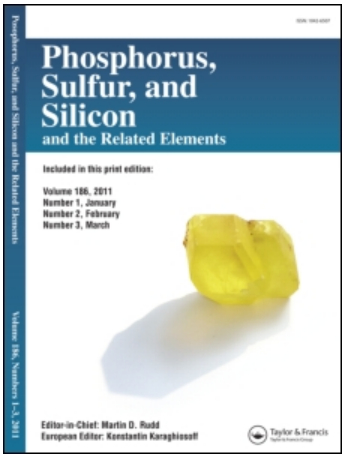

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SYNTHESES AND SOME PROPERTIES OF SULFOXIDES, SULFILIMINES, AMINOSULFONIUM SALTS AND SULFOXIMINES CONTAINING PYRIDINE NUCLEI

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SYNTHESES AND SOME PROPERTIES OF SULFOXIDES, SULFILIMINES, AMINOSULFONIUM SALTS AND SULFOXIMINES CONTAINING PYRIDINE NUCLEI

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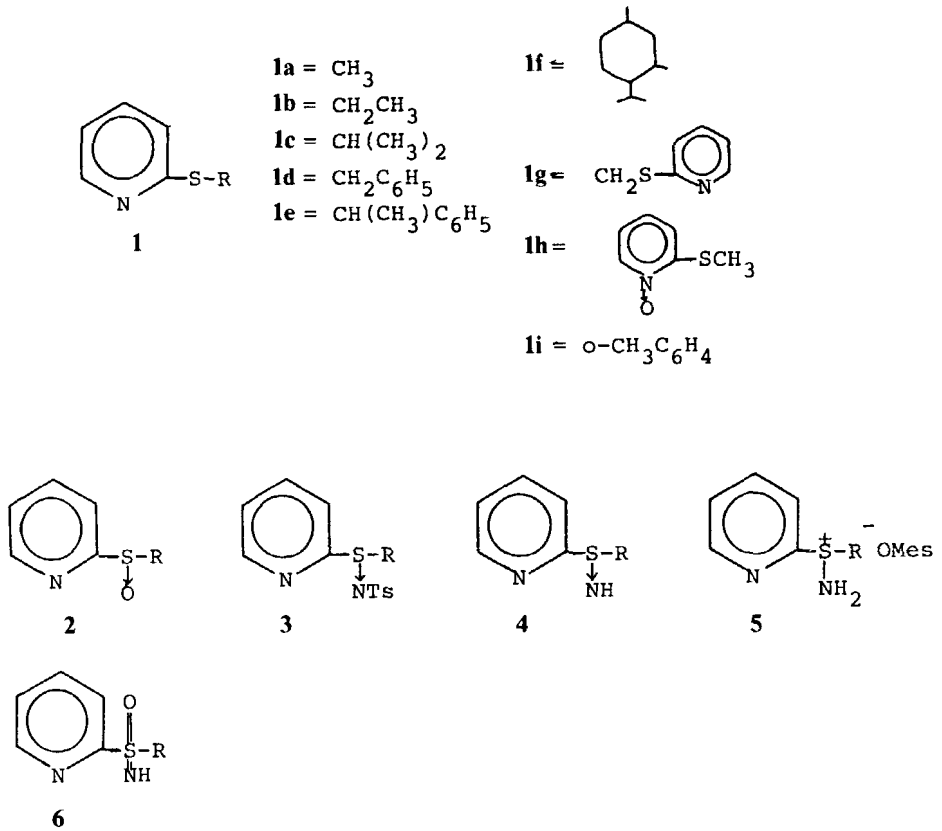
Several 2-pyridyl sulfides (**1**) (e.g., methyl (**1a**), ethyl (**1b**), isopropyl (**1c**), benzyl (**1d**), 1-phenylethyl (**1e**), *l*-menthyl (**1f**) 2-pyridyl sulfides; and bis(2-pyridylthio)methane (**1g**), and methyl 2-(*N*-oxy-pyridyl) sulfide (**1h**) were prepared by the usual method. Sulfoxides (**2**) were prepared by oxidation of the corresponding sulfides with *m*-chloroperbenzoic acid in good yields. A few sulfoxides were found to work as phase-transfer catalysts for some typical nucleophilic reactions in nonpolar solvents such as benzene, and in two-phase systems such as benzene–water. S-2-Pyridyl-*N*-(*p*-toluenesulfonyl) sulfilimines (**3**) were prepared upon treatment of sulfides with Chloramine-T. Hydrolysis of *N*-(*p*-toluenesulfonyl)-2-pyridyl-*o*-tolylsulfilimine (**3i**) with conc. sulfuric acid gave the corresponding free sulfilimine in a moderate yield. S-2-Pyridyl sulfoximines (**4**) were not obtained by the general method from the sulfoxides and hydrazoic acid. Alkyl-2-pyridyl sulfoximines, however, were obtained by oxidation of the free sulfilimines derived from the corresponding aminosulfonium salts (**5**) prepared by reaction of the sulfides with mesitylene-sulfonylhydroxylamine (MSH). These free sulfilimines and sulfoximines thus prepared were found to give adducts with a few copper salts.

Sulfoxides have been accepted as versatile starting materials for modern organic syntheses[1] and their chemistry has been widely investigated.[2] On the other hand, sulfilimines and sulfoximines are rather newcomers among organosulfur compounds and have received attention only recently.[3] A remarkable feature of these S—N compounds is the strong basic nature of terminal imino group of the semipolar S—N bonds, e.g., the pK_a value of diphenylsulfilimine is 8.5.[4] As reflected in the following reactions, free sulfilimines can undergo Michael-type addition to electrophilic olefins to yield aziridines or the corresponding adducts in high yields,[5] and also react with various alkylating and acylating agents to afford the corresponding *N*-substituted sulfilimines.[6] Although sulfoximines undergo many similar reactions, the reactions are limited by the relatively weaker basicities and higher stabilities of the sulfoximines than those of the sulfilimines. However, we have recently found that some sulfoximines have strong affinities toward several metal cations.[7] When dimethyl sulfoximine was used as the solvent in S_N2 type nucleophilic substitutions or E2 eliminations, large rate enhancements were always observed like those in common polar aprotic solvents such as DMSO or DMF.[8] These large rate enhancements are undoubtedly the result of the strong activation of nucleophilic anions, namely, forming "naked anions" owing to the strong solvation of the metal cation by the sulfoximino group. Further, dichlorocarbene generated *in situ* from chloroform and sodium hydroxide powder was found to react with the sulfoximines. In this study of the carbene reactions, we have found that new adducts are formed between the



SCHEME Organic sulfur compounds containing pyridine nuclei.

sulfoximines and copper salts. Therefore, in order to explore further the chemical behavior of sulfilimines and sulfoximines, several sulfoxides, aminosulfonium salts, *N*-substituted and unsubstituted sulfilimines and sulfoximines containing pyridine nuclei have been prepared to provide tricoordinate and tetracoordinate sulfur compounds that have stronger affinities for metals; and their characteristic properties and the applications for organic reactions have been investigated.

