl chlorides and bromides could be synthesized by means of three essentially similar methods involving the action of chlorine or bromine on aryl disulfides, thiophenols, or aryl benzyl sulfides.

$$ArSSAr + X_2 \rightarrow 2ArSX \quad (15)$$

$$ArSH + X_2 \rightarrow ArSX + HX \quad (16)$$

$$ArSCH_2C_6H_5 + 2X_2 \rightarrow ArSX + C_6H_5CHX_2 + HX \quad (17)$$

In a number of instances, Zincke used these methods alternatively to synthesize the same sulfenyl halide (104).

1. Sulfenyl halides from disulfides

The preparation of sulfenyl halides from aryl disulfides was subsequently extended by Zincke and coworkers (106, 108, 109, 113, 114, 116), and its use by other workers (see table 1) has indicated its rather general application in the synthesis of aromatic sulfenyl chlorides and bromides. The halogenation is conducted at relatively low temperatures, under anhydrous conditions, in solvents such as carbon tetrachloride, chloroform, ethylene chloride, and occasionally benzene, pentane, or other hydrocarbon solvents capable of dissolving both reactants. Although the yields have not always been recorded in the literature, they have been found to be nearly quantitative in some instances and, except where this method encounters serious limitations, are generally indicated

as satisfactory. The synthesis of 2-benzothiazolesulfenyl iodide by this method has been claimed in a patent (69), but this is the only record of the synthesis of a sulfenyl iodide by this means. In a paper as early as 1868, Otto (78) anticipated the existence of sulfenyl halides, and reported the preparation of benzenesulfenyl bromide by the reaction of bromine with phenyl disulfide. It was later shown by Zincke, however, that under the conditions employed by Otto (absence of a diluent solvent) nuclear substitution rather than scission of the disulfide linkage occurs, and that the product described by Otto was in reality 4-bromophenyl disulfide and not benzenesulfenyl bromide (104).

The reaction of halogens with disulfides has certain restrictions as a method for the preparation of sulfenyl halides. In the first place, the ease of formation of the sulfenyl halide by reaction of the disulfide with one molar proportion of halogen seems to decrease in passing from chlorine to iodine. It is indicated in the work of Zincke, for example, that in the synthesis of nitrobenzenesulfenyl halides the formation of the sulfenyl chlorides occurred more readily than did that of the sulfenyl bromides; and in the anthraquinone series it has been already indicated (page 274) that in some instances bromine failed to effect the scission of certain symmetrical anthraquinonyl disulfides (33). It therefore seems reasonable to expect that disulfides will not generally be cleaved by the action of one molecular proportion of iodine under the conditions illustrated in table 1 for the similar reactions of chlorine and bromine (85). On the other hand, the action of excess halogen on some disulfides may result in the formation of tetrahalogen derivatives, such as the disulfide tetrabromides and tetraiodides, which on hydrolysis yield thiolsulfonic esters (21, 34). In the presence of hydroxylic solvents or moisture from the air, the action of chlorine may also effect oxidation of the disulfide past the sulfenyl chloride stage and result in the formation of sulfonyl chlorides (33, 88, 97, 98).

Another difficulty in the synthesis of sulfenyl chlorides and bromides from disulfides is the fact that halogenation of the aromatic ring or aliphatic chain may occur in preference to scission of the disulfide linkage (33, 67, 85, 104). This effect is particularly pronounced in the synthesis of aliphatic sulfenyl halides from disulfides, and is largely responsible for the fact that so few of these have been prepared (67). Of the aliphatic sulfenyl halides which have been synthesized, the molecules were so chosen as to minimize the tendency for chain halogenation to occur (table 1). When nitro groups are present in the aromatic nucleus, the tendency for substitution by halogen is greatly reduced, and such sulfenyl halides as *o*-nitrobenzenesulfenyl chloride are particularly easy to prepare in good yields from the disulfides. On the other hand, in the preparation of such compounds as benzenesulfenyl chloride or naphthalenesulfenyl halides, substitution in the aromatic nucleus becomes a problem which requires special attention. The use of low temperatures, dilution of reagents, and exclusion of light and moisture are measures which have been effective in the synthesis of sulfenyl halides in instances where this problem was encountered (63, 67).

There are not sufficient data available to permit generally valid statements to be made in regard to the influence which various groups may have in restricting

the effectiveness of the synthesis of sulfenyl halides from disulfides. Obviously, the nitro group does not interfere; the same is probably true of the sulfonyl chloride group, SO_2Cl (101). Groups containing active hydrogen will generally react with the sulfenyl halides formed. Apparently, if the amino group in aminoaryl disulfides is first acetylated, the disulfide linkage may then be cleaved by halogen to yield acetamido aromatic sulfenyl halides (19, 116). Another possible means for protection of the amino group, during cleavage of the disulfide by bromine, may be the formation of the amine hydrobromide (33).

In an excellent paper (67), Lecher and Wittwer have briefly summarized the difficulties attendant on the synthesis of aliphatic sulfenyl halides, as well as such aromatic derivatives as 2-naphthalenesulfenyl halides, in which the nucleus is easily subject to halogenation. Since, in many respects, the sulfenyl thiocyanates (RSSCN) markedly resemble the sulfenyl halides, Lecher and coworkers (66, 67) showed that a number of these could be prepared more readily than the corresponding sulfenyl halides, and suggested the use of the sulfenyl thiocyanates for synthetic work in those instances where the sulfenyl halides proved difficult or impossible to prepare. The sulfenyl thiocyanates will be discussed in some detail in the next section.

2. Sulfenyl halides from thiophenols and mercaptans

The action of chlorine or bromine on thiophenols has been reported as a useful method for the synthesis of aromatic sulfenyl chlorides and bromides (26, 32, 63, 104, 107, 108, 112). Since sulfenyl halides react readily with compounds containing the thiol group, a side reaction is the formation of the disulfides (61, 63, 84, 87, 108, 112, 116). By further reaction of the halogen with disulfide, however, the final product is the sulfenyl halide.

$$RSH + X_2 \rightarrow RSX + HX \quad (18)$$

$$RSH + RSX \rightarrow RSSR + HX \quad (19)$$

$$RSSR + X_2 \rightarrow 2RSX \quad (20)$$

The conditions required in this method, in instances which do not involve secondary difficulties to be described below, are essentially the same as those used in the preparation of sulfenyl halides from disulfides. Thus, in the synthesis of nitro-substituted benzenesulfenyl halides, the use of excess halogen does not cause difficulty, and the yields of such sulfenyl halides obtainable from the nitro-substituted thiophenols are good. In this case, the reactions occur as indicated in equations 18, 19, and 20. In the preparation of a sulfenyl halide such as benzenesulfenyl chloride, however, it is desirable to avoid conversion of the thiophenol to the disulfide. If phenyl disulfide is formed, and the conditions are then made sufficiently vigorous to effect cleavage of the S—S linkage, extensive chlorination of the ring occurs simultaneously (64). In contrast, the conditions required for the formation of the sulfenyl halide by the reaction of the halogen with the thiophenol (equation 18) are mild enough so that ring chlorination is considerably reduced. To avoid disulfide formation, the expedient of gradually adding the thiophenol to a solution of chlorine in an inert solvent maintains a low

concentration of the thiophenol; reaction according to equation 19 is thereby reduced to a minimum, and this allows the sulfenyl halide to accumulate in high yield (63). It is to be seen, therefore, that this method for the preparation of sulfenyl halides is subject to essentially the same limitations as is the one employing the disulfides but may be more advantageous, as was illustrated above for the synthesis of benzenesulfenyl chloride. It is interesting to note that if the chlorination of thiophenols is carried out in inert solvents, such as chloroform or carbon tetrachloride, the sulfenyl chlorides are formed; but in glacial acetic acid, sulfonyl chlorides are obtained (107, 110, 115).

As has already been indicated, the preparation of sulfenyl halides from mercaptans encounters difficulties which prevent this method of synthesis from being generally useful. The action of halogens on mercaptides also generally leads to the formation of disulfides, but under controlled conditions it may be used for the preparation of certain sulfenyl halides. Thus, Rheinboldt and coworkers (84, 85, 87) obtained trimethylmethanesulfenyl bromide or the corresponding iodide by reaction of the halogen with *tert*-butyl mercaptides, as shown in equation 21.

$$(CH_3)_3CSHgSC(CH_3)_3 + 2I_2 \rightarrow 2(CH_3)_3CSI + HgI_2 \qquad (21)$$

These workers also indicated that *tert*-amyl mercaptides underwent similar reactions. In a patent citation (92) it was claimed that the reaction of sodium hypochlorite with *tert*-butyl mercaptan allowed the quantitative formation of the corresponding sulfenyl chloride, $(CH_3)_3CSCl$. If this is the case it would be extremely interesting, for one would expect the simultaneous formation of *tert*-butyl disulfide, as well as other products formed by hydrolysis of the sulfenyl chloride.

3. Sulfenyl halides from sulfides

The original method employed by Zincke for the synthesis of aromatic sulfenyl chlorides was the reaction between chlorine and an aryl benzyl sulfide, as indicated in equation 17. The conditions required for the scission of the carbon-to-sulfur bond in this type of sulfide are practically identical with those used for the preparation of sulfenyl halides from disulfides. Zincke used this reaction with aryl benzyl sulfides only for the synthesis of aromatic sulfenyl chlorides. Apparently it has not been used by other workers, since it has no particular advantages over the other methods available. It may be noted that while the reaction of chlorine with a methyl aryl sulfide, $ArSCH_3$, leads to the chlorination of the methyl group to give $ArSCCl_3$, the low electronegativity of the benzyl radical permits easy scission of the benzyl sulfides and formation of the sulfenyl halide (104). However, the preparation of 4-methyl-2-nitrobenzenesulfenyl chloride by reaction of chlorine with methyl 4-methyl-2-nitrophenyl sulfide (as well as from the corresponding ethyl sulfide) has been reported (115). Also, not all aryl benzyl sulfides can be converted to aromatic sulfenyl halides by this method. Thus, 2,5-dichloro-3-methyl-6-hydroxybenzenesulfenyl chloride could not be prepared from the corresponding benzyl sulfide (105). It was also observed that if the chlorination of the benzyl sulfides was carried out in glacial

acetic acid solution in place of inert solvents, sulfonyl chlorides rather than sulfenyl chlorides were obtained (107, 115).

4. Sulfenyl bromides from sulfinic acids

In 1912, Fries found that the reduction of 1-anthraquinonesulfinic acid with hydrogen bromide, in glacial acetic acid solution, led to the formation of 1-anthraquinonesulfenyl bromide (30). In a later paper (31), this work was extended to show that other aromatic sulfinic acids participated in this reaction. Besides the example already cited, 2-nitrobenzenesulfenyl bromide and 4-chloro-2-nitrobenzenesulfenyl bromide were prepared from the corresponding sulfinic acids. The general equation for the reaction may be written as shown below:

$$RSO_2H + 3HBr \rightarrow RSBr + 2H_2O + Br_2 \qquad (22)$$

In the reaction of hydrogen bromide with other sulfinic acids, under the same conditions as were employed for the reaction with the sulfinic acids mentioned above, reduction to the disulfides rather than to sulfenyl halides was observed. Thus, disulfides were the products obtained by the reaction of hydrogen bromide with the following sulfinic acids: benzenesulfinic acid, *p*-nitrobenzenesulfinic acid, 2-naphthalenesulfinic acid, 5-nitro-1-naphthalenesulfinic acid, and 4-hydroxy-1-anthraquinonesulfinic acid. These reactions may be summarized in equation 23.

$$2RSO_2H + 6HBr \rightarrow RSSR + 4H_2O + 3Br_2 \qquad (23)$$

It was implied (31) that in the latter reactions sulfenyl bromides were formed initially, but that these were unstable and decomposed to yield disulfides. A pertinent observation in this connection was the fact that if 2-nitrobenzenesulfinic acid was reduced by an insufficient amount of the hot hydrogen bromide–acetic acid mixture, 2-nitrophenyl disulfide was obtained, whereas with a larger proportion of the hydrogen bromide solution, the sulfenyl halide was isolated. Since even this relatively stable sulfenyl bromide can be reduced to the disulfide under these conditions, it is not surprising to find that such a conversion occurs at lower temperatures for sulfenyl bromides, whose stabilities have been reported to be of a lower order than that of 2-nitrobenzenesulfenyl bromide. The conversion of the intermediate sulfenyl bromide to the disulfide could occur either by reaction with mercaptans (which may be present in the reaction mixture by decomposition of the sulfinic acids), equation 19, or by thermal decomposition into the disulfide and bromine (equation 24).

$$2RSBr \rightarrow RSSR + Br_2 \qquad (24)$$

Since hydrogen bromide is a rather selective reducing agent, practical advantage of the reaction of this substance with substituted sulfinic acids may be taken to reduce the sulfinic acid group without the simultaneous reduction of other groups, such as the nitro group (31).

In those cases in which sulfenyl bromides were obtained from the sulfinic acids, the reaction took place smoothly and rapidly. The yield of 2-nitrobenzenesul-

fenyl bromide was stated to be good, but the yields of sulfenyl bromides in the other instances were not reported. Fries (31) also found that "disulfoxides" were easily reduced by hydrogen bromide, in glacial acetic acid solution, either to sulfenyl bromides or to disulfides. Because sulfones are not reduced by hydrogen bromide under these conditions, he considered that the thiolsulfonic ester structure (I, page 271) was not correct, and preferred the symmetrical structure (II, page 271) for substances of the formula $R_2S_2O_2$. In view of later work concerning the structure of the thiolsulfonic esters, this analogy proposed by Fries does not seem valid.

5. Other methods for the preparation of sulfenyl halides

There are a number of other reactions whereby sulfenyl halides are produced. In general, these are not useful as methods of preparation, because the reactants employed are usually best obtained from the sulfenyl halides themselves. However, certain of these reactions may prove useful in particular instances. Thus, sulfenamides may be obtained without resorting to the use of sulfenyl halides (see Section V), and these may then be converted to sulfenyl halides by reaction with hydrogen halides, as shown in equation 25. Some examples of such syntheses are cited in table 1. An interesting one is the preparation of benzenesulfenyl chloride. Earlier attempts to prepare this compound were not satisfactory, and it was variously considered that it was either too unstable to exist or that it could not be prepared from thiophenol or phenyl disulfide without simultaneous chlorination of the ring. Although, as has already been pointed out (page 285), the synthesis from thiophenol or phenyl disulfide can be effected by proper control of the experimental conditions, benzenesulfenyl chloride was first synthesized by scission of benzenesulfenodiethylamide with hydrogen chloride in absolute ether as solvent (63).

$$C_6H_5SN(C_2H_5)_2 + 2HCl \rightarrow C_6H_5SCl + (C_2H_5)_2NH_2Cl \qquad (25)$$

Miscellaneous methods which result in the formation of sulfenyl halides are listed below. Specific instances of these reactions will be considered under later headings.

(*1*) Reaction of hydrogen halide with sulfenic esters:

$$RSOR' + HX \rightarrow RSX + R'OH \qquad (26)$$

(*2*) Reaction of hydrogen halide with sulfenamides, as illustrated in equation 25.

(*3*) Reaction of hydrogen halide with the free sulfenic acids:

$$RSOH + HX \rightarrow RSX + H_2O \qquad (27)$$

The only instances of this type of reaction are to be found in the anthraquinone series and have already been mentioned.

(*4*) Reaction of hydrogen halides or phosphorus pentachloride with sulfenic anhydrides:

$$RSOSR \xrightarrow[(\text{ether})]{HCl \text{ or } PCl_5} RSCl \qquad (28)$$

(5) Reduction of certain thiolsulfonic esters with hydrogen bromide under the same conditions as are required for the reduction of sulfinic acids to sulfenyl bromides (31).

