Heteroatom Chemistry
Volume 3, Number 5/6, 1992

Generation and Characterization of New Sulfenate Salts via Ipso-substitution of Azaheterocyclic Sulfoxides

Naomichi Furukawa,* Yasuo Konno, Masayuki Tsuruoka, and Satoshi Ogawa

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Received 8 May 1992

ABSTRACT

New stable sulfenate salts, sodium 2-pyridinesulfenate **9a** and sodium 2-(3-trimethylsilyl)pyridinesulfenate **9b**, were prepared by the ipso-substitution reactions of azaheterocyclic sulfoxides (**1c**/**3a** and **4a**, respectively) with sodium ethoxide or sodium butanethiolate under mild conditions and were characterized by physical and spectroscopic properties. The FT-IR spectra of compounds **9a** and **9b** showed characteristic S—O absorptions at 870 and 890 cm^{-1}, respectively. These sulfenate salts were converted rapidly to the corresponding sulfinate salts on contact with oxygen. A number of other sulfenates were prepared and trapped by alkylation to give sulfoxides (as were **9a** and **9b**).

INTRODUCTION

It has long been known that sulfenic acids and sulfenate salts are key intermediates in organic and bioorganic sulfur reactions [1]. Although some stable derivatives or salts of sulfenic acids have been made, study of these species has progressed little due to their high reactivity. Davis and his co-workers have reported the generation and reactions of some sulfenic acids in detailed mechanistic studies of the pyrolysis of sulfoxides. The stability of the sulfenic acids was explained in terms of steric, electronic, and intramolecular hydrogen-bonding effects around the acid group [2]. Sulfenic acids are generally generated either by pyrolysis of sulfoxides or oxidation of thiols, but they are extremely labile and dimerize rapidly to thiosulfinates [3]. Only a few stable sulfenic acids have been isolated and their structures determined; in these, the SOH group is protected from facile dimerization by intramolecular hydrogen bonding, by steric effects of bulky substituents, and/or by electronic effects of electron-withdrawing groups [4].

Similarly, some procedures have been reported for the preparation of sulfenate salts, which are the conjugate bases of sulfenic acids and are relatively stable in solution [5]. Only one sulfenate salt which has Ag^+ as a counter cation has been isolated [6]. We reported recently that numerous 2-sulfonyl-substituted azaheterocycles underwent facile ipso-substitution to liberate the corresponding sulfinate salts [7]. These results prompted us to try to isolate sulfenate salts by treatment of 2-sulfinyl-substituted azaheterocycles with nucleophiles. We report herein the generation and reactions of several sodium sulfenates, together with the first isolation and characterization of stable sodium 2-pyridinesulfenate **9a** and sodium 2-(3-trimethylsilyl)pyridinesulfenate **9b** from the ipso-substitution of 2-(2-pyridylsulfinyl)benzothiazole **3a** and 2-[2-(3-trimethylsilyl)-pyridylsulfinyl]-benzothiazole **4a**, respectively, with sodium ethoxide or sodium butanethiolate under mild conditions.

Dedicated to Professor Yao-Zeng Huang on the occasion of his eightieth birthday.

*To whom correspondence should be addressed.

1042-7163/92/$3.50 + .25

RESULTS AND DISCUSSION

Synthesis of Azaheterocyclic Sulfoxides

The azaheterocyclic sulfoxides **1**, **3**, and **4** (Scheme 1), used as a source of sulfenate salts, were prepared from the sodium salts of 2-mercaptopyridine-1-oxide and of 2-mercaptobenzothiazole by using a modification of a method previously reported [8]. The 1-oxides **1a–f** were prepared by the ipso-substitution reaction of 2-(methylsulfonyl) pyridine-1-oxide with appropriate thiolate anions, followed by oxidation with *m*-chloroperbenzoic acid (*m*-CPBA). The 1-oxide **1g** also was prepared by oxidation of the corresponding sulfide with *m*-CPBA. In this case, however, the 2-nitrophenyl group was introduced by reaction of the sodium salt of 2-mercaptopyridine-1-oxide with a 2-nitrobenezenediazonium salt. 2-(2-Pyridylsulfinyl)benzothiazole **3a** and bis(2-benzothiazolyl) sulfoxide **3b** were also prepared by the same procedures as for **1a–f**. 2-[2-(3-Substituted)pyridylsulfinyl]benzothiazoles **4a–c** were synthesized by oxidation with *m*-CPBA of the corresponding sulfides in which the substituents had been introduced by regiospecific ortho lithiation of the pyridine ring and subsequent treatment with electrophiles [9].

