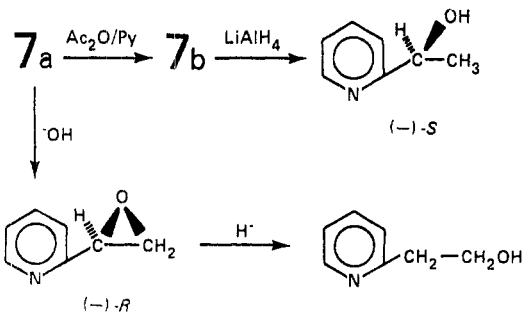
Scheme I



and the resulting **6** was purified by distillation: bp 110 °C (0.3 mm); NMR ($CDCl_3$) 4.88 (2 H, s), 7.55 (1 H, dd, J = 9, 5 Hz), 7.90 (1 H, dd, J = 9, 9 Hz), 8.10 (1 H, d, J = 9 Hz), 8.70 (1 H, d, J = 5 Hz).

Microbial Reduction of 6. To each of four flasks containing a 2-day-old shake culture of *C. macerans* was added 250 mg (total 1.0 g) of **6**. The flasks were shaken for 4 days. The combined aqueous phases were concentrated to half their original volume, made alkaline with $NaHCO_3$, and extracted with ethyl acetate. The organic layer was concentrated and the residue purified by thick-layer chromatography to yield 237 mg of **7a**, whose NMR spectrum was identical with that of an authentic sample prepared from 2-vinylpyridine by the procedure of Hanzlik et al.;[7] $[\alpha]^{25}_D$ −33.2° (*c* 4.06, $CHCl_3$).

Acetylation of (1*R*)-(2-Pyridyl)-2-bromoethanol (7a). The bromo alcohol **7a** (230 mg) was acetylated in the usual manner in pyridine–acetic anhydride (Scheme I) and purified by preparative thick-layer chromatography to yield 213 mg (77%) of the acetate, $[\alpha]^{25}_D$ −49.7° (*c* 1.45, $CHCl_3$). Its NMR spectrum was identical with one prepared from racemic **7a** by the same procedure.

$LiAlH_4$ Reduction of (1*R*)-(2-Pyridyl)-2-bromo-1-acetoxyethane (7b). An ether solution of (1*R*)-(2-pyridyl)-2-bromo-1-acetoxyethane (200 mg) was added slowly to an ether suspension of excess $LiAlH_4$ at 0 °C. The mixture was stirred for 2 h, decomposed with ice, and extracted with ether. The ether solution was dried and concentrated, and the residue was purified by thick-layer chromatography (EtOAc–hexane, 1:1) to yield 34 mg (34%) of (1*S*)-(2-pyridyl)ethanol (**7c**):$[\alpha]^{25}_D$ −49.8° (*c* 3.1, EtOH); ee 88%.[4]

Preparation of 2-Pyridylethylene Oxide. To a solution of **7a** (90 mg) in MeOH (7 mL) was slowly added 7 mL of 0.4 N NaOH at 0 °C and the mixture stirred for 1 h. The reaction mixture was extracted into ether, washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by thick-layer chromatography (EtOAc–hexane, 1:4) and distillation (bp 100 °C, 5 mm) to give (2*R*)-pyridylethylene oxide, $[\alpha]^{25}_D$ −15.0° (*c* 0.41, $CHCl_3$). The NMR spectrum was identical with that of racemic material.

Microbial Reduction of 2-Chloroindan-1-one (1b). When **1b** (500 mg) was subjected to the procedure described above for **4a**, 74 mg of the *trans*-chlorohydrin **2b** ($[\alpha]^{25}_D$ +16.5° (*c* 3.7, $CHCl_3$)) was isolated by thick-layer chromatography, and 424 mg of **1b** was recovered.

Conversion of (+)-2b to (1*R*)-Indanol. Acetylation of (+)-**2b** was carried out in the usual manner to yield 65 mg of the (+)-acetate, $[\alpha]^{25}_D$ +97.1° (*c* 1.4, $CHCl_3$).