C. PHYSICAL PROPERTIES

An interesting characteristic of sulfenyl halides is that those reported are invariably colored. Zincke (108) was the first to observe this general property and ascribed the color to the SX group. Lecher and Holschneider (63) compared the absorption spectrum of sulfur dichloride (ClSCl) with that of benzenesulfenyl chloride and found considerable similarity. They suggested that in sulfur dichloride no further alteration of the molecule can take place, and that the color of this substance as well as of benzenesulfenyl chloride was associated with the chromophoric SCl group. Gebauer-Fülnegg (37) limited his discussion to aromatic derivatives and suggested that in aromatic sulfenyl chlorides, for example, the "loose" nature of the sulfur-to-chlorine bond " . . . seems to cause an alteration of the benzoid structure of the molecule and, as a consequence of the shifting of the valences, a quinoid structure in the benzene ring is approached." He considered that it was this latter structure, and not the sulfenyl chloride group itself, which was responsible for the production of color. While all of the sulfenyl halides are colored, the sulfenamides into which they may be converted may or may not be colored. Zincke had noted that those sulfenamides which contained a nitro group were always colored, and he ascribed their color to the presence of the nitro group. Gebauer-Fülnegg (37) considered that the substitution of the more strongly bonded sulfenamide group, in place of the sulfenyl halide function, largely eliminated the tendency for approach to the "quinoid" structure, and that for this reason the sulfenamides which lacked a nitro group were colorless. If a nitro group was present, however, the tendency for the sulfenamide to approach the quinoid structure was again enhanced and color resulted. A graphic model to depict the approached "quinoid" state was used by this author. According to this reasoning, it would be predicted that the absorption spectra of the nitro-substituted sulfenamides and of the corresponding aromatic sulfenyl halides would be similar. Some of these were compared and found to have definite resemblances,—being nearly identical in the case of 2-nitrobenzenesulfenyl chloride and 2-nitrobenzenesulfenanilide. While these considerations are of interest, and the type of experimental evidence gained in the studies of Gebauer-Fülnegg is valuable, the definite indications that aliphatic sulfenyl halides are also colored (see table 1), and the fact that these were not taken into account by this investigator, considerably lower the validity of his conclusions.

The melting points and distillation temperatures of various sulfenyl halides have been listed in table 1. All of the aromatic sulfenyl halides which contain nitro groups are crystalline solids. Others, such as benzenesulfenyl chloride and its analogs, are liquids which may be distilled at reduced pressure, but which decompose when distilled at ordinary pressures. Although there are only scant indications, it seems that the sulfenyl halides of lower molecular weight are

possessed of definite, penetrating odors. For example, benzenesulfenyl chloride is described as having an odor similar to that of sulfur dichloride (63), and Rheinboldt (87) noted that solutions of trimethylmethanesulfenyl iodide and of the corresponding bromide possess sharp irritating odors.

The aromatic sulfenyl halides are generally soluble in solvents such as benzene and chloroform. Water and alcohol are not good solvents for the sulfenyl halides and, in addition, they effect hydrolysis with varying degrees of rapidity. The sulfenyl halides also react with acetone and other compounds containing active hydrogen, so that these are not suitable solvents. There are no specific data given on the solubilities of aliphatic sulfenyl halides. Rheinboldt (85, 87) generally prepared solutions of trimethylmethanesulfenyl halides in absolute ether or carbon tetrachloride, and it may be inferred from the slowness of the reactions of such solutions of the sulfenyl halides with water that their solubilities in the latter are low. This notion is substantiated by the observation that trichloromethanesulfenyl chloride can be steam distilled with little loss by decomposition (25).

D. CHEMICAL PROPERTIES OF SULFENYL HALIDES

The sulfenyl halides enter into a variety of reactions which have already established their value as synthetic intermediates. In the following discussion, these reactions will be classified under the following headings: (*1*) oxidations, (*2*) formation of disulfides, (*3*) thioalkylation and thioarylation reactions, (*4*) hydrolytic reactions, (*5*) exchange reactions with metallic salts, and (*6*) formation of sulfenamides. A section concerning sulfenyl halides as postulated intermediates has also been included.

In his fundamental studies, Zincke found that the general reactions of aromatic sulfenyl chlorides and bromides were essentially similar. In nearly all the synthetic studies, however, the sulfenyl chlorides rather than the bromides have been used. Besides the work of Zincke there have been no extensive, systematic studies of the comparative reactivities of sulfenyl halides toward specific reagents. Nevertheless, significant differences have been noted in some instances. For example, Fries and Schürmann (32) found that 2-anthraquinonesulfenyl chloride, as well as the corresponding bromide, showed remarkably greater reactivities than the isomeric 1-anthraquinonesulfenyl halides in reactions with acetone, glacial acetic acid, and acetoacetic ester, but such differences were not noted in reactions with ammonia, amines, and phenols. Similarly, *p*-nitrobenzenesulfenyl chloride was found to be decidedly more subject to hydrolytic decomposition than was the ortho isomer (113), and 1-chloro-2-naphthalenesulfenyl chloride was far more stable than 2-naphthalenesulfenyl chloride itself (108). It has also been clearly established that the halogen atom in sulfenyl halides is generally decidedly reactive, and seems, at least in some instances, to be even more reactive than is the halogen atom in corresponding sulfonyl halides. The majority of reactions involving sulfenyl halides occur rapidly; in many instances they occur spontaneously at room temperature.

Zincke (109, 113) emphasized the observation that in some reactions aromatic

sulfenyl halides displayed properties of acid halides, whereas, in others, their behavior recalled that of diazonium salts (compare, for example, equations 3 and 4, page 272). Gebauer-Fülnegg (37) also commented on the dual behavior of the chlorine atom in aromatic sulfenyl chlorides. He suggested that these substances behaved as "electromers," the chlorine atom sometimes acting as a negative group, while in other reactions it displayed properties characteristic of positive chlorine, as in hypochlorites or chloroamines.[5] Thus, in inert solvents, even with rigorous exclusion of moisture, Gebauer-Fülnegg recorded that reaction with silver nitrate precipitated silver chloride, while in reactions with iodides, free iodine was liberated. Rather than to ascribe such differences to the existence of two electromeric species of the sulfenyl chloride, it would seem preferable to consider that, depending on the nature of the reagents and the experimental conditions, the mechanism of the reaction differs,—occurring by an ionic mechanism in some cases, and by a free-atom mechanism in others (see also page 298).

Although both sulfenyl chlorides and bromides are highly reactive, it appears that the former are decidedly more stable with respect to thermal decomposition (19, 64, 71, 84, 85). Sulfenyl iodides, however, are virtually unknown, and very little can therefore be said about their properties. Apparently, the tendency for these to undergo thermal decomposition is very great. The few facts which are known about trimethylmethanesulfenyl iodide in solution (84, 87) will be mentioned below (see also table 1), but the thermal instability of this substance has thus far precluded its isolation.

1. Oxidation reactions

Relatively little work has been done on the oxidation of sulfenyl halides. Zincke and Farr (109) found that *o*-nitrobenzenesulfenyl chloride reacted with warm nitric acid (d = 1.4), in glacial acetic acid solution, to yield a readily separable mixture of the corresponding sulfonyl chloride and sulfonic acid. *p*-Nitrobenzenesulfenyl chloride reacted similarly, but in this case it was observed that some of the "disulfoxide" was also formed (113). 1-Chloro-2-naphthalenesulfenyl chloride (108) and 4,4′-biphenyldisulfenyl chloride (107) were oxidized to the corresponding sulfonyl chlorides, either by hot nitric acid, or by chlorine in glacial acetic acid solution. The fact that chlorine, in acetic acid, converts these sulfenyl chlorides, as well as 4-methyl-2-nitrobenzenesulfenyl chloride (114), to the sulfonyl chlorides recalls the observations that disulfides, thiophenols, and aryl benzyl sulfides also react with chlorine in glacial acetic acid solution to give sulfonyl chlorides. This indicates the possibility that the sulfenyl chlorides may be intermediates in these reactions—since, as has already

[5] Since the chloroamines (ArNHCl) are not appreciably colored, Gebauer-Fülnegg used the above analogy between sulfenyl chlorides and chloroamines in support of his conclusion that the SCl group, as such, is not chromophoric. This is questionable, for it assumes that color depends on the nature of the chlorine atom rather than on the group as a whole. In this connection, it may be pointed out that the thiocarbonyl group is itself a chromophore (thiobenzophenone and thioacetophenone, for example, are blue), and it may be that the attachment of the chlorine atom results in a new chromophoric group.

been stated, if the chlorinations are carried out in inert solvents instead of acetic acid, sulfenyl chlorides may actually be obtained (see page 283). A number of hydrolytic reactions of the sulfenyl halides are accompanied by the formation of products such as sulfinic acids and thiolsulfonic esters, which are presumed to arise by dismutation of the intermediate sulfenic acids. Although such reactions may in part be classified as oxidations, they will be considered separately below.

2. Formation of disulfides

In a number of reactions of sulfenyl halides, disulfides are obtained as the main products. The mercaptans or mercaptides may be intermediate products in such reactions, but the ease with which each of these reacts with sulfenyl halides to give disulfides probably explains why the latter are the products actually isolated. A few examples of such reactions follow. *o*-Nitrobenzenesulfenyl chloride, dissolved in dry ether, reacted with thiophenol to give a nearly quantitative yield of the corresponding disulfide (61). Benzenesulfenyl chloride reacted with zinc to give phenyl disulfide (63). 2-Thionaphthol or its mercury derivative, $Hg(SC_{10}H_7)_2$, readily reacted with ethereal solutions of trimethylmethanesulfenyl iodide to give the unsymmetrical disulfide (87). Trimethylmethanesulfenyl iodide reacted with magnesium or mercury to form *tert*-butyl disulfide in nearly quantitative yield. The formation of this disulfide from the sulfenyl iodide also occurred upon shaking with water or upon heating. Even at low temperatures, slow decomposition occurred; iodine was eliminated, and *tert*-butyl disulfide was formed. At room temperatures, or at the boiling point of ethereal solutions, this change occurred much more rapidly. However, anhydrous ether solutions of the sulfenyl iodide could be kept at 0°C. for several days. With aqueous sodium thiosulfate solutions, reduction to *tert*-butyl disulfide was also the main reaction. In this case it was observed that the reduction was accelerated by exposure to sunlight (87). In absolute alcohol solution, at room temperatures, potassium hydrogen sulfide reduced 2-nitrobenzenesulfenyl chloride to the corresponding disulfide (24). The formation of disulfides by the reduction of sulfinic acids with hydrogen bromide or hydrogen iodide, or by the reduction of 1-anthraquinonesulfenic acid with hydrogen iodide (31), possibly involves the sulfenyl halides as intermediates. Disulfides were also reported as products in the reactions of aromatic sulfenyl halides with certain compounds which contain active methylene groups, such as benzyl cyanide, malonic ester, and acetonylacetone (106), but the exact nature of these reactions has not been carefully established (see also page 294). Iodide ion can also effect the reduction of sulfenyl halides to disulfides. Thus, benzenesulfenyl chloride, dissolved in carbon tetrachloride, reacted quantitatively with an aqueous solution of potassium iodide to liberate one equivalent of iodine and to form phenyl disulfide (16). In hydrolytic reactions of sulfenyl halides, disulfides have often been observed among the products, but such reactions will be enumerated in a later paragraph (page 296). Heating of sulfenyl halides generally leads to disulfides; the process seems to be facilitated in the presence of a tertiary amine. Thus, 4-acetamino-1-naphthalenesulfenyl bromide hydrobromide decomposed to the disulfide when

heated (116), and 2-nitrobenzenesulfenyl bromide when heated with pyridine likewise gave 2-nitrophenyl disulfide (74). Sulfenyl halides also react with hydrogen sulfide to form trisulfides. Thus, the reaction of benzenesulfenyl chloride with hydrogen sulfide results in the formation of phenyl trisulfide, $C_6H_5SSSC_6H_5$. Benzenesulfenyl thiocyanate (C_6H_5SSCN) gives the same trisulfide by reaction with hydrogen sulfide (62).

3. Thioalkylation and thioarylation reactions

Under this heading will be included those reactions of the sulfenyl halides which lead to the formation of a sulfur-to-carbon bond. The nature of the groups which may be attached to the sulfur atom by these reactions may be aliphatic or aromatic, and they may be variously substituted. Furthermore, it is probable that the formation of the sulfur-to-carbon bond sometimes results from a secondary process, such as the rearrangement of a sulfenamide to an amino sulfide, rather than from direct replacement of the halogen atom from the sulfenyl halide by the organic radical.

(a) Reactions with Grignard reagents

Lecher and coworkers (64) found that benzenesulfenyl chloride and *p*-toluenesulfenyl chloride reacted smoothly with ethereal solutions of phenylmagnesium bromide to give 65–70 per cent yields of the corresponding sulfides.

$$C_6H_5MgBr + ArSCl \rightarrow C_6H_5SAr + MgBrCl \qquad (29)$$

The reaction was suggested as a suitable method for the preparation of unsymmetrical organic sulfides.

(b) Additions to olefins

The formation of "mustard gas," $ClCH_2CH_2SCH_2CH_2Cl$, from ethylene may involve 2-chloroethanesulfenyl chloride as an intermediate in the manner indicated below:

$$CH_2{=}CH_2 + SCl_2 \rightarrow ClCH_2CH_2SCl \xrightarrow{CH_2=CH_2} ClCH_2CH_2SCH_2CH_2Cl \qquad (30)$$

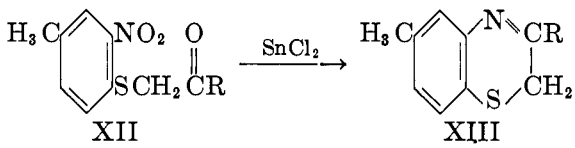
This would suggest that other sulfenyl halides could add to the ethylenic bond Lecher and coworkers (64) found that benzenesulfenyl chloride and *p*-toluenesulfenyl chloride reacted with ethylene, in carbon tetrachloride solution, to give the corresponding 2-chloroethyl sulfides.

$$CH_2{=}CH_2 + p\text{-}CH_3C_6H_4SCl \rightarrow ClCH_2CH_2SC_6H_4CH_3 \qquad (31)$$

These reactions occurred at room temperatures and the yields of products were high. 2-Nitrobenzenesulfenyl chloride underwent a similar addition to ethylene at an elevated temperature (100°C.). 2-Nitrobenzenesulfenyl chloride and 2,4-dinitrobenzenesulfenyl chloride undergo similar addition reactions with cyclohexene (59).

(c) Reactions with ketones and compounds containing active methylene groups

Zincke (104, 106, 109, 113, 114, 116) demonstrated that the aromatic sulfenyl chlorides reacted readily with ketones such as acetone and acetophenone, as well as with diethyl ketone and acetoacetic ester. The products were readily isolated and may be generally formulated as ketones in which hydrogen from an active methylene or methyl group has been replaced by an ArS— radical. These reactions occurred when the reactants were gently heated, either alone, or in solution with an inert solvent such as chloroform. For example, when 2-nitro-4-methylbenzenesulfenyl chloride reacted with acetone and acetophenone (114), compounds such as XII (R = methyl or phenyl) were obtained. Upon reduction of the nitro group of XII with stannous chloride ring closure occurred, and this afforded a method for the synthesis of 3-substituted 1,4-benzothiazines such as XIII (106, 114). Additional examples of the reactions of sulfenyl chlorides with methyl ketones have been found, and will be reported in the near future (59).



XII XIII (32)

The sulfenyl bromides do not necessarily react with ketones in a similar manner. For example, 2-nitro-4-methylbenzenesulfenyl bromide reacted with acetone, causing bromination of the latter and yielding 2-nitro-4-methylphenyl disulfide. The formation of a compound corresponding to XII was, however, not observed (114). The greater ease of thermal decomposition of the sulfenyl bromide, in comparison with the corresponding sulfenyl chloride, may account for this observed difference. Zincke has furnished numerous other examples of the reactions of various aromatic sulfenyl chlorides with ketones to form compounds such as XII. Introduction of the ArS— group also occurred readily upon reaction of the sulfenyl chlorides with the sodium or copper derivative of acetoacetic ester (32, 106). While reaction with acetoacetic ester itself may occur as expected (106), it is not always smooth (32).

In the same way, while 2-nitro-4-chlorobenzenesulfenyl chloride reacted with a number of methyl ketones, as well as with diethyl ketone and acetylacetone, as would be expected from the above examples, its reactions with acetonylacetone, benzyl cyanide, and malonic ester did not lead to the expected sulfides, but rather to the corresponding disulfide $(NO_2ClC_6H_3S)_2$ and various more complex products from the carbonyl components. Acetaldehyde also reacted with the above sulfenyl chloride to yield the disulfide, paraldehyde, and other products (106).

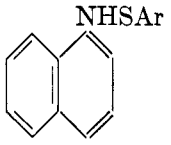
(d) Reactions with dimethylaniline, naphthylamines, phenols, and benzene

With activated aromatic nuclei, such as in naphthols, phenols, dimethylaniline, and naphthylamines, reactions with aromatic sulfenyl halides have been reported to introduce an ArS— group into the aromatic nucleus. The following examples may demonstrate the scope and nature of these reactions.