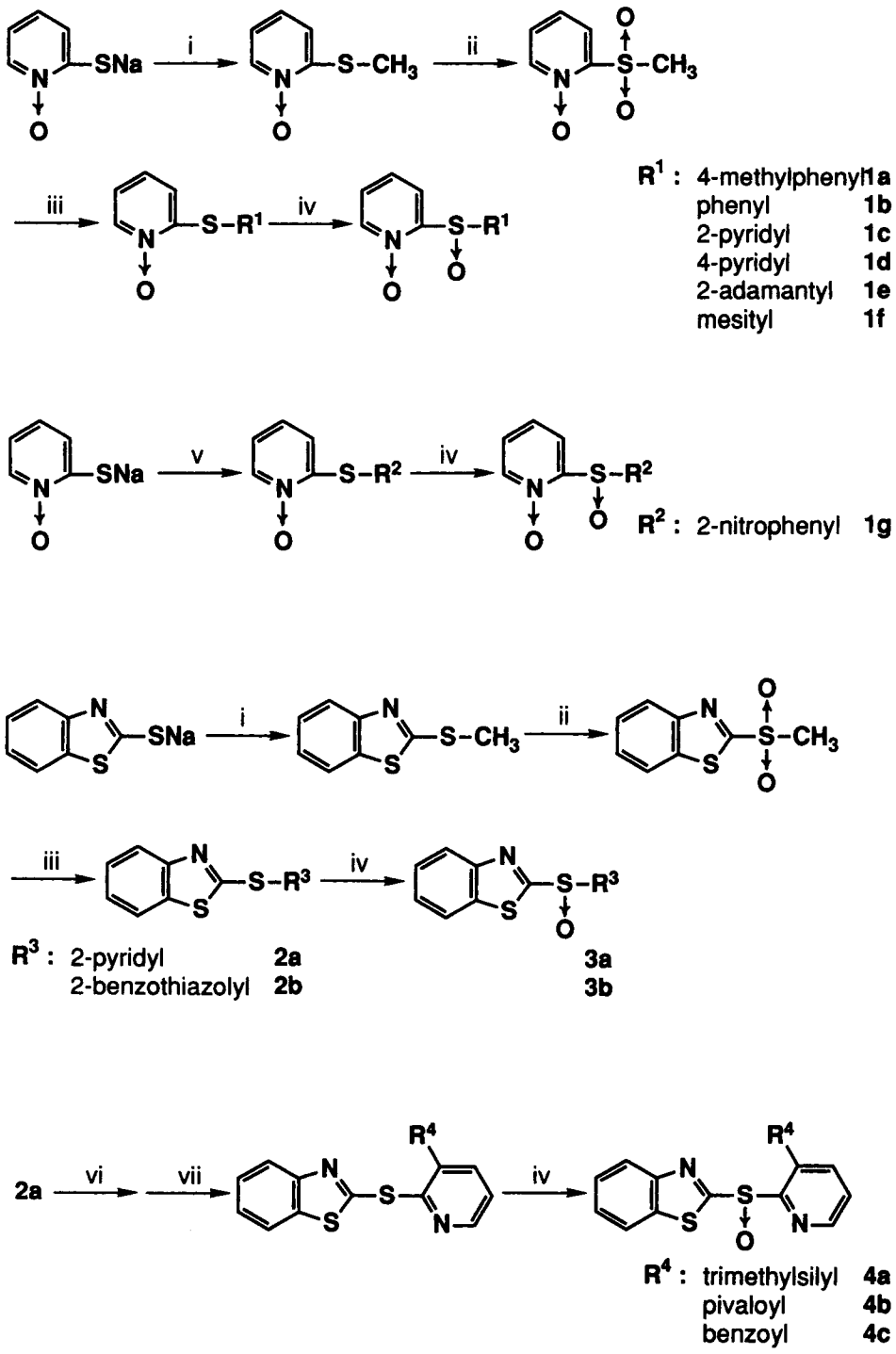
Generation of Sulfenate Salts

Sulfoxides **1**, **3**, and **4** were subjected to reaction with sodium ethoxide in acetonitrile or sodium (or lithium) butanethiolate in tetrahydrofuran (THF) under an argon atmosphere for 0.5 hour. Nucleophilic substitution took place at the ipso-position of the pyridine-1-oxide or the benzothiazole ring, liberating the corresponding sulfenate anions. Excess iodomethane was then added as a trapping reagent to give the corresponding methyl aryl (or alkyl) sulfoxides **5a–h** in moderate yields (Scheme 2, Table 1). 2-Sulfinylpyridine-1-oxides **1a–g** and 2-sulfinylbenzothiazoles **3a,b** are convenient sources for generation of the sulfenate salts. On the basis of the yield of each trapped product, we concluded that sulfoxides bound to the electron-withdrawing pyridine ring of **1c** and **3a** afforded the relatively stable sodium 2-pyridinesulfenate **9a**. Trapping experiments showed that sodium 2-pyridinesulfenate **9a** was more stable than sodium 4-pyridinesulfenate. This is presumably due to the stabilizing effect provided by intramolecular chelation of the sodium cation with the nitrogen atom of the pyridine ring.

Bulky substituents also are known to stabilize sulfenate salts. Sulfoxides **4a–c** have a bulky or electron-withdrawing substituent at the 3-position of the pyridine ring. When **4a** reacted with sodium ethoxide, nucleophilic attack took place at both the benzothiazole ring and the silicon atom attached to the pyridine ring to afford methyl 2-(3-trimethylsilyl)pyridyl sulfoxide **5h** and 2-(2-pyridylsulfinyl)benzothiazole **3a**, which reacted with sodium ethoxide and iodomethane affording methyl 2-pyridyl sulfoxide **5c**. When sulfoxide **4a** was allowed to react with sodium or lithium butanethiolate in THF under the same conditions described above, ipso-substitution took place readily on the benzothiazole ring to afford only sulfoxide **5h** in a quantitative yield. This result indicates that sulfoxide **4a** is also a convenient source for the preparation of the stable sodium 2-(3-trimethylsilyl)-pyridinesulfenate **9b**. However, ipso-substitution reactions of sulfoxide **4b** and **4c** with lithium butanethiolate took place, not on the benzothiazole ring, but on the pyridine ring to give 2-(methylsulfinyl)-benzothiazole **5g**, presumably because of the strongly electron-withdrawing ability of the substituents attached to the 3-position of the pyridine ring. By this procedure, the sulfenates having a strongly electron-withdrawing substituent and also intramolecular metal chelating ability, such as the 2- pyridyl group, preferably with an additional bulky trimethylsilyl group at the 3-position of the pyridine ring, can be prepared as stable salts if oxygen and moisture are rigorously excluded during and after the reaction. Other sulfenates thus generated are extremely reactive with oxygen and moisture and hence are too unstable to be isolated.