RESULTS AND DISCUSSION

Sulfides Containing Pyridine

Several 2-pyridyl sulfides (**1**) were prepared by the following general procedures. Methyl (**1a**),[10] ethyl (**1b**),[10] isopropyl (**1c**),[11] benzyl (**1d**)[12] and 1-phenylethyl (**1e**)[13] 2-pyridyl sulfides were prepared from 2-mercaptopyridine and the corresponding alkyl halides in acetonitrile in the presence of triethylamine as a base. *l*-Menthyl 2-pyridyl sulfide (**1f**), which was identified by spectroscopic and elemental analyses, was prepared by the reaction of the sodium salt of 2-mercaptopyridine with *l*-menthyl tosylate, $[\alpha]_D^{25°} - 71.1°$ (c 3.248 acetone), in dimethyl sulfoxide acetonitrile

TABLE I

The yields, Bps (Mps), and Nmr spectra of 2-pyridyl sulfides (**1**)

Sulfide	Yield (%)	Bp (Mp) (°C)	Nmr (δ-values, ppm)[a]
1a[b]	67	60/4 mmHg	2.54 (s, 3 H, CH_3), 6.77–7.67 (m, 3 H, β, γ-H), 8.24–8.48 (m, 1 H, α-H)
1b[b]	77	64/5 mmHg	1.38 (t, 3 H, J = 7.2 Hz, CH_3), 2.92 (q, 2 H, J = 7.2 Hz, CH_2) 6.79–7.62 (m, 3 H, β, γ-H), 8.33–8.50 (m, 1 H, α-H)
1c[c]	71	68/4 mmHg	1.40 (d, 6 H, J = 6.9 Hz, CH_3), 4.00 (Sept, 1 H, J = 6.9, CH) 6.81–7.66 (m, 3 H, β, γ-H), 8.38–8.55 (m, 1 H, α-H)
1d[d]	86	(29–30)	4.41 (s, 2 H, CH_2), 6.76–7.56 (m, 8 H, C_6H_5, β, γ-H), 8.33–8.50 (m, 1 H, α-H)
1e[e]	94	(48–49)	1.73 (d, 3 H, J = 7.2 Hz, CH_3), 5.13 (q, 1 H, J = 7.2 Hz, CH), 6.76–7.60 (m, 3 H, β, γ-H), 8.36–8.55 (m, 1 H, α-H)
1f[f]	50	(50–51)	0.98–2.25 (m, 18 H, Alkyl), 4.50 (m, 1 H, S-CH), 7.34–7.54 (m, 3 H, β, γ-H), 8.28–8.45 (m, 1 H, α-H)
1g[g]	70	(93–94)	5.08 (s, 2 H, CH_2), 6.88–7.54 (m, 6 H, β, γ-H), 8.29–8.60 (m, 1 H, α-H)
1h[h]	58	(64–65)	2.46 (s, 3 H, CH_3), 6.93–7.50 (m, 3 H, β, γ-H), 8.04–8.38 (m, 1 H, α-H)
1i[i]	83	158/5 mmHg[g]	2.40 (s, 3 H, CH_3), 6.63–7.73 (m, 7 H, C_6H_4, β, γ-H) 8.35–8.53 (m, 1 H, α-H)

[a] In $CDCl_3$ at 35°C.
[b] Ref. 9.
[c] Ref. 11.
[d] Ref. 10.
[e] Ref. 13.
[f] $[\alpha]_D^{25°} = +95.6°$ (c 4.008 acetone).
[g] Ref. 15.
[h] Ref. 14.
[i] Ref. 16.

mixed solvent since a facile elimination reaction of *l*-menthyl tosylate occurred in protic solvents such as alcohol. *l*-Menthyl 2-pyridyl sulfide (**1f**) thus obtained in 50% yield has an optical rotation of $[\alpha]_D^{25°} = +95.6°$ (c 4.008 acetone). Methyl 2-(*N*-oxy-pyridyl) sulfide (**1h**)[14] was prepared by treating an aqueous solution of the sodium salt of 2-mercaptopyridine *N*-oxide with dimethyl sulfate. Bis(2-pyridylthio)-methane[15] was also prepared by treatment of 2-mercaptopyridine with dichloro-methane in the presence of triethylamine. 2-Pyridyl *o*-tolyl sulfide (**1i**)[16] was obtained in good yield by the direct displacement of bromide from 2-bromopyridine with sodium *o*-toluenethiolate in *N*,*N*-dimethylacetamide. The sulfides thus prepared were purified by recrystallization or vacuum distillation. Their yields, mps (bps) and nmr spectra are summarized in Table I.

Sulfoxides Containing Pyridine

Generally, sulfoxides (**2**) were prepared by oxidation of the corresponding sulfides using *m*-chloroperbenzoic acid (mCPBA) as an oxidizing reagent in dichloro-methane. The product obtained was identified by spectroscopic and elemental analyses. However, methyl 2-(*N*-oxy-pyridyl) sulfoxide was not obtained by the oxidation of the corresponding sulfide using mCPBA. The sulfoxide was prepared

from the reaction of the sulfide with Chloramine-T in methanol in the presence of a catalytic amount of acetic acid or with hydrogen peroxide in acetic acid. Upon oxidation of *l*-menthyl 2-pyridyl sulfide (**1f**), two stereoisomers of *l*-menthyl 2-pyridyl sulfoxide (**2f**) were obtained and they were cleanly separated by means of column chromatography using chloroform as the eluent. One was obtained as white crystals, mp. 81–83° in 57% yield having $[\alpha]_D^{25°} = +166.9°$ (c 2.04 acetone). The other was also obtained as a colorless oil in 30% yield having $[\alpha]_D^{25°} = -74.7°$ (c 1.006, acetone). The configurations of these sulfoxides have not been determined.

Diastereoselective reaction was observed when 1-phenylethyl 2-pyridyl sulfide (**1e**) was converted to the corresponding diastereomeric sulfoxide (**2e**) by oxidation using mCPBA in dichloromethane, to give both erythro (RR/SS) and threo (RS/SR) isomers in a 1 : 2.2 ratio. The chemical shifts of the methyl groups of the sulfoxides (**2e**) appear at 1.86 (minor product) and 1.44 (major product) ppm, respectively, as double doublets. Thus, the ratio of the two stereoisomers was readily calculated and was found to be 1 : 2.2. Similar diastereoselective oxidation of sulfides has also been observed in the literature.[17] For example, the chemical shifts of the methyl group at the α-position of 1-phenylethyl *p*-tolyl sulfoxides appear at 1.52 ppm for the erythro isomer and 1.56 ppm for the threo isomer, respectively. The ratio is 1 : 2.0. The differences of the ratio of diastereoselectivities between 1-phenylethyl 2-pyridyl sulfoxide (**2e**) and 1-phenylethyl *p*-tolyl sulfoxide in the oxidation of the corresponding sulfides with mCPBA are almost negligible but their methyl group chemical shifts were exactly opposite if the major products of both oxidations of the corresponding sulfides are threo isomers. Methylation of benzyl 2-pyridyl sulfoxide (**2d**) was carried out via the initial formation of the corresponding carbanion derived from the reaction with butyllithium in THF followed by the treatment with excess methyliodide and both *erythro*- and *threo*-1-phenylethyl 2-pyridyl sulfoxides (**2e**) were obtained in total yield of 92%. The ratio of these stereoisomers was 2.1 : 1 and that of the 1-phenylethyl *p*-tolyl sulfoxides obtained from the similar reaction of benzyl *p*-tolyl sulfoxide was 2.3 : 1.[18] Here again, the difference in the ratios is quite small. In order to assign the structure of each stereoisomer, namely whether erythro or threo, a mixture of stereoisomeric 1-phenylethyl 2-pyridyl sulfoxides (**2e**) prepared by the oxidation of the corresponding sulfide (**1e**) with mCPBA was thermally decomposed at 80°C for 110 min in $CDCl_3$ in a sealed tube to afford styrene via an Ei process. The ratio was found to be changed from *erythro* : *threo* = 1 : 2.2 to 1 : 5.5. This trend for the El rate of 2-pyridyl sulfoxides (**2e**) is similar to that of 1-phenylethyl *p*-tolyl sulfoxides, namely the Ei ratio for *erythro* : *threo* of 1-phenylethyl *p*-tolyl sulfoxides is about 2 at 100°C. Therefore, the structural assignment of the products obtained by the oxidation of 1-phenylethyl 2-pyridyl sulfide (**1e**) or methylation of benzyl 2-pyridyl sulfoxide (**2d**) should be as follows: the chemical shift of the peak appearing at 1.86 ppm (CH_3) should be assigned as the *erythro* isomer and that of 1.44 ppm as the *threo* isomer. Namely, the orientation in the formation of *erythro*- and *threo*-1-phenylethyl 2-pyridyl sulfoxides (**2e**) should be quite opposite to that of 1-phenylethyl *p*-tolyl sulfoxides. The reasons for these differences in nmr chemical shifts are not understood but the most important factor seems to be the participation of the pyridine ring in the transition states of the oxidation or the methylation reaction.[19] The sulfoxides (**2**) thus prepared are summarized in Table II with their yields, mps (or bps), ir and nmr spectra.

