purity by using thin-layer and gas–liquid chromatography.

**Preparation and Analysis of Pyridinium Hydrobromide Perbromide Complexes.** Complex 1 could be prepared according to the method of Fieser.[6a] The complex is also available from Aldrich Chemical Company, Inc. Recrystallization of 10 g of the crude complex from 5.5 mL of acetic acid yields 7.5 g of pure material melting at 132–34 °C. Anal. Calcd for $C_5H_5N{\cdot}HBr{\cdot}Br_2$: reducible Br, 49.96; total Br, 74.95. Found: reducible Br, 49.9; total Br, 75.0. Complex 2 could be prepared according to the method of Englert and McElvain.[6b] Complex 1 may also be converted into complex 2. Recrystallization of 10 g of complex 1 from 8.5 mL of acetic acid yields 8.2 g of complex 2 melting at 104–106 °C. Anal. Calcd for $3(C_5H_5N{\cdot}HBr){\cdot}2Br_2$: reducible Br, 39.97; total Br, 69.95. Found: reducible Br, 39.9; total Br, 70.4.

**General Procedure for Hydrolysis of Thioacetals and Thioketals. (a) Phase-Transfer Method.** (This method is preferred in most cases.) With vigorous stirring, 1 mmol of tetrabutylammonium bromide was added to a mixture of 10 mmol of thioacetal, 10 mmol of pyridine, and 10 mmol of complex 1 (or 5 mmol of complex 2) in 10 mL of dichloromethane and 2 mL of water at 0 °C.

The red-orange color of the bromine complex faded to colorless or a pale yellow within a few minutes. Stirring was continued at room temperature for 2 h to complete the hydrolysis. The dichloromethane layer was separated and the aqueous phase was extracted with two 10-mL portions of dichloromethane. The combined organic phase was washed with water and then was filtered through a loose cotton plug to remove suspended water. The solvent was evaporated and the crude carbonyl compound was purified by distillation or chromatography through a short column of Florisil to yield essentially (>98%) pure material.

**(b) Aqueous Acetonitrile.** (This procedure is recommended for α-thioketalized acids.) A solution of 10 mmol of bromine complex 1 (or 5 mmol of complex 2) in 2 mL of aqueous 50% acetonitrile was added dropwise at 0 °C to a stirred solution of 10 mmol of thioacetal dissolved in 15 mL of aqueous 10% acetonitrile. Pyridine (1 equiv) may be added to the reaction mixture if desired. Hydrolysis to give an α-keto acid should be carried out in the absence of pyridine. The orange color of the bromine complex rapidly discharges to colorless or a pale yellow. The reaction mixture was stirred at room temperature for 30 min. After the acetonitrile had been evaporated, the residue was taken up in ether, washed with water, and dried over anhydrous magnesium sulfate. The ether was evaporated and the crude carbonyl compound purified as above.

**2-(Heptadec-8-enyl)-1,3-dithiacyclohexane**: NMR δ 0.9 (t, 3, $J$ = 7), 1.1–1.8 (br m, 26), 1.8–2.4 (m, 4), 2.8–2.95 (m, 4), 4.05 (t, 1, $J$ = 6), 5.4 (t, 2, $J$ = 5); mol wt calcd for $C_{21}H_{40}S_2$ 356.2571, found 356.2568. Anal. Calcd for $C_{21}H_{40}S_2$ (mol wt 356.68): C, 70.72; H, 11.30; S, 17.98. Found: C, 70.55; H, 11.25; S, 17.81.

**2-Methyl-2-nonyl-1,3-dithiacyclohexane**: NMR δ 0.85 (t, 3, $J$ = 7), 1.1–1.5 (br m, 14), 1.6 (s, 3), 1.8–2.1 (m, 4), 2.8 (t, 4, $J$ = 6); mol wt calcd for $C_{14}H_{28}S_2$ 260.1633, found 260.1633. Anal. Calcd for $C_{14}H_{28}S_2$ (mol wt 260.51): C, 64.55; H, 10.83; S, 24.62. Found: C, 64.29; H, 10.77; S, 24.71.

