

Table 1. Chemical shifts of substituted selenophenes relative to the α - and β -hydrogens of selenophene in solution.

	δ_3^2	δ_4^2	δ_5^2	δ_3^3	δ_4^3	δ_5^3
OCH ₃	+1.14	+0.54	+0.88	+1.40	+0.32	+0.25
SCH ₃	+0.20	+0.20	+0.07	+0.49	+0.14	+0.06
Br	+0.07	+0.32	+0.16			
CN	-0.5	-0.037	-0.335	-0.675	-0.22	-0.17
COCH ₃	-0.48	-0.01	-0.31	-0.89	-0.52	-0.04
COOH	-0.50	-0.02	-0.30	-0.66	-0.71	-0.24
NO ₂	-0.78	-0.03	-0.38	-0.98	-0.29	+0.09
F	-0.78	+0.73	+0.50			
I	+0.16	+0.40	-0.05			
CH ₃				+0.15	+0.23	+0.54

Table 2. Regression equations relating proton chemical shift δ of monosubstituted selenophenes to substituent constants F and R .

Equation	b^b	c^c	N^d
$\delta_3^2 = (0.04 \pm 0.23) - (0.37 \pm 0.39)F - (2.21 \pm 1.04)R$	0.23	0.93	9
$\delta_4^2 = (0.01 \pm 0.14) + (0.21 \pm 0.19)F - (1.10 \pm 0.48)R$	0.12	0.91	9
$\delta_5^2 = (0.05 \pm 0.18) - (0.07 \pm 0.26)F - (1.57 \pm 0.63)R$	0.15	0.94	9
$\delta_3^3 = -(0.35 \pm 0.14) + (0.22 \pm 0.23)F - (3.43 \pm 0.42)R$	0.17	0.98	7
$\delta_4^3 = -(0.14 \pm 0.20) - (0.06 \pm 0.33)F - (1.21 \pm 0.67)R$	0.25	0.77	7
$\delta_5^3 = (0.21 \pm 0.18) - (0.28 \pm 0.30)F - (0.40 \pm 0.55)R$	0.23	0.49	7

^a The shifts are given in ppm relative to those of selenophene. The notations δ_i^2 , δ_j^3 denote the shifts of the i - and j -proton of 2- and 3-substituted selenophenes, respectively.

^b Standard deviation in ppm.

^c Correlation coefficient.

^d Number of substituents in the regression analysis.

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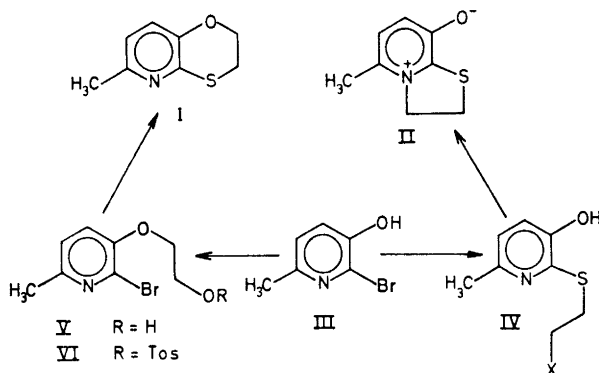
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Synthesis of a [1,4]Oxathiano-[3,2-b]pyridine Derivative

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Studies^{1,2} of the evaporation process of S_N -quaternary salts in the mass spectrometer required for comparative purposes a [1,4]oxathiano[3,2-b]pyridine derivative to be synthesized. This ring system does not appear to have previously been described. Previous findings³ show that a 2-ethio derivative with a displaceable group on the ethyl β -carbon (IV) is cyclized with preferential 5-membered ring formation over the pyridyl nitrogen (II). Cyclisa-



tion over the *ortho* phenolic oxygen to I was not seen. *N*-Cyclisation can be excluded, however, by initial *O*-alkylation with the ethyl reagent which is to become part of the oxathiano ring system.

For this purpose 2-bromo-3-hydroxy-6-methylpyridine (III) was *O*-alkylated with ethylene bromohydrin in aqueous alkali. At high pH the phenolic group is dissociated and this favours *O*-alkylation rather than *N*-alkylation. The alcohol (V) was next tosylated and VI readily thiated by heating with thiourea in ethanol. The nuclear bromine is not displaced by this sulphur nucleophile except at elevated temperature such as by heating in ethylene glycol.³ The 3-bromine in analogous compounds can be substituted on heating with potassium hydrogen sulphide in ethylene glycol.³ When the isothiuronium salt was decomposed in saturated sodium bicarbonate at 80°C, cyclisation was achieved without isolation of the intermediate thiol. The greater ease of bromine displacement in the formation of I is due to this being an intramolecular process with favourable ring size formation.

The spectroscopic properties of the isomers I and II differ. While the betaine (II) in alkaline solution has long-wave UV maximum at about 360 nm,³ the highest wave-length band for I is at 310 nm. In acid solution both compounds absorb around 340 nm. The NMR signals at 6.5 and 5.4 τ in trifluoroacetic acid due to the S-CH₂-CH₂-O methylene protons in I are shifted downfield to 6.1 and 4.9 τ (S-CH₂-CH₂- $\overset{+}{\text{N}}\equiv$) in the pyridinium isomer (II).³ The methyl groups and the pyridyl protons have very similar chemical shifts.