Isolation and Stabilization of New Sodium Sulfenates

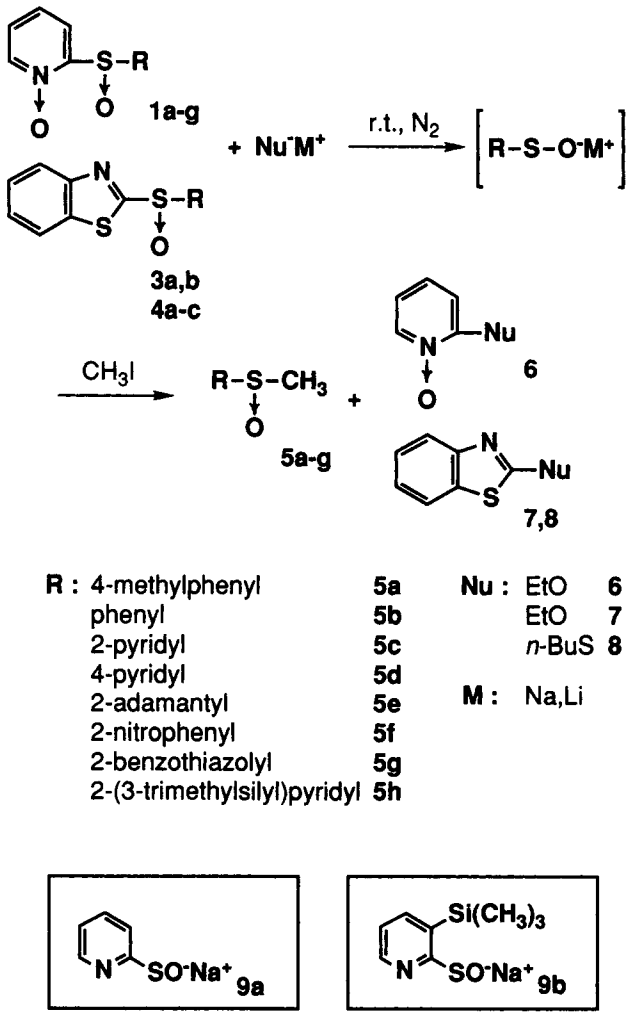
In order to isolate and characterize sodium sulfenates, 2-(2-pyridylsulfinyl)-pyridine-1-oxide **1c** and 2-(2-pyridylsulfinyl)benzothiazole **3a** were treated with sodium ethoxide in acetonitrile under an argon atmosphere. Similarly, 2-[2-(3-trimethylsilyl)pyridyl-sulfinyl]benzothiazole **4a** was treated with sodium butanethiolate in THF under an argon atmosphere. After the reaction, workup was carried out carefully in a dry-box with rigorous exclusion of air and moisture. In the case of **1c**, after removal of the solvent, the residual products were washed with anhydrous ether to remove the ipso-substitution product, 2-ethoxypyridine-1-oxide **6**. A pale yellow powder **9a** was obtained in more than 80% yield. This compound showed a strong IR-absorption at 870 cm^{-1}. However, the solid was still contaminated with 2-ethoxypyridine-1-oxide **6**, even upon repeated washing with anhydrous ether. Sulfoxide **3a** also was treated with an equivalent of sodium ethoxide in acetonitrile at room temperature for 0.5 hour. After removal of the solvent under an N_2 atmosphere, the residue was washed with anhydrous ether in a dry-box. In this case, 2-pyridinesulfenate **9a** was easily separated from 2-ethoxybenzothiazole **7** to afford a pale yellow crystalline material in 90% yield. A strong IR absorption band appears at 870 cm^{-1} which is assigned as the S—O stretching vibration. On exposure of



SCHEME 1

this KBr disk to air for about an hour, the IR spectrum gradually changed mostly to that of a sulfinate. The SO-band due to the sulfenate disappeared, and new bands appeared corresponding to the SO_2 of the sulfinate salt, sodium 2-pyridinesulfinate **10** at 1050, 1040, and 990 cm^{-1}. If one stored this sulfenate **9a** under an N_2 or argon atmosphere, the compound was stable even at room temperature and did not disproportionate after having been allowed to stand for one month.

Sulfoxide **4a** reacted with an equivalent amount of sodium butanethiolate in THF to afford sodium 2-(3-trimethylsilyl)pyridinesulfenate **9b** as a pale yellow crystalline material which was also stable



SCHEME 2

and in which a strong IR absorption band of S—O appeared at 890 cm^{-1}. The FT-IR spectra of these compounds are shown in Figure 1. The results indicate that the sulfenate salts are unstable in air and are quickly converted to the sulfenate salts even in the solid state. However, sulfenate salts attached to the 2-pyridyl or 2-(3-trimethylsilyl)pyridyl group could be isolated under an N_2 atmosphere. These are the first examples of isolation and characterization of sodium sulfenates.

The stabilities of the sulfenate salts **9a** and **9b** toward oxygen could not be determined quantitatively. We tried to compare their stabilities in the presence of water. Sodium sulfenates **9a** and **9b** were generated in situ by similar procedures to those described previously (in this case, sodium butanethiolate was used as a nucleophile) in the presence of water. The reaction mixtures were stirred at room temperature for 10, 20, and 40 minutes, respectively, under an argon atmosphere and then treated with iodomethane. After workup, the yields of the trapped products (sulfoxide **5c** and **5h**) were plotted against the reaction time (Figure 2). Sulfenate salt **9a** was less stable than **9b** in the presence of water. These results suggest that the steric effect of a substituent near the sulfenate moiety has a large effect upon its stability, and, overall, for isolation of stable sulfenate salts, the presence of ligands having a combination of electron-withdrawing, intramolecular metal chelating ability, and steric bulk is required.