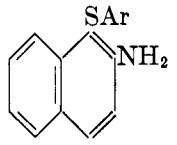
(*1*) As already indicated (page 272), 1-anthraquinonesulfenyl bromide reacted with β-naphthol at 110°C. to eliminate hydrogen bromide and to form 1-anthraquinonyl 2-hydroxy-1-naphthyl sulfide (equation 4). Anthraquinonesulfenyl halides also reacted especially easily with resorcinol to introduce the anthraquinonylthio radical in position 4 of the resorcinol molecule.

(*2*) Heating 1-anthraquinonesulfenyl bromide with an equal weight of dimethylaniline on the steam bath for 3 hr. yielded 1-anthraquinonyl 4-dimethylaminophenyl sulfide (32). 2-Nitrobenzenesulfenyl chloride reacted similarly when refluxed for a short time with dimethylaniline (109).

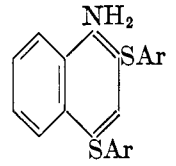
(*3*) With α- and β-naphthylamines, there may be obtained sulfenamides such as XIV. However, if the reaction between the sulfenyl halide and amine was effected in hot glacial acetic acid, amino sulfides such as XV and XVI were formed instead (109, 114).



XIV

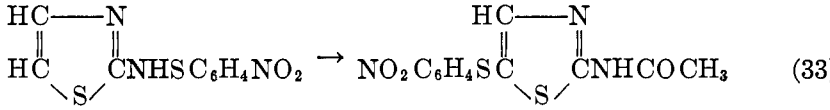


XV



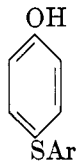
XVI

It is likely that the formation of the amino sulfides involves rearrangements of the sulfenamides (see page 321). Bambas (5) found that the reaction of *p*-nitrobenzenesulfenyl chloride with 2-thiazolylamine in glacial acetic acid at 20°C., followed by heating with acetic anhydride at 85°C., gave 4-nitrophenyl 2-acetamino-5-thiazolyl sulfide (XVIII). It was suggested that the formation of the sulfide involved rearrangement, accompanied by acetylation, of XVII to XVIII.

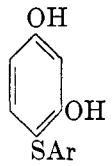


XVII XVIII (33)

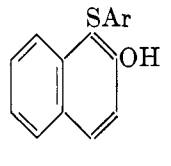
Phenol, resorcinol, *o*- and *m*-cresols, catechol, thymol, and the naphthols reacted readily with aromatic sulfenyl chlorides to give hydroxy sulfides (28, 29, 64, 106, 109, 113, 114). The reactions are similar to those which occur with dimethylaniline, and the products obtained may be exemplified by structures XIX to XXII.



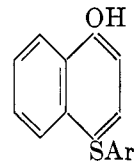
XIX



XX



XXI



XXII

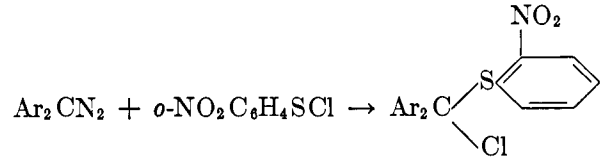
The substitution of the ArS— group always occurred in a position para to the phenolic hydroxyl group. While reactions with phenols which possess free para-

positions, such as those mentioned above, occurred readily, it was found (114) that 2-nitro-4-methylbenzenesulfenyl chloride did not react with *p*-cresol or hydroquinone, nor did the substitution of the ArS— group occur with simple phenyl ethers such as anisole. At least superficially, the above reactions of sulfenyl halides appear similar to the coupling reactions of phenols with diazonium salts. Various other examples of sulfide formation by the reaction of sulfenyl halides with phenols are included in the papers of Zincke and also of Foss and coworkers (28, 29). Such reactions serve as suitable preparative methods for the hydroxy sulfides. It may be pointed out, however, that with the exception of the work of Fries (30) and of Stevenson and Smiles (96), nearly all of the reactions of sulfenyl halides with phenols have been carried out with nitro-substituted benzenesulfenyl chlorides. This is probably a result of the greater ease of preparation of these chlorides, and also of their lesser tendency to undergo hydrolytic decomposition.

It has also been reported that the introduction of the ArS— radical into the benzene nucleus may be effected by reaction of the hydrocarbon with 1-anthraquinonesulfenyl chloride in the presence of aluminum chloride (32). However, Lecher and coworkers (64) reported that attempts to use benzenesulfenyl chloride and *p*-toluenesulfenyl chloride in modified Friedel–Crafts syntheses were not successful. An additional interesting example is the reported reaction between trichloromethanesulfenyl chloride and benzene, in the presence of aluminum chloride, to yield thiobenzophenone (100).

(e) Reactions with diazomethanes

Schönberg and coworkers (90, 91) found that aromatic sulfenyl chlorides reacted smoothly with diazomethane and diaryl diazomethanes to form hemimercaptol halides, as indicated in equation 34.



(34)

These reactions occurred spontaneously when the sulfenyl chloride was added to an ethereal solution of the diazomethane. The yields of products reported for several instances were satisfactory.

4. Hydrolytic reactions

Under this heading will be included the reactions of sulfenyl halides with hydroxylic solvents such as water, alcohols, or glacial acetic acid, under neutral, acidic, or basic conditions. In a few instances, the products reported were those which would be expected from a metathetic exchange of groups (see, for example, the reaction of 1-anthraquinonesulfenyl bromide with methanol, page 271). However, the great majority of the examples cited in the literature list products which cannot be accounted for by such a simple expression. In most of the

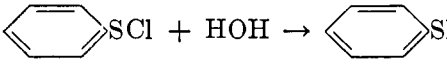
recorded examples, there were reported disulfides, sulfinic acids, the so-called "disulfoxides" or thiolsulfonic esters, sulfenic anhydrides, and in some cases sulfonyl halides and sulfonic acids. Some typical illustrations follow: Zincke and Farr (109) reported that 2-nitrobenzenesulfenyl chloride reacted with cold water to give the sulfenic anhydride. This hydrolysis was found to be reversible, for by the action of concentrated hydrochloric acid on the sulfenic anhydride, the sulfenyl chloride was once more obtained.

$$2NO_2C_6H_4SCl + H_2O \leftrightarrows (NO_2C_6H_4S)_2O + 2HCl \qquad (35)$$

When 2-nitrobenzenesulfenyl chloride was dissolved in cold methyl or ethyl alcohol, it decomposed slowly to give the disulfide, $(NO_2C_6H_4S)_2$, the disulfoxide, formulated as $NO_2C_6H_4S\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{}}SC_6H_4NO_2$, and a smaller amount of 2-nitrobenzenesulfinic acid. If the sulfenyl chloride was boiled with methyl alcohol, however, the disulfide and the sulfinic acid were the main products. With aqueous methyl alcohol, at reflux temperature, considerable amounts of the disulfide and orthanilic acid were obtained, as well as some of the sulfinic acid and *o*-nitrobenzenesulfonic acid. With dilute sodium hydroxide solution, the main product of the reaction was 2-nitrobenzenesulfinic acid and there was also formed a smaller quantity of 2-nitrophenyl disulfide. Lecher and Holscheider (64) found that reaction of benzenesulfenyl chloride with cold dilute aqueous sodium hydroxide solution gave nearly the theoretically expected quantities of phenyl disulfide and benzenesulfinic acid. Miller and Smiles (71) recorded a similar reaction for 2,5-dichlorobenzenesulfenyl chloride. The hydrolytic reactions of the anthraquinonesulfenyl halides, in which products similar to those listed above were reported, have already been mentioned (see Section I and references 30, 31, 32, 33). Other nitrobenzenesulfenyl halides undergo reactions similar to those described for *o*-nitrobenzenesulfenyl chloride. For example, *p*-nitrobenzenesulfenyl chloride (113) was readily decomposed into a mixture of the disulfide and "disulfoxide" when exposed to moist air. The reaction of this sulfenyl halide with methyl or ethyl alcohol yielded, first, the sulfenic anhydride, $(NO_2C_6H_4S)_2O$, but on longer contact with the alcohols there was formed a mixture of the disulfide and "disulfoxide". With dilute sodium hydroxide solution, the main product was *p*-nitrobenzenesulfinic acid. Under the same circumstances, 2-nitro-4-methylbenzenesulfenyl chloride (114) and 2-nitro-4-chlorobenzenesulfenyl chloride (106) reacted in the same manner as the examples already cited.

It is possible to correlate the various products observed in the above reactions by assuming that free sulfenic acids are formed as intermediates, and that these can then undergo disproportionation into products which may interact among themselves as shown in equations 11 (page 276). While there are several indications which substantiate the belief that sulfenic acids or their salts occur as intermediate products in the hydrolysis of sulfenyl halides, the representation in equations 11 is simply a geometrical model which predicts the main products

observed, but gives no information as to the mechanisms whereby the various reactions occur. On the basis of their studies of the hydrolysis of sulfur dichloride, Böhme and Schneider (16) proposed that the first step in the hydrolysis of sulfenyl chlorides is the formation of the thiophenol and hypochlorous acid.



(36)

They considered that the hypochlorous acid then acts in its capacity as an oxidizing agent to form products which interact among themselves to give the ones actually isolated. One of their main arguments in support of this viewpoint was the observation that 2 moles of benzenesulfenyl chloride reacted quantitatively with aqueous potassium iodide solution to yield 1 mole of iodine. On this basis, they proposed that the charge on the chlorine atom is positive and that the formula for the sulfenyl halide should be written $C_6H_5\overset{-}{S}\overset{+}{Cl}$. While this type of evidence may be in the right direction, a more complete, experimentally verified statement of the mechanism of these reactions is still to be advanced. One additional reaction of interest is the conversion of trichloromethanesulfenyl chloride to thiophosgene (3, 49). Böhme and Schneider (16) interpreted the hydrolysis to occur as indicated in equation 37.

$$Cl_3CSCl \xrightarrow{H_2O} HOCl + Cl_3CSH \rightarrow HCl + Cl_2C{=}S \qquad (37)$$

In practice the reaction is carried out in the presence of tin and hydrochloric acid and is looked upon by other authors (25) as a reduction by hydrogen (see also reference 83).

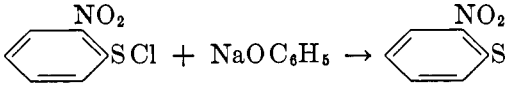
$$Cl_3CSCl + 2H \rightarrow Cl_2C{=}S + HCl \qquad (38)$$

Certain other hydrolytic reactions which lead to sulfenic anhydrides, sulfenates, and sulfenamides will be considered when the methods of preparation of these sudstances are taken up.

5. Exchange reactions with metallic salts

The sulfenyl halides undergo a variety of reactions with metallic salts. Although it is true that, in some instances, only a few examples of a certain reaction may be known, the majority of these should prove to be of general character.

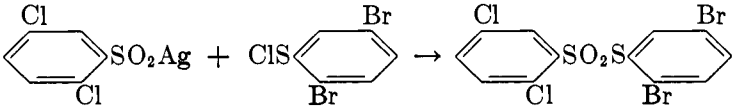
(*a*) With sodium alkoxides or phenoxides, the formation of the alkyl and aryl sulfenates is reported. A typical reaction from the work of Zincke (109) is shown below (see also Section VI).



(39)

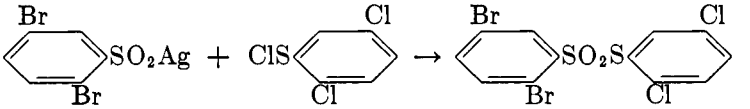
(*b*) Silver salts of sulfinic acids react to give thiosulfonic esters. Thus, benzenesulfenyl chloride reacted with silver benzenesulfinate, in dry ether, to give a nearly quantitative yield of the product designated as "diphenyl disulfoxide" (64). Zincke (109) described a similar reaction for 2-nitrobenzenesulfenyl

chloride and silver benzenesulfinate. A particularly interesting example of this reaction was furnished by Miller and Smiles (71). These workers found that compounds XXIII and XXIV were isomeric but were distinctly different. The formation of these two compounds, as shown in equations 40 and 41, was proposed as evidence for the correctness of the unsymmetrical structure for thiolsulfonic esters (see also footnote 3, page 271).



(40)

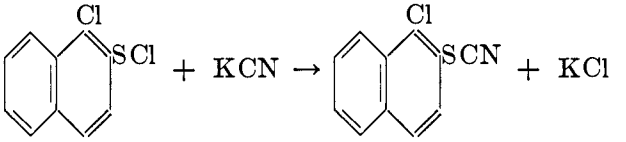
XXIII



(41)

XXIV

(*c*) With potassium cyanide in glacial acetic acid, the sulfenyl halides react readily to give thiocyanates (106, 108, 109, 113).



(42)

(*d*) With metal thiocyanates, there are formed the sulfenyl thiocyanates (see Section IV).

(*e*) The formation of disulfides by reaction of sulfenyl halides with mercaptides has already been mentioned (page 286).

$$RSX + R'SM \rightarrow RSSR' + MX \tag{43}$$

6. Formation of sulfenamides

The sulfenyl halides react with ammonia and amines to yield sulfenamides. These reactions will be dealt with in detail under the preparation of sulfenamides (page 314). With excess of the sulfenyl halides, sulfenimides may be obtained (see table 3 and page 319).

$$2ArSX + 3NH_3 \rightarrow ArS\overset{H}{N}SAr + 2NH_4X \tag{44}$$

7. Sulfenyl halides as postulated intermediates

Sulfenyl halides have been postulated as intermediate products in certain reactions. Their probable rôle as intermediates during the reduction of sulfinic acids and thiolsulfonic esters to disulfides by means of hydrogen bromide has been mentioned previously. The reduction of thiolsulfonic esters with hydrogen iodide gives only disulfides. Although sulfenyl iodides may occur as intermediates, these have never been isolated (71). Another instance is the postulation

of methanesulfenyl iodide (95) to explain the very easy formation of equivalent amounts of trimethylsulfonium iodide and trimethylsulfonium triiodide in the reaction of methyl iodide with methyl disulfide, as shown below:

$$CH_3SS|CH_3 \xrightarrow{CH_3I} (CH_3)_2S + CH_3SI \qquad (45)$$

$$(CH_3)_2S \xrightarrow{CH_3I} (CH_3)_3SI$$

$$CH_3SI \xrightarrow{CH_3I} (CH_3)_2SI_2 \xrightarrow{CH_3I} (CH_3)_3SI_3$$

The possible rôle of 2-chloroethanesulfenyl chloride in the synthesis of "mustard gas" has already been mentioned (page 293). It is probable, also, that trichloromethanesulfenyl chloride (CCl_3SCl) is an intermediate product in the preparation of carbon tetrachloride from carbon disulfide and chlorine (49). Sulfenyl chlorides have also been postulated in the synthesis of diphenylene disulfides (thianthrenes) by reaction of benzenoid compounds and sulfur monochloride (30) (*cf.* also the formation of thioxanthones and thianthrenes from disulfides, page 275).

IV. The Sulfenyl Thiocyanates

The original studies of the sulfenyl thiocyanates (RSSCN) are recorded in two papers by Lecher and coworkers (66, 67). The striking similarities between thiocyanate and halide ions, as well as between thiocyanogen, $(SCN)_2$, and the elementary halogens (X_2), led these workers to consider that the sulfenyl thiocyanates should be similar in their properties to the sulfenyl halides. Furthermore, in view of the difficulties encountered in the synthesis of certain sulfenyl halides (see Section III,B), it was suggested that the corresponding sulfenyl thiocyanates might prove easier to prepare. As the following discussion will show, these expectations were realized in some measure.

A. Preparation of Sulfenyl Thiocyanates

The sulfenyl thiocyanates may be prepared in two ways: (*a*) By reaction of a sulfenyl halide with a metal thiocyanate:

$$RSCl + KSCN \rightarrow RSSCN + KCl \qquad (46)$$

(*b*) By reaction of a thiophenol or mercaptan with thiocyanogen:

$$RSH + (SCN)_2 \rightarrow RSSCN + HSCN \qquad (47)$$

Method (*a*) illustrates a general property of the sulfenyl halides and affords a method for the preparation of sulfenyl thiocyanates in those cases where the halide is available, but is, obviously, of no assistance in those instances where the sulfenyl thiocyanates are required to serve as substitutes for sulfenyl halides

which cannot be easily prepared. In the examples studied (66), the reaction of a sulfenyl halide with the thiocyanate was readily achieved by shaking equivalent amounts of the reactants for extended periods in a solvent such as benzene. The yields of 2-nitrobenzenesulfenyl thiocyanate and of triphenylmethanesulfenyl thiocyanate, from the corresponding sulfenyl chlorides, were found to be practically quantitative. 2,4-Dinitrobenzenesulfenyl thiocyanate has been similarly prepared (59).