TABLE II

The yields, Mps (Bps), Ir and Nmr spectra of 2-pyridyl sulfoxides (**2**)

Sulfoxide	Yield (%)	Mp (BP) (°C)	Ir ($SO\ cm^{-1}$)	Nmr (δ-values, ppm)[a]
2a[b]	88	(117/6 mmHg)	1055	2.83 (s, 3 H, CH_3), 7.20–7.50 (m, 1 H, γ-H), 7.74–8.16 (m, 2 H, β-H), 8.32–8.58 (m, 1 H, α-H)
2b	66	—	1050	1.20 (t, 3 H, J = 7.2 Hz, CH_3), 3.08 (m, 2 H, CH_2), 7.30–7.63 (m, 1 H, γ-H), 7.80–8.15 (m, 2 H, β-H) 8.61–8.80 (m, 1 H, α-H)
2c	90	—	1025	7.38–7.60 (m, 1 H, γ-H), 7.86–8.73 (m, 2 H, β-H), 8.55–8.73 (m, 1 H, α-H)
2d[c]	91	84–85	1035	4.05, 4.34 (dd, 2 H, J = 13.4 Hz, CH_2), 6.88–7.93 (m, 8 H, C_6H_5, β, γ-H), 8.56–8.73 (m, 1 H, α-H)
2e	94	—	1060	1.44, 1.86 (dd, 3 H, CH_3), 4.30 (m, 1 H, CH_3), 6.73–8.04 (m, 4 H, C_5H_4N), 7.35 (s, 5 H, C_6H_5)
2f	57[d]	81–83	1040	0.65–2.53 (m, 18 H, Alkyl), 3.38 (m, 1 H, S-CH), 7.15–7.40 (m, 1 H, γ-H), 7.70–8.06 (m, 2 H, β-H), 8.49–8.69 (m, 1 H, α-H)
	30[e]	—		0.73–2.43 (m, 18 H, Alkyl), 3.55 (m, 1 H, S-CH), 7.18–7.44 (m, 1 H, γ-H), 7.68–8.14 (m, 2 H, β-H), 8.49–8.65 (m, 1 H, α-H)
2h	38[f]	122–123	1025	3.10 (s, 3 H, CH_3), 7.35–8.03 (m, 3 H, β, γ-H), 8.19–8.35 (m, 1 H, α-H)
2i	87	113–114	1035	2.66 (s, 3 H, CH_3), 7.15–8.20 (m, 7 H, C_6H_4, β, γ-H), 8.44–8.59 (m, 1 H, α-H)

[a] In $CDCl_3$ at 35°C.
[b] Ref. 21.
[c] Ref. 22.
[d] $[\alpha]_D^{25°} = +166.9°$ (c 2.040 acetone).
[e] $[\alpha]_D^{25°} = -74.7°$ (c 1.066 acetone).
[f] Prepared from the corresponding sulfide by treating with Chloramine-T.

Methyl 2-pyridyl sulfoxide (**2a**) was found to have strong affinities toward alkali cations and was found consequently to enhance the nucleophilic reactivities of the gegen anions.[20] Actually, nucleophilic substitution of benzyl bromide with lithium chloride (the Finkelstein reaction) occurred smoothly in benzene or benzene–water in the presence of a catalytic amount of the sulfoxide (**2a**). This reaction did not proceed at all in the absence of the sulfoxide. Other S_N2 type reactions were also found to proceed in benzene or benzene–water in the presence of methyl 2-pyridyl sulfoxide (**2a**).[20]

The reactions of benzyl bromide with sodium thiophenolate, sodium cyanide and potassium cyanide in benzene–water at 70°C were carried out and gave the substituted products in quantitative yields. These results indicate that methyl 2-pyridyl sulfoxide (**2a**) can be employed as a phase-transfer catalyst in two-phase heterogeneous reactions.

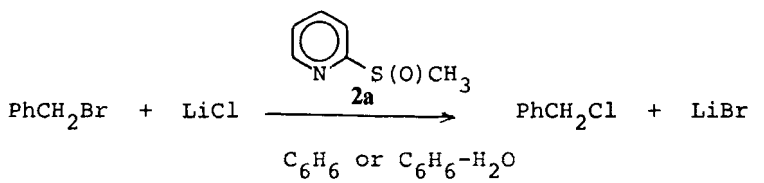


TABLE III

The yields, Mps, Ir, and Nmr spectra of 2-pyridylsulfilimines (**3**)

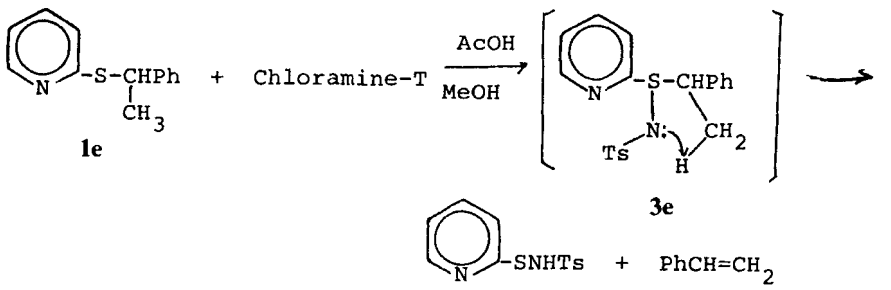
Sulfilimine	Yield (%)	Mp (°C)	Ir (S=N, cm^{-1})	Nmr (δ-values, ppm)[a]
3a	31	126–127	955	2.40 (s, 3 H, *p*-CH_3), 2.99 (s, 3 H, S-CH_3), 7.10–7.56 (m, 3 H, m-H, γ-H), 7.70–8.25 (m, 4 H, *o*-H, β-H), 8.35–8.72 (m, 1 H, α-H)
3b	37	91–92	980	1.19 (t, 3 H, J = 7.1 Hz, CH_3), 2.40 (s, 3 H, *p*-CH_3) 3.28 (m, 2 H, CH_2), 7.14–8.22 (m, 7 H, C_6H_4, β, γ-H), 8.49–8.73 (m, 1 H, α-H)
3c	46	92–93	1000	1.05, 1.26 (dd, 6 H, J = 6.7 Hz, CH_3), 2.38 (s, 3 H, *p*-CH_3), 3.70 (sept, 1 H, J = 6.7 Hz, CH), 7.13–7.56 (m, 3 H, m-H, γ-H), 7.72–8.05 (m, 4 H, *o*-H, β-H), 8.54–8.70 (m, 1 H, α-H)
3d	25	124–125	960	2.34 (s, 3 H, *p*-CH_3), 4.28, 4.65 (dd, 2 H, J = 13.4 Hz, CH_2), 6.95–8.06 (m, 12 H, C_6H_4, C_6H_5, β, γ-H), 8.59–8.75 (m, 1 H, α-H)
3h	27	180–181	925	2.40 (s, 3 H, *p*-CH_3), 3.10 (s, 3 H, S-CH_3), 7.15–8.35 (m, 8 H, C_6H_4, C_5H_4N)
3i	44	111–112	970	2.33 (s, 3 H, *p*-CH_3), 2.55 (s, 3 H, *o*-CH_3), 7.00–8.60 (m, 12 H, C_6H_4, C_5H_4N)
4i[b]		61.5–63	925 (NH)	2.52(s, 1 H, NH), 2.58 (s, 3 H, *o*-CH_3), 7.13–8.09 (m, 7 H, C_6H_4, β, γ-H), 8.31–8.59 (m, 1 H, α-H)

[a] In $CDCl_3$ at 35°C.
[b] Free sulfilimine.