**2,2-Dibutyl-1,3-dithiacyclohexane**: NMR δ 0.9 (t, 6, $J$ = 7), 1.2–1.5 (m, 8), 1.8–2.0 (m, 6), 2.75 (t, 4, $J$ = 6); mol wt calcd for $C_{12}H_{24}S_2$ 232.1319, found 232.1320. Anal. Calcd for $C_{12}H_{24}S_2$ (mol wt 232.45): C, 62.00; H, 10.41; S, 27.59. Found: C, 62.05; H, 10.33; S, 27.41.

**(*E*)-Methyl 4,4-bis(ethylthio)pent-2-enoate**: IR 1645, 1725 $cm^{-1}$; NMR δ 1.1 (t, 6, $J$ = 7), 1.6 (s, 3), 2.5 (q, 4, $J$ = 7), 3.6 (s, 3), 5.7 (d, 1, $J$ = 16), 6.7 (d, 1, $J$ = 16); mol wt calcd for $C_{10}H_{18}O_2S_2$ 234.0748, found 234.0746. Anal. Calcd for $C_{10}H_{18}O_2S_2$ (mol wt 234.38): C, 51.25; H, 7.74; S, 27.36. Found: C, 51.11; H, 7.69; S, 27.30.

**2,2-Bis(ethylthio)hexanal**: IR 1710 $cm^{-1}$; NMR δ 0.8–2.0 (m, 15), 2.4 (q, 4, $J$ = 7), 8.75 (s, 1); mol wt calcd for $C_{10}H_{20}OS_2$ 220.0955, found 220.0956. Anal. Calcd for $C_{10}H_{20}OS_2$ (mol wt 220.40): C, 54.50; H, 9.15; S, 29.10. Found: C, 54.25; H, 9.13; S, 28.78.

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**Registry No.** 1, 39416-48-3; 2, 53913-80-7; 2-hexyl-1,3-dithiane, 26958-42-9; (*Z*)-8-heptadecenyl-1,3-dithiane, 76467-37-3; 2-phenyl-1,3-dithiane, 5425-44-5; 2-methyl-2-nonyl-1,3-dithiane, 70499-19-3; 2,2-dibutyl-1,3-dithiane, 76467-38-4; 1,5-dithiaspiro[5.5]undecane, 180-59-6; 2-methyl-2-phenyl-1,3-dithiane, 6331-22-2; spiro[1,3-dithiane-2,9′-[9H]fluorene], 165-06-0; ethyl 2-butyl-1,3-dithiane-2-carboxylate, 32557-27-0; ethyl 2,2-bis(ethylthio)hexanoate, 76467-39-5; methyl(*E*)-4,4-bis(ethylthio)pent-2-enoate, 76467-40-8; 2,2-bis(ethylthio)hexanoic acid, 71535-47-2; 2,2-bis(ethylthio)hexanal, 76371-99-8; heptanal, 111-71-7; (*Z*)-9-octadecenal, 2423-10-1; benzaldehyde, 100-52-7; 2-undecanone, 112-12-9; 5-nonanone, 502-56-7; cyclohexanone, 108-94-1; 1-phenylethanone, 98-86-2; 9*H*-fluoren-9-one, 486-25-9; ethyl 2-oxohexanoate, 5753-96-8; methyl *trans*-4-oxo-2-pentenoate, 2833-24-1; 2-oxohexanoic acid, 2492-75-3; 2-oxohexanal, 2363-84-0.

## Synthesis and Conformational Mobility of [2.2](2,6)Pyridinophan-1-ene

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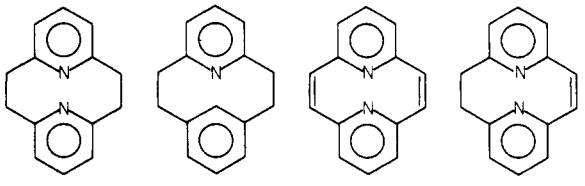
There has been considerable interest in the synthesis and properties of [2.2]metacyclophanes over the past two decades.[1] Many of these cyclophanes have proven highly useful in investigations of steric interactions through studies of the effects of substituents on the rates of conformational processes.[2] Particularly intriquing are the pyridinophanes 1 and 2 where conformational flipping



1 2 3 4

involves lone pair–lone pair and lone pair–CH interactions, respectively. In the former case, $\Delta G^{\ddagger}$ = 14.8 kcal/mol has been reported[3] for the conformational interchange while the value for 2 is too large for determination by the dynamic NMR technique.[4] Boekelheide has reported the preparation of diene 3 and suggests that the ethylene bridges render this cyclophane conformationally rigid based on the absence of NMR spectral changes over a wide temperature range.[5] The absence of nonequivalent exchange sites in this molecule makes this interpretation questionable, however. We report the synthesis [2.2]-(2,6)pyridinophan-1-ene (4) and more definitive results from dynamic NMR studies of its conformational behavior.