The preparation of sulfenyl thiocyanates from the mercaptan or thiophenol by reaction with thiocyanogen also seems to be capable of general application. This reaction probably proceeds by the same mechanism as does the reaction between a mercaptan and halogen, but seems to have two points in its favor. In the first place, the reaction between the sulfenyl thiocyanate and the unreacted mercaptan, to give the disulfide (equation 48), takes place sufficiently slowly so that with an excess of thiocyanogen present the formation of the sulfenyl thiocyanate is the main reaction.

$$RSSCN + HSR' \rightarrow RSSR' + HSCN \qquad (48)$$

Secondly, the tendency for nuclear or chain substitution of hydrogen by thiocyanogen is lower than is the corresponding tendency for halogenation to occur. Thus, the major difficulties associated with the synthesis of sulfenyl halides from mercaptans are largely discounted in the synthesis of sulfenyl thiocyanates. In contrast to the failures of attempts to prepare sulfenyl halides, such as ethanesulfenyl chloride, it was therefore found possible to synthesize the corresponding sulfenyl thiocyanate.

In the preparation of sulfenyl thiocyanates by method (*b*), a slightly greater than 1 molar proportion of thiocyanogen (prepared in absolute ether solution by reaction of lead thiocyanate with bromine) is reacted with the chosen mercaptan or thiophenol at low temperatures. The reaction is complete in a short time. The excess thiocyanogen and thiocyanic acid are separated by decomposing the reaction mixture with ice, and the sulfenyl thiocyanate is then isolated from the ether solution (67).

B. TABULATION OF SULFENYL THIOCYANATES

A number of examples of sulfenyl thiocyanates are listed in table 2.

C. PROPERTIES OF SULFENYL THIOCYANATES

Some of the physical characteristics of the sulfenyl thiocyanates have been recorded in table 2. In contrast to the sulfenyl halides, the sulfenyl thiocyanates are not necessarily colored. Thus, while 2-nitrobenzenesulfenyl thiocyanate and 2-naphthalenesulfenyl thiocyanate are yellow, ethanesulfenyl thiocyanate and benzenesulfenyl thiocyanate are colorless. While the 2-nitrobenzene and the 2-naphthalene derivatives were found to be odorless, the sulfenyl thiocyanates derived from ethane and benzene possessed sufficiently remarkable odors to warrant special notice.

The thermal stability of ethanesulfenyl thiocyanate was found to be suffi-

ciently great to permit purification by distillation at reduced pressure (see table 2). On standing at room temperature, most of the sulfenyl thiocyanates tend to decompose. Ethanesulfenyl thiocyanate was the most difficult to keep, and underwent extensive decomposition in a period of half an hour. Benzenesulfenyl thiocyanate was also very subject to decomposition on keeping. 2-Naphthalenesulfenyl thiocyanate, however, was fairly stable and underwent only

TABLE 2

Sulfenyl thiocyanates

Benzenesulfenyl thiocyanate, C_6H_5SSCN	Colorless crystals of pungent odor. Liquefy when removed from ice–salt bath. Could not be distilled without decomposition. Prepared from thiophenol and thiocyanogen (1:2 molar ratio) in absolute ether. Yield not stated (63, 67).
2,4-Dinitrobenzenesulfenyl thiocyanate, $(NO_2)_2C_6H_3SSCN$	Yellow crystals. M.p. 74.5–76°C. From 2, 4-dinitrobenzenesulfenyl chloride and potassium thiocyanate, by shaking for 20 hr. at room temperature, in high yield (59).
Ethanesulfenyl thiocyanate, C_2H_5SSCN	Colorless liquid. B.p. 52°C./1.5 mm., with some decomposition. Possesses strong irritating odor. From 0.06 mole of thiocyanogen and 0.05 mole of ethyl mercaptan in ether. Yield, 50–60 per cent. Density > 1. Immiscible with water; soluble in ether. Dissolves in alcohol with liberation of cyanic acid (67).
2-Naphthalenesulfenyl thiocyanate, $C_{10}H_7SSCN$	Pale yellow crystals. M.p. 64.5–65°C. Odorless. From thiocyanogen and 2-mercaptonaphthalene (2:1 molar ratio) in ether solution. Insoluble in water; readily soluble in non-polar solvents (67, 87).
2-Nitrobenzenesulfenyl thiocyanate, $NO_2C_6H_4SSCN$	Yellow crystals from carbon tetrachloride. M.p. 93–94°C. From 2-nitrobenzenesulfenyl chloride and equivalent quantity of potassium thiocyanate, in benzene, by shaking for 20 hr. at room temperature. Quantitative yield (66). Also from *o*-nitrothiophenol and thiocyanogen; 75 per cent yield (67). Soluble in benzene and ethyl acetate; difficultly soluble in ether, ligroin, and carbon tetrachloride.

slight decomposition in a period of weeks. In ether solution, the above compounds could be kept for longer periods. 2-Nitrobenzenesulfenyl thiocyanate, however, is a very stable compound, which requires no special storage precautions and may be recovered unchanged after heating in ethylene bromide solution at 90°C. for 2 hr. (59).

In many respects, the sulfenyl thiocyanates resemble the sulfenyl halides in chemical behavior.

(*1*) By reactions with mercaptans and thiophenols a considerable number of disulfides have been prepared (66, 67).

(*2*) The reaction with an excess of ammonia or amines leads to sulfenamides. Thus, 2-nitrobenzenesulfenyl thiocyanate reacted with ammonia to give a quantitative yield of 2-nitrobenzenesulfenamide (66). Similarly, benzenesulfenyl thiocyanate reacted with diethylamine to give a 70 per cent yield of the corresponding diethylamide (63). The amides thus obtained were identical with the ones prepared from the corresponding sulfenyl chlorides (63, 108). Reactions of this type confirm the structure RSSCN for the sulfenyl thiocyanates. If these compounds were derivatives of isothiocyanic acid (HNCS), reaction with ammonia and amines would be expected to lead to derivatives of thiourea ($RSNHCSNH_2$).

(*3*) With dimethylaniline, 2-nitrobenzenesulfenyl thiocyanate reacted in the same manner as the sulfenyl chloride to give 4-dimethylaminophenyl 2-nitrophenyl sulfide (66).

(*4*) In the reaction of 2-nitrobenzenesulfenyl thiocyanate with potassium hydroxide solution, there was formed the same characteristic color as was observed in the case of the corresponding sulfenyl chloride (109). In both instances, it was presumed that the salt of the sulfenic acid was formed as an intermediate product, but the products of alkaline hydrolysis of the thiocyanate were not further described.

(*5*) In a recent patent (U.S. 2,390,713; December 11, 1945) Hunt describes the reaction of aliphatic sulfenyl thiocyanates with alkali metal salts of *N*-substituted dithiocarbamates to form sulfenyl derivatives, as shown below:

$$\mathrm{R{-}N(R'){-}C(=S){-}SNa} \xrightarrow{\mathrm{R''SSCN}} \mathrm{R{-}N(R'){-}C(=S){-}S{-}SR''}$$

(*6*) 2-Nitrobenzenesulfenyl thiocyanate and 2,4-dinitrobenzenesulfenyl thiocyanate react with acetone or acetophenone to give the corresponding acetonyl or phenacyl aryl sulfides (*cf.* Section III, D, 3, (c) on page 294 for the corresponding reactions of sulfenyl halides).

Examples of reactions such as the above are, to be sure, restricted in number. The analogy to the sulfenyl halides, nevertheless, is rather clear. Lecher and coworkers were convinced of this relationship and of the correctness of classifying the sulfenyl thiocyanates as derivatives of sulfenic acids rather than as disulfides. In contrast to ordinary disulfides, they considered the sulfur-to-sulfur linkage in RS—SCN to be of a polar nature and even attempted to establish a tendency for ionic dissociation. However, 2-nitrobenzenesulfenyl thiocyanate proved to be a non-conductor of electricity in liquid sulfur dioxide solution (66).

A few differences in the properties of the sulfenyl halides and the sulfenyl thiocyanates have been noted, mainly in the greater hydrolytic stability which the latter compounds display in contrast, for example, to the sulfenyl chlorides. In their thermal stabilities they appear to be quite comparable to the sulfenyl chlorides. The hydrolytic stabilities toward water and alcohol vary widely,

depending on the particular thiocyanate. Ethanesulfenyl thiocyanate was slowly hydrolyzed by cold water, and rapidly by hot water or alcohol. 2-Naphthalenesulfenyl thiocyanate was hydrolyzed very slowly by cold water, but was decomposed more rapidly by hot water or alcohol. 2-Nitrobenzenesulfenyl thiocyanate was found to be very indifferent to the action of water (66), whereas the analogous sulfenyl chloride underwent complete hydrolysis under comparable conditions (109). A study to extend the chemistry of sulfenyl thiocyanates, and particularly the reactions of these substances with olefins, is now in progress in the laboratories of the authors (59).

V. SULFENAMIDES

A considerable literature dealing with sulfenamides has been developed. Industrial investigators have been interested in these substances primarily because of their utility as accelerators for the vulcanization of rubber. Articles in the general literature have as their central interests the preparation of the sulfenamides and the study of their chemical properties. In this paper, references to the patent literature concerned with the applications of sulfenamides as rubber accelerators have been collected, and the contributions made to sulfenamide chemistry by these efforts have been noted. A discussion of the uses of sulfenamides in the manufacture of rubber, however, will not be undertaken.

A. TABULATION OF SULFENAMIDES

Table 3 lists the sulfenamides which were encountered in the course of this literature survey. The number of these which have been definitely characterized and recorded in the literature decidedly exceeds that of the sulfenyl halides known with an equal degree of exactness. As was true also of the sulfenyl halides, however, there are several references which merely imply that certain sulfenamides were prepared, but give little or no specific information. It may also be noted that the experimental studies cited in the patent literature are primarily concerned with the sulfenamides obtainable from 2-mercaptobenzothiazole and amines such as cyclohexylamine, butylamines, and piperidine. These sulfenamides have been found to be especially effective as accelerators for the vulcanization of rubber.

The sulfenamides have been designated in various ways: as sulfamines, sulfur amines, mercaptoamines, aminothio compounds, amino sulfides, sulfur amides, and thiohydroxylamines. The most convenient system of denoting these compounds would seem to be the one which considers them as derivatives of sulfenic acids. The names should be chosen in the same way as for sulfonamides, but the prefix "sulfon" should be changed to "sulfen." The examples in table 3 illustrate this nomenclature.

B. PREPARATION OF SULFENAMIDES

1. Sulfenamides from sulfenyl halides

The earliest instances of the preparation of sulfenamides were reported in the original papers of Zincke, who showed that the reaction of aromatic sulfenyl

TABLE 3

Sulfenamides

4-Acetamidobenzenesulfen(2-pyridylamide), $C_{13}H_{13}ON_3S$	Not isolated. From 4-acetamidobenzenesulfenyl chloride or bromide and 2-pyridylamine in inert solvents. Oxidized to corresponding sulfonamide (6a, 8).
4-Acetamidobenzenesulfen(4,6-dimethyl-2-pyrimidylamide), $C_{14}H_{16}ON_4S$	White powder. From the sulfenyl halide and amine in benzene (6b).
4-Acetamidobenzenesulfenoguanidide, $C_9H_{11}ON_3S$	Not isolated. Oxidized to the sulfonamide. From 4-acetamidobenzenesulfenyl chloride and guanidine nitrate in presence of sodium ethoxide, in ether at room temperature (6).
4-Amino-1-anthraquinonesulfenanilide, $C_{20}H_{14}O_2N_2S$	Violet-red needles. M.p. 180°C. (decomposition). From 4-amino-1-anthraquinonesulfenyl bromide hydrobromide and aniline in benzene solution (33).
2-Aminobenzenesulfenopiperidide, $C_{11}H_{16}N_2S$	Well-shaped crystals. M.p. 66–68°C. From 2-aminophenyl disulfide and piperidine with aqueous sodium hypochlorite in presence of excess pyridine at 50°C. (99).
1-Anthraquinonesulfenamide, $C_{14}H_9O_2NS$	Orange needles. Color lightens at 215°C., but solid does not melt even at 300°C. From the sulfenyl bromide and alcoholic ammonia (32).
1-Anthraquinonesulfenanilide, $C_{20}H_{13}O_2NS$	Red needles. M.p. 210°C. From the sulfenyl bromide and aniline in benzene (32).
2-Anthraquinonesulfenanilide, $C_{20}H_{13}O_2NS$	Orange needles from methyl alcohol. M.p. 171°C. From the sulfenyl chloride and aniline (32).
Benzenediazo triphenylmethyl sulfide, $(C_6H_5)_3CSN{=}NC_6H_5$	Yellow leaves. M.p. 108°C. (decomposition). From benzenediazonium chloride and triphenylmethylthiol (100).
Benzenesulfenanilide, $C_{12}H_{11}NS$	Colorless crystals. M.p. 53–55°C. From benzenesulfenyl chloride and aniline in ether (64).
Benzenesulfenodiethylamide, $C_{10}H_{15}NS$	Colorless liquid. B.p. 90°C./3.5 mm.; 94–96°C./5 mm. From benzenesulfenyl thiocyanate and diethylamine (70 per cent yield), or from the sulfenyl chloride (76 per cent yield) (63). Also from the sulfenyl bromide (64).
Benzenesulfenodimethylamide, $C_8H_{11}NS$	B.p. 63.5–64°C./3 mm. From benzenesulfenyl chloride and dimethylamine in absolute ether. Yield, 92 per cent (64).
Benzenesulfen(4,6-dimethyl-2-pyrimidylamide), $C_{12}H_{13}N_3S$	From benzenesulfenyl chloride and 4,6-dimethyl-2-pyrimidylamine. Crystals from alcohol. Oxidized to the sulfonamide (6b).

TABLE 3—*Continued*

Benzenesulfenoguanidide, $C_7H_9N_3S$	From the sulfenyl chloride, guanidine nitrate, and sodium ethoxide in dry benzene. Converted to the sulfonamide (6).
Benzenesulfen(2-pyridylamide), $C_{11}H_{10}N_2S$	Crystals from alcohol. Prepared from the sulfenyl chloride and 2-pyridylamine (6a).
2-Benzimidazolesulfenopiperidide, $C_{12}H_{15}N_3S$	M.p. 190–193°C. From 2-mercaptobenzimidazole and piperidine, with aqueous sodium hypochlorite (99).
2-Benzothiazolesulfenamide, $C_7H_6N_2S_2$	M.p. 128–129°C. From 2-mercaptobenzothiazole and cold concentrated aqueous ammonia with sodium hypochlorite, or from sodium 2-mercaptobenzothiazole and chloroamine at 0–5°C. Nearly quantitative yields (17, 18, 47).
2-Benzothiazolesulfen(2-aminoethylamide), $C_9H_{11}N_3S_2$	M.p. 122–123°C. From 2-benzothiazolesulfenamide and ethylenediamine (53). From the mercaptan and amine with aqueous hypochlorite; white powder, m.p. 115°C. (1, 17, 18).
2-Benzothiazolesulfenanilide, $C_{13}H_{10}M_2S_2$	M.p. 119–122°C. From the sulfenyl chloride and amine (70).
2-Benzothiazolesulfenobenzylamide, $C_{14}H_{21}N_2S_2$	M.p. 115°C. From 2-mercaptobenzothiazole and benzylamine with aqueous sodium hypochlorite (18). From 2-benzothiazolesulfenamide and benzylamine, m.p. 111–114°C. (53).
2-Benzothiazolesulfenobenzylmethylamide, $C_{15}H_{14}N_2S_2$	From the mercaptan and amine with aqueous hypochlorite; about 85 per cent yield (99).
2-Benzothiazolesulfenobutylamide, $C_{11}H_{16}N_2S_2$	Red oil. From sodium 2-mercaptobenzothiazole and butylamine with aqueous hypochlorite, about 85 per cent yield (1).
2-Benzothiazolesulfen-*sec*-butylamide, $C_{11}H_{14}N_2S_2$	White. M.p. 59–61°C. (1, 22, 94).
2-Benzothiazolesulfenocyclohexylamide, $C_{13}H_{16}N_2S_2$	M.p. 99–101°C. (1, 18, 22, 48, 53).
2-Benzothiazolesulfen(2-cyclohexylcyclohexylamide), $C_{19}H_{26}N_2S_2$	Waxy, buff-colored solid (22).
2-Benzothiazolesulfeno(dibutylamide), $C_{15}H_{22}N_2S_2$	Oil. From 2-benzothiazolesulfenamide and dibutylamine (53), or from 2-mercaptobenzothiazole and the amine with sdium hypochlorite, 70 per cent yield (99).