A solution of the acetate in THF was refluxed overnight with excess $LiAlH_4$, and the resulting (*R*)-indanol (38 mg) was isolated by chromatography, $[\alpha]^{25}_D$ −13.3° (*c* 1.75, $CHCl_3$) (lit.[17] for (*R*)-indanol $[\alpha]^{25}_D$ −17° (*c* 5, $CHCl_3$).

Acknowledgment. We wish to express our appreciation to Dr. U. Weiss for stimulating and valuable discussions.

Registry No. **1b**, 73908-22-2; **2b**, 73951-59-4; **2b** acetate, 73951-60-7; **4a**, 70-11-1; **4b**, 532-27-4; **5a**, 73908-23-3; **5a** acetate, 73908-24-4; **5b**, 56751-12-3; **5b** acetate, 33942-01-7; **5c**, 1445-91-6; **6**, 40086-66-6; **7a**, 73951-61-8; **7b**, 73908-25-5; **7c**, 59042-90-9; **8**, 73908-26-6; **9**, 73908-27-7; **10a**, 73908-28-8; **10b**, 73908-29-9; (+)-(*R*)-styrene oxide, 20780-53-4; *p*-methylbenzoin, 66749-62-0; (+)-(1*R*,2*S*)-*cis*-1-(4-methylphenyl)-2-phenylethylene oxide, 62137-65-9; butyrophenone, 495-40-9; *threo*-1-phenyl-2-chloro-1-butanol, 73951-62-9; *erythro*-1-phenyl-2-chloro-1-butanol, 73951-63-0; *cis*-1-phenyl-2-ethyloxirane, 73951-64-1; *trans*-1-phenyl-2-ethyloxirane, 73951-65-2; (−)-(*S*)-phenylpropylcarbinol, 22135-49-5; (2*R*)-pyridylethylene oxide, 73908-30-2; (*R*)-indanol, 697-64-3.

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Protonation of Methoxyphenyl Alkyl Sulfides in Pentafluoroantimony–Fluorosulfonic Acid

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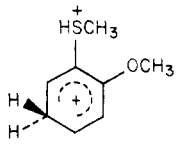
Aromatic sulfides protonate in strong acids exclusively at the sulfur atom,[2,3] unlike aromatic ethers[4,5] where the protonation sites involve both oxygen and ring carbon. The site of electrophilic attack in substitution reactions of alkoxy-substituted aromatic sulfides was found to be strongly affected by the presence of the alkoxy group.[6,7] It is, therefore, of considerable interest to examine the mode of protonation of these compounds. We present here some results on the protonation behavior of methoxyphenyl alkyl sulfides in SbF_5–FSO_3H solution.

o-, *m*-, and *p*-Methoxyphenyl sulfides (**1–3**, respectively) were protonated in 11.5 mol % SbF_5–FSO_3H at −80 °C. In addition, protonation of isomer **1** was carried out in pure FSO_3H solution. The site of protonation was determined on the basis of ^1H and ^{13}C NMR data of the ions formed, at −60 °C. The assignments of the ^{13}C resonances were made on the basis of their multiplicities in the off-resonance, ^1H-decoupled, ^{13}C NMR spectra and by comparison of their chemical shifts with the ^{13}C NMR chemical shifts of related positions in the *p*-methoxybenzenium ion[4] and the dimethyl phenyl sulfonium ion,[8] respectively.

The most interesting feature was exhibited by the ortho isomer. Its ^1H and ^{13}C NMR spectra are shown in Figures 1 and 2. The measured NMR data are best explaned by formation of a diprotonated species **4**.