While a number of [2.2]cyclophanedienes are known,[5,6] compounds with single ethylenic bridges are relatively rare,[7] especially in heterocyclic systems.[6b] the usual strategy for construction of such systems involves ring

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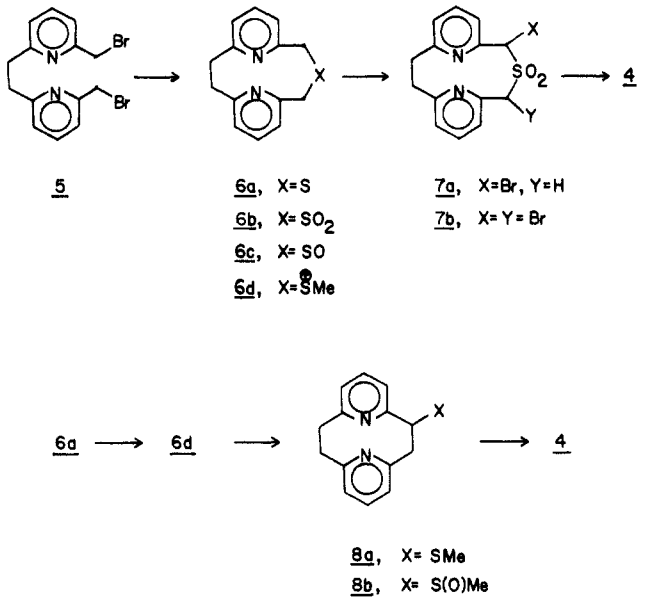
Scheme I




contractions of 2-thia[2.3]cyclophanes which are generally prepared from bridged benzylic halides and $Na_2S$ under high-dilution conditions.

In our synthesis of [2.2](2,6)pyridinophan-1-ene (**4**), shown in Scheme I, treatment of dibromide **5**[8] with $Na_2S$ gave the corresponding 2-thiapyridinophane **6a** in 76% yield. Initial attempts to oxidize this sulfide to sulfone **6b** with 30% $H_2O_2$ in acetic acid gave mixtures of **6b** and its *N*-oxide. Similar difficulties in oxidations of pyridine-containing thiacyclophanes have been previously noted.[6e,f] Sulfide **6a** could be oxidized cleanly to **6b** in 88% yield by the method of Schultz[9] with $H_2O_2$ in aqueous THF for 1 h at 50–60 °C in the presence of catalytic amounts of tungstic acid. The oxidation was slower in the absence of the catalyst and at 20 °C gave largely sulfoxide **6c**. Bromination with $Br_2$ of the anion formed from **6b** and *n*-BuLi at −78 °C gave unstable α-bromo sulfone **7a** in 60% yield. Upon standing in solution **7a** tended to disproportionate to α,α-dibromo sulfone **7b** and **6b**. Prompt isolation of **7a** prevents this difficulty. Treatment of **7a** with NaOH gave the desired olefin **4** by Ramberg–Backlund rearrangement[10] in 43% yield along with a modest amount of sulfone **6b** which presumably presumably arises by displacement of the rather stable anion of **6b** upon attack of hydroxide anion on bromine. The olefinic cyclophane **4** was readily isolated by preparative layer chromatography and further purified by sublimation and recrystallization. The $^1H$ NMR spectrum of **4** shows, in addition to resonances from aromatic protons, a sharp resonance at δ 6.80 from the olefinic bridge protons and a single resonance at δ 2.87 from the saturated bridge protons (Figure 1).

The generation of **4** by a Ramberg–Backlund rearrangement is especially noteworthy in that failures in closely related cases have led to the general belief that this approach is not useful for the construction of ethylene-bridged [2.2]cyclophanes.[6f,10,11] Subtle differences in the degree of conformational freedom present in the carbanionic rearrangement precursor may be responsible for the sucess in this case.