TABLE 3—*Continued*

2-Benzothiazolesulfeno(diethylamide), $C_{11}H_{14}N_2S_2$	Oil. Prepared in same ways as the dibutyl derivative (53, 99).
2-Benzothiazolesulfeno(dipropylamide), $C_{13}H_{18}N_2S_2$	Oil. From 2-benzothiazolesulfenamide and dipropylamine (53).
2-Benzothiazolesulfenethylamide, $C_9H_{10}N_2S_2$	White. M.p. 52–53°C. (53); m.p. 55–57°C. (17).
2-Benzothiazolesulfen(2-hydroxyethylamide), $C_9H_{10}ON_2S_2$	M.p. 96–99°C. (1, 22).
2-Benzothiazolesulfen(isopropylamide), $C_{10}H_{12}N_2S_2$	White crystals. M.p. 93–94°C. (53, 94).
2-Benzothiazolesulfenomethylamide, $C_8H_8N_2S_2$	Amber liquid or low-melting solid (17, 22).
2-Benzothiazolesulfen(1-methylbutylamide), $C_{12}H_{16}N_2S_2$	White solid. M.p. 58–60°C. From sodium 2-mercaptobenzothiazole and 1-methylbutylamine, with sodium hypoiodite, in good yield (94).
2-Benzothiazolesulfen(1-methylisopentylamide), $C_{13}H_{18}N_2S_2$	White. M.p. 52–64°C. (94).
2-Benzothiazolesulfenomorpholide, $C_{11}H_{12}ON_2S_2$	M.p. 86–87°C. From 2-benzothiazolesulfenamide and morpholine (53).
2-Benzothiazolesulfen(*N*-ethylcyclohexylamide), $C_{15}H_{20}N_2S_2$	Oil (99).
2-Benzothiazolesulfenopentylamide, $C_{12}H_{16}N_2S_2$	White. M.p. 35–37°C. (1, 17).
2-Benzothiazolesulfen-*tert*-pentylamide, $C_{12}H_{16}N_2S_2$	M.p. 80–82°C. (94).
2-Benzothiazolesulfenopiperidide, $C_{12}H_{14}N_2S_2$	White crystals. M.p. 80°C. Obtained by various oxidative methods from the mercaptan and amine (1, 53, 99).
2-Benzothiazolesulfenopropylamide, $C_{10}H_{12}N_2S_2$	White. M.p. 32–33°C. (17).
Bis(benzenesulfen)imide, $C_6H_5SNHSC_6H_5$	Colorless, odorless crystals. Melt with evolution of ammonia at 126.5–128°C. (corr.). From ammonia and excess benzenesulfenyl chloride, in ether. Poor yield (64).
Bis(1-chloro-2-naphthalenesulfeno)-methylimide, $C_{21}H_{15}NS_2Cl_2$	Shiny leaves from benzene–petroleum ether. M.p. 177–178°C. (108).

TABLE 3—*Continued*

Bis(4-chloro-2-nitrobenzenesulfen)-imide, $C_{12}H_7O_4N_3S_2Cl_2$	Pale yellow needles. M.p. 210°C. (decomposition) (106).
Bis(4-chloro-2-nitrobenzenesulfen)-*o*-phenylenediamide, $C_{18}H_{12}O_4N_4S_2Cl_2$	M.p. 181°C. From 4-chloro-2-nitrobenzenesulfenyl chloride and *o*-phenylenediamine in ether, 2:1 molar ratio (40).
Bis(4-chloro-2-nitrobenzenesulfen)-*m*-phenylenediamide	Brown-red powder. Decomposes at 70–80°C. (41).
Bis(4-chloro-2-nitrobenzenesulfen)-*p*-phenylenediamide	M.p. 212°C. (40).
Bis(4-methyl-2-nitrobenzenesulfen)-imide, $C_{14}H_{13}O_4N_3S_2$	Yellow needles. M.p. 241°C. From 4-methyl-2-nitrobenzenesulfenamide by boiling with acetic acid (114).
Bis(4-methyl-2-nitrobenzenesulfeno)methylimide, $C_{15}H_{15}O_4N_3S_2$	Yellow crystals. M.p. 226°C. (decomposition). From 4-methyl-2-nitrobenzenesulfenomethylamide by heating with acetic acid (114).
Bis(2-nitrobenzenesulfen)imide, $C_{12}H_9O_4N_3S_2$	Lemon-yellow needles or powder. M.p. 217°C. (decomposition). From the amide by boiling with dilute acetic acid, or from the sulfenyl chloride and dilute aqueous ammonia (109).
Bis(4-nitrobenzenesulfen)imide, $O_2NC_6H_4SNHSC_6H_4NO_2$	Pale yellow needles. M.p. 155°C. From ammonia and excess 4-nitrobenzenesulfenyl chloride, or more simply by boiling the corresponding amide with dilute acetic acid (113).
Bis(2-nitrobenzenesulfeno)methylimide, $C_{13}H_{11}O_4N_3S_2$	Yellow. M.p. 204–5°C. (decomposition). Prepared in same manner as the corresponding sulfenimide above (109).
Bis(4-nitrobenzenesulfeno)methylimide, $C_{13}H_{11}O_4N_3S_2$	Pale yellow needles from glacial acetic acid. M.p. 156°C. (113).
Bis(*p*-toluenesulfen)imide, $CH_3C_6H_4SNHSC_6H_4CH_3$	Could not be obtained pure; very unstable. From *p*-toluenesulfenyl chloride and ammonia (64).
4-Chlorobenzenesulfen(4,6-dimethyl-2-pyrimidylamide), $C_{12}H_{12}N_3SCl$	From the sulfenyl chloride and the amine, in benzene at room temperature. Recrystallized from alcohol (6b).
4-Chlorobenzenesulfenoguanidide, $C_7H_8N_2SCl$	Not isolated. From the sulfenyl chloride and guanidine nitrate with sodium ethoxide in benzene. Oxidized to sulfonamide (6).
4-Chlorobenzenesulfen(2-pyridylamide), $C_7H_8N_3SCl$	Not isolated; oxidized to sulfonamide (6a).

TABLE 3—*Continued*

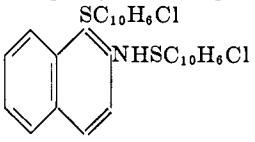
1-Chloro-2-naphthalenesulfenamide, $C_{10}H_8NSCl$	Needles which easily turn to red color. Melt at about 160°C. with previous decomposition at about 105–110°C. (108).
1-Chloro-2-naphthalenesulfenanilide, $C_6H_{12}NSCl$	M.p. 132°C. From the sulfenyl chloride and aniline, 1:2 molar ratio (108).
Bis(1-chloro-2-naphthalenesulfen)-imide, $C_{20}H_{13}NS_2Cl_2$	Red, flocculent crystals. M.p. 213–214°C. From 1-chloro-2-naphthalenesulfenamide by treatment with cold acetic acid or by action of excess ammonia and the sulfenyl chloride (108).
1-Chloro-2-naphthalene(1-(1-chloro-2-naphthylthio)2-naphthylamide) 	Nearly colorless needles. M.p. 187–188°C. From 1-chloro-2-naphthalenesulfenyl chloride and 1-chloro-2-naphthylthio(2-naphthylamine) in 1:2 molar ratio (108).
1-Chloro-2-naphthalenesulfeno-methylamide, $C_{11}H_{10}NSCl$	Leaves from aqueous methyl alcohol. M.p. 89–90°C. (108).
1-Chloro-2-naphthalenesulfen-α-naphthylamide, $C_{20}H_{14}NSCl$	M.p. 154°C. From the sulfenyl chloride and α-naphthylamine (108).
1-Chloro-2-naphthalenesulfen-β-naphthylamide	Colorless needles. M.p. 132–133°C. (108).
4-Chloro-2-nitrobenzenesulfenamide, $C_6H_5O_2N_2SCl$	Bright yellow needles. M.p. 126–127°C. From the sulfenyl chloride and ammonia in cold chloroform solution. Converted to an acetyl derivative (106).
4-Chloro-2-nitrobenzenesulfenanilide, $C_{12}H_9O_2N_2SCl$	Orange-yellow crystals from alcohol. M.p. 102°C. From the sulfenyl chloride and aniline in ether (76); m.p. 100°C. (42).
4-Chloro-2-nitrobenzenesulfen-*o*-chloroanilide, $C_{12}H_8O_2N_2SCl_2$	Orange needles. M.p. 112°C. From the sulfenyl chloride and *o*-chloroaniline (42, 77).
4-Chloro-2-nitrobenzenesulfen-*p*-chloroanilide	Brown-red crystals. M.p. 172°C. (41).
4-Chloro-2-nitrobenzenesulfen(2,4-dichloroanilide), $C_{12}H_7O_2N_2SCl_3$	Golden yellow needles. M.p. 154°C. (41).
4-Chloro-2-nitrobenzenesulfen(2,4-dihydroxyanilide), $C_{12}H_9O_4N_2SCl$	Poorly crystalline. Appeared to melt at 133°C. From the sulfenyl chloride and 2,4-dihydroxyaniline (38).
4-Chloro-2-nitrobenzenesulfen-*p*-dimethylaminoanilide, $C_{14}H_{14}O_2N_3SCl$	Crystals from ether. M.p. 152°C. (40).

TABLE 3—*Continued*

4-Chloro-2-nitrobenzenesulfenodiphenylamide, $C_{18}H_{13}O_2N_2SCl$	M.p. 127°C. (42). Compare 2-nitrobenzenesulfenodiphenylamide (below).
4-Chloro-2-nitrobenzenesulfen-*p*-ethoxyanilide, $C_{14}H_{13}O_3N_2SCl$	Red crystals. M.p. 86°C. From the sulfenyl chloride and *p*-phenetidine.
4-Chloro-2-nitrobenzenesulfenethylanilide, $C_{14}H_{13}O_2N_2SCl$	Red crystals. M.p. 74°C. (41).
4-Chloro-2-nitrobenzenesulfen-*o*-hydroxyanilide, $C_{12}H_8O_3N_2SCl$	Red-brown crystals. M.p. 143°C. From the sulfenyl chloride and *o*-aminophenol in ether (40).
4-Chloro-2-nitrobenzenesulfen-*p*-hydroxyanilide	Red leaves from benzene. M.p. 118–119°C. (38, 39).
4-Chloro-2-nitrobenzenesulfenomethylanilide, $C_{13}H_{11}O_2N_2SCl$	Orange-red. Did not crystallize well, but analyzed correctly (37).
4-Chloro-2-nitrobenzenesulfen-α-naphthylamide, $C_{16}H_{11}O_2N_2SCl$	Red crystals. M.p. 180°C. (41).
4-Chloro-2-nitrobenzenesulfen-β-naphthylamide	Brown-red crystals. M.p. 176°C. (41).
4-Chloro-2-nitrobenzenesulfen(*p*-phenylazoanilide), $ClNO_2C_6H_3SNHC_6H_4N{=}NC_6H_5$	Red crystals from ether. M.p. 188°C. From the sulfenyl chloride and aminoazobenzene (37).
4-Chloro-2-nitrobenzenesulfen-*o*-toluidide, $C_{13}H_{11}O_2N_2SCl$	Orange-red plates from alcohol. M.p. 127°C. (76); pale yellow crystals, m.p. 123°C. (41).
4-Chloro-2-nitrobenzenesulfen-*p*-toluidide	Red crystals. M.p. 137°C. (41).
4-Chloro-2-nitrobenzenesulfen(2,4,6-trimethylanilide), $C_{15}H_{15}O_2N_2SCl$	Golden yellow needles. M.p. 178°C. (41).
2,5-Dichlorobenzenesulfenanilide, $C_{12}H_9NSCl_2$	White needles. M.p. 85°C. (37).
2,4-Dinitrobenzenesulfenanilide, $C_{12}H_9O_4N_3S$	M.p. 142.5–143°C. (14). This compound and the other 2,4-dinitrobenzenesulfenamides listed below were prepared from the sulfenyl chloride and amines in ether solution.
2,4-Dinitrobenzenesulfenobutylamide, $C_{10}H_{13}O_4N_3S$	M.p. 88.5–89°C. (14).
2,4-Dinitrobenzenesulfen-*p*-bromoanilide, $C_{12}H_8O_4N_3SBr$	M.p. 180.5–181°C. (14).
2,4-Dinitrobenzenesulfen-*p*-chloroanilide, $C_{12}H_8O_4N_3SCl$	M.p. 164–164.5°C. (14).

TABLE 3—*Continued*

2,4-Dinitrobenzenesulfenocyclohexylamide, $C_{12}H_{15}O_4N_3S$	M.p. 109.5–110°C. (14).
2,4-Dinitrobenzenesulfen(*N*-cyclohexylmethylamide), $C_{13}H_{17}O_4N_3S$	M.p. 95.5–96°C. (14).
2,4-Dinitrobenzenesulfenethylamide, $C_8H_9O_4N_3S$	M.p. 66–66.5°C. (14).
2,4-Dinitrobenzenesulfenomethylamide, $C_7H_7O_4N_3S$	M.p. 99–99.5°C. (14).
2,4-Dinitrobenzenesulfen-*p*-methoxyanilide, $C_{13}H_{11}O_5N_3S$	M.p. 158–159°C. (14).
2,4-Dinitrobenzenesulfen-α-naphthylamide, $C_{16}H_{11}O_4N_3S$	M.p. 188.5–189°C. (14).
2,4-Dinitrobenzenesulfen-β-naphthylamide	M.p. 167–168°C. (14).
2,4-Dinitrobenzenesulfenopentylamide, $C_{11}H_{15}O_4N_3S$	Oil (14).
2,4-Dinitrobenzenesulfenopropylamide, $C_9H_{11}O_4N_3S$	M.p. 94–94.5°C. (14).
2,4-Dinitrobenzenesulfen-*o*-toluidide, $C_{13}H_{11}O_4N_3S$	M.p. 155–156°C. (14).
2,4-Dinitrobenzenesulfen-*p*-toluidide	M.p. 161–161.5°C. (14).
2-Methyl-2-butanesulfenopiperidide, $C_{10}H_{21}NS$	Colorless liquid. B.p. 100°C./12 mm. From the sulfenyl iodide and piperidine in ether (87).
4-Methyl-2-nitrobenzenesulfenamide, $C_7H_8O_2N_2S$	Orange-red needles. M.p. 147°C. Acetyl derivative, m.p. 188°C. (decomposition) (114).
4-Methyl-2-nitrobenzenesulfenanilide, $C_{13}H_{12}O_2N_2S$	Pale orange crystals. M.p. 91°C. (114).
4-Methyl-2-nitrobenzenesulfenodimethylamide, $C_9H_{12}O_2N_2S$	Yellow needles. M.p. 76°C. (114).
4-Methyl-2-nitrobenzenesulfenomethylamide, $C_8H_{10}O_2N_2S$	Deep yellow needles. M.p. 46°C. (114).
4-Methyl-2-nitrobenzenesulfenomethylanilide, $C_{14}H_{14}O_2N_2S$	Yellow crystals. M.p. 78°C. (114).
4-Methyl-2-nitrobenzenesulfen(1-(4-methyl-2-nitrophenylthio)-2-naphthylamide), $C_{24}H_{19}O_4N_3S_2$	Yellow-brown crusts. M.p. 184°C. (114).