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The ^1H NMR spectra (Figure 1, Table I) showed a well-resolved doublet at δ 3.36 (J = 7 Hz, total area 3) assigned to the SCH_3 protons, two partially overlapped

(1) Present address: Organisch-chemisches Institut der Universität, D-69 Heidelberg 1, West Germany.
(2) G. G. Furin and G. G. Yakobson, *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk*, 1, 109 (1977); *Chem. Abstr.*, **87**, 21855 (1977).
(3) M. Eckert-Maksić, submitted for publication.
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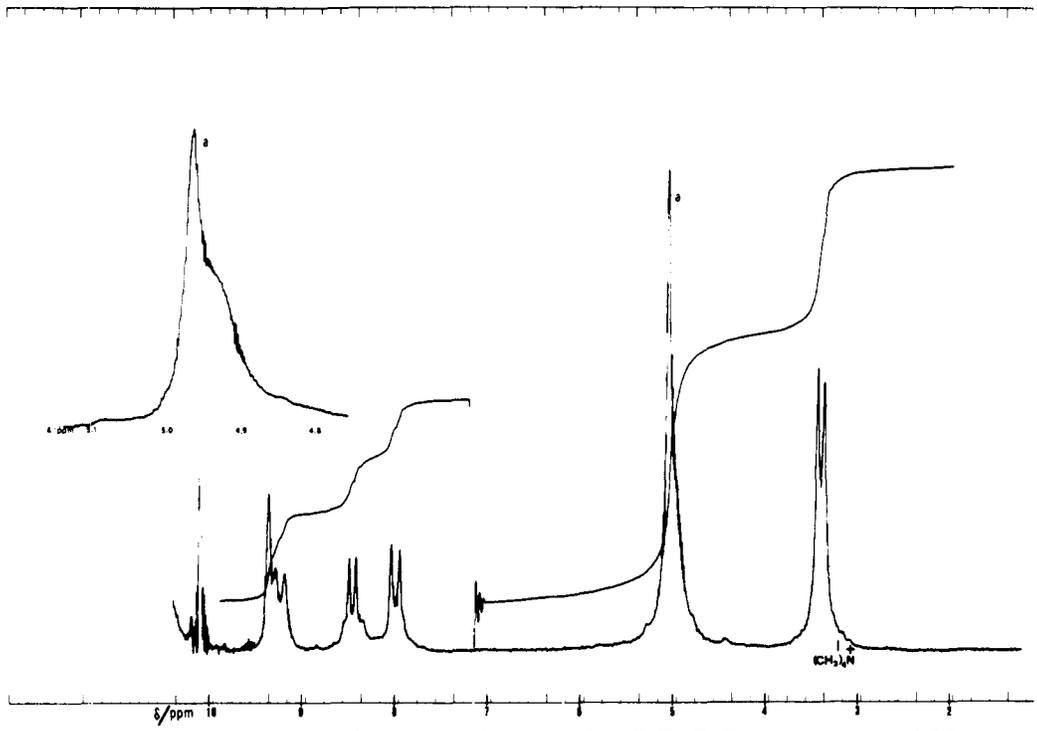
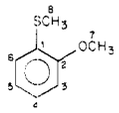
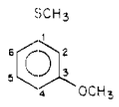
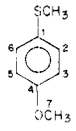


Figure 1. ^1H NMR spectrum of the o-methoxythioanisole **1** in 11.5 mol % SbF_5–FSO_3H solution at −60 °C.

Table I. ^1H NMR Parameters of Protonated Methoxythioanisoles in 11.5 mol % SbF_5-FSO_3H at −60 °C

	^1H NMR chemical shifts and multiplicities[a]				
starting base	SCH_3	OCH_3	ring protons	SH^+	CH_2
 **1**	3.36 (d, J = 7)	4.96 (s)	7.96 (d, J = 9), 9.20 (d, J = 9), 9.32 (s, br)	8.44 (q, J = 7)	4.9[b] (s, br)
 **2**	3.36 (d, J = 7)	5.02 (s, br)	8.10 (m)	[c]	
 **3**	3.32 (d, J = 7)	5.04 (s, br)	7.88 (d, J = 9), 8.22 (d, J = 9)	[c]	

[a] ^1H NMR chemical shifts are in parts per million from $(CH_3)_4N^+$ as internal standard, the chemical shift of $(CH_3)_4N^+$ was taken as −3.20 ppm relative to Me_4Si; multiplicities and coupling constants (J, in hertz) are given in parentheses: s = singlet, d = doublet, q = quartet, m = multiplet, br = broad. [b] Partially hindered by OCH_3 signal. [c] The ^+SH signal has not been observed as a separate signal; however, on the basis of integral ratios and the appearance of the spectra it can be concluded that it coincides with the ring protons.