We were also able to prepare **4** by using the Stevens rearrangement procedure developed by Boekelheide.[11] Treatment of **6a** with trimethyloxonium hexafluorophosphate gave the corresponding *S*-methyl sulfonium salt, **6d**, which, without isolation, underwent a Stevens rearrangement in the presence of NaH to give 1-methylthio-[2.2](2,6)pyridinophane (**8a**) in 35% yield. This sulfide was oxidized at 20 °C to sulfoxide **8b** in 74% yield by the action of $H_2O_2$ in aqueous THF. Thermolysis[12] of **8b** in refluxing xylene for 30 h gave **4** in 42% yield.

The sharp bridge methylene proton resonance at δ 2.87 in the 27 °C $^1H$ NMR spectrum of **4** suggests that rapid conformational flipping is occurring at this temperature. At lower temperatures the conformational flipping process is slowed as evidenced by broadening of the bridge methylene proton peak (Figure 1). The coalescence temperature, $T_c$, is reached at −43 °C and the frozen spectrum showing the expected AA'BB' pattern for the axial and equatorial protons on the methylene bridge is seen at −65 °C. Calculation of the free energy of activation for the flipping process using the coalescence temperature method[13] with an approximation of the spectrum as an AB system[14] ($\Delta\nu$ = 85 Hz, $J_{AB}$ = 8 Hz) gives $k_c$ = 194 $s^{-1}$ and $\Delta G^{\ddagger}_{230K}$ = 10.9 kcal $mol^{-1}$ (45.7 kJ $mol^{-1}$). The same results were obtained from curve matching with computed AA'BB' spectra[15] generated by the DNMR 3 program of Kleier and Binsch.[16]

Replacement of one of the saturated bridges in **1** ($\Delta G^{\ddagger}_{287K}$ = 14.8 kcal $mol^{-1}$)[3] with an ethylenic bridge thereby lowers the activation barrier to conformational flipping. While the unsaturated bridge in **4** would be expected to decrease the distance between the stepped pyridine rings owing to a shorter olefinic bond length, the increased bond angles resulting from the $sp^2$-hybridized bridge carbons would tend to increase the bridge length and thus decrease the nitrogen–nitrogen repulsion component of the activation barrier. While an increase in conformational mobility from bond-angle spreading has been observed in [2.2]metaparacyclophane-1,9-diene,[6d] molecular models suggest that a reduction in the ring plane separation in **4** results in an increase in the nitrogen–nitrogen interaction. This decrease in distance between the pyridine rings in **4** relative to **1** would raise the energy of the ground state of **4** relative to its transition state for the flipping process and thus lower the value of $\Delta G^{\ddagger}$.

In light of these results it seems likely that diene **3**, reported by Boekelheide,[5] would be even more mobile than **4**. Boekelheide inferred from a dynamic NMR study that **3** is conformationally frozen since no change in its $^1H$ NMR spectrum was observed over a wide temperature range. This conclusion was based on the assumption that the average chemical shifts of rapidly inverting **3** would differ significantly from those of frozen **3**. When one considers

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(15) Exact coupling constants for the AA'BB' analysis could not be extracted from the frozen spectrum of **4** owing to uncertainties in the positions of the weaker transitions. The constants used for our calculation were those obtained from an analysis of the frozen spectrum of 1:[3] $J_{AB}$ = −12.0, $J_{AA'}$ = 12.6, $J_{BB'}$ = 3.7, $J_{AB'}$ = 4.0 Hz. A chemical shift difference $\Delta\nu$ = 85 Hz was obtained from the spectrum of **4** at −65 °C in $CH_2Cl_2$ (100 MHz). A computer-generated spectrum for frozen **4**, using these values, closely matched the observed spectrum.
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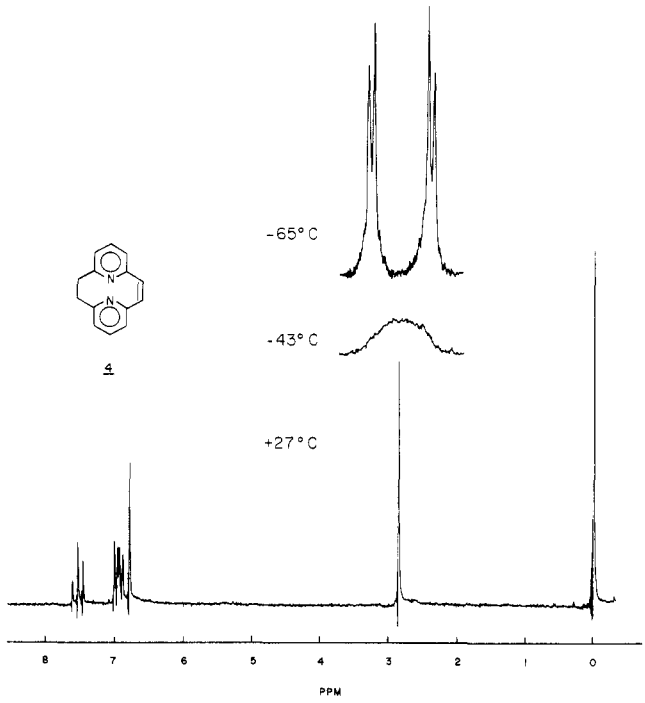


