sity of the bands at 3, 7.6, 8.0, 8.9, 11.9 μ which may be associated with the vibration of the hydroperoxy group were decreased. The band at 9.8 μ shifted to 9.9 μ indicating decomposition of the hydroperoxide to a peroxide.

Removal of Dienes from Severely Cracked Naphtha by Co-oxidation with 2-Naphthalenethiol.—a. 2-Naphthalenethiol (16 g., 0.1 mole) was dissolved in 100 ml. (82 g.) of severely cracked naphtha of diene number 34. Air was introduced into the solution at room temperature for 3 hr. Then the solution was cooled to 0° and the air introduction was continued for another 3 hr. At the end of this period, the clear orange-colored reaction mixture was placed in a cold box at −15°. At this temperature, an almost colorless solid precipitated. It was filtered off by suction and washed with cold *n*-heptane. In this manner, 0.4 g. of substance having peroxide equivalent 242 was obtained. When the filtrate (65.3 g.) was diluted with an equal volume of *n*-heptane, 24 g. of orange-colored co-oxidation product separated as a bottom phase at room temperature. The latter product had a peroxide equivalent of 393. The diene number of the severely cracked naphtha decreased to one third of the original as a result of the treatment.

The solid peroxidic product showed the following composition on analysis: C, 72.72; H, 5.05; S, 7.2; 0 (by difference), 15.03. The liquid peroxide isolated had a sulfur content of 8.35%. The infrared spectrum of both is shown in Fig. 3.

b. In 100 ml. of severely cracked naphtha of diene number 14, 16 g. (0.1 mole) of 2-naphthalenethiol was dissolved while air was introduced into the mixture. Then the solution was cooled by ice water to about 0°, while the introduction of air was continued. At 0°, however, some of the naphthalenethiol precipitated. Therefore the mixture was allowed to come to room temperature. During the second cooling period, no precipitation was observed. This showed the progress of the reaction. After a total of 4 hr. of air introduction, the solution was kept overnight at −29°, when 4.4 g. of light yellow liquid separated. On further cooling to −73°, 16 g. more substance crystallized, which turned to a yellow liquid at room temperature. These liquids gave a positive qualitative peroxide test.

The naphtha filtrate after this treatment was distilled at 10 mm. on a steam bath to yield 80 ml. of a colorless distillate with a diene number of 1.6. This distillate remained colorless for 5 days when left standing in an open Erlenmeyer flask at 43°. The distillation residue deposited 2.4 g. of crystals which had a peroxide equivalent of 1692.

Air Oxidation of Severely Cracked Naphtha.—A 100-ml. sample of the severely cracked naphtha used in experiment b was air oxidized in the same manner as in (b), but at 0° without the addition of naphthalenethiol. After 8 hr. of air introduction, the naphtha was distilled at 10 mm. (maximum bath temperature 100°). The distillate obtained (89 ml.) contained more low boiling constituents than the corresponding distillate of experiment b above, but was colored (Rob. 18.5) and had a diene number of 13.

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Sulfobenzoic Acid Esters. III. The Correct Structures of the Aryl Esters

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The structures of the compounds previously assumed to be phenyl 2-sulfamylbenzoate and its isomer, phenyl 2-sulfobenzamide, have both been shown to be incorrect; the various reactions involving these compounds have been elucidated.

Previous papers in this series[1] described the synthesis of aliphatic esters of 2-sulfamylbenzoic acid for evaluation as potential anticonvulsant agents. As part of this study the corresponding aryl esters were also desired.

The preparation of such a compound (*4*) and its isomer (*3*) (Fig. 1) was reported by Remsen[2,3] more than 60 years ago. We have discovered, in repeating Remsen's work, that certain of the structures which he assigned to his products are incorrect.

The reactions carried out by Remsen and the structures which he assigned to his products are shown in Fig. 1.