Sulfilimines Containing Pyridine

Several *N*-(*p*-toluenesulfonyl)-2-pyridylsulfilimines (**3**) were prepared by our general procedure.[23] The reaction of the sulfides and Chloramine-T did not proceed at all in the absence of a catalytic amount of acetic acid although, in general, alkyl aryl or diarylsulfilimines were obtained under the same conditions without acid catalyst. This difference seems to result from the strong electron-withdrawing property of the pyridine nuclei.[24] 2-Pyridylsulfilimines (**3**) were obtained in moderate yields together with the corresponding sulfoxides. The products obtained were identified by spectroscopic and elemental analyses. Their yields, mps, ir and nmr spectra are summarized in Table III.

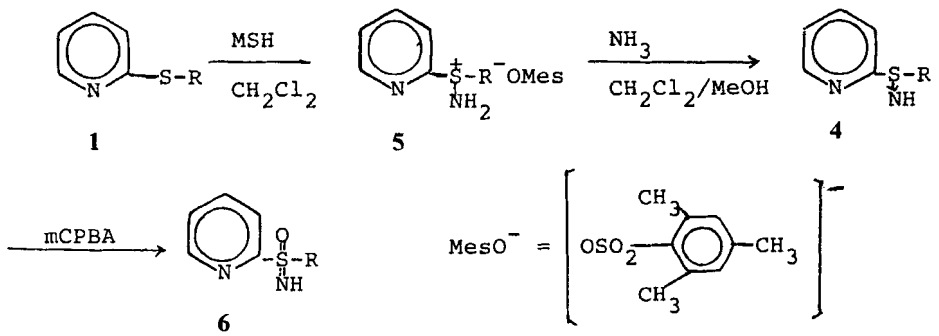
The ir absorption bands of the S—N bonds of these 2-pyridylsulfilimines (**3**) were identical with those of alkyl aryl or diarylsulfilimines. Similarly, when 1-phenylethyl 2-pyridyl sulfide (**1e**) was treated with Chloramine-T in methanol at low temperature (0 ~ −10°C), the corresponding sulfilimine (**3e**) was obtained in 78% yield. This sulfilimine (**3e**) was identified as a single diastereoisomer which was identified by nmr spectra and its sharp melting point. However, the configuration of this isomer was not determined. On the other hand, when the reaction was carried out at room temperature, the products obtained were *N*-(*p*-toluenesulfonyl)-2-pyridinesulfenamide and styrene in 82% and 68% yields, respectively. These products are undoubtedly formed via the initial formation of the corresponding sulfilimine (**3e**) followed by the intramolecular elimination reaction (Ei), as shown in the scheme.



Aminosulfonium Salts and Sulfoximines Containing Pyridine

A few general methods[4a] for the preparation of 2-pyridyl sulfoximines (**6**) were tested with *l*-menthyl 2-pyridyl sulfoxide (**2f**) in order to obtain the optically active sulfoximine (**6**). The reaction of the sulfoxide with sodium azide in chloroform in the presence of conc. sulfuric acid conditions similar to the Schmidt reaction, failed to give the desired result and the product thus obtained was 2-pyridyl disulfide in 49% yield. In this reaction, elimination reactions may take place and 2-pyridylsulfenic acid thus formed is considered disproportionate to the corresponding thiosulfinate and consequently afforded the resulting disulfide. The other products should be *l*-menthene and 2-pyridinesulfonic acid since it has been known that the thiolsulfonate is not stable and the final product actually obtained was 2-pyridinesulfonic acid.[25]

The reaction of the sulfoxide (**2**) and tosyl azide in methanol in the presence of a copper salt also did not afford the corresponding sulfoximine (**6**) but instead gave many products, suggesting that the reaction may proceed by the nitrene abstraction of a hydrogen atom from the menthyl group. The best preparative method of the sulfoximines (**6**) containing pyridine nuclei is the oxidation of the corresponding free sulfilimines (**4**) with peracid without isolation during the experimental procedures as shown in the following equation.



The free sulfilimines (**4**) were derived from 2-pyridylaminosulfonium salts (**5**) via the reaction of the sulfide (**1**) with mesitylenesulfonylhydroxylamine (MSH)[26] by treating with ammonia at low temperature. Various 2-pyridylaminosulfonium salts (**5**) were thus prepared by the reaction of the corresponding sulfides (**1**) with MSH. The products obtained were identified by spectroscopic and elemental analyses. The

TABLE IV

The yields, Mps, and Nmr spectra of 2-pyridylaminosulfonium salts

Sulfonium Salt	Yield (%)	Mp (°C)	Nmr (δ-values, ppm)[a]
5a	80	94–95	2.29 (s, 3 H, *p*-CH_3), 2.48 (s, 6 H, *o*-CH_3), 3.33 (s, 3 H, S-CH_3), 6.72 (s, 2 H, C_6H_2), 6.90–7.16 (br s, 2 H, NH_2), 7.12–7.50 (m, 1 H, γ-H), 7.62–8.30 (m, 2 H, β-H), 8.40–8.56 (m, 1 H, α-H)
5b	67	118–119	1.41 (t, 3 H, J = 7.2 Hz, CH_3), 2.19 (s, 3 H, *p*-CH_3), 2.53 (s, 6 H, *o*-CH_3), 3.66 (m, 2 H, CH_2), 6.63–6.78 (br s, 2 H, C_6H_2), 6.93–7.16 (br s, 2 H, NH_2), 7.33–8.63 (m, 4 H, C_5H_4N)
5c	75	93–94	1.36 (t, 6 H, J = 6.5 Hz, CH_3), 2.20 (s, 3 H, *p*-CH_3), 2.58 (s, 6 H, *o*-CH_3), 3.97 (sept, 1 H, J = 6.5 Hz, CH), 6.68–6.78 (br s, 2 H, C_6H_2), 6.88–7.10 (br s, 2 H, NH_2), 7.249–8.66 (m, 4 H, C_5H_4N)
5d	68	unstable	2.18 (s, 3 H, *p*-CH_3), 2.44 (s, 6 H, *o*-CH_3), 4.90, 4.97 (dd, 2 H, J = 13.4 Hz, CH_2), 6.56–6.75 (br s, 2 H, C_6H_2), 6.91–8.55 (m, 11 H, C_6H_5, NH_2, C_5H_4N)
5e	52		unstable
5f[c]	52	159–161 (dec)	0.74–2.13 (m, 18 H, Alkyl), 2.19 (s, 3 H, *p*-CH_3), 2.61 (s, 6 H, *o*-CH_3), 3.90 (m, 1 H, S-CH), 6.78 (br s, 2 H, C_6H_2), 7.25–8.20 (m, 6 H, NH_2, C_5H_4N)
5g	88		unstable
5h[c]	79	155–156 (dec)	2.04 (s, 3 H, *p*-CH_3), 2.35 (s, 6 H, *o*-CH_3), 3.26 (s, 3 H, S-CH_3), 6.64 (br s, 2 H, C_6H_2), 6.75 (br s, 2 H, NH_2), 7.55–8.58 (m, 4 H, C_5H_4N)