**Figure 1.** 100-MHz $^1H$ NMR spectrum of **4** at 27 °C with changes in the methylene bridged proton region at −43 and −65 °C.

the relatively short time spent by such a molecule in other than its ground state, this assumption seems highly questionable.

It will be highly interesting to see if unsaturation in one of the bridges in **2** lowers the flipping barrier to the point where the topomerization can be observed by using the dynamic NMR technique.

## Experimental Section[17]

**2-Thia[2.3](2,6)pyridinophane (6a).** To 800 mL of anhydrous MeOH stirred under an inert atmosphere was added 2 mL of a 12-mL solution containing 650 mg (2.7 mmol) of $Na_2S·9H_2O$ in MeOH and 100 mg of 1,2-bis[6-(bromomethyl)-2-pyridyl]ethane (**5**).[8] Stirring was continued for 1 h whereupon another 2-mL portion of the $Na_2S$ solution and another 100 mg of dibromide **5** were added. New additions were made after each hour until all of the $Na_2S$ solution and a total of 600 mg (1.63 mmol) of dibromide **5** had been added. The mixture was stirred overnight and concentrated to near dryness by distillation of the MeOH from the reaction vessel. The remaining MeOH was removed under reduced pressure and the residue extracted with several portions of $CH_2Cl_2$. The residue was purified by preparative layer chromatography (alumina, $CHCl_3$), giving 300 mg (76%) of **6a**: mp 140.5–141 °C (from benzene–pentane); IR (KBr) 3060, 2957, 2920, 1584, 1568, 1452, 1425, 1408, 1272, 1180, 1074, 1000, 991 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.00 (s, 4, $CH_2$), 3.73 (s, 4, $CH_2S$), 7.0–7.8 (m, 6, PyH).

Anal. Calcd for $C_{14}H_{14}N_2S$: C, 69.39; H, 5.82; N, 11.56. Found: C, 69.36; H, 5.96; N, 11.46.

**2-Thia[2.3](2,6)pyridinophane *S,S*-Dioxide (6b).** By use of the procedure of Schultz and co-workers[9] a tungstic acid catalyst solution was prepared by slurrying 66 mg of $H_2WO_4$ in 2 mL of distilled water and adding several drops of 6 N NaOH until the pH was 11–12. The solution was treated with drops of glacial HOAc until the pH was approximately 5. A portion of this turbid solution (0.5 mL) was added to a solution containing 300 mg of **6a** (1.24 mmol), 3 mL of the THF, and 3 mL of water followed by the addition of 270 $\mu$L of 30% $H_2O_2$ (3.3 mmol). The mixture was heated at 50–60 °C for 2 h followed by removal of most of the THF under reduced pressure. The remaining mixture was extracted with $CHCl_3$ and the extracts were washed with water and dried over $Na_2SO_4$. Concentration followed by recrystallization of the residue from benzene–pentane gave 300 mg of **6b** (88%): mp 233–233.5 °C; IR ($CHCl_3$) 3012, 1587, 1567, 1447, 1305, 1099 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.10 (s, 4, $CH_2$), 4.37 (s, 4, $CH_2SO_2$), 7.0–8.0 (m, 6, PyH).

Anal. Calcd for $C_{14}H_{14}N_2O_2S$: C, 61.29; H, 5.14; N, 10.21. Found: C, 61.26; H, 5.14; N, 10.06.