According to Remsen,[2] the diacid chloride of *o*-sulfobenzoic acid on heating with phenol gave an oil (*1*) which on stirring with ammonium hydroxide gave a mixture of the diphenyl ester (*3*) and another substance (*4*), m.p. 130°, whose analysis agreed with the structure he assigned to it (Fig. 1). Subsequently,[3] the half ester (*2*) was isolated from

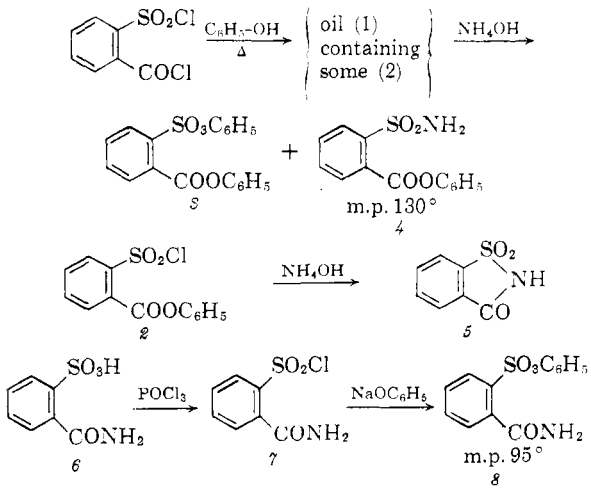


Fig. 1.—Reactions showing structures assigned by Remsen.

(1) B. Loev and Minerva Kormendy, Part I, *J. Org. Chem.*, **27**, 1703 (1962); Part II, *ibid.*, **27**, 2177 (1962).

(2) I. Remsen and S. R. McKee, *Am. Chem. J.*, **18**, 794 (1896).

(3) I. Remsen and R. E. Humphreys, *ibid.*, **30**, 292 (1903).

the oil (*1*), but treatment of pure *2* with ammonia gave saccharin (*5*) rather than the expected sulfamyl benzoate (*4*).

To support the assignment of structure *4*, a compound claimed to be the isomeric substance (*8*), was synthesized from *o*-sulfobenzamide by the route shown in the lower part of Fig. 1.[3] The analysis (N and S) agreed with the structure indicated.

On the basis of the evidence to be presented below, we have established that Remsen's compound (*4*) actually has the structure A and his compound (*8*) is in fact the nitrile B.

We have repeated the reactions described by Remsen (Fig. 1) and have isolated compounds whose physical properties and analyses agree essentially with those he reported.[4] Although the intermediate (*2*) could not be isolated following Remsen's procedure, this compound, identical in all respects to Remsen's material was prepared unambiguously as shown in Fig. 2.

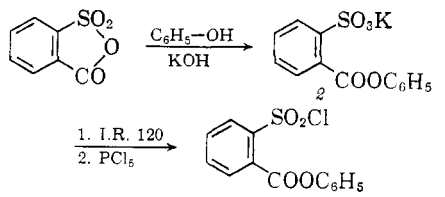


Figure 2

On the basis of our previous experience with aliphatic esters of sulfobenzoic acid,[1] it appeared that many of the reactions shown in Fig. 1 were inconsistent with the structures assigned by Remsen.

For example: (a) Although *4* could be obtained by treatment of the crude oil (*1*) with aqueous ammonia, it could not be prepared from pure *2*, the presumed precursor, under the same conditions. (b) Compound *4* could be obtained on treatment of *1* with *aqueous* ammonia, whereas in the aliphatic ester series,[1] compounds corresponding to *4* could *only* be prepared by the use of *anhydrous* ammonia—with aqueous ammonia only saccharin resulted. (c) When an *aliphatic* ester corresponding to *4* is treated with dilute aqueous base, it immediately dissolves as it is converted to a water-soluble salt of saccharin—in contrast, *4* is insoluble even in concentrated base and dissolves only slowly on heating, with evolution of ammonia, and the formation of only traces of saccharin. It seems most unlikely that the phenyl ester should be more resistant to cyclization than were the alkyl esters. (d) If *4* has the structure assumed by Remsen, then *3* and *4* should show almost identical infrared absorption characteristics in the carbonyl region—however, *3* absorbs at 5.7 μ, whereas *4* absorbs at 6.0 μ. The observation concerning the difference in absorption characteristics,[5] the marked difference in behavior of *2* and *4* with ammonia, and the marked difference in the behavior of *4* and the aliphatic counterpart with aqueous base, left no alternative but that the structure assigned to *4* was incorrect.

It became clear that only structure A was consistent with the analyses and reactions observed for *4*.