[a] In $CDCl_3$ at 35°C.
[b] In DMSO-d_6 at 35°C.
[c] $[\alpha]_D^{25°} = +41.7°$ (c 2.130 chloroform).

reaction of amino compounds containing a sulfide group with MSH has already been reported. It was shown that MSH initially reacts with the nitrogen atom but not sulfur and the corresponding aminosulfonium salt is not obtained.[27] The facile reaction of several pyridine derivatives and MSH was also reported under very mild conditions.[28] In the case of 2-pyridyl sulfides (**1**) of lower alkyl homologs, e.g., methyl, ethyl, and isopropyl derivatives, the corresponding aminosulfonium salts (**5**) were undoubtedly obtained since the chemical shifts of the α-protons adjacent to the sulfur shifted to lower fields comparing to that of the sulfides (**1**) (see nmr spectra in Table IV as well as yields and mps).

Aminosulfonium salts (**5**) of benzyl (**5d**), 1-phenylethyl (**5e**) 2-pyridyl sulfides and bis(2-pyridylthio)methane (**5g**) were not sufficiently stable to obtain accurate nmr spectra. 2-Pyridyl sulfoximines (**6**) prepared in moderate yields were the methyl (**6a**), ethyl (**6b**) and isopropyl (**6c**) derivatives. The products were identified by their spectroscopic and elemental analyses. The results are summarized in Table V.

Although 2-pyridyl *o*-tolyl sulfide (**1i**) was found to react with MSH, the corresponding aminosulfonium salt (**5i**) was not isolated in crystalline form. Treatment of the product with ammonia gas at low temperature gave the recovered sulfide (**1i**) (22%), di-*o*-tolyl disulfide (19%) and *N*,*N*-bis(*o*-tolylthio)amine (16%), respectively.

A similar reaction of *l*-menthyl-2-pyridylaminosulfonium salt afforded the rearrangement product but the correct structure was not determined.

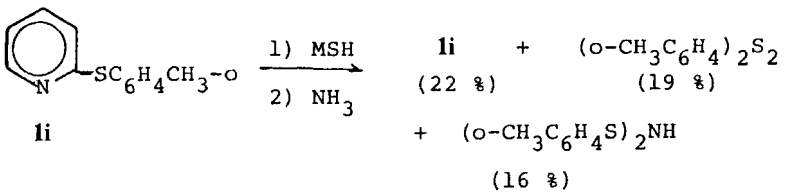


TABLE V

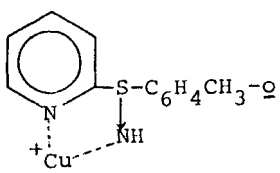
The yields, Mps, Ir, and Nmr spectra of 2-pyridylsulfoximines (**5**)

Sulfoximine	Yield (%)	Mp (°C)	Ir (O=S=N)	(NH)	Nmr (δ-values, ppm)[a]
6a	65	64.5–66	1010 1225	3250	2.80–3.07 (br s, 1 H, NH), 3.28 (s, 3 H, CH_3) 7.40–7.68 (m, 1 H, γ-H), 7.80–8.31 (m, 2 H, β-H), 8.70–8.87 (m, 1 H, α-H)
6b	43	—	990 1210	3300	1.29 (t, 3 H, J = 7.2 Hz, CH_3), 2.95 (s, 1 H, NH), 3.47 (m, 2 H, CH_2), 7.38–7.69 (m, 1 H, γ-H), 7.84–8.33 (m, 2 H, β-H), 8.73–8.90 (m, 1 H, α-H)
6c	36	65–66.5	950 1210	3250	1.30, 1.36 (dd, 6 H, J = 7.2 Hz, CH_3), 3.13 (s, 1 H, NH), 3.75 (sept, 1 H, J = 7.2 Hz, CH), 7.48–7.68 (m, 1 H, γ-H), 7.80–8.30 (m, 2 H, β-H), 8.70–8.88 (m, 1 H, α-H)

[a]In $CDCl_3$ at 35°C.

The chemical shifts of the α- or β-protons of these sulfoxides (**2**), sulfilimines (**3**) and sulfoximines (**6**) often appear at low fields as compared with those of the sulfides (**1**). This seems to be due to the anisotropic effects of the pyridine ring or the S—O and S—N bonds.

All free sulfilimines (**4**) and sulfoximines (**6**) prepared easily afforded the copper adducts by treating them with e.g., cupric chloride in methanol. The absorption band of the S—N bond of the adduct of 2-pyridyl-*o*-tolyl-sulfilimine (**4i**) with cupric chloride was found to have lower frequency, ν_{SN} = 900 cm^{-1}, as compared to that of the sulfilimine (**4i**), ν_{SN} = 930 cm^{-1}. This indicates that the lone pair of the basic nitrogen atom of the sulfilimine (**4**) coordinates rather strongly with the vacant *d*-orbital of the copper atom. Study of the ir spectra of these adducts suggests that the structure of the adduct with cupric chloride may be described as below.



Thus, the compounds prepared in this study may be useful as surface-active reagents and could have some pharmacological activity, e.g., in treatment of Wilson's disease which is caused by copper.

EXPERIMENTAL

Chemicals used were of reagent grade unless otherwise specified. All melting and boiling points were uncorrected. Infrared spectra were measured on a Hitachi 215 or JASCO A-3 spectrometer. Nuclear magnetic resonance spectra were obtained with a Hitachi R-24 or Hitachi Perkin-Elmer R-20 spectrometer in dilute solutions in $CDCl_3$ using TMS as the internal standard. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. A Yanako Model G-80 gas chromatograph was used for gas chromatography with nitrogen as a carrier gas. Optical rotations were taken at 25° with a Yanako OR-50D spectropolarimeter or a JASCO DIP-140 digital polarimeter in a 0.5 dm quartz cell. Silica gel and activated alumina used for column chromatography were of either Wako or Merck chromatographic grade; for thin-layer chromatography Merck DC-Plastikfolien Kieselgel 60F 254 with fluorescent indicator was used. Development was followed with UV light or by coloring with iodine.