Oxidation of **6a** as above at 25 °C and without the tungstic acid catalyst gave a mixture of sulfide **6a** and sulfoxide **6c** which was separated by preparative layer chromatography (alumina, EtOAc–MeOH, 97:3). Pure **6c** was obtained by recrystallization from benzene–pentane: mp 134–135 °C; IR ($CHCl_3$) 3010, 1587, 1572, 1449, 1022 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.07 (s, 4, $CH_2$), 4.00, 4.33 (dd, 4, $CH_2SO$, $J_{AB}$ = 13 Hz), 7.0–8.0 (m, 6, PyH).

Anal. Calcd for $C_{14}H_{14}N_2OS$: C, 65.09; H, 5.46; N, 10.84. Found: C, 64.92; H, 5.54; N, 10.76.

**1-Bromo-2-thia[2.3](2,6)pyridinophane *S,S*-Dioxide (7a).** A solution containing 27.4 mg (0.10 mmol) of **6b** in 2 mL of dry THF was stirred at −78 °C under an inert atmosphere and treated with drops of *n*-butyllithium solution (1.25 N in hexane) until the light yellow color of the monoanion persisted. The addition of butyllithium solution (90 $\mu$L) was continued until all of **6b** had been converted to its monoanion. The endpoint for this titration was signaled by a sudden change in the color of the solution to dark orange, presumably owing to the formation of a dianion. Bromine (6 $\mu$L, 0.12 mmol) was then rapidly added with vigorous stirring whereupon the yellow color of the reaction solution was discharged. The mixture was warmed to 20 °C, concentrated under reduced pressure, and the residue chromatographed (preparative layer chromatography, alumina, $CHCl_3$), giving 21 mg (60%) of **7a**: mp 213–215 °C (from benzene–pentane); IR ($CHCl_3$) 2924, 1587, 1567, 1451, 1330, 1159, 1125, 1114, 1077, 998 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.6–3.5 (m, 4, $CH_2$), 4.08, 4.71 (dd, 2, $CH_2SO_2$, $J_{AB}$ = 13.5 Hz), 5.38 (s, 1, CHBr), 7.1–7.9 (m, 6, PyH).

Anal. Calcd for $C_{14}H_{13}BrN_2O_2S$: C, 47.60, H, 3.71; N, 7.93. Found: C, 47.37; H, 3.79; N, 7.86.

Solutions of **7a** were found to be unstable, disproportionating into **6b** and a higher $R_f$ product believed to be the 1,3-dibromosulfone **7b** which was isolated by preparative layer chromatography (alumina, $CHCl_3$): mp 200–205 °C dec; IR ($CHCl_3$) 2874, 1587, 1565, 1451, 1348, 1179, 1161, 1136, 1085, 1000 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.6–3.6 (m, 4, $CH_2$), 5.32, 5.66 (2 s, 2, CHBr, 2 isomers), 7.1–7.9 (m, 6, PyH).

Anal. Calcd for $C_{14}H_{12}Br_2N_2O_2S$: C, 38.91; H, 2.80; N, 6.48. Found: C, 38.80; H, 2.78; N, 6.49.

**[2.2](2,6)Pyridophan-1-ene (4).** To 23 mg (0.065 mmol) of bromo sulfone **7a** in 1.0 mL of dioxane was added with stirring 0.4 mL of water and 20 drops of 1 N NaOH. The yellow solution was allowed to sit for 2 h whereupon it was concentrated to a low volume under reduced pressure, diluted with 2 mL of water, and extracted with $CH_2Cl_2$. The extracts were washed with water, dried over $Na_2SO_4$, and concentrated. The residue was chromatographed (preparative layer chromatography, alumina, $CHCl_3$), giving 3.8 mg of debrominated sulfone **6b** and 5.8 mg (43%) of **4**. An analytical sample was obtained by sublimation (100 °C, 0.5 mm) followed by recrystallization from hexane: mp 181.5–182.5 °C; IR (KBr) 3060, 3030, 2960, 2925, 1570, 1555, 1440, 1410, 1230, 1200, 1140, 1079, 992, 878, 815 $cm^{-1}$; UV (EtOH) 221 ($\epsilon$ 12 200), 270 (7300); $^1H$ NMR ($CDCl_3$) $\delta$ 2.87 (s, 4, $CH_2$), 6.80 (s, 2, CH=CH), 6.83–7.75 (m, 6, PyH).

Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.57; H, 5.97; N, 13.23.