Table 1 Generation and Trapping of Sulfenate Salts in the Reactions of Azaheterocyclic Sulfoxides with Nucleophiles and Iodomethane under an N_2 Atmosphere

Compound	*Nu^-M^+*	*solvent*	*product*	*yield (%)*
1a	EtO^-Na^+	CH_3CN	**5a**	trace
1b	EtO^-Na^+	CH_3CN	**5b**	54
1c	EtO^-Na^+	CH_3CN	**5c**	94
1d	EtO^-Na^+	CH_3CN	**5d**	53
1e	EtO^-Na^+	CH_3CN	**5e**	21[a]
1f	EtO^-Na^+	CH_3CN		
1g	EtO^-Na^+	CH_3CN	**5f**	**55**
3a	EtO^-Na^+	CH_3CN	**5c**	89
3b	EtO^-Na^+	CH_3CN	**5g**	61
4a	EtO^-Na^+	CH_3CN	**5h**	34[b]
4a	*n*-BuS^-Na^+	THF	**5h**	90
4a	*n*-BuS^-Li^+	THF	**5h**	91
4b	*n*-BuS^-Li^+	THF	**5g**	84[c]
4c	*n*-BuS^-Li^+	THF	**5g**	87[c]

[a]Many products were obtained.
[b]Also, **5c** was obtained in 25% yield.
[c]Substitution took place at the ipso-position of the R group. See Scheme 2.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. The ^1H NMR spectra were obtained with a Hitachi R-600 instrument. Mass spectra were taken with a Hitachi RMU-6MG or a JEOL JMS-SX 102 mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center at this University. All reagents were obtained from Wako Pure Chemical Industries, Ltd. or Aldrich Chemical Co. The reaction solvents were further purified and dried by general methods.

Preparation of Sulfoxides **1a–g**

Iodomethane (2.5 mL, 39.6 mmol) was added to a stirred solution of the sodium salt of 2-mercaptopyridine-1-oxide (5.0 g, 33.5 mmol) in ethanol (150 mL) at room temperature. After 1 hour the resulting salt was separated by filtration and the filtrate was evaporated under reduced pressure. The residue was treated with a small amount of water and extracted with chloroform ($CHCl_3$) (3 × 100 mL). The extract was dried with anhydrous magnesium