Preparation of sulfides (**1**). A typical experimental procedure to prepare the 2-pyridyl sulfides (**1**) is as follows: to a solution of 2-mercaptopyridine (3.65 g, 320 mmol) and triethylamine (4.0 g, 400 mmol) in 5 ml CH_3CN was added dropwise methyl iodide (5.6 g, 390 mmol) in 5 ml CH_3CN with stirring and cooling with an ice-water bath. Then the mixture was stirred at room temperature overnight and the solvent was evaporated. After addition of excess ethyl acetate to the residue, triethylammonium iodide was filtrated and the solvent was evaporated. The resulting residue was separated by column chromatography using $CHCl_3$ as the eluent. Methyl 2-pyridyl sulfide (**1a**) was obtained as a colorless liquid in 67% yield after being purified by distillation under reduced pressure. The sulfides thus prepared are summarized in Table I together with their yields, mps, (or bps) and nmr spectra.

l-Menthyl 2-pyridyl sulfide (**1f**). The sulfide (**1f**) was prepared as follows: 2-mercaptopyridine (2.7 g, 240 mmol) was dissolved in 15 ml ethanol. Sodium (0.56 g, 24 mmol) was added slowly to the solution and removal of the solvent yielded the sodium salt of 2-mercaptopyridine. To a solution of this salt in 15 ml dry dimethyl sulfoxide was added *l*-menthyl tosylate (10.3 g, 330 mmol), $[\alpha]_D^{25°} = -71.1°$ (c 3.248 acetone), in 30 ml DMSO and 10 ml CH_3CN mixed solvent. The mixture was stirred for 2 h at room temperature and heated at 70°C overnight. Then the mixture was poured into ice water and extracted four times with 50 ml portions of $CHCl_3$. The combined $CHCl_3$ layer was dried over $MgSO_4$ and the solvent was evaporated. The resulting residue was separated by column chromatography using hexane as the eluent. *l*-Menthyl 2-pyridyl sulfide (**1f**) was obtained in 50% yield as white crystals by recrystallization from hexane after cooling to −78°C. Mass; 249 (M^+). Anal. Calcd. for $C_{15}H_{23}NS$: C, 72.23; H, 9.29; N, 5.61. Found: C, 71.90; H, 9.43; N, 5.59.

Methyl 2-N-oxy-pyridyl sulfide (**1h**). This sulfide (**1h**) was prepared by the reaction of the sodium salt of 2-mercaptopyridine *N*-oxide with dimethyl sulfate. To a 50% aqueous solution of 2-mercaptopyridine *N*-oxide sodium salt (17.3 g, 580 mmol) cooled with an ice-water bath was added dimethyl sulfate (4.4 g, 300 mmol) dropwise. The mixture was stirred at room temperature for 2 h. Then the aqueous solution was evaporated and extracted three times with 50 ml portions of $CHCl_3$. The $CHCl_3$ layer was dried over Na_2SO_4 and the solvent was again evaporated. Methyl 2(*N*-oxy-pyridyl) sulfide (**1h**), upon purification by column chromatography using acetone as the eluent and followed by distillation under the reduced pressure, was obtained in 58% yield as hygroscopic white crystals. Bp. 178° at 6 mm Hg.

2-Pyridyl o-tolyl sulfide (**1i**). This sulfide (**1i**) was prepared as follows: a mixture of *o*-methylthiophenol (24.5 g, 0.2 mol) and NaOH (8 g, 0.2 mol) in 80 ml *N,N*-dimethylacetamide was heated to 150°C to remove the H_2O formed. After the mixture was cooled to 80°C, 2-bromopyridine (30 g, 0.19 mol) was carefully added dropwise. Then the mixture was refluxed overnight. After the mixture was cooled to room temperature, *N,N*-dimethylacetamide was removed by distillation under reduced pressure. The resulting residue was poured into H_2O, and the product was extracted four times with 50 ml portions of CH_2Cl_2. The combined CH_2Cl_2 layer was dried over Na_2SO_4 and the solvent was evaporated. Pure 2-pyridyl *o*-tolyl sulfide (**1i**) was obtained in 83% yield by vacuum distillation as a colorless liquid.

Preparation of the sulfoxides (**2**) *containing pyridine nuclei*. A typical experimental procedure to prepare 2-pyridyl sulfoxides (**2**) is as follows: to a solution of benzyl 2-pyridyl sulfide (**1d**) (2.307 g, 110 mmol) in 5 ml $CHCl_3$ cooled with an ice-water bath was added mCPBA (2.361 g, 140 mmol) in 30 ml $CHCl_3$ and stirred at 0°C for 30 min. Then 10 ml methanol was added to the solution and then neutralized with dry NH_3 gas. The ammonium salt then formed was filtrated and the solvent was evaporated. The resulting residue was purified by column chromatography using benzene or $CHCl_3$ as the eluent. Further purification of the sulfoxides (**2**) was carried out by distillation or recrystallization from hexane or benzene, if possible. Benzyl 2-pyridyl sulfoxide (**2d**) was obtained in 91% yield as white needles by recrystallization from benzene–hexane. 2-Pyridyl sulfoxides (**2**) thus prepared are summarized in Table II together with their yields, mps (or bps), ir and nmr spectra.

TABLE VI

Elemental analyses of (**2**)

Sulfoxide	Analyses
2b[a]	Found: C, 53.61; H, 5.66; N, 8.66
	Calcd.: C, 54.16; H, 5.84; N, 9.02
2c[a]	Found: C, 56.29; H, 6.48; N, 8.20
	Calcd.: C, 56.78; H, 6.55; N, 8.28
2e[b]	Found: C, 66.97; H, 5.11; N, 5.67
	Calcd.: C, 67.50; H, 5.66; N, 6.05
2f	Found: C, 67.72; H, 8.67; N, 5.29
	Calcd.: C, 67.88; H, 8.73; N, 5.27
2h[d]	Found: C, 46.15; H, 4.41; N, 8.90
	Calcd.: C, 45.84; H, 4.48; N, 8.91
2i[c]	Found: C, 66.11; H, 5.03; N, 6.50
	Calcd.: C, 66.33; H, 5.10; N, 6.44

[a]A hygroscopic colorless liquid.
[b]A hygroscopic colorless oil.
[c]White crystals recrystallized from ether.
[d]White crystals.

Methyl 2(N-oxy-pyridyl) sulfoxide (**2h**). To a solution of Chloramine-T (2.472 g, 8.7 mmol) and a few drops of acetic acid in 15 ml methanol, stirred and cooled with an ice-water bath, was added dropwise methyl 2(*N*-oxy-pyridyl) sulfide (**1h**) (1.073 g, 7.6 mmol). Then a solution was heated at 45°C for 5 h. The solution was evaporated and the resulting residue was separated through column chromatography using acetone as the eluent. The products obtained were methyl 2(*N*-oxy-pyridyl) sulfoxide (**2h**) as white crystals in 38% yield by recrystallization from benzene and *N*-(*p*-toluenesulfonyl)methyl-2-(*N*-oxy-pyridyl)sulfilimine (**3h**) as white crystals in 27% yield by recrystallization from ethanol. Mass spectra and elemental analyses of the sulfoxides are summarized in Table VI.

Preparation of sulfilimines (**3**). A typical experimental procedure to prepare *N*-(*p*-toluenesulfonyl)-2-pyridylsulfilimines (**3**) is the following: to a solution of Chloramine-T (1.931 g, 6.8 mmol) and a few drops of acetic acid in 20 ml methanol with stirring and cooling with an ice-water bath was added methyl 2-pyridyl sulfide (**1a**) (0.762 g, 6.1 mmol) in 5 ml methanol. The solution was heated at 45°C for 3 h. Then the solution was poured into dil. aqueous NaOH. The white precipitate which formed immediately was filtered. *N*-(*p*-Toluenesulfonyl)methyl-2-pyridylsulfilimine (**3a**) was obtained in 31% yield as white crystals after recrystallization from benzene–hexane. The aqueous layer was extracted three times with 20 ml portions of $CHCl_3$. The combined $CHCl_3$ solution was dried over Na_2SO_4 and then the solvent was evaporated. The resulting residue gave methyl 2-pyridyl sulfoxide (**2a**) in 22% yield. These sulfilimines (**3**) thus obtained were white crystals after recrystallization from benzene–hexane or ethanol. Their yields, mps, ir, and nmr spectra are summarized in Table III. Their mass spectra and elemental analyses are summarized in Table VII.