This conclusion was further substantiated by a comparison of the infrared absorption spectra of *3* and *4* with those of various authentic materials (Table I). It can be seen that *4* clearly shows the presence of a carboxamide and the absence of sulfonamide and carboxylic ester groups.[6]

Having thus shown that the structure of *4* is really A (the structure which Remsen had erroneously assigned to compound *8*), it then became necessary to elucidate the reactions involving compounds *6*, *7*, and *8* (Fig. 1).

We found that *8* showed *no absorption in the carbonyl region* of the infrared absorption spectrum —instead, it showed nitrile absorption. The compound was therefore assigned structure B.

The structure of *8* as B was confirmed by hydrolysis of *8* to a compound identical to *4* (*i.e.*, A) (see Fig. 3).

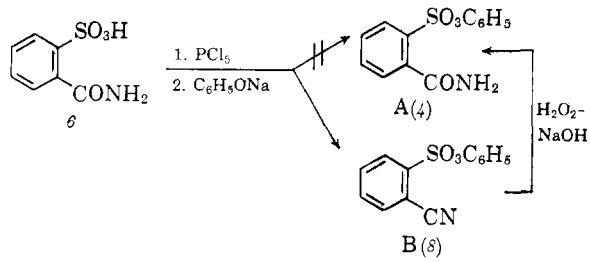


Figure 3

Microanalytical data are consistent with both assignments of structure. The previous workers, unfortunately, analyzed *8* only for nitrogen and

(4) Something of a polemic occurred between R. List and M. Stein, *Ber.*, **31**, 1648 (1898) and Remsen.[3] List and Stein claimed that they could not duplicate the preparation of *4* and made the following sweeping statement: "Despite the most careful research, we have been unable to obtain the *o*-sulfamylbenzoate described by Remsen. According to our experiments this ester does not appear to be capable of existence." As it turns out, they were wrong with respect to the *preparation* of *4*, but prophetic with respect to the *o*-sulfamylbenzoate A *structure*.

(5) In the early stages of this work, in order to account for the discrepancy in spectra, we considered that the structure of *3* might be incorrect, and that an acid-catalyzed rearrangement to a hydroxybenzophenone or a cyclic ortho ester might have occurred. Such assumptions proved to be physically and chemically inconsistent with the properties of *3*.

(6) The absorption of aryl sulfonates was not sufficiently characteristic to be used for structural proof, hence was not included in the table.

TABLE I
INFRARED ABSORPTION PEAKS

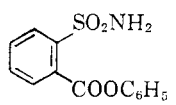
Compound	Position of absorption (μ) —COOR	—CONH₂	—SO₂NH₂
(4) or A	...	6.0	...
(3)	5.7, 7.8, 8.05, 9.2	...	...
C_6H_5—COO—C_6H_5	5.7, 7.9, —, 9.2	...	...
C_6H_5—$CONH_2$	...	6.0	...
C_6H_5—SO_2NH_2	...	...	7.5
1,3-$NH_2SO_2C_6H_4CONH_2$	...	6.0	7.5
1,3-$NH_2SO_2C_6H_4COOPr$-i[a]	5.8, 7.9, —, 9.1	...	7.5
1,2-$Me_2NSO_2C_6H_4COOC_6H_5$ (9)	5.7, 7.7, 8.0, 9.1	...	7.45
1,2-$C_6H_5OSO_2C_6H_4CN$ ((8) or B)[b]	...	..	...

[a] Ref. 1. [b] Showed CN absorption at 4.49 μ.

sulfur, and the percentages of these two elements are not very different in structures A and B.[7]

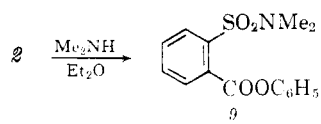
Having thus established the correct structure of *4* as A, and *8* as B, we can now satisfactorily explain the earlier apparent anomalies.

It is now obvious why pure *2* did not give *4* (now A). Furthermore, the fact that *2* did not give a new substance (which would be the desired compound C), but gave only saccharin, even with an-



C

hydrous ammonia, indicates that the aryl esters are even more sensitive to alkaline conditions than are the alkyl esters. When cyclization to saccharin is prevented, as on treatment of *2* with dimethylamine, a good yield of *9*, the *N,N*-dimethyl derivative of the unstable C, was formed.[8]



9

The infrared absorption of *9* (Table I) was entirely different from *4* and clearly consistent with that expected for the structure drawn.