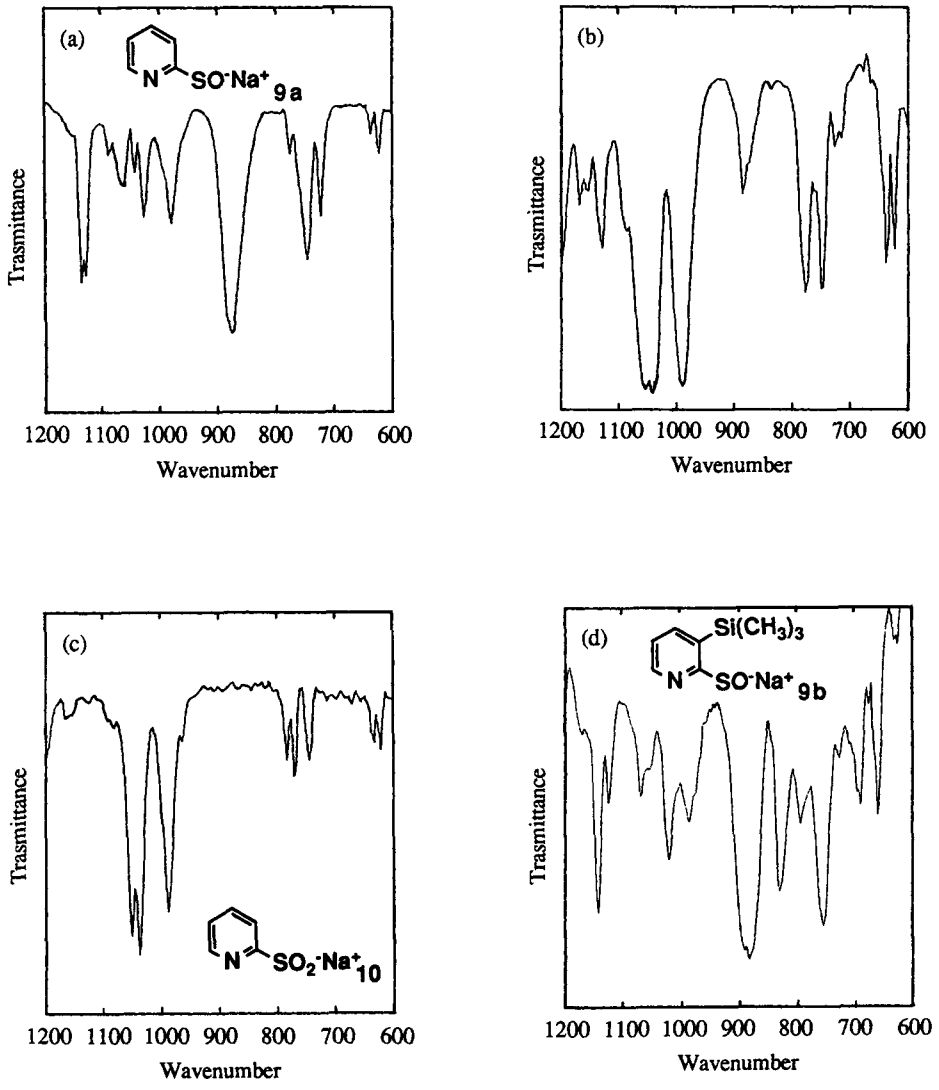


FIGURE 1

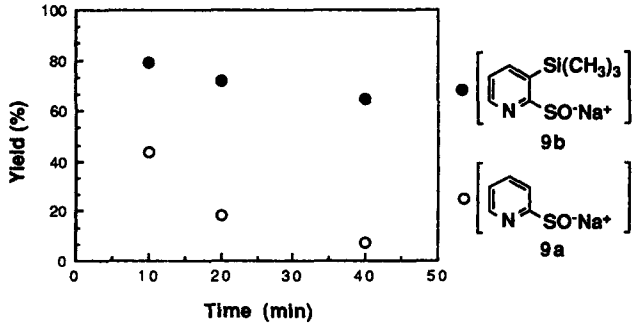


FIGURE 2

sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, $CHCl_3$) to give 2-methylthiopyridine-1-oxide as a colorless liquid in 97% yield; ^1H NMR ($CDCl_3$) δ 2.47 (m, 3H, CH_3), 6.80–7.43 (m, 3H, 3,4,5-PyH), and 8.34–8.90 (m, 1H, 6-PyH). Thirty percent aqueous hydrogen peroxide (13.2 g, 116.4 mmol) was added to a stirred solution of 2-methylthiopyridine-1-oxide (6.6 g, 46.7 mmol) in acetic acid (130 mL). The mixture was stirred for 6 hours at 80°C. After removal of the solvent, the residue was neutralized with aqueous ammonia and was extracted with $CHCl_3$ (3 × 100 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was recrystallized from hexane/ethyl acetate to give 2-methylsulfonylpyridine-1-oxide in 45% yield; mp 102–

103°C; ^{1}H NMR ($CDCl_3$) δ 3.44 (s, 3H, CH_3), 6.80–7.43 (m, 2H, 4,5-PyH), and 7.90–8.36 (m, 2H, 3,6-PyH); IR (KBr) 1130, 1155, and 1310 cm^{-1} (SO_2). *p*-Thiocresol (3.0 g, 24.2 mmol) was added to a stirred solution of sodium ethoxide (prepared from 0.5 g, 21.7 mmol of sodium) in ethanol (100 mL). The mixture was stirred at room temperature for 10 minutes under an N_2 atmosphere and then was treated with 2-methylsulfonylpyridine-1-oxide (3.0 g, 17.3 mmol).

After having been stirred for 15 hours under an N_2 atmosphere, the solvent was removed under reduced pressure. The residue was treated with a small amount of water and extracted with $CHCl_3$ (3 × 100 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was recrystallized from hexane/ethyl acetate to give 2-(4-methylphenylthio)pyridine-1-oxide in 80% yield; mp 144–146°C; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 6.30–7.60 (m, 7H, 3,4,5-PyH, ArH), and 8.07–8.29 (m, 1H, 6-PyH); IR (KBr) 1250 cm^{-1} (NO). A stirred solution of 2-(4-methylphenylthio)pyridine-1-oxide (3.0 g, 13.8 mmol) in dichloromethane (CH_2Cl_2) (100 mL) at −20°C was treated with 90% m-CPBA (2.6 g, 13.6 mmol) in CH_2Cl_2 (100 mL). The mixture was stirred at −20°C for 4 hours and then treated with anhydrous ammonia. The resulting solid was separated by filtration and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (alumina—eluent, ethyl acetate; then silica gel—eluent, ether/ethanol = 10/1) to give sulfoxide **1a**. Recrystallization from ethanol gave colorless crystals of pure sulfoxide **1a** in 56% yield. Other sulfoxides **1b–f** were prepared by a similar procedure to that used for sulfoxide **1a**.

2-(4-Methylphenylsulfinyl)pyridine-1-oxide

1a: mp 151.5–152.5°C; ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H, CH_3), 7.07–8.13 (m, 8H, ArH, PyH); IR (KBr) 1045 (SO), 1252 cm^{-1} (NO); MS (*m/z*): 233 (M^+); anal calcd for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00%. Found: C, 61.82; H, 4.68; N, 6.00%.

2-(Phenylsulfinyl)pyridine-1-oxide

1b: mp 145.0–146.0°C; ^{1}H NMR ($CDCl_3$) δ 7.20–8.17 (m, ArH, PyH); IR (KBr) 1050 (SO), 1260 cm^{-1} (NO); MS (*m/z*): 219 (M^+); anal calcd for $C_{11}H_9NO_2S$: C, 60.26; H, 4.14; N, 6.39%. Found: C, 60.32; H, 4.07; N, 6.36%.

2-(2-Pyridylsulfinyl)pyridine-1-oxide

1c: mp 165.5°C; ^{1}H NMR ($CDCl_3$) δ 7.15–8.14 (m, 8H, PyH); IR (KBr) 1050 (SO), 1258 cm^{-1} (NO); MS (*m/z*): 220 (M^+); anal calcd for $C_{10}H_8N_2O_2S$: C, 54.53; H, 3.66; N, 12.72%. Found: C, 54.37; H, 3.71; N, 12.69%.