Experimental. 2-Bromo-3- β -hydroxyethoxy-6-methylpyridine (V). Ethylene bromohydrin (12.5 g, 0.10 mol) was added dropwise over 15 min to a stirred solution of 2-bromo-3-hydroxy-6-methylpyridine (9.4 g, 0.05 mol) in N NaOH (40 ml) at room temperature. The solution was then heated at 100°C for 1 h, allowed to cool, the oily precipitate extracted into chloroform, the extracts washed with 0.5 N NaOH and water, the organic solution dried, evaporated and the residual solid recrystallized from dilute ethanol; yield 9.8 g (85%), m.p. 73–75°C. (Found: C 41.29; H 4.21; N 6.18. Calc. for C₈H₁₀BrNO₂: C 41.35; H 4.35; N 6.04.) UV maxima in 0.1 HCl/EtOH at 288 nm (log ϵ 3.87); in 0.1 N NaOH/EtOH at 288 nm (log ϵ 4.00) and at 223 nm (log ϵ 4.15).

2-Bromo-6-methyl-3- β -tosyloxyethoxypyridine (VI). Tosyl chloride (6.1 g, 0.032 mol) was added in small portions to a stirred solution of 2-bromo-3- β -hydroxyethoxy-6-methylpyridine (7.0 g, 0.03 mol) in anhydrous pyridine (40 ml), the temperature being 0–5°C. The reaction mixture was left in the cold overnight, poured into water, the product extracted into chloroform, the chloroform solution washed well with water, dried and evaporated. The residual solid was crystallized in white needles from carbon tetrachloride; yield 9.4 g (81%), m.p. 114°C (Found: C 46.44; H 4.27; N 3.87. Calc. for C₁₅H₁₆BrNO₄S: C 46.64; H 4.18; N 3.63.)

6-Methyl[1,4]oxathiano[3,2-*b*]pyridine (I). The above tosylate (VI) (2.30 g, 0.006 mol) was added in small portions to a stirred solution of thiourea (0.45 g, 0.006 mol) in ethanol at 75°C. After 1 h at this temperature the ethanol was evaporated, the residual isothiuronium salt dissolved in saturated sodium bicarbonate solution (100 ml) and this solution kept at 80°C for 3 days. The oily

material formed was then extracted from the cold reaction mixture into chloroform. Evaporation of the washed and dried solution left an oily material which was converted to the solid HBr salt by addition of HBr to an ethyl acetate solution and the precipitated material recrystallized from ethyl acetate/acetone; yield 0.8 g (49%), m.p. 170°C (decomp). (Found: C 38.85; H 4.19; N 5.65. Calc. for $C_8H_9NOS \cdot HBr$: C 38.72; H 4.06; N 5.46.)

NMR spectrum in TFA: 7.30 τ ($-CH_2$, singlet), 6.54 and 5.39 τ ($-S-CH_2-CH_2-O-$ triplets), 2.25–2.63 (H^7-H^8 , AB-quartet with $J=9$ cps). UV maxima in 0.1 N HCl/EtOH at 338 nm ($\log \epsilon=4.10$) and at 256 nm (3.76); in 0.1 N NaOH/EtOH at 311 nm ($\log \epsilon=4.07$) and at 250 nm (3.90).

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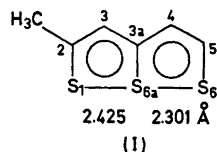
The Structure of 2-Methyl-6a-thiathiophthene

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The results from CNDO/2 calculations on mono-methyl substituted 6a-thiathiophthene show that a 2-methyl group causes a lengthening of the S(1)–S(6a) bond.¹ A structure study of 2-methyl-6a-thiathiophthene (I) has been carried out in order to test the CNDO/2 predictions, and the preliminary results from this study are given.

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The sulphur–sulphur bonds in I are S(1)–S(6a) = 2.425(2) Å and S(6a)–S(6) = 2.301(2) Å in agreement with the results from the CNDO/2 calculations.¹

Other bond lengths in the molecule are S(1)–C(2) = 1.688(4) Å, S(6a)–C(3a) = 1.747(5) Å, S(6)–C(5) = 1.672(5) Å, C(2)–C(3) = 1.353(7) Å, C(3)–C(3a) = 1.403(6) Å, C(3a)–C(4) = 1.425(7) Å, C(4)–C(5) = 1.365(7) Å and C(2)–C(6) = 1.520(8) Å.

A sample of I was generously supplied by Reid.² Crystallisation from cyclohexane yielded orange red plates with {001} predominant. The crystals belong to the monoclinic space group $P2_1/c$ with unit cell dimensions $a=5.9558(9)$ Å, $b=7.8563(8)$ Å, $c=16.014(4)$ Å, and $\beta=91.31(2)^\circ$. There are four molecules per unit cell; $D_c=1.545$ g cm⁻³, $D_m=1.54$ g cm⁻³.

The structure was solved by direct methods³ and refined by full matrix least squares. With anisotropic temperature factor coefficients for all atoms except hydrogen, the present R is 0.05.

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