Olefin **4** was more conveniently prepared on a larger scale directly from **6b** without isolation of bromo sulfone **7a** as illustrated in the following procedure. Sulfone **6b** (109 mg, 0.4 mmol) in 7 mL of dry THF was treated at −78 °C with BuLi solution as described above in the preparation of **7a** until the orange endpoint of the dianion was just apparent. Neat $Br_2$ (25 $\mu$L) was added via a pipet and the mixture was warmed to 0 °C and treated

(17) Melting points are uncorrected. Routine $^1H$ NMR spectra were recorded with a Varian EM-360 spectrometer with $Me_4Si$ as an internal standard. The dynamic NMR spectra were obtained by using a JEOL JNM-MH-100 spectrometer with a variable-temperature controller which was calibrated by using methanol chemical shift differences.[18] Infrared spectra were obtained by using a Beckman AccuLab 1 spectrometer. Merck precoated type E aluminum oxide $F_{254}$ plates were used for TLC. Preparative thin-layer chromatography was performed on 20 × 20 cm plates containing 1-mm layers of Merck aluminum oxide PF-254 (type E).

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with 3 drops of glacial HOAc to retard disproportionation. The solvent was removed at 10–15 °C on a rotary evaporator and the residue dissolved in 4 mL of dioxane. Water (1.5 mL) was added followed by drops of 2 N NaOH until the reaction mixture became yellow. The mixture was stirred for 1 h, concentrated under reduced pressure, treated with water, and extracted as previously described. Sublimation of the crude product (110 °C, 0.5 mm) gave 25 mg (30%) of pure **4**.

**1-Methylthio[2.2](2,6)pyridinophane (8a).** To 120 mg (0.50 mmol) of **6a** in 3 mL of dry $CH_2Cl_2$ was added over 1 min 120 mg (0.58 mmol) of solid trimethyloxonium hexafluorophosphate. The initially homogeneous mixture became bright yellow after approximately 5 min and then colorless followed by the separation of sulfonium salt **6d**. The reaction was monitored by TLC (alumina, $CH_2Cl_2$) and upon disappearance of all of the sulfide (approximately 0.5 h) the mixture was evaporated to dryness and the residue suspended in 3 mL of dry THF. To this stirred slurry was added an excess (approximately 75 mg) of NaH likewise slurried in a small amount of THF. The mixture immediately became orange in color and $H_2$ was evolved. After the mixture was stirred for 3 h water was cautiously added to distroy excess NaH and the mixture was evaporated to dryness. The residue was extracted with $CH_2Cl_2$ and the extracts were washed with water, dried over $Na_2SO_4$, and concentrated. The concentrate was passed through a short plug (4 cm) of Woelm neutral alumina (activity grade II), giving 45 mg (35%) of **8a** which was pure by TLC. An analytical sample was recrystallized from benzene–pentane: mp 124–126 °C; IR (KBr) 3080, 3060, 2960, 2908, 2865, 1587, 1569, 1452, 1306, 1148, 1080, 996 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.16 (s, 3, $CH_3$), 3.0–4.0 (m, 7, $CH_2$, CHS), 7.0–8.0 (m, 6, PyH).

Anal. Calcd for $C_{15}H_{16}N_2S$: C, 70.28; H, 6.29; N, 10.93. Found: C, 70.18; H, 6.38; N, 10.77.

**1-(Methanesulfinyl)[2.2](2,6)pyridinophane (8b).** A solution containing 32 mg (0.125 mmol) of **8a** in 0.5 mL of THF was treated with 0.5 mL of water and 3 drops of 30% $H_2O_2$. Several additional drops of 30% $H_2O_2$ were added after 0.5 h and stirring was continued all of the sulfide had been consumed as evidenced by TLC analysis (alumina, $CH_2Cl_2$). Excess $H_2O_2$ was destroyed by the addition of $Na_2SO_3$ solution and the mixture was concentrated to near dryness. The residue was extracted with $CH_2Cl_2$ and the extracts were washed with brine, dried over $Na_2SO_4$, and concentrated. Preparative layer chromatography (alumina, 15:1 EtOAc–MeOH) gave 25 mg (74%) of **8b** as an oil which crystallized from benzene–pentane: mp 160–164 °C; IR (KBr) 3060, 2995, 2950, 2920, 2850, 1580, 1562, 1449, 1080, 1040 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.56, 2.68 (2 br s, 3, diastereomeric $CH_3$), 3.0–3.48 (br m, 6, $CH_2$), 4.12 (br d, 1, CHSO), 7.0–8.0 (m, 6, PyH).