2-(4-Pyridylsulfinyl)pyridine-1-oxide

1d: mp 141.0–143.0°C; ^{1}H NMR ($CDCl_3$) δ 7.27–8.78 (m, PyH); IR (KBr) 1053 (SO), 1241 cm^{-1} (NO); MS (*m/z*): 220 (M^+); anal calcd for $C_{10}H_8N_2O_2S$: C, 54.53; H, 3.66; N, 12.72%. Found: C, 54.47; H, 3.64; N, 12.65%.

2-(Adamantylsulfinyl)pyridine-1-oxide

1e: mp 192.0–193.0°C; ^{1}H NMR ($CDCl_3$) δ 1.07–2.74 (m, 14H, AdmH), 3.32–3.55 (m, 1H, 2-AdmH), 7.15–8.26 (m, 4H, PyH); IR (KBr) 1050 (SO), 1255 cm^{-1} (NO); MS (*m/z*): 277 (M^+); anal calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90; N, 5.05%. Found: C, 65.06; H, 7.00; N, 5.05%.

2-(Mesitylsulfinyl)pyridine-1-oxide

1f: mp 136.0–137.0°C; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H, 4-CH_3), 2.56 (s, 6H, 2,6-CH_3), 6.84 (s, 2H, ArH), 7.23–7.50 (m, 2H, 4,5-PyH), 7.86–8.15 (m, 2H, 3,6-PyH); IR (KBr) 1055 (SO), 1260 cm^{-1} (NO); MS (*m/z*): 261 (M^+); anal calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36%. Found: C, 64.29; H, 5.84; N, 5.36%.

2-(2-Nitrophenylsulfinyl)pyridine-1-oxide

1g: A solution of sodium nitrite (2.88 g, 41.7 mmol) in water (5 mL) was added dropwise to a stirred solution of 2-nitroaniline (1.98 g, 14.3 mmol) in concd hydrochloric acid (10.4 mL) the mixture being maintained below 0°C. After having been stirred for 15 minutes, the mixture was treated with sodium tetrafluoroborate (2.4 g, 21.9 mmol) in water (5 mL) and was stirred for 1 hour at 0°C. The resulting salt was filtered off, washed with benzene, and dissolved in dimethyl sulfoxide (DMSO) (30 mL). The sodium salt of 2-mercaptopyridine-1-oxide (2.0 g, 13.4 mmol) was carefully added to this stirred solution maintained below 0°C. After the mixture had been stirred for 1 hour at room temperature and then for 1 hour at 100°C, the solvent was removed under reduced pressure. The residue was purified by column chromatography (alumina—eluent, ethyl acetate/methanol = 20/1) and then by recrystallization from ethanol to give 2-(2-nitrophenylthio)pyridine-1-oxide in 12% yield; ^{1}H NMR ($CDCl_3$) δ 6.93–7.75 (m, 6H, 3,4,5-PyH, 4,5,6-ArH), 7.88–8.35 (m, 2H, 6-PyH, 3-ArH). Oxidation of the sulfide to the corresponding sulfoxide **1g** was carried out by a similar procedure to those used for sulfoxides **1a–f**. **1g**: mp 157.0–159.0°C; ^{1}H NMR ($CDCl_3$) δ 7.22–8.31 (m, PyH, ArH); IR (KBr) 1050 (SO), 1260 cm^{-1} (NO); MS (*m/z*): 264 (M^+); anal calcd for

$C_{11}H_8N_2O_4S$: C, 49.99; H, 3.05; N, 10.60; S, 12.13%. Found: C, 49.55; H, 3.07; N, 10.36, S, 12.13%.

Preparation of Sulfoxides **3a,b**

Sulfoxides **3a,b** were prepared by a similar procedure to those used for sulfoxides **1a–f** via the corresponding sulfide (**2a,b**), in which the sodium salt of 2-benzothiazole was used as a starting material.

2-(2-Pyridylthio)benzothiazole

2a: colorless liquid [9]; ^{1}H NMR ($CDCl_3$) δ 7.00–8.06 (m, 7H, ArH, 3,4,5-PyH), 8.40–8.64 (m, 1H, 6-PyH); MS (*m/z*): 244 (M^+).

Bis(2,2'-benzothiazolyl) Sulfide

2b: mp 104.0°C; ^{1}H NMR ($CDCl_3$) δ 7.26–8.14 (m, ArH); MS (*m/z*): 300 (M^+); anal calcd for $C_{14}H_8N_2S_3$: C, 55.98; H, 2.68; N, 9.32%. Found: C, 55.99; H, 2.69; N, 9.13%.

2-(2-Pyridylsulfinyl)benzothiazole

3a: mp 134.0°C; ^{1}H NMR ($CDCl_3$) δ 7.38–8.23 (m, 7H, ArH, 3,4,5-PyH), 8.50–8.73 (m, 1H, 6-PyH); IR (KBr) 1060 cm^{-1} (SO); MS (*m/z*): 260 (M^+); anal calcd for $C_{12}H_8N_2OS_2$: C, 55.37; H, 3.10; N, 10.75%. Found: C, 55.17; H, 3.13; N, 10.74%.

Bis(2,2'-benzothiazolyl) Sulfoxide

3b: mp 191.5–192.0°C; ^{1}H NMR ($CDCl_3$) δ 7.31–7.64 (m, 4H, ArH), 7.78–8.22 (m, 4H, ArH); IR (KBr) 1070 cm^{-1} (SO); MS (*m/z*): 316 (M^+); anal calcd for $C_{14}H_8N_2OS_3$: C, 53.14; H, 2.55; N, 8.85%. Found: C, 53.12; H, 2.52; N, 8.75%.