The products obtained in the reaction of *1* with ammonia can be explained as shown in Fig. 4. The oil *1*, undoubtedly contains a mixture of all possible products and some unreacted starting material. The presence of *2* and *3* was established by Remsen.[8,9] Compound *2*, which might be expected to be the major constituent, on treatment with ammonia may form C, but this is immediately converted to saccharin. Any unchanged starting material (dichloride) would also give saccharin. *10* must be present as the precursor of A.

(7) For A: $C_{13}H_{11}NO_4S$: Calcd.: N, 5.07; S, 11.57. For B: $C_{13}H_9NO_3S$: Calcd.: N, 5.4; S, 12.35. Found[3]: N, 5.32; 5.27; S, 12.11; 11.81.

(8) Reaction of II with monomethyl amine gave only *N*-methylsaccharin.

(9) *3* has been isolated[3] from the crude oil *1* as well as after ammonia treatment as shown in Fig. 1. It is quite stable to ammonia; only after heating with aqueous ammonia under pressure for several hours does it react to give some saccharin.

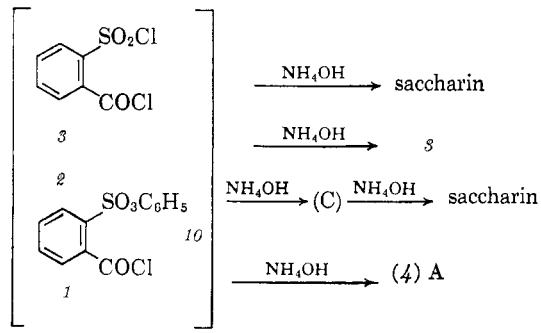
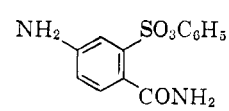


Figure 4

The stability of A to base, in contrast to the lability of C, is not really surprising. In C the phenoxide is easily displaced by the sulfamyl anion and the formation of saccharin from various sulfamyl derivatives is well known.[10a] In the case of the isomeric substance, A, one now has to contend with the extraordinary stability of aryl sulfonates to nucleophilic displacement reactions.[10b,11] The instability of the aromatic ester C compared to the corresponding aliphatic ester is also not surprising, for one is here encountering the well known reactivity of aryl esters to nucleophilic reagents.[12]

One of the most surprising features in this work was the formation of a sulfonic ester from phenol and a sulfonyl chloride under strongly acidic conditions. This reaction has always been claimed to require a base or other acid acceptor.[13]

The *p*-chlorophenyl esters, corresponding to *3* and A, and the phenyl ester of 4-amino-2-sulfobenzamide (*11*) have also been prepared.



11

(10) (a) "The Organic Chemistry of Tetravalent Sulfur Compounds," C. M. Suter, J. Wiley and Sons, Inc., New York, N. Y., 1944, p. 618; (b) *ibid.*, p. 539.

(11) Another example of the difference in tendency of the isomers to cyclize is illustrated by the two isomeric sulfobenzoic acid amides. 2-Sulfamylbenzoic acid cyclizes to saccharin with such facility that it is difficult to prepare this acid pure. On the other hand, 2-sulfobenzamide cannot be converted to saccharin even on prolonged heating at 300°.

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 211.

(13) R. Connor, "Organic Chemistry," Vol. 1, H. Gilman, ed., J. Wiley and Sons, Inc., New York, N. Y., 1943, p. 898.

Compound *11* was prepared in the same manner as was A, starting with 4-nitro-2-chlorosulfonylbenzoyl chloride,[1] followed by a final reduction step.

Experimental[14]

Diphenyl 2-Sulfobenzoate (*3*) and the Oil (*1*).—A mixture of 23.9 g. (0.1 mole) of 2-chlorosulfonylbenzoyl chloride[1] and 18.8 g. (0.2 mole) of phenol was heated under reduced pressure at 40–45° for 5 hr. The resulting red oil (*1*) was treated with concentrated ammonium hydroxide. The color changed to yellow and a new oil separated which crystallized on standing. This solid was dissolved in hot ethanol, then water was added to reach a cloud point; the solution was left to cool slowly. White crystals separated, were filtered, and were recrystallized again from ethanol, m.p. 118–120° (lit.,[3] m.p. 118–120°), 7.3 g. (20%).