broad singlets around δ 4.9 (5 H) ascribed to the OCH_3 and the "methylenic" CH_2 protons, and a quartet centered at δ 8.44 (J = 7 Hz, 1 H) assigned to the ^+SH proton. The ortho vinylic protons showed a slightly broadened doublet at δ 9.20 (J = 9 Hz, 1 H) and a broad singlet at δ 9.32 (1 H), respectively, while the meta vinylic proton appeared as a broad doublet at δ 7.96 (J = 9 Hz, 1 H). No significant change, except further broadening of the signals, occurs on raising the temperature to −30 °C. At this and higher temperatures, decomposition of the ion was observed.

A still better insight into the structure of the ion **4** was obtained on the basis of its ^{13}C NMR spectrum (Figure 2, Table II). The spectrum shows typical changes of the ^{13}C chemical shifts for the benzene derivatives upon protonation at the ring carbon.[10] In addition, the ring carbon atom to which the thiomethoxy group is attached shows a remarkable upfield shift (21.0 ppm) in comparison to its position in $CDCl_3$,[9] undoubtedly indicating protonation at sulfur. The assignment of the resonance at δ 43.4 to the methylenic carbon is unequivocal on the basis of its typical aliphatic shift magnitude.[4] The broadness of the signal as well as its failure to display completely resolved fine structure in the off-resonance decoupled spectrum indicates that rapid exchange with the superacid occurs under the conditions of measurement.

When neat fluorosulfonic acid was used instead of SbF_5–FSO_3H, base **1** was found to be protonated exclu-

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Table II. ^{13}C NMR Parameters of Protonated Methoxythioanisoles in 11.5 mol % SbF_5-FSO_3H at -60 °C

starting base	^{13}C NMR chemical shifts and multiplicities[a]							
	C1	C2	C3	C4	C5	C6	C7	C8
1	119.4 (s)	186.5 (s)	121.6 (d)	180.8 (d)*	43.4 (br)	179.6 (d)*	66.2 (q)	20.5 (q)
2	121.4 (s)	135.0 (d)*	151.9 (s)	125.3 (d)	122.6 (d)	134.7 (d)*	74.4 (q)	23.0 (q)
3	121.0 (s)	135.9 (d)	121.1 (d)	155.3 (s)	121.1 (d)	135.9 (d)	73.4 (q)	23.2 (q)

[a] ^{13}C NMR chemical shifts are in parts per million from external (capillary) Me_4Si, multiplicities are given in parentheses: s = singlet, d = doublet, q = quartet, br = broad. Resonances which are labeled with asterisks have interchangeable assignments. Numbering of the atoms is the same as in Table I.

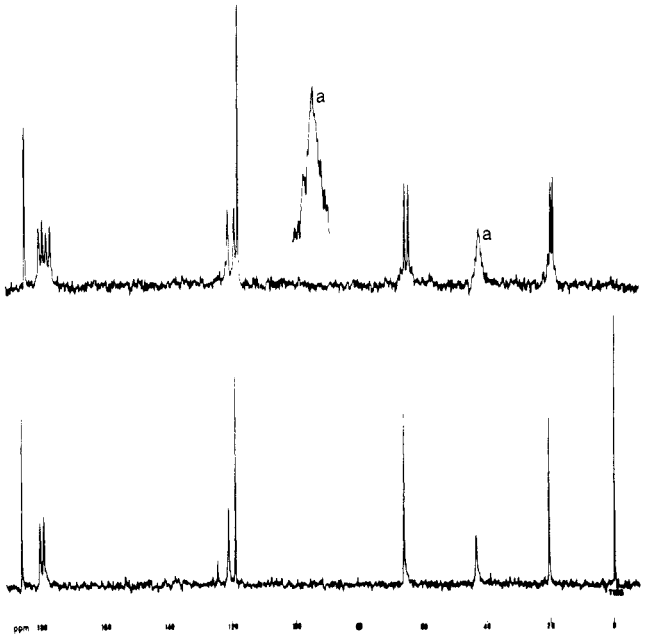

Figure 2. ^{13}C NMR spectra of the *o*-methoxythioanisole **1** in 11.5 mol % SbF_5-FSO_3H solution at -60 °C. The lower portion is the proton-decoupled spectrum, and the upper is the off-resonance proton-decoupled spectrum.

sively at sulfur. The ^1H NMR spectrum of the solution shows a thiomethoxy doublet at δ 3.09 (J = 7 Hz, 3 H), a OCH_3 singlet at δ 4.31 (3 H), a ring-proton multiplet between δ 7.19 and 7.83 (4 H), and an ^+SH quartet centered at δ 8.11 (J = 7 Hz, 1 H).