Preparation of Sulfoxides **4a–c**

A stirred solution of sulfide **2a** (4.0 g, 16.4 mmol) in THF (10 mL) maintained at −78°C under an N_2 atmosphere was treated with 3.75 M lithium diisopropylamide (4.8 mL, 18.0 mmol) in THF solution. The mixture was stirred for 1 hour at −78°C under an N_2 atmosphere and then treated with trimethylsilyl chloride (5.0 mL, 39.4 mmol).

The mixture was stirred for 4 hours at −78°C under an N_2 atmosphere. After hydrolysis and extraction with CH_2Cl_2 (3 × 50 mL), the extract was dried with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel—eluent, CH_2Cl_2) to give a crude product. Recrystallization from hexane gave 2-[2-(3-trimethylsilyl)pyridylthio]benzothiazole in 53% yield; mp 96.5–97.0°C (Ref. [9] mp 97–98°C); ^{1}H NMR ($CDCl_3$) δ 0.42 (m, 9H, CH_3), 7.01–7.43 (m, 3H, PyH, ArH), 7.57–7.98 (m, 3H, PyH, ArH), 8.41–8.61 (m, 1H, 6-PyH). Oxidation of the sulfides to sulfoxides **4a–c** was carried out by a similar procedure to those used for sulfoxides **1a–f**.

2-[2-(3-Trimethylsilyl)pyridylsulfinyl]benzothiazole

4a: mp 107.0–107.5°C; ^{1}H NMR ($CDCl_3$) δ 0.55 (m, 9H, CH_3), 7.16–7.59 (m, 3H, ArH, PyH), 7.78–8.08 (m, 3H, ArH, PyH), 8.52–8.71 (m, 1H, 6-PyH); IR (KBr) 1050 cm^{-1} (SO); MS (*m/z*): 332 (M^+); anal calcd for $C_{15}H_{16}N_2OS_2Si$: C, 54.18; H, 4.85; N, 8.42%. Found: C, 53.93; H, 4.81; N, 8.21%.

2-[2-(3-Pivaloyl)pyridylsulfinyl]benzothiazole

4b: mp 166.0–167.0°C; ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 9H, CH_3), 7.27–7.57 (m, 3H, ArH, PyH), 7.71–8.19 (m, 3H, ArH, PyH), 8.59–8.78 (m, 1H, 6-PyH); IR (KBr) 1055 (SO), 1670 cm^{-1} (CO); MS (*m/z*): 328 (M^+ − 16); anal calcd for $C_{17}H_{16}N_2O_2S_2$: C, 59.28; H, 4.68; N, 8.13%. Found: C, 59.34; H, 4.64; N, 8.12%.

2-[2-(3-Benzoyl)pyridylsulfinyl]benzothiazole

4c: mp 63.0–65.0°C; ^{1}H NMR ($CDCl_3$) δ 7.17–8.06 (m, 11H, ArH, PyH), 8.75–8.94 (m, 1H, 6-PyH); IR (KBr) 1060 (SO), 1645 cm^{-1} (CO); MS (*m/z*): 348 (M^+); anal calcd for $C_{19}H_{12}N_2OS_2$: C, 62.62; H, 3.32; N, 7.69%. Found: C, 62.37; H, 3.40; N, 7.48%.

Trapping Experiments of Sulfenate Salts

In a typical run, a stirred solution of sulfoxide **1c** (80 mg, 0.362 mmol) in acetonitrile (5 mL) under an argon atmosphere was treated with 1.0 M sodium ethoxide (0.38 mL, 0.38 mmol) in ethanol. The mixture was stirred for 30 minutes at room temperature under an argon atmosphere and treated with iodomethane (0.5 mL, 8.0 mmol). After having been stirred for 12 hours, the reaction mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The residue was purified by column chromatography (alumina, eluent, ethyl acetate, and then ethanol) to give methyl 2-pyridyl sulfoxide **5c** and 2-ethoxypyridine-1-oxide **6** in 94% and quantitative yields, respectively.

Methyl 4-Methylphenyl Sulfoxide

5a: mp 40.5–42.0°C (Ref. [10] 41–42°C); ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H, CH_3Ph), 2.71 (s, 3H, CH_3), 7.29, 7.75 (ABq, J = 8 Hz, 4H, To1H).

Methyl Phenyl Sulfoxide

5b: colorless liquid [11]; ^{1}H NMR ($CDCl_3$) δ 2.72 (s, 3H, CH_3), 7.37–7.78 (m, 5H, PhH).

Methyl 2-Pyridyl Sulfoxide

5c: colorless liquid [8]; ^{1}H NMR ($CDCl_3$) δ 2.85 (s, 3H, CH_3), 7.16–7.47 (m, 1H, 5-PyH), 7.80–8.02 (m, 2H, 3,4-PyH), 8.44–8.67 (m, 1H, 6-PyH).

Methyl 4-Pyridyl Sulfoxide

5d: hygroscopic colorless crystals, mp 42–43°C, bp 137.0–137.5°C/4.0 Torr; ^{1}H NMR ($CDCl_3$) δ 2.79 (s, 3H, CH_3), 7.56, 8.80 (ABq, J = 6 Hz, 4H, PyH); IR (neat) 1056 cm^{-1} (SO); exact mass calcd for C_6H_7NOS 141.0248, found 141.0249.

2-Adamantyl Methyl Sulfoxide

5e: mp 121.5–123.0°C (Ref. [12] 122–123°C); ^{1}H NMR ($CDCl_3$) δ 2.58 (s, 3H, CH_3), 1.38–2.90 (m, 15H, AdmH).