Anal. Calcd. for $C_{19}H_{14}SO_5$: C, 64.34; H, 3.96. Found: C, 64.24; H, 4.12.

Phenyl 2-Carbamylbenzenesulfonate (*4*, A).—The alcoholic filtrates of the above were concentrated; addition of water and cooling gave a solid that melted at 113–119°. Purification of this was carried out by chromatography over neutral alumina and using tetrahydrofuran as solvent. The product had a m.p. 129–131° (lit.,[3] m.p. 132°), 1.8 g. (6%).

Anal. Calcd. for $C_{13}H_{11}SNO_4$: C, 56.31; H, 4.00. Found: C, 56.64; H, 4.07.

Phenyl 2-Chlorosulfonylbenzoate (*2*).—To a stirred solution of 11.2 g. (0.2 mole) of potassium hydroxide and 20 g. (0.24 mole) of phenol in ice water (200 ml.) was added 36.8 g. (0.2 mole) of *o*-sulfobenzoic anhydride. Stirring was continued until all of the solid had dissolved. The solution was extracted with ether to eliminate the excess of phenol and then concentrated under reduced pressure. The potassium salt of phenyl *o*-sulfobenzoate separated as a white solid, m.p. 160–163°, 27 g. This was heated with 1.5 equivalents of phosphorus pentachloride on a steam bath for 2.5 hr. and then concentrated under reduced pressure. The residue was suspended in ether, filtered, and the filtrate was then concentrated. The residue was treated with ethanol to give 9.3 g. (16% over-all yield) of sulfonylchloride, m.p. 103–105° (lit.,[3] m.p. 103–104°).

Anal. Calcd. for $C_{13}H_9ClO_4S$: C, 52.62; H, 3.06. Found: C, 52.68; H, 3.52.

A suspension of 1 g. of phenyl 2-chlorosulfonylbenzoate in 35 ml. of *t*-butyl alcohol was treated with gaseous ammonia for 2 hr. while cooling. The volatile materials were removed *in vacuo* and the residue was taken up in water. Most of the solid dissolved. On acidification, saccharin was isolated in 90% yield. Similar results were obtained on treatment of *2* with aqueous ammonia.

Phenyl 2-Cyanobenzenesulfonate (*3*, B).—A solution of 15 g. (0.0815 mole) of *o*-sulfobenzoic anhydride (National Aniline) in tetrahydrofuran was treated with gaseous ammonia. The white flocculent solid which separated was filtered, rinsed with ethanol, and recrystallized from methanol, m.p. 257–259°, 9.0 g. (*o*-carbamylbenzenesulfonic acid, ammonium salt). It was dissolved in a small amount of water, passed through ion exchange resin IR-120 and collected as long as the effluent was acidic. Concentration under reduced pressure gave a glass which solidified in contact with ethanol, m.p. 195–196°, 3.3 g. (*o*-carbamylbenzenesulfonic acid (*6*), lit.,[15] m.p. 193–194°). The acid (0.015 mole) was neutralized with potassium hydroxide solution and concentrated to dryness to give 3.5 g. of the potassium salt. This solid was heated with 10 ml. of phosphorus oxychloride for 1.5 hr. at the end of which time almost all of the solid had dissolved. The suspension was concentrated under reduced pressure to give an oil, 2-cyanobenzenesulfonyl chloride. The sulfonyl chloride was treated with the theoretical amount of phenol (1.51 g., 0.015 mole) and potassium hydroxide (0.9 g., 0.0165 mole) in 20 ml. of water. There was a vigorous reaction; more potassium hydroxide was added to keep the solution basic. A solid separated, m.p. 89–91°. It was filtered and recrystallized from ethanol–water, 2.1 g. of B (54% yield), m.p. 90–92°. The literature[3] melting point of this compound, erroneously assigned structure *8*, is 95°.

Anal. Calcd. for $C_{13}H_9NO_3S$: C, 60.25; H, 3.48; Found: C, 60.21; H, 3.62.

Both B and the intermediate, 2-cyanobenzenesulfonyl chloride, showed strong characteristic nitrile absorption in the infrared at 4.49 μ.