Contrary to *o*-methoxythioanisole, isomers **2** and **3** did not display ring protonation in 11.5 mol % SbF_5-FSO_3H solution. Both bases give similar ^1H NMR spectra (Table I), indicative of S-protonation. The spectra show a doublet around δ 3.3 assigned to the SCH_3 protons and a rather broad singlet around δ 5.0 ascribed to the methoxy protons. The aromatic protons of protonated base **2** are centered as a multiplet at δ 8.10, while those of protonated isomer **3** show two doublets between δ 7.88 and 8.22 (Table I). The ^{13}C NMR spectra (Table II) of protonated **2** and **3** show also the typical changes of sulfur-protonated ions,[3,8] although on the basis of a significant downfield chemical shift for the methoxy carbon atoms and an observed upfield shift of the ring carbon atom ipso to the OCH_3 group (7.0 ppm for isomer **2** and 3.0 ppm for isomer **3**) attachment of the proton to the oxygen atom cannot be excluded.

Experimental Section

The sulfides **1-3** were prepared by methylation of the related thiophenols with methyl sufate in base.[11] Thiophenols were synthetized by routine methods, either from the corresponding anisidines[12] (ortho and meta isomers) or by reduction of the corresponding sulfonyl chloride[13] (para isomer). All compounds were purified by vacuum distillation prior to the protonation study.

The fluorosulfonic acid (Fluka) and antimony pentafluoride (Merck) were purged with dry nitrogen for several hours and distilled in vacuo before use. Ions for NMR measurements were prepared by low-temperature dissolution of base in an excess of superacid under nitrogen.[5] After their NMR analyses, the solutions were quenched as previously described.[5] The starting sulfides were recovered quantitatively in all cases, as indicated by their GC, IR, and NMR analyses.

The ^1H NMR spectra were measured on a JEOL PS-100 spectrometer equipped with a variable-temperature probe. The ^{13}C NMR studies were performed on a JEOL JNM FX-100 spectrometer, also equipped with a variable-temperature probe, by using the Fourier transform method.

Acknowledgment. This work was financially supported by the Self-managing Authority for Scientific Research of the SR of Croatia SIZ II). We thank Dr. J. Kidrič and Dr. Z. Meić for arranging the use of ^1H NMR and ^{13}C NMR spectrometers, respectively. We also thank our referees for helpful comments.

Registry No. 1, 2388-73-0; 1 S-protonated, 73891-69-7; 1 diprotonated, 73953-50-1; 2, 2388-74-1; 2 S-protonated, 73891-70-0; 3, 1879-16-9; 3 S-protonated, 73926-77-9; SbF_5, 7783-70-2; FSO_3H, 7789-21-1.

(10) G. L. Nelson and E. A. Williams, *Prog. Phys. Org. Chem.*, 12, 229-342 (1976), and references therein.
(11) E. I. Vogel "Textbook of Practical Organic Chemistry", 3rd ed., Longmans, Green and Co., London, New York, Toronto, 1956, p 670.
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(13) R. Adams and C. S. Marvel, "Organic Syntheses", Collect. Vol. I, Wiley, New York, 1941, p 504.

A New Route to Simple Monoterpenes by Remote Functionalization

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We have developed a new method which enables remote functionalization of a nonactivated methylene or methine carbon.[1,2] The synthetic utility of this procedure is illustrated by the preparation of some monoterpenes.

We believe that this stereospecific approach, applied here to simple models, could be extended to other synthetic problems such as specific labeling or preparation of new steroid compounds.[3]

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