N-(p-Toluenesulfonyl)-1-phenylethyl-2-pyridylsulfilimine (**3e**). This sulfilimine (**3e**) was prepared similarly as above starting with 15 mmol of 1-phenylethyl 2-pyridyl sulfide (**1e**), 18 mmol of Chloramine-T under cooling with ice water. The product was obtained after pouring the reaction mixture in ice-cooled dil. NaOH solution. The recrystallization was carried out from methanol at 0 ~ −70°C. The sulfilimine (**3**) thus obtained consists of one stereoisomer which was identified by nmr and ^{13}Cmr analyses. Mp. 150–152°C. Yield was 77.8%.

Reaction of 1-phenylethyl 2-pyridyl sulfide (**1e**) *with Chloramine-T At room temperature.* 1-Phenylethyl 2-pyridyl sulfide (**1e**) (1.519 g, 7.1 mmol) and Chloramine-T (2.407 g, 8.5 mmol) were treated in 30 ml MeOH in the manner described above. After the reaction, the product was analyzed by gas chromatography by comparing with authentic samples and the yield was determined using bromobenzene as the internal standard. The column used was 2 m stainless tube (3 mm i.d.) packed with 5% silicone G.E. SE-30 (60–80 mesh) on chromosorb W. The oven temperature was 100° and the flow of carrier gas was 20 ml/min. The product obtained in 68% yield was styrene. Then the reaction mixture was poured into dil. aqueous NaOH solution, and a white precipitate was formed. The precipitate was collected and identified by spectroscopic and elemental analyses. The product obtained in 82% yield as white crystals upon

TABLE VII

Elemental Analyses of **3**

Sulfilimine	Analyses	Mass (M^+)
3a	Found: C, 53.31; H, 4.75; N, 9.43	294
	Calcd.: C, 53.04; H, 4.79; N, 9.51	
3b	Found: C, 54.48; H, 5.11; N, 9.05	308
	Calcd.: C, 54.52; H, 5.22; N, 9.08	
3c	Found: C, 55.90; H, 5.54; N, 8.65	a)
	Calcd.: C, 55.87; H, 5.62; N, 8.68	
3d	Found: C, 61.47; H, 4.82; N, 7.57	370
	Calcd.: C, 61.59; H, 4.89; N, 7.56	
3h	Found: C, 50.55; H, 4.51; N, 8.91	310
	Calcd.: C, 50.31; H, 4.55; N, 9.03	
3i	Found: C, 51.99; H, 4.87; N, 8.56	370
	Calcd.: C, 51.83; H, 4.97; N, 8.63	

[a] 280 $[2\text{-}C_5H_4N\text{-}SNHTs]^+$ (95.3%), 171 $[TsNH_2]^+$ (46.9%), 155 $[Ts]^+$ (30.3%), 91 $[Tol]^+$ (85.3%), 78% $[C_5H_4N]^+$ (11.6%), 42 $[CH{=}CHCH_3]^+$ (100%).

recrystallization from ethanol was *N*-(*p*-toluenesulfonyl)-2-pyridinesulfenamide. mp. 152–153° (dec.). Mass; 280 (M^+). Ir (KBr); 1160, 1320 cm^{-1} (SO_2) Nmr (δ) 2.29 (s, 3 H, Ar-H), 7.13–8.00 (m, 8 H, C_6H_4, β, γ-H, NH), 8.28–8.45 (m, 1 H, α-H). Anal. Calcd. for $C_{12}H_{12}N_2O_2S_2$: C, 51.40; H, 4.31; N, 9.99. Found: C, 51.41; H, 4.23; N, 9.95.

Hydrolysis of N-(p-toluenesulfonyl)-2-pyridyl-o-tolylsulfilimine (**3i**) *with conc. sulfuric acid.* *N*-(*p*-Toluenesulfonyl)-2-pyridyl-*o*-tolylsulfilimine (**3i**) (4.01 g, 110 mmol) was dissolved in 10 ml conc. H_2SO_4 and heated 45° for 1 h. Then the H_2SO_4 solution was poured into ice water. After keeping the solution for 10 min., a colorless oil was formed. The residue was immediately decanted and dissolved in 50 ml methanol. The solution was cooled with a dry ice–methanol bath and neutralized with dry NH_3 gas. After removal of the solvent with an evaporator, 70 ml $CHCl_3$ was added. Ammonium sulfate was filtrated and the filtrate was evaporated. To the resulting residue dissolved in 5 ml methanol was added $CuCl_2$ (1.48 g, 110 mmol) in 40 ml methanol. After keeping the solution for 6 h, a greenish adduct was formed in 64% yield which was filtrated and washed with methanol. Mp. 185–192°C (dec.). Ir (KBr); 900 cm^{-1} (S=N). To the greenish adduct, 0.076 g in 2 ml methanol, was added ethylenediamine (0.058 g, 0.97 mmol) in 1 ml methanol. The solution then became homogeneous and blue in color. The mixture was separated by chromatography on an activated alumina column using methanol as the eluent. 2-Pyridyl-*o*-tolylsulfilimine (**4i**) was obtained in 98% yield as white crystals upon recrystallization from benzene–hexane. Mp. 61.5–63°C. Anal. Calcd for $C_{12}H_{12}N_2S$: C, 66.63; H, 5.59; N, 12.95. Found: C, 65.82; H, 5.49; N, 12.91. The ir and nmr spectra are shown in Table III.

Preparation of aminosulfonium salts (**5**) *containing pyridine.* A typical experimental procedure to prepare 2-pyridylaminosulfonium mesitylenesulfonates (**5**) is as follows: to a solution of methyl 2-pyridyl sulfide (**1a**) (0.375 g, 3.0 mmol) in 3 ml CH_2Cl_2 under stirring and cooling in an ice-water bath was added 1.5 equivalents of Na_2SO_4-dried mesitylenesulfonylhydroxylamine (MSH) (1.3 g, 4.65 mmol), which was prepared according to the general method,[22] in 4 ml CH_2Cl_2. The solution was stirred at 0°C for 30 min., then poured into ether. The white precipitate then formed was filtered and recrystallized from CH_2Cl_2–ether. Methyl-2-pyridylaminosulfonium mesitylenesulfonate (**5a**) was obtained in 80% yield as white crystals. Yields, mps, and nmr spectra are summarized in Table IV, and the ir spectra and elemental analyses are summarized in Table VIII.

Preparation of sulfoximines (**6**) *containing pyridine nuclei* (**6**). A typical procedure to prepare 2-pyridylsulfoximines (**6**) is as follows: a solution of methyl-2-pyridylaminosulfonium mesitylenesulfonate (**5a**) (0.491 g, 1.4 mmol) in 30 ml CH_2Cl_2 under stirring and cooling with a dry ice–methanol bath was saturated with dry NH_3 gas. Then the solution was warmed to 0°C and mCPBA (0.285 g, 1.6 mmol) in 10 ml CH_2Cl_2 was added dropwise. A yellow precipitate formed at once. Then 5 ml methanol was added to the solution and the mixture was neutralized with dry NH_3 gas at 0°C. A yellow precipitate formed again. The precipitates were filtrated and the solvent was removed with an evaporator. The resulting residue was

TABLE VIII

Ir spectra and elemental analyses of aminosulfonium salt (**5**)