Anal. Calcd for $C_{15}H_{16}N_2OS$: C, 66.15; H, 5.92; N, 10.28. Found: C, 66.02; H, 5.92; N, 10.22.

**Pyrolysis of 8b.** A solution containing 25 mg (0.9 mmol) of **8b** in 1.0 mL of xylene was heated at reflux for 30 h. The mixture was concentrated on a steam bath and chromatographed (preparative layer chromatography, alumina, $CH_2Cl_2$), giving 8 mg (42%) of **4**.

**Registry No.** **4**, 76467-41-9; **5**, 76467-42-0; **6a**, 76467-43-1; **6b**, 76467-44-2; **6c**, 76467-45-3; **6d**·$PF_6^-$, 76467-47-5; **7a**, 76467-48-6; **7b**, 76467-49-7; **8a**, 76467-50-0; **8b**, 76467-51-1.

## An Unusually Stable α-Chloro Epoxide

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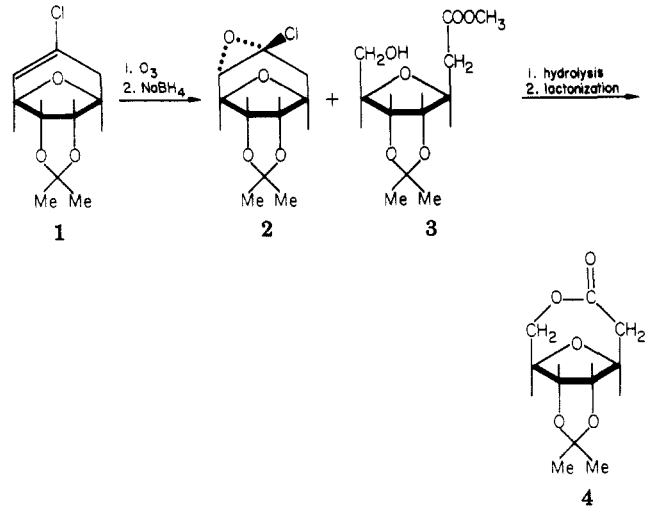
A key step in our synthesis of a homo-*C*-nucleoside[1] calls for cleavage of the vinyl chloride double bond in compound **1** with ozone. Although slow, ozonolysis of this kind of olefin is well recognized.[2] In our case, the ozonolysis proceeded smoothly at 0 °C, with methanol as solvent in the presence of a cation exchange resin. The oxidative cleavage was followed directly by reduction with sodium borohydride to form the methyl ester **3**, then hydrolysis of the crude reaction mixture, and finally azeotropic dehydration. The goal was to reach intermediate lactone **4**, which we initially took to be the crystalline product (mp 120 °C) isolated in low yield. But continued investigation made this untenable. Thus, we found that the crystalline product was already present in the borohydride product mixture, in which the main product as expected (72%) was the oily methyl ester **3**. Also, after authentic lactone **4** (mp 140–141 °C) had been prepared,[1] it became clear that the crystalline material was different from the lactone. The present note discusses this compound, to which we have now assigned the chloro epoxide structure **2**.[3]




The composition and molecular weight corresponded to $C_{10}H_{13}ClO_4$, as required by **2**. No molecular mass peak was evident in the high-resolution mass fragmentation pattern. However, the most intense peak corresponded to $M^+ - CH_3$, a fragment generated by loss of one of the two isopropylidene methyl groups to form a carbonium ion stabilized by the two neighboring oxygen atoms.[4] The infrared absorption spectrum showed no maxima in the carbonyl region at 1700–1800 $cm^{-1}$. A maximum at 870 $cm^{-1}$ is present, one that can be ascribed to an asymmetrical stretch vibration of the three-membered ring; also the observed maximum at 1270 $cm^{-1}$ corresponds to the symmetrical "breathing" vibration.[5] The proton magnetic resonance spectrum was consistent with that expected for structure **2**. The carbon-13 NMR results proved to be particularly informative. Thus a doublet at 57 ppm, ascribed to the methine carbon of the epoxide function, corresponded well to the relatively high-field signals reported before for related epoxides.[6] Even more significant

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