TABLE 3—*Continued*

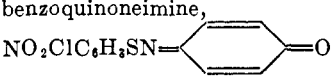
4-Methyl-2-nitrobenzenesulfen-α-naphthylamide, $C_{17}H_{14}O_2N_2S$	Pale orange needles. M.p. 143°C. (114).
4-Methyl-2-nitrobenzenesulfen-β-naphthylamide	Pale orange needles. M.p. 177°C. (114).
4-Methyl-2-nitrobenzenesulfen-*o*-toluidide, $C_{14}H_{14}O_2N_2S$	Brown-red plates or leaves. M.p. 140°C. (114).
4-Methyl-2-nitrobenzenesulfen-*p*-toluidide	Yellow-brown prisms. M.p. 81°C. (114).
N-Benzylidene-1-chloro-2-naphthalenesulfenamide, $ClC_{10}H_6SN{=}CHC_6H_5$	Colorless needles. M.p. 106–107°C. From 1-chloronaphthalene-2-sulfenamide and benzaldehyde in alcohol at room temperature for 24 hr. (108).
N-Benzylidene-4-chloro-2-nitrobenzenesulfenamide, $ClNO_2C_6H_3SN{=}CHC_6H_5$	Yellow needles. M.p. 161°C. From 4-chloro-2-nitrobenzenesulfenamide and benzaldehyde in boiling alcohol (106).
N-Benzylidene-4-methyl-2-nitrobenzenesulfenamide, $C_{14}H_{12}O_2N_2S$	Yellow needles. M.p. 146°C. (114).
N-Benzylidene-2-nitrobenzenesulfenamide, $C_{13}H_{10}O_2N_2S$	Golden yellow needles. M.p. 159°C. (109).
N-Benzylidene-4-nitrobenzenesulfenamide, $C_{13}H_{10}O_2N_2S$	Shining, silken needles. M.p. 130°C. (113).
N-Benzylidenetriphenylmethanesulfenamide, $C_{26}H_{21}NS$	Yellow needles. M.p. 128°C. From triphenylmethanesulfenamide and benzaldehyde in benzene in presence of sodium ethoxide (100).
N-(4-Chloro-2-nitrophenylthio)-*p*-benzoquinoneimine, 	Orange crystals. M.p. 194°C. By oxidation of 4-chloro-2-nitrobenzenesulfen-*p*-hydroxyanilide with hydrogen peroxide (39).
N-(4-Chloro-2-nitrophenylthio)-2-hydroxy-*p*-benzoquinoneimine, $C_{12}H_7O_4N_2SCl$	By oxidation of 4-chloro-2-nitrobenzenesulfen(2,4-dihydroxyanilide) with hydrogen peroxide (38).
N-Isopropylidene-4-methyl-2-nitrobenzenesulfenamide, $CH_3NO_2C_6H_3SN{=}C(CH_3)_2$	Yellow needles. M.p. 116°C. From 4-methyl-2-nitrobenzenesulfenamide by refluxing with acetone (114).
N-Isopropylidene-2-nitrobenzenesulfenamide, $C_9H_{10}O_2N_2S$	Yellow needles. M.p. 86°C. (109).
2-Naphthoxazolesulfenopiperidide, $C_{16}H_{16}ON_2S$	Crystals from alcohol. M.p. 71–73°C. From 2-mercaptonaphthoxazole and piperidine with aqueous sodium hypochlorite (99).

TABLE 3—*Continued*

2-Nitrobenzenesulfenamide, $C_6H_6O_2N_2S$	Golden needles. M.p. 124–125°C. Acetyl derivative, m.p. 179°C. From the sulfenyl chloride and ammonia in ether (15, 109); or from 2-nitrobenzenesulfenyl thiocyanate and ammonia in benzene (66).
2-Nitrobenzenesulfenanilide, $C_{12}H_{10}O_2N_2S$	Brick-red crystals. M.p. 95°C. (74); m.p. 94°C. (109); 88.5–89°C. (corr.) (15).
2-Nitrobenzenesulfenobutylamide, $C_{10}H_{14}O_2N_2S$	M.p. 27–28°C. (corr.) (15).
2-Nitrobenzenesulfen-*p*-bromoanilide, $C_{12}H_9O_2N_2SBr$	M.p. 146–146.5°C. (corr.) (15).
2-Nitrobenzenesulfen-*o*-chloroanilide, $C_{12}H_9O_2N_2SCl$	Crystals from alcohol. M.p. 130°C. (56, 76).
2-Nitrobenzenesulfen-*p*-chloroanilide	M.p. 143.5–144°C. (corr.) (15).
2-Nitrobenzenesulfenocyclohexylamide, $C_{12}H_{16}O_2N_2S$	M.p. 51.5–52°C. (corr.) (15).
2-Nitrobenzenesulfenodiethylamide, $C_{10}H_{14}O_2N_2S$	Oil (15).
2-Nitrobenzenesulfenodimethylamide, $C_8H_{10}O_2N_2S$	Yellow leaves or needles from methyl alcohol. M.p. 62.5–63°C. (corr.) (15); 63°C. (109).
2-Nitrobenzenesulfenodiphenylamide, $C_{18}H_{14}O_2N_2S$	Could not be prepared from the sulfenyl chloride and diphenylamine (15).
2-Nitrobenzenesulfenethylamide, $C_8H_{10}O_2N_2S$	M.p. 32.5–33°C. (15).
2-Nitrobenzenesulfen-4-methoxyanilide, $C_{13}H_{12}O_3N_2S$	M.p. 138–138.5°C. (corr.) (15).
2-Nitrobenzenesulfenomethylamide, $C_7H_8O_2N_2S$	Deep yellow needles. M.p. 36°C. (15, 109).
2-Nitrobenzenesulfenomethylanilide, $C_{13}H_{12}O_2N_2S$	M.p. 86–86.5°C. (corr.) (15).
2-Nitrobenzenesulfen-*o*-nitroanilide, $C_{12}H_9O_4N_3S$	Could not be prepared from the sulfenyl chloride and *o*-nitroaniline (15).
2-Nitrobenzenesulfen-α-naphthylamide, $C_{16}H_{12}O_2N_2S$	M.p. 130.5–131°C. (corr.) (15); 129°C. (109).
2-Nitrobenzenesulfen-β-naphthylamide, $C_{16}H_{12}O_2N_2S$	M.p. 202–202.5°C. (corr.) (15); 188°C. (109).

TABLE 3—*Continued*

2-Nitrobenzenesulfen-(1-(2-nitrophenylthio)-2-naphthylamide), $C_{22}H_{15}O_4N_3S_2$	Yellow crystals. M.p. 186–187°C. (109).
2-Nitrobenzenesulfenopropylamide, $C_9H_{12}O_2N_2S$	Oil (15).
2-Nitrobenzenesulfen-*o*-toluidide, $C_{13}H_{12}O_2N_2S$	Reddish orange crystals. M.p. 119.5–120°C. (74); 115.5–116°C. (corr.) (15).
2-Nitrobenzenesulfen-*m*-toluidide	M.p. 106.5–107°C. (15).
2-Nitrobenzenesulfen-*p*-toluidide	Golden yellow needles or leaves. M.p. 136–136.5°C. (corr.) (15); 135°C. (74); 133°C. (109).
4-Nitrobenzenesulfen(2-benzothiazolylamide), $C_{13}H_9O_2N_3S_2$	Yellow needles. M.p. 193°C. From 4-nitrobenzenesulfenyl chloride and 2-benzothiazolylamine (8).
4-Nitrobenzenesulfenamide, $C_6H_6O_2N_2S$	Deep yellow needles. M.p. 103°C. (113).
4-Nitrobenzenesulfenanilide, $C_{12}H_{10}O_2N_2S$	Yellow leaves or needles. M.p. 75°C. (74, 113).
4-Nitrobenzenesulfen-*o*-chloroanilide, $C_{12}H_9O_2N_2SCl$	Crystals from alcohol. M.p. 99–101°C. (76).
4-Nitrobenzenesulfenodimethylamide, $C_8H_{10}O_2N_2S$	Yellow. M.p. 48°C. (113).
4-Nitrobenzenesulfen(4,6-dimethyl-2-pyrimidylamide), $C_{12}H_{12}O_2N_4S$	Crystals from alcohol. From ethyl 4-nitrobenzenesulfenate and the amine in dry benzene. Oxidized to the sulfonamide (6b).
4-Nitrobenzenesulfenoguanidide, $C_7H_8O_2N_4S$	Not isolated. Oxidized to the sulfonamide. From ethyl 4-nitrobenzenesulfenate or the corresponding sulfenyl chloride plus guanidine nitrate and sodium ethoxide in benzene (6).
4-Nitrobenzenesulfenomethylamide, $C_7H_8O_2N_2S$	Yellow needles. M.p. 48°C. (113).
4-Nitrobenzenesulfen(4-methyl-2-thiazolylamide), $C_{10}H_9O_2N_3S_2$	Not isolated; used in synthesis (6c).
4-Nitrobenzenesulfen(4-methyl-2-thiazolylmethylamide), $C_{11}H_{11}O_2N_3S_2$	Not isolated; used in synthesis. From the sulfenyl chloride and *N*-methyl(4-methyl-2-thiazolylamine) (5).
4-Nitrobenzenesulfen(1-(4-nitrophenylthio)-2-naphthylamide), $C_{22}H_{15}O_4N_3S_2$	Yellow crystals. M.p. 195°C. (113).

TABLE 3—*Concluded*

4-Nitrobenzenesulfen(2-pyridylamide), $C_{11}H_9O_2N_3S$	Prisms from benzene. M.p. 170–173°C. From the sulfenyl chloride or ethyl sulfenate and 2-pyridylamine (6a, 8).
4-Nitrobenzenesulfen(2-pyrimidylamide), $C_{10}H_8O_2N_4S$	Not isolated. Oxidized to the corresponding sulfonamide (6b).
4-Nitrobenzenesulfen-*p*-toluidide, $C_{13}H_{12}O_2N_2S$	Yellow needles. M.p. 73°C. (113).
N,*N*′-(Bis-4-chloro-2-nitrobenzenesulfenyl)benzidine, $(ClNO_2C_6H_3SNHC_6H_4)_2$	M.p. 235°C. (decomposition) (42).
N,*N*-Bis(trimethylmethanesulfenyl)piperazine, $C_{12}H_{26}N_2S_2$	Colorless leaves. M.p. 120°C. From the sulfenyl chloride, bromide, or iodide plus piperazine in ether (85, 87).
p-Toluenesulfenanilide, $C_{13}H_{13}NS$	Colorless needles. M.p. 80–81°C. (64, 65).
Trimethylmethanesulfenodimethylamide, $C_6H_{15}NS$	B.p. 55.5°C./82 mm.; 58.5°C./90 mm.; 60.5°C./96 mm.; 47–51 per cent yield from the sulfenyl iodide and amine (87).
Trimethylmethanesulfenomethylamide, $C_5H_{13}NS$	Colorless liquid of amine-like odor. B.p. 56.5°C./58 mm.; 61.5°C./70 mm.; 65°C./80 mm.; 68.5°C./94 mm.; 54–56 per cent yield (87).
Triphenylmethanesulfenamide, $C_{19}H_{17}NS$	Colorless crystals. M.p. 126°C. Acetyl derivative, m.p. 187°C. (100).
Triphenylmethanesulfenanilide, $C_{25}H_{21}NS$	White plates. M.p. 103°C. (100).
Triphenylmethanesulfenodimethylamide, $C_{21}H_{21}NS$	Colorless leaves. M.p. 105–108°C. (100).
Triphenylmethanesulfenomethylamide, $C_{20}H_{19}NS$	Colorless leaves from chloroform–alcohol. M.p. 119–120°C. Acetyl derivative, m.p. 133°C.; *N*-nitroso derivative, m.p. 102–103°C. (100).
Triphenylmethanesulfen-*o*-toluidide, $C_{26}H_{23}NS$	Crystals from toluene. M.p. 141°C. (100).

halides with ammonia and primary or secondary amines provided a general method for the preparation of the corresponding sulfenamides.

$$RSX + 2HNR_2 \rightarrow RSNR_2 + R_2NH_2X \qquad (49)$$

This method has been used for the synthesis of a variety of sulfenamides (see table 3). The formation of the sulfenamide is generally achieved by adding ammonia or the amine to the sulfenyl halide dissolved in ether or another appro-

priate solvent. The hydrogen halide generated in the reaction may be conveniently removed by the use of an excess of the reacting amine. The yields of sulfenamides obtainable by this method are usually reported to be high. The reactions proceed smoothly, at low temperatures, and usually occur spontaneously. However, not all amines react with equal facility. Thus, Billman and O'Mahony reported that weakly basic amines such as diphenylamine and *o*-nitroaniline did not react with 2-nitrobenzenesulfenyl chloride, whereas reaction with ammonia, aliphatic amines, aniline, *p*-anisidine, and *p*-bromoaniline occurred with ease (15). In boiling ether solution, however, Gebauer-Fülnegg found that 4-chloro-2-nitrobenzenesulfenyl chloride reacted with diphenylamine to give the expected sulfenamide (see table 3). He reported also that 2,4,6-trichloroaniline, 2,4,6-tribromoaniline, and 2,4-dichloro-1-naphthylamine did not react with 4-chloro-2-nitrobenzenesulfenyl chloride (41). If the sulfenyl halide is subject to hydrolysis, anhydrous conditions are required. However, with a sulfenyl halide such as 2-nitrobenzenesulfenyl chloride, which is not readily decomposed by water, the presence of hydroxylic solvents is not objectionable. As a matter of fact, the reaction of the above sulfenyl chloride with amines has been recommended as a method for identification of the latter in aqueous solutions (15).

2. Sulfenamides from mercaptans

A second procedure for the preparation of certain sulfenamides consists in the reaction between aromatic mercaptans and amines in the presence of oxidizing agents.

$$\mathrm{ArSH} + \mathrm{HNR_2} \xrightarrow{(O)} \mathrm{ArSNR_2} + \mathrm{H_2O} \qquad (50)$$

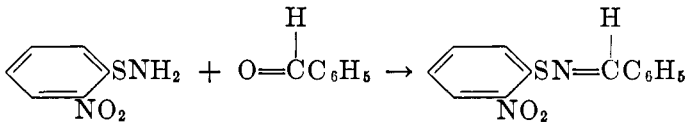
Various modifications for effecting the oxidative elimination of hydrogen between compounds such as 2-mercaptobenzothiazoles and amines have been described in the patent literature (1, 17, 18, 22, 47, 48, 92, 94, 99, 103). Reagents such as hypochlorites, hydrogen peroxide, potassium persulfate, potassium ferricyanide, and the halogens have been reported to be useful for this purpose. However, the number of examples illustrating the application of these oxidizing agents in such reactions is definitely insufficient to permit sound evaluations of their relative efficiencies for the preparation of different types of sulfenamides. Such a comparative study of the synthesis of selected sulfenamides by various methods is now being made in the laboratories of the authors (58).

It is clear that in the synthesis of sulfenamides by reaction of thiophenols or mercaptans with amines in the presence of oxidizing agents, the main competing reaction is the formation of disulfides by oxidation of the thiol. The authors (58) have not been able to verify patent claims for the oxidative formation of sulfenamides, using hydrogen peroxide or potassium ferricyanide as oxidizing agents, with various combinations of thiols and amines. Disulfides were the only products isolated. The oxidative elimination of hydrogen between 2-mercaptobenzothiazole and aliphatic amines whose basicities are equal to or greater than that of ammonia has, however, been achieved by various workers (see

references above) by employing mild alkaline conditions and aqueous solutions of hypochlorites as oxidizing agents. The method does not seem applicable to aliphatic mercaptans, in which case disulfide formation predominates. Thus, with benzyl mercaptan and various amines, benzyl disulfide was the only product isolated in yields of over 90 per cent (58). The preparation of sulfenamides from aromatic thiols and aromatic amines has been claimed in patents, but such claims still await confirmation.

3. Sulfenamides by other methods

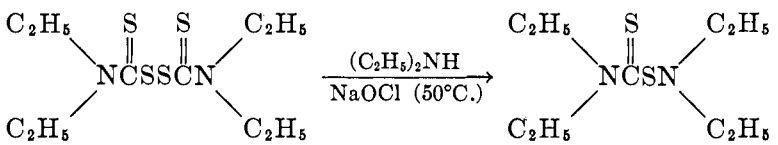
The reaction of sulfenyl thiocyanates with amines affords another synthetic approach to the sulfenamides, but its use has been demonstrated in only a few instances to date (see page 303). It has also been found that certain sulfenamides derived from ammonia react readily with aldehydes and ketones in a manner similar to the formation of Schiff bases from amines and carbonyl compounds. For example:



(51)

XXV

This reaction may therefore serve as a method of preparation for sulfenamides such as compound XXV. In the patent literature (103) it has also been indicated that disulfides such as 2-benzothiazolyl disulfide and aliphatic amines such as piperidine react at temperatures of from 40–150°C. to yield corresponding sulfenamides. It has also been reported that the reaction of tetraethylthiuram disulfide with diethylamine, in the presence of aqueous sodium hypochlorite, leads to the formation of the sulfenamide XXVI (99).



(52)

XXVI

Examples of the formation of the related sulfenimides have been noted on pages 299 and 319, and have been included in table 3.