Alkaline Hydrolysis of B to A.—A suspension of 0.52 g. (0.002 mole) of B in 5 ml. of ethanol was made basic with a few drops of a 10% solution of sodium hydroxide. One-half milliliter of 30% hydrogen peroxide was added, and the suspension was warmed on a steam bath at 45° for 2 hr. The addition of base and hydrogen peroxide was repeated several times and warming was continued for 4 hr. The resulting solution was diluted with water, following which a solid slowly separated, m.p. 130–132°, 0.15 g. The solid proved to be identical to A previously prepared as shown by mixed melting point determination and comparison of infrared spectra.

Phenyl 2-(Dimethylsulfamyl)benzoate (*9*).—A solution of dimethylamine in diisopropyl ether was mixed with a solution of 4.0 g. (0.013 mole) of the sulfonyl chloride (*2*) in ether, and the solution was left at room temperature for 28 hr. The resulting suspension was filtered, and the filtrate was concentrated to dryness to give a solid which was recrystallized from a mixture of ethanol and water, m.p. 78–79°, 3.2 g. (78%).

Anal. Calcd. for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.95. Found: C, 58.81; H, 5.25.

***o*-Sulfobenzoic Acid, Bis-*p*-chlorophenyl Ester.**—A mixture of 19.45 g. (0.0813 mole) of 2-chlorosulfonylbenzoyl chloride,[1] *p*-chlorophenol (20.85 g., 0.163 mole), and 0.3 g. of anhydrous magnesium chloride was stirred at 40–45° for 5 hr. After cooling, the oil was treated with 50% aqueous ammonia and stirred for 5–10 min. A solid slowly separated. The aqueous solution was decanted, and the solid was recrystallized from 150 ml. of hot ethanol, 10 g., m.p. 103–106°.

Anal. Calcd. for $C_{19}H_{12}Cl_2O_5S$: C, 53.91; H, 2.86. Found: C, 54.0; H, 3.16.

***p*-Chlorophenyl *o*-Carbamylbenzenesulfonate.**—The filtrate from the recrystallization of the preceding compound was concentrated and diluted with water. The oil which separated had a strong phenolic odor. It was rinsed several times with 50% aqueous ammonia and then it solidified, m.p. 140–145°, 4.5 g. Several recrystallizations from ethanol–water gave 2.0 g. (8%), m.p. 160–163°.

Anal. Calcd. for $C_{13}H_{10}ClNO_4S$: C, 50.08; H, 3.23. Found: C, 50.06; H, 3.54.

Phenyl 2-Carbamyl-5-nitrobenzenesulfonate.—A mixture of 21.3 g. (0.075 mole) of 4-nitro-2-chlorosulfonylbenzoyl chloride,[1] 10.7 g. (0.1125 mole) of phenol, and 0.3 g. of magnesium chloride was stirred at 45° for 5 hr. The resulting reddish yellow oil was cooled and stirred with 50% aqueous ammonia. The aqueous layer was decanted and the residue was suspended in ether and filtered. Some ammonium salt of 6-nitrosaccharin separated. The ethereal solution was rinsed with water, dried, filtered, and concentrated to give an oil which slowly solidified to give 8.9 g., m.p. 124–130°. Recrystallization from ethanol gave 7.0 g. (29%) phenyl 2-carbamyl-5-nitrobenzenesulfonate, m.p. 129–131°.

Anal. Calcd. for $C_{13}H_{10}N_2O_6S$: C, 48.44; H, 3.13; N, 8.69. Found: C, 48.50; H, 3.22; N, 8.44.

(14) All melting points are corrected. The microanalyses were performed by Mrs. D. Rolston and her staff of these laboratories. Infrared spectra were determined in mineral oil mulls.

(15) F. D. Wilson, *Am. Chem. J.*, **30**, 353 (1903).

Phenyl 2-Carbamyl-5-aminobenzenesulfonate (*11*).—The above nitro compound (3.5 g., 0.0109 mole) was dissolved in 200 ml. of ethyl acetate and reduced in the presence of palladium and carbon. The reaction proceeded very smoothly and at the end, the suspension was filtered and concentrated to give an oil which slowly solidified. The solid was recrystallized from isopropyl alcohol, m.p. 136–140°, 1.8 g. (57%).