Aminosulfonium Salt	Ir (SO_3, KBr, cm^{-1})			Analyses
5a	1170	675		Found: C, 52.69; H, 5.89; N, 8.12 Calcd.: C, 52.91; H, 5.92; N, 8.22
5b	1215	1145	675	Found: C, 54.19; H, 6.22; N, 7.94 Calcd.: C, 54.21; H, 6.25; N, 7.90
5c	1180	580		Found: C, 55.23; H, 6.49; N, 7.53 Calcd.: C, 55.40; H, 6.56; N, 7.60
5d	1210	1165	680	unstable
5e	1220	1180	680	unstable
5g	1200	1170	680	unstable
5f	1180	675		Found: C, 61.43; H, 7.84; N, 6.02 Calcd.: C, 62.03; H, 7.80; N, 6.02
5h	1210	1175	680	Found: C, 50.72; H, 5.58; N, 7.63 Calcd.: C, 50.54; H, 5.66; N, 7.86

TABLE IX

Elemental analyses of (**6**)

Sulfoximine	Analyses	Mass (M^+)
6a	Found: C, 46.34; H, 5.01; N, 17.85 Calcd.: C, 46.13; H, 5.16; N, 17.93	156
6b[a]	Found: C, 48.94; H, 5.97; N, 16.20 Calcd.: C, 49.39; H, 5.92; N, 16.45	170
6c[b]	Found: C, 52.04; H, 6.45; N, 15.25 Calcd.: C, 52.14; H, 6.56; N, 15.20	184

[a]A colorless oil.
[b]Recrystallized from benzene–hexane.

separated by column chromatography using $CHCl_3$ as the eluent. Methyl-2-pyridylsulfoximine (**6a**) was obtained in 60% yield as white crystals. Yields, mps, ir and nmr are summarized in Table V. Mass spectra and elemental analyses are summarized in Table IX.

Reaction of 2-pyridyl o-tolyl sulfide (**1i**) *with mesitylenesulfonylhydroxylamine (MSH).* To a solution of 2-pyridyl *o*-tolyl sulfide (**1i**) (2.027 g, 10 mmol) in 5 ml CH_2Cl_2 under stirring and cooling with an ice-water bath was added 1.5 equivalent of MSH (3.87 g, 12.6 mmol) in 20 ml of CH_2Cl_2. The solution was stirred at 0°C for 20 min. and then poured into ether. The colorless oil formed was dissolved in 50 ml CH_2Cl_2 and cooled with a dry ice–methanol bath. Then the solution was saturated with dry NH_3 gas. The products were analyzed by gas chromatography or by comparing the GC-MS spectra with those of authentic samples. The products obtained were the recovered sulfide (**1i**) (22%), di-tolyl disulfide (19%) and bis(*o*-tolylthio)amine (16%), respectively.

Adduct of methyl-2-pyridylsulfoximine (**6a**) *with cupric chloride.* To a solution of $CuCl_2$ (0.184 g, 1.4 mmol) in 2 ml MeOH was added methyl-2-pyridylsulfoximine (**6a**) (0.230 g, 1.4 mmol) in 1 ml methanol at room temperature. Greenish crystals slowly formed. The crystals were filtered and washed well with methanol. The adduct was obtained in 88% yield as greenish crystals. Mp. 181–182°C (dec.). Ir (KBr); 1230, 1130, 1090, 1015 (O=S=N). Anal. Calcd for $C_6H_8Cl_2NOSCu$: C, 24.79; H, 2.77; N, 9.64. Found: C, 25.33; H, 3.33; N, 9.39.

REFERENCES AND NOTES

1. (a) E. Block, "Reactions of Organosulfur Compounds", Academic Press, New York, 1978; (b) T. Durst, D. N. Jones ed., "Comprehensive Organic Chemistry", Vol. 3, p. 121, 1979, Pergamon Press.
2. J. Drabowicz and M. Mikolajzyk, *Org. Prepn. and Procedures Int.*, **14**, 45 (1982).
3. (a) N. Furukawa and S. Oae, *I & EC Product Research & Development*, **20**, 260 (1981); (b) S. Oae and N. Furukawa, "Chemistry of Sulfilimines and their Derivatives", in press, 1983, American Chemical Society.
4. (a) S. Oae, K. Harada, K. Tsujihara and N. Furukawa, *Int. J. Sulfur Chem., Part A*, **2**, 49 (1972); (b) N. Furukawa, T. Yoshimura, T. Omata and S. Oae, *Chem. & Ind.*, 702 (1974).
5. (a) Y. Tamura, K. Sumoto, H. Matsushima, H. Taniguchi and M. Ikeda, *J. Org. Chem.*, **38**, 4324 (1973); (b) N. Furukawa, S. Oae and T. Yoshimura, *Synthesis*, 30 (1976).
6. (a) T. Yoshimura, T. Omata, N. Furukawa and S. Oae, *J. Org. Chem.*, **41**, 1728 (1976).
7. N. Furukawa, F. Takahashi, T. Yoshimura and S. Oae, *Tetrahedron Lett.*, 3633 (1977).
8. N. Furukawa, F. Takahashi, T. Yoshimura and S. Oae, *Chem. Lett.*, 1359 (1977). Idem., *J. Chem. Soc., Perkin-2*, 432 (1981).
9. N. Furukawa, F. Takahashi, T. Yoshimura and S. Oae, *Tetrahedron*, **35**, 317 (1979).
10. R. Lawrence and E. S. Waight, *J. Chem. Soc.*, **B**, 1 (1968).
11. J. J. D'Amico, *U.S.P. 3295946*, Jan. 3, 1967.
12. W. E. Stewart and T. H. Siddall, *J. Phys. Chem.*, **74**, 2027 (1970).
13. T. Mukaiyama, S. Ikeda and S. Kobayashi, *Chem. Lett.*, 1159 (1975).
14. R. E. Kohrman, D. X. West and M. A. Little, *J. Heterocycle Chem.*, **11**, 101 (1974).
15. B. S. Jackson, R. F. Brookes, J. E. Graham, W. A. Cummings, D. Greenwood and H. A. Stevenson, *J. Sci. Food Agr.*, **8**, 31 (1957).
16. C. K. Bradsher, L. D. Quinin, R. E. LeBleu and J. W. McDonald, *J. Org. Chem.*, **26**, 4644 (1961).
17. K. Nishihata and M. Nishio, *J. Chem. Soc., Perkin-2*, 748 (1973).
18. K. Nishihata and M. Nishio, *Chem. Commun.*, 958 (1971).
19. Detailed analyses of the configurations of these stereoisomers will be published elsewhere.
20. (a) N. Furukawa, K. Kishimoto, S. Ogawa, T. Kawai, H. Fujihara and S. Oae, *Tetrahedron Lett.*, **22**, 4409 (1981). (b) N. Furukawa, S. Ogawa, T. Kawai, K. Kishimoto, H. Fujihara and S. Oae, *Heterocycles*, **16**, 1927 (1981).
21. G. B. Berlin and W. V. Brown, *J. Chem. Soc.*, **B**, 1435 (1968).
22. W. Walter, J. Voss and J. Curts, *Ann. Chem.*, **695**, 77 (1966).
23. K. Tsujihara, N. Furukawa, K. Oae and S. Oae, *Bull. Chem. Soc. Japan*, **42**, 2631 (1969).
24. L. Field, H. Haule, T. C. Owen and A. Ferretti, *J. Org. Chem.*, **29**, 1632 (1964).
25. This compound was not isolated.
26. Y. Tamura, J. Minamikawa, K. Sumoto, S. Fujii and M. Ikeda, *J. Org. Chem.*, **38**, 1239 (1973).
27. Y. Tamura, H. Matsushima, J. Minamikawa, M. Ikeda and K. Sumoto, *Tetrahedron*, **31**, 3035 (1975).
28. (a) Y. Tamura, Y. Miki, Y. Sumida and M. Ikeda, *J. Chem. Soc., Perkin, 1*, 2580 (1973); (b) Idem., *ibid.*, 406 (1974).