The spontaneous displacement of the amino group from 2-benzothiazolesulfenamide by other amines whose base strengths are greater than that of ammonia has been reported in a recent patent (53). Thus, mixing 2-benzothiazolesulfenamide with cyclohexylamine results in the formation of 2-benzothiazolesulfenocyclohexylamide and ammonia. Similar reactions have been reported for 2-benzothiazolesulfenamide and ethylamine, ethylenediamine, isopropylamine, benzylamine, morpholine, piperidine, dipropylamine, and dibutylamine (see table 3). These displacement reactions permit the formation of certain types of sulfenamides and are also reminiscent of the displacement reactions observed in

studies of the sulfenanilides (see page 322). It may also be pointed out that the synthesis of sulfenamides may be carried out by using the sulfenic acid esters in place of sulfenyl halides or thiocyanates. Thus, the reaction of 4-nitrobenzenesulfenyl chloride or of ethyl 4-nitrobenzenesulfenate with 2-pyridylamine leads to the same sulfenamide (see table 3).

C. PHYSICAL PROPERTIES OF SULFENAMIDES

The sulfenamides are generally crystalline substances, possessed of sharp melting points, although some members of low molecular weight are liquids. Nitro-substituted aromatic sulfenamides are always reported to be colored, but the sulfenamide group itself is not a chromophore. The solubilities of the sulfenamides vary with the nature of the substituents present, but as a rule, they are more soluble in non-polar solvents, such as benzene and chloroform, than they are in the more polar solvents. Specific physical properties are recorded in table 3.

D. CHEMICAL PROPERTIES OF SULFENAMIDES

1. Thermal stability

The sulfenamides display considerable thermal stability. They may be recrystallized unchanged from various solvents, and the liquid members may be purified by distillation at reduced pressures. When heated at 150–160°C. for several hours, some sulfenanilides rearrange to amino sulfides (see page 321).

2. Acylation

In some respects, the sulfenamides resemble amines rather than amides. The ease of formation of acetyl and benzoyl derivatives by conventional methods (85, 100, 109, 114) seems to be one instance in support of this observation. The reaction with carbonyl compounds (equation 51) is another example of this similarity to amines, as is also the formation of *N*-nitroso derivatives from an amide such as triphenylmethanesulfenamide (100).

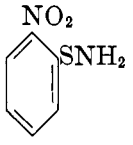
3. Acidic and basic character

In contrast to sulfonamides, the sulfenamides do not display acidic character in aqueous solution. For example, it has been found that various 2-nitrobenzenesulfenamides are not soluble in 10 per cent aqueous sodium hydroxide solution (15). While the sulfenamides probably do possess weakly basic properties, these are not sufficient to allow the formation of salts such as hydrochlorides in aqueous solution. Acid solutions readily effect hydrolysis of the sulfenamide linkage, and it is likely that in this process, the first step is the coördination of the proton by the nitrogen atom of the sulfenamide linkage.

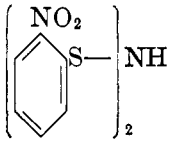
4. Hydrolytic scissions

Billman and coworkers (14, 15) found that various 2-nitrobenzenesulfenamides were cleaved by the passage of hydrogen chloride, for 3 min., into their ethereal solutions. The corresponding sulfenyl halides and amine hydrochlorides were recovered in this procedure in nearly quantitative amounts. Hydrolytic cleav-

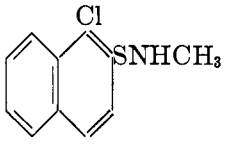
age of the sulfenamides has also been observed by other workers and has even been used to advantage in the synthesis of certain sulfenyl chlorides and bromides (63, 85, 86). Zincke (106, 109, 113, 114) established that it was a general property of nitro-substituted benzenesulfenamides to undergo cleavage, with formation of the sulfenyl chloride, when reacted with concentrated hydrochloric acid, either alone or in conjunction with glacial acetic acid. However, the cleavage of sulfenamides by halogen acids does not always lead to the formation of the sulfenyl chloride. If the particular sulfenyl halide is unstable, the disulfide may be obtained instead. Thus, cleavage of benzenesulfenodiethylamide with hydrogen chloride led to the formation of benzenesulfenyl chloride (equation 25), but the action of hydrogen bromide in carbon tetrachloride solution gave phenyl disulfide (64). In contrast to the formation of sulfenyl chlorides from the sulfenamides by heating with concentrated hydrochloric acid, it was found that the action of hot dilute acids resulted in the formation of sulfenimides. Thus, Zincke found that by heating sulfenamides such as XXVII and XXVIII with dilute hydrochloric or acetic acid, ammonia or methylamine was eliminated and the sulfenimides XXVII-A and XXVIII-A were obtained.



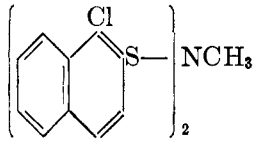
XXVII



XXVII-A

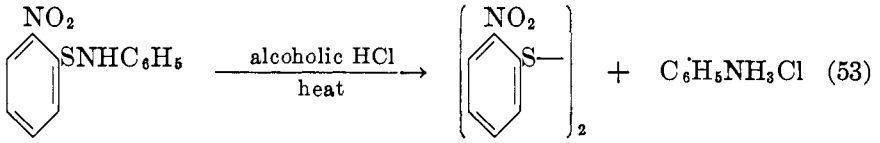


XXVIII



XXVIII-A

Moore and Johnson reported that gentle refluxing of sulfenanilides for extended periods with alcoholic or aqueous solutions of hydrogen chloride resulted in the formation of disulfides and amine hydrochlorides (74, 76).



(53)

Zincke and Eismayer (108) likewise reported that the action of concentrated hydrochloric acid on 2-chloro-1-naphthalenesulfenanilides led to the formation of disulfides and "disulfoxides", but the sulfenyl chloride could not be isolated.

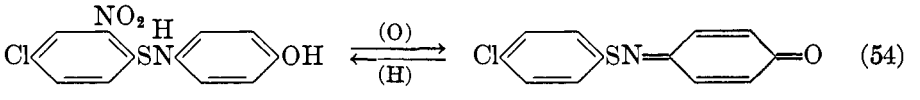
The sulfenamides are more resistant to hydrolytic scission in cold alkaline media than they are in acid solutions. The action of hot alcoholic solutions of sodium hydroxide, however, effects rearrangements of the sulfenanilides to mercapto diarylamines (see page 323). In attempting to reduce nitro-substituted sulfenanilides, such as 4-chloro-2-nitrobenzenesulfen-*p*-hydroxyanilide, to amino derivatives, Gebauer-Fülnegg and Beatty (38) found that this could not be achieved because cleavage of the sulfenamide linkage occurred even under the mildest conditions which were effective for the reduction of the nitro group, for example, by the use of aluminum amalgam in neutral or aqueous solution.

Because of their resemblances to amines, Zincke attempted to diazotize compounds such as 2-nitrobenzenesulfenamide (109). However, the action of nitrite

plus acid resulted in hydrolysis of the sulfenamide. The products obtained were the disulfide and the "disulfoxide," but no indications of products which would be analogous to diazonium chlorides were found. Lecher (64) similarly reported that *p*-toluenesulfenanilide was cleaved by nitrous acid in acetic acid solution. The products reported in this instance were *p*-toluenediazonium acetate and "*p*-tolyl disulfoxide."

5. Oxidations

Although the examples are restricted in number, it seems that oxidation of sulfenamides to the corresponding sulfonamides can readily be effected by alkaline solutions of permanganate or of hydrogen peroxide. This procedure has served as an alternative method for the synthesis of certain sulfonamide derivatives (6, 7, 8). The oxidation of sulfenamides in acid media does not proceed in the same manner. Apparently, hydrolytic scissions accompany the oxidative process, and there results a mixture of more complicated products. Zincke and Farr (109) reported that the action of nitric acid (d = 1.5) on 2-nitrobenzenesulfenamide resulted in a very vigorous reaction, accompanied by deflagration of the sulfenamide. Gebauer-Fülnegg and coworkers (40, 41, 42) made a study of the oxidation of certain sulfenanilides with oxidizing agents such as nitric acid, and potassium dichromate or hydrogen peroxide in conjunction with glacial acetic acid. In none of the experiments were sulfonamides unequivocally identified in the reaction mixtures. The products were generally complex, and in several instances could not be identified. These workers, however, had found that nitrobenzenesulfenyl chlorides reacted with *o*- or *p*-aminophenol to give the corresponding hydroxyanilides (for example, XXIX), and that the latter could be oxidized to the corresponding quinoneimine derivative (XXX) by hydrogen peroxide or potassium dichromate in glacial acetic acid solution (38, 39, 40). By gentle reduction, compound XXX could be reconverted to XXIX.



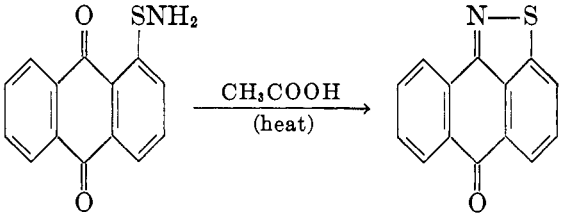
XXIX XXX (54)

Compounds such as XXIX were denoted as "quinonesulfurimines," and their properties and proofs of their structures were reported in the papers already cited. Although these derivatives of benzoquinoneimine could be obtained by the method described above, they were not obtainable by direct reaction of the sulfenyl chloride and quinoneimine. In attempts to obtain an oxime or hydrazone from compound XXX, hydrolysis of the sulfur-to-nitrogen bond occurred and prevented the preparation of such derivatives. The main product of the hydrolytic scissions in these instances was 4-chloro-2-nitrophenyl disulfide (39). In an effort to obtain substances which would be of interest as dyes, Gebauer-Fülnegg and Beatty attempted to introduce auxochrome groups into the "quinonesulfurimines" by reducing the nitro group to the amine. This also could not be achieved because scission of the S—N linkage occurred during the reduction. It was found, however, that the "quinonesulfurimines" formed chelate

compounds with chromium, and the possibility of using them as dyes was investigated. While the required chemical processes for mordanting with chromium salts could be achieved, the colors produced were uninteresting and the investigation was not extended (38).

6. Reactions with carbonyl compounds

Zincke and coworkers (106, 109, 113, 114) demonstrated that it was a general property of sulfenamides, such as 2-nitrobenzenesulfenamide, 4-chloro-2-nitrobenzenesulfenamide, and 1-chloro-2-naphthalenesulfenamide, to react with acetone and benzaldehyde in a manner which resembles the formation of Schiff bases from primary amines (see, for example, equation 51). These reactions were carried out by heating the sulfenamides with excess acetone in a sealed tube at 100°C. for a few hours, or by boiling with alcoholic solutions of benzaldehyde. The reactions with benzaldehyde took place more readily than with acetone. The products obtained (for example, XXV) were excellently crystalline substances which may find use as derivatives for the sulfenamides. Similar reactions with other ketones and with aldehydes other than benzaldehyde, or with other types of sulfenamides, were not investigated by Zincke, although Vörlander and Mittag (100) reported such reactions for triphenylmethanesulfenamide. An interesting example was also described by Fries and Schürmann (32). These workers obtained the isothiazole analog (XXXI) by heating 1-anthraquinonesulfenamide in glacial acetic acid solution.



(55)

XXXI

7. Rearrangements of sulfenanilides

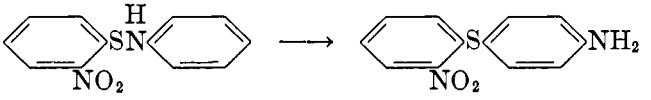
In studies of the reaction between aromatic amines and sulfur, Moore and Johnson (73) corroborated the reports of earlier workers that amino sulfides were formed as products in this reaction, and noted that only those amines which had at least one labile hydrogen atom attached to nitrogen could react with sulfur to yield such products. They therefore postulated that the formation of the amino sulfides was a two-step process as indicated in equation 56.

$$C_6H_5NH_2 \xrightarrow[135\text{–}145°C.]{(S)} C_6H_5NHSNHC_6H_5 \rightarrow H_2NC_6H_4SC_6H_4NH_2 \quad (56)$$

XXXII XXXIII

The isolation of an intermediate product corresponding to XXXII could not be achieved because, at the temperature of the aniline–sulfur reaction, even if the intermediate was actually formed, it was completely decomposed. Because the structures of sulfenanilides, ArSNHAr, are analogous to that of the proposed

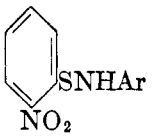
intermediate, Moore and Johnson undertook studies of the rearrangements of these substances. The results of these investigations were subsequently reported in a series of papers. It was found (74, 76) that sulfenanilides such as XXXIV yielded small amounts of amino sulfides, such as XXXV, when simply heated at 150–160°C. for about 5 hr.



(57)

XXXIV XXXV

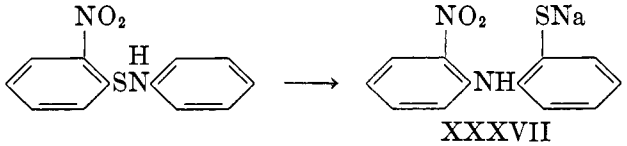
Because rearrangements from nitrogen to carbon are generally favored by the presence of acid, such conditions were studied. Mineral acids could not be used, however, for in their presence hydrolysis of the sulfenamide linkage invariably occurred in preference to rearrangement. Thus, with dilute hydrochloric acid, disulfides were isolated as the products of hydrolytic scission, but products of rearrangement could not be detected (74, 76). Disulfides were also formed when sulfenanilides were heated in the presence of amine hydrochlorides, and also on long digestion with glacial acetic acid. If the sulfenanilides were heated in the presence of excess aromatic amine, however, the amino sulfides were obtained in satisfactory yields. Thus, when 2-nitrobenzenesulfenanilide (XXXIV) was heated for 6 hr. at 180–190°C., with excess of aniline present, *p*-(2-nitrophenylthio)aniline (XXXV) was obtained in 70 per cent yield. In such experiments, in every case but one, the rearrangement reaction gave only a single product. In the one variant instance, when 2-nitrobenzenesulfen-*o*-toluidide was heated with excess *o*-toluidine, two isomeric amino sulfides were obtained. This result was interpreted to indicate that ortho as well as para rearrangement may occur, and to imply that the rearrangement of sulfenanilides occurred in two steps: formation of the ortho isomer, followed by rearrangement of this to the more stable *p*-amino sulfide. It was later determined that if the para-position of the sulfenanilide was blocked, rearrangement to the ortho-position occurred. Whenever possible, however, rearrangement to the para-position predominated. It was also found that in the course of the reaction the anilide group in one sulfenanilide could be displaced by another, and that in this way, there could be formed an amino sulfide corresponding to the externally added amine (76). Thus, when 2-nitrobenzenesulfenanilide was heated at 180–190°C. with an excess of *o*-toluidine, *p*-(2-nitrophenylthio)-*o*-toluidide was obtained. It was established that aniline, *o*-toluidine, and *p*-toluidine were able to displace one another in the rearrangements of the respective sulfenamides to the amino sulfides. *o*-Chloroaniline, however, did not displace the anilide groups in structures corresponding to XXXVI (Ar = phenyl, *o*- or *p*-tolyl).



XXXVI

For example, when 2-nitrobenzenesulfenanilide (Ar = C_6H_5) was heated at 180–190°C. in the presence of excess *o*-chloroaniline, compound XXXV was obtained in 70 per cent yield. Moreover, it was found that *o*-chloroaniline was replaced from its anilides by other aromatic amines, such as aniline or *o*-toluidine, with particular ease. Tabulations of such experiments concerning displacements of one amine by another in the rearrangements of sulfenanilides have been prepared by Moore and Johnson (76). A similar discussion of such rearrangements is given in a patent (56).

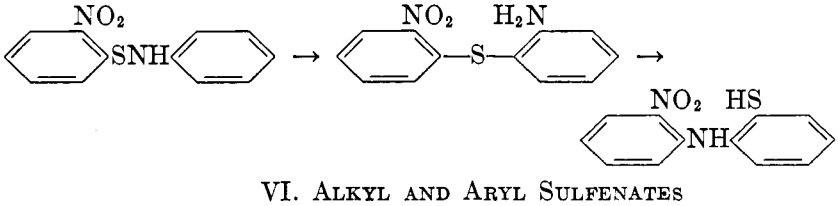
When certain nitro-substituted benzenesulfenanilides are heated in alcoholic sodium hydroxide solutions, the rearrangement takes a different course from the one just described above. Instead of amino sulfides, the products obtained were the corresponding *o*-mercapto diaryl amines (75). For example, if 2-nitrobenzenesulfenanilide was refluxed with dilute alcoholic sodium hydroxide solution for 3 hr., an 87 per cent yield of product XXXVII was obtained.