Anal. Calcd. for $C_{13}H_{12}N_2O_4S$: C, 53.44; H, 4.14; N, 9.58. Found: C, 53.99; H, 4.51; N, 9.39.

N-(Heteroaromatic-Substituted Methyl) Derivatives of 2-Aminoethanethiol[1,2]

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Several methods for the preparation of *N*-(heteroaromatic-substituted methyl) derivatives of 2-aminoethanethiol have been investigated. The sodium borohydride reduction of Schiff bases derivable from cystamine and heteroaromatic aldehydes (for example, Ia and Ib) may have general utility for the preparation of this type of *N*-substituted 2-aminoethanethiols. The iodine oxidation of the thiazolidines IIa and IIb has been demonstrated to be an advantageous source of the corresponding Schiff bases. The direct aralkylation of cystamine with 8-(bromomethyl)quinoline was shown to be controllable so as to give as the predominant product either a tetra- or a disubstituted cystamine (IX and X, respectively). Sulfite cleavage of the disubstituted cystamines VIa and X afforded the corresponding intra Bunté salts.

Although simple 2-alkylaminoethanethiols have been reported to be less protective against radiation injury in experimental animals than 2-aminoethanethiol itself,[3] *N*-(heteroaromatic-substituted methyl) derivatives of 2-aminoethanethiol warrant antiradiation screening because their structure combines heteroaromatic nuclei of potential biological importance with 2-aminoethanethiol without profoundly affecting the basicity of the amino group and its relation to the thiol group. The compounds selected for synthesis are represented by the structure $ArCH_2NHCH_2CH_2SH$ where Ar is the heterocyclic groups 3-pyridyl, 2-thienyl, 3-indolyl, and 8-quinolyl.

Of the synthetic methods that we examined, one that appears to have general utility is the reduction of Schiff bases derivable from 2,2′-dithiobisethylamine (cystamine) and heteroaromatic aldehydes, a number of which are commercially available or readily prepared. 2,2′-Dithiobis[*N*-(3-pyridylmethylene)ethylamine] (IVa), the Schiff base from nicotinaldehyde (Ia), was obtained as a pure solid, whereas 2-thiophenecarboxaldehyde (Ib) afforded 2,2′-dithiobis[*N*-(2-thenylidine)ethylamine] (IVb) as a viscous oil, which was used in the subsequent reduction without further purification. The infrared absorption spectrum of each was characterized by strong absorption near 1640 cm.$^{-1}$ assigned to the conjugated exocyclic —CH=N— group,[4] which disappeared on subsequent reduction. Attempts to characterize the Schiff bases IVa and IVb as picrates resulted in hydrolysis, and in each case the dipicrate of 2,2′-dithiobisethylamine was obtained.

As an alternative procedure, the iodine oxidation of the thiazolidines IIa and IIb, prepared by the condensation of 2-aminoethanethiol with nicotinaldehyde and 2-thiophenecarboxaldehyde, respectively, in a manner modeled after previously described[5,6] general procedures, was demonstrated to produce conveniently the desired Schiff bases. That certain thiazolidines unsubstituted on the nitrogen atom undergo many reactions typical of thiols has previously been observed.[7] Thus, 2-(3-pyridyl)thiazolidine (IIa), isolated as an analytically pure water-soluble oil, gave a positive nitroprusside test for a thiol and consumed a nearly quantitative volume of standard iodine–potassium iodide solution to give a Schiff base that was identical with the authentic sample of 2,2′-dithiobis[*N*-(3-pyridylmethylene)ethylamine] (IVa). These results are in agreement with the proposed equilibrium between a thiazolidine and the corresponding methyleneaminoethanethiol (in this case, IIa⇌IIIa).[7,8] Significant antiradiation protection of rats by the intraperitoneal injection of 4-thiazolidinecarboxylic acid (in hydrolytic equilibrium with cysteine) has recently been reported.[9] The properties of the thiazolidine IIa, which showed a strong NH stretching band (3250 cm.$^{-1}$) in the infrared and formed a pure dipicrate, do not agree with those described recently[10] for the water-insoluble product obtained from a condensation of 2-aminoethanethiol and nicotinaldehyde carried

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