Methyl 2-Nitrophenyl Sulfoxide

5f: mp 99.5–101.5°C (Ref. [13] 101–102°C); ^{1}H NMR ($CDCl_3$) δ 2.93 (s, 3H, CH_3), 7.50–8.46 (m, 4H, ArH).

2-Benzothiazolyl Methyl Sulfoxide

5g: mp 66.0–67.5°C (Ref. [14] 66–68°C); ^{1}H NMR ($CDCl_3$) δ 3.08 (s, 3H, CH_3), 7.37–7.63 (m, 2H, 5,6-ArH), 7.86–8.17 (m, 2H, 4,7-ArH).

Methyl 2-(3-Trimethylsilyl)pyridyl Sulfoxide

5h: colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.43 (s, 9H, $Si(CH_3)_3$), 2.83 (s, 3H, CH_3), 7.29–7.48 (m, 1H, 4-PyH), 7.96–8.02 (m, 1H, 5-PyH), 8.70–8.80 (m, 1H, 6-PyH); IR (neat) 1040 cm^{-1} (SO); exact mass calcd for $C_9H_{15}NOSSi$ 213.0644, found 213.0638.

2-Ethoxypyridine-1-oxide

6: mp 131.0–133.0°C (Ref. [15] 131–133°C); ^{1}H NMR ($CDCl_3$) δ 1.38 (t, J = 7 Hz, 3H, CH_3), 4.36 (q, J = 7 Hz, 2H, CH_2), 6.54–7.67 (m, 3H, 3,4,5-PyH), 7.97–8.23 (m, 1H, 6-PyH).

2-Ethoxybenzothiazole

7: colorless liquid [16]; ^{1}H NMR ($CDCl_3$) δ 1.47 (t, J = 7 Hz, 3H, CH_3), 4.61 (q, J = 7 Hz, 2H, CH_2), 7.08–7.77 (m, 4H, ArH).

2-Butylthiobenzothiazole

8: colorless liquid [17]; ^{1}H NMR ($CDCl_3$) δ 0.70–1.96 (m, 7H, $CH_2CH_2CH_3$), 3.03–3.35 (m, 2H, SCH_2), 7.11–7.95 (m, 4H, ArH).

Isolation of Sulfenate Salts **9a** *and* **9b**

A typical procedure is as follows. A stirred solution of sulfoxide **3a** (214 mg, 0.82 mmol) in acetonitrile (5 mL) under an argon atmosphere was treated with 1.14 M sodium ethoxide (0.75 mL, 1.52 mmol) in ethanol. The mixture was stirred at room temperature for 1 hour under an argon atmosphere and then was treated with anhydrous ether (1 mL). The resulting salt was filtered off, washed with anhydrous ether, and a trace amount of solvent was removed under reduced pressure in a dry-box under a dry-N_2 stream to give sulfenate salt **9a** in 90% yield. Sulfenate salt **9b** was also isolated in quantitative yield from **4a** by the same procedure applied to the product of the reaction of sulfoxide **9a** with sodium butanethiolate in THF.

Sodium 2-Pyridinesulfenate

9a: mp 157–161°C (decomp); ^{1}H NMR (CD_3CN) δ 6.42–7.17 (m, 3H, 3,4,5-PyH), 8.07–8.17 (m, 1H, 6-PyH); IR (KBr) 870 cm^{-1} (S—O); anal calcd for C_5H_4NNaOS: C, 40.27; H, 2.70; N, 9.39%. Found: C, 39.81; H, 2.76; N, 9.45%.

Sodium 2-(3-Trimethylsilyl)pyridinesulfenate

9b: mp 176–182°C (decomp); ^{1}H NMR (DMF-d_7) δ 0.40 (s, 9H, CH_3), 6.59–6.69 (m, 1H, 5-PyH), 7.32–7.44 (m, 1H, 4-PyH), 8.35–8.46 (m, 1H, 6-PyH); IR (nujol) 890 cm^{-1} (S—O); anal calcd for $C_8H_{12}NNaOSSi$: C, 43.41; H, 5.47; N, 6.33%. Found: C, 42.56; H, 4.89; N, 6.22%.

Sodium 2-Pyridinesulfinate

10: mp 280–285°C (decomp); ^{1}H NMR (D_2O, DSS) δ 7.28–8.18 (m, 3H, 3,4,5-PyH), 8.35–8.56 (m, 1H, 6-PyH); IR (KBr) 990, 1040, 1050 (SO_2); anal calcd for $C_5H_4NNaO_2S$: C, 36.37; H, 2.44; N, 8.48%. Found: C, 36.72; H, 2.82; N, 8.34%.

Test of Stability of Sulfenate Salts **9a,b** *in Water*

A typical procedure is as follows. A stirred solution of sulfoxide **3a** (100 mg, 0.38 mmol) in THF (10 mL) under an argon atmosphere was treated with 1.2 M sodium butanethiolate (0.33 mL, 0.40 mmol) in methanol. Then water (1 mL, 55.5 mmol) was added quickly to the mixture. The mixture was stirred for 10 minutes (other runs, 20 and 40 minutes) at room temperature under an argon atmosphere and was treated with iodomethane (0.3 mL, 4.8 mmol). After having been stirred for 6 hours at room temperature, the mixture was extracted with $CHCl_3$ (3 × 20 mL) and dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, ethyl acetate) to give sulfoxide **5c** in 46% yield (other runs, 18 and 7% yields, respectively). When sulfoxide **4a** was treated with water under the same conditions

for 10, 20, and 40 minutes the trapped products **5h** were obtained in 79, 72, and 65% yields, respectively.

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for Scientific Research No. 02453018 from the Ministry of Education, Science and Culture, Japan.

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