(58)

XXXVII

The isolation product XXXVII, whose structure was established by conversion to the known thiomethyl ether as described by Wight and Smiles (102), definitely established that 2-nitrobenzenesulfenanilides were capable of undergoing ortho as well as para rearrangements (75). That is, direct heating resulted in the formation of *p*-amino sulfides, while treatment with alcoholic sodium hydroxide favored ortho rearrangement to mercapto diarylamines. In the latter type of rearrangement, it is interesting to note that while 2-nitrobenzenesulfenanilide rearranged very easily to product XXXVII, 4-nitrobenzenesulfenanilides did not rearrange under the same conditions. 2-Nitro-4-chlorobenzenesulfenanilides did, however, rearrange. These differences were considered to indicate that the substitution of the nitrogroup in the para-position did not activate the carbon atom attached to the amino nitrogen to the same extent as was done by a nitro group in the ortho-position. A tabulation of these rearrangements may be found in reference 77. The possibility that the rearrangement of 2-nitrobenzenesulfenanilides to diarylamines occurs through the intermediate formation of the ortho amino sulfides was suggested by Moore and Johnson (75), but they considered that the evidence available for its support was not adequate (equation 59).



(59)

VI. Alkyl and Aryl Sulfenates

Substances corresponding to the formula RSOR′, in which R′ may be an alkyl or aryl radical, may be considered as esters of the sulfenic acids. In accord with

this viewpoint, they have also been designated as sulfenates. These compounds are isomeric with the sulfoxide, but it has been clearly established that the two classes of substances are distinctly different.

A. PREPARATION

The only instances of the direct esterification of a sulfenic acid are the preparations of methyl and ethyl 1-anthraquinonesulfenates (table 4). The most general procedure, however, consists in the reaction of sodium alkoxides or phenoxides with sulfenyl halides (60, 64, 84, 106, 108, 109, 113, 114).

$$RSCl + NaOR' \rightarrow RSOR' + NaCl \quad (60)$$

Presumably, sulfenyl thiocyanates may also be used in place of the sulfenyl halides. Connor (21) calls attention to the fact that the reaction of alkyl hypochlorites with mercaptides does not give sulfenic esters, but that disulfides are formed instead.

$$2RSNa + R'OCl \rightarrow RSSR + R'ONa + NaCl \quad (61)$$

As already mentioned (page 272), 1-anthraquinonesulfenyl bromide reacted with boiling methanol to give the corresponding methyl sulfenate (30).

B. TABULATION

Table 4 lists those alkyl and aryl sulfenates which were encountered in the course of this literature survey.

TABLE 4

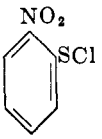
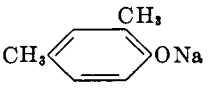
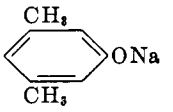
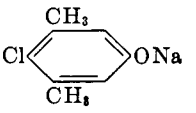
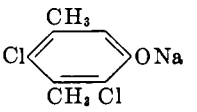
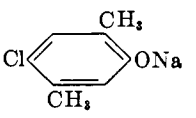
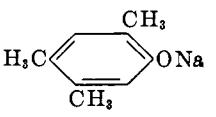
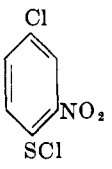
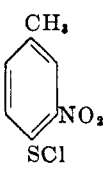
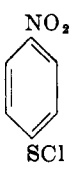
Alkyl and aryl sulfenates

Ethyl 1-anthraquinonesulfenate, $C_{16}H_{12}O_3S$	Red needles. M.p. 149°C. Prepared from the sulfenyl chloride or bromide by reaction with ethyl alcohol, or from the sulfenic acid and ethyl sulfate (30, 32).
Ethyl trimethylmethanesulfenate, $C_6H_{14}OS$	Colorless liquid. B.p. 64°C./89 mm. From the sulfenyl iodide and sodium ethoxide in ether solution (84). The methyl ester was prepared in similar manner (87).
Methyl 1-anthraquinonesulfenate, $C_{15}H_{10}O_3S$	Orange-red needles. M.p. 189°C. From the sulfenyl bromide or the sulfenic acid by boiling with methanol (30).
Methyl benzenesulfenate, C_7H_8OS	Colorless liquid. B.p. 88–89°C./4 mm. (corr.). From benzenesulfenyl chloride and sodium methoxide, in methanol, at 0°C. Yield, 36 per cent. Considerable phenyl disulfide formed simultaneously. Odor resembles that of thiophenol (64).
Methyl 1-chloronaphthalene-2-sulfenate, $C_{11}H_9OSCl$	Nearly colorless oil. From the sulfenyl chloride and sodium ethoxide, in hexane, by shaking at room temperature (108).

TABLE 4—*Concluded*

Nitrobenzenesulfenates

All of the examples listed below were prepared from the corresponding sulfenyl chlorides and sodium alkoxides or phenoxides

SULFENYL CHLORIDE	ALKOXIDE OR PHENOXIDE	MELTING POINT	REFERENCE
		°C.	
	CH_3ONa	54	(109)
	C_2H_5ONa	26	(109)
	C_6H_5ONa	72	(109)
		85	(60)
		74	(60)
		118–120	(60)
		125–127	(60)
		120	(60)
		103	(60)
	CH_3ONa	111–112	(106)
	C_2H_5ONa	73–74	(106)
	C_6H_5ONa	75	(106)
	CH_3ONa		(114)
	CH_3ONa	49	(113)

C. PROPERTIES

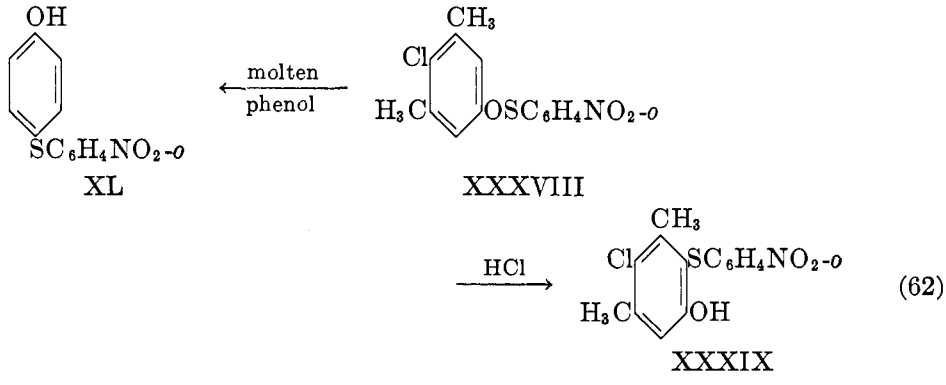
The majority of the reported sulfenic acid esters are solids of definite melting points. The thermal stabilities of these compounds are reflected in the reports that methyl trimethylmethanesulfenate and methyl benzenesulfenate were isolated by distillation at relatively high pressures (see table 4), as well as by the fact that the aryl 2-nitrobenzenesulfenates did not decompose until heated to 120°C. (60). The 2-nitrobenzenesulfenates were invariably reported to be yellow, but since some of the other members were found to be colorless, color is apparently not associated with the sulfenate linkage. In general, the sulfenates were found to be insoluble in water, sparingly soluble in alcohol, and more soluble in ether, benzene, etc.

It might be expected that the oxidation of sulfenates would lead progressively to esters of sulfinic acids and then to sulfonates. This simple addition of oxygen does not seem to occur. Zincke found that the oxidation of alkyl 2-nitrobenzenesulfenates with hydrogen peroxide led to the formation of the free sulfinic acids rather than the esters. At the same time, the formation of smaller proportions of "disulfoxides" was observed. In the oxidation of aryl 2-nitrobenzenesulfenates, the corresponding sulfonic acid ester could also not be obtained. The action of hydrogen peroxide or other oxidizing agents, in warm glacial acetic acid, resulted in disruption of the sulfenates (60).

The hydrolytic stabilities of alkyl sulfenates appear to be somewhat greater than those of the corresponding aryl derivatives. Zincke (109) found that if the phenyl sulfenates were not kept in a vacuum desiccator, rapid decomposition, with the formation of phenol, occurred. Methyl 1-chloro-2-naphthalenesulfenate, however, was also very readily decomposed by exposure to the air (108). In comparing various phenyl 2-nitrobenzenesulfenates, Learmonth and Smiles (60) remarked that those of the esters which contained more fully substituted phenyl groups were more stable than phenyl 2-nitrobenzenesulfenate itself. In passing, it may be noted that methyl *p*-nitrobenzenesulfenate was reported to be less stable than the corresponding *o*-nitrobenzenesulfenate. This is reminiscent of the similar relation between *p*-nitrobenzenesulfenyl chloride and *o*-nitrobenzenesulfenyl chloride.

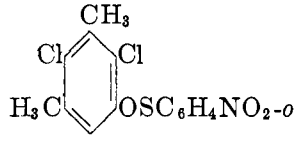
Concentrated hydrochloric acid converts certain sulfenic acid esters to the corresponding sulfenyl chlorides (106, 108, 109, 113, 114). On the other hand, alkaline or neutral hydrolysis leads to the formation of disulfides and "disulfoxides" (108). Zincke observed that the reactions of the sulfenates with sodium hydroxide resulted in the formation of characteristic colors which he ascribed to the intermediate existence of the salts of sulfenic acids. Learmonth and Smiles (60) reported that warm alkali effected the hydrolysis of aryl 2-nitrobenzenesulfenates, but they did not indicate the products obtained.

Corresponding to the rearrangements of the sulfenanilides, as demonstrated by Moore and Johnson, the work of Learmonth and Smiles has shown that phenyl 2-nitrobenzenesulfenates are converted, under the influence of hydrogen chloride in benzene solution, into hydroxy sulfides. The conversion of the sulfenate XXXVIII into the hydroxy sulfide XXXIX is a suitable example.



XL XXXVIII XXXIX (62)

It should be noted, however, that in the rearrangements of sulfenanilides acid conditions could not be used, while in the rearrangements of the aryl sulfenates such conditions are required (see page 322). The yields of hydroxy sulfides obtained in such rearrangements permit this reaction to serve as a convenient means for their preparation. It was also found (60) that an external phenol could displace the original aryl group present in the sulfenate. For example, in the presence of molten phenol, the sulfenate XXXVIII yielded the sulfide XL (equation 62). This ability for one phenol to displace another in the course of the rearrangement reaction, together with other evidence concerning the orientation of the sulfides produced, led Learmonth and Smiles to consider that the conversion of the aryl sulfenates to hydroxy sulfides was not a true intramolecular rearrangement. It was also noted that rearrangement does not always occur. Thus, in the attempt to rearrange 3,5-dimethyl-2,4-dichlorophenyl 2-nitrobenzenesulfenate (XLI) by the standard procedure which was effective in other



XLI

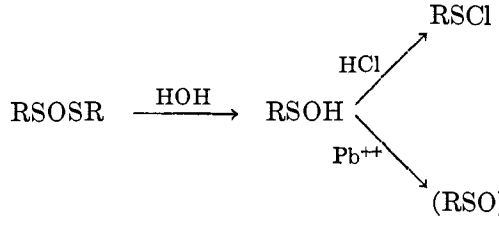
instances, there was obtained the chlorophenol and 2-nitrobenzenesulfenyl chloride; but the hydroxy sulfide, to be expected if rearrangement occurred, was not to be found among the reaction products (60). The possibility that such cleavage of the sulfenic ester may also occur in cases where rearrangement is observed, and that the hydroxy sulfide then results from a secondary reaction between the sulfenyl chloride and the phenol, deserves consideration.

VII. Sulfenic Anhydrides

The sulfenic anhydrides (RSOSR) are formed mainly as the products of hydrolysis of sulfenyl chlorides (106, 108, 109, 113, 114). Presumably they arise in the following fashion:

$$\mathrm{ArSCl} \xrightarrow{\mathrm{HOH}} \mathrm{ArSOH} \xrightarrow{\mathrm{ArSCl}} \mathrm{ArSOSAr} \qquad (63)$$

While each of the nitro-substituted benzenesulfenyl chlorides investigated by Zincke was reconverted to a corresponding sulfenic anhydride, the experiences with these were so nearly alike, and compare so closely to instances cited by other authors, that the description of the experiments with 2-nitrobenzenesulfenic anhydride (109) will serve for illustrative purposes. When 2-nitrobenzenesulfenyl chloride was shaken for about 5 hr. with twenty times its weight of water, at room temperature, a smooth hydrolysis ensued to form 2-nitrobenzenesulfenic anhydride. This substance, like the other members of its class, was difficultly soluble in petroleum ether, ether, and alcohol, but more readily soluble in benzene, glacial acetic acid, chloroform, or acetone. With concentrated hydrochloric acid, the anhydride was converted to 2-nitrobenzenesulfenyl chloride in nearly quantitative yield. The conversion to the sulfenyl chloride could also be readily effected by use of phosphorus pentachloride in ether solution. Accompanying the reaction of the anhydride with aqueous ammonia or sodium hydroxide, there was the development of the characteristic color of the salts of sulfenic acids. This color disappeared on heating, on addition of acid, or if the solution was allowed to stand for some time at room temperature. In alcohol, ammoniacal solutions retained their color for considerably longer periods than aqueous solutions. If a freshly prepared ammoniacal solution was treated with lead acetate, there was precipitated a blue product, presumably the lead salt, which rapidly became colorless. Zincke suggested that such reactions implied an amphoteric character for sulfenic acids. That is, the reaction of the anhydrides with hydrochloric acid indicated their basic character, and their reaction with lead acetate or bases, to give the transitory metal sulfenates, showed an acidic character.



(64)

The products isolated from the alkaline hydrolysis of 2-nitrobenzenesulfenic anhydride were chiefly 2-nitrophenyl disulfide and 2-nitrobenzenesulfinic acid. The "disulfoxide" was considered to be an intermediate product in the formation of the disulfide and sulfinic acid, but it was not actually isolated in this instance. In other cases (113) the "disulfoxide" was reported among the products of hydrolysis. It was found that the decomposition of 2-nitrobenzenesulfenic anhydride into the disulfide and sulfinic acid occurred spontaneously when the anhydride was covered with a layer of aqueous sodium hydroxide. This immediate formation of the insoluble disulfide explained why the sulfenic anhydrides never seemed to dissolve completely in sodium hydroxide solutions. (Notations regarding 1-chloro-2-naphthalenesulfenic anhydride are recorded in reference 108, and the anhydrides of the anthraquinonesulfenic acids have already

been referred to in Section II.) The various nitro-substituted benzenesulfenic anhydrides which were prepared by Zincke were definite products which gave correct analyses for the elements, but they did not display sharp melting temperatures. Examples of the sulfenic anhydrides which were encountered in this literature survey are listed in table 5.

TABLE 5

Sulfenic anhydrides

1-Anthraquinonesulfenic anhydride, $C_{28}H_{14}O_5S_2$	From 1-anthraquinonesulfenic acid by heating. Not obtained pure (30).
2-Anthraquinonesulfenic anhydride, $C_{28}H_{14}O_5S_2$	Colorless crystals. M.p. 260°C. (decomposition). From 2-anthraquinonesulfenyl chloride by hydrolysis (32).
1-Chloro-2-naphthalenesulfenic anhydride, $C_{20}H_{12}OS_2Cl_2$	Pale yellow crystals from toluene. M.p. 149°C. (decomposition). From the sulfenyl chloride by alkaline hydrolysis (108).
4-Chloro-2-nitrobenzenesulfenic anhydride, $C_{12}H_6O_5N_2S_2Cl_2$	Yellow plates. Sinter at 115–116°C. but do not melt unless heated above 200°C. May be recrystallized from glacial acetic acid (106).
2-Nitrobenzenesulfenic anhydride, $C_{12}H_8O_5N_2S_2$	Yellow plates from benzene. Darken at 92–93°C., fuse, and do not remelt until heated above 180°C. By hydrolysis of the chloride with water at room temperature. Some disulfide formed as side product (109).
4-Nitrobenzenesulfenic anhydride, $C_{12}H_8O_5N_2S_2$	Yellow leaves. Darken at 126°C. and melt with decomposition at 160°C. By hydrolysis of the chloride with dilute alcohol or acetic acid (113).
2-Nitro-4-methylbenzenesulfenic anhydride, $C_{14}H_{12}O_5N_2S_2$	Pale yellow crystalline powder. M.p. 194°C. with previous discoloration. By hydrolysis of the sulfenyl chloride with water (114).

The authors are grateful to Professor Charles D. Hurd for his critical reading of the manuscript, and to the Abbott Fund of Northwestern University for a fellowship to support certain experimental studies in this work.

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