# Benzo[*b*]thiophene Derivatives. XIV. Derivatives of Naphtho[1,8-*c*]thiophene (1)

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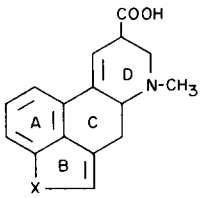
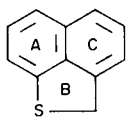
In the course of our efforts to synthesize the sulfur isostere of lysergic acid, we have prepared a number of derivatives of the little known naphtho[1,8-*bc*]thiophene ring system. Two previously reported compounds, 2-bromo-3,4-dihydro-5-oxo-5*H*-naphtho[1,8-*bc*]thiophene and 2-bromo-5-hydroxy-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene have been obtained pure for the first time, and the syntheses and spectral data of eighteen new compounds are presented. The new compounds include alcohols, ketones, and halogen derivatives of partially reduced naphtho-[1,8-*bc*]thiophene, as well as the sulfones of several of these compounds.

In line with our continuing interest in the synthesis of benzo[*b*]thiophene isosteres of biologically active indole derivatives (2,3), we have attempted the synthesis of 1-deaza-1-thialysergic acid (Ia), the sulfur isostere of lysergic acid (Ib). In the course of this work we have prepared a number of derivatives of the little known naphtho-[1,8-*bc*]thiophene ring system (shown as II). There has been only one synthetic study on this heterocycle published (4). Prior to this publication only two examples of the naphtho[1,8-*bc*]thiophene ring system had been reported, IIIa (5) and IIIb (6). Hawthorne and Porter (4) prepared a series of naphtho[1,8-*bc*]thiophene derivatives with methyl, phenyl, and bromo substituents in the 2-position. In a second publication (7) they gave a detailed analysis of the mass spectra of these compounds. One of the compounds (Va) reported by Hawthorne and Porter (4) was the key intermediate in our work.

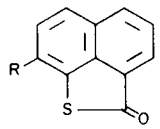
Compound Va was prepared by cyclization of 2-bromo-3-(2′-carboxyethyl)benzo[*b*]thiophene (IVb). Hawthorne and Porter (4) prepared IVb *via* a malonic ester synthesis using a 2-bromo-3-bromomethylbenzo[*b*]thiophene. We found it more convenient to prepare IVb by brominating the unsubstituted acid IVa which was prepared *via* a malonic ester synthesis using 3-chloromethylbenzo[*b*]-thiophene (8). An interesting side product was obtained in the preparation of IVa. The dialkylated malonic ester, diethyl 2,2-di(3′-benzo[*b*]thenyl)malonate, was recovered from the reaction mixture when the malonic ester substitution product was subjected to alkaline hydrolysis. This dialkylated ester could not be hydrolyzed even in boiling concentrated base. Its extreme resistance to hydrolysis is apparently due to the steric hindrance afforded by the two bulky substituents (9). Hawthorne and Porter (4) converted IVb to the acid chloride with thionyl chloride and accomplished the Friedel-Crafts cyclization to Va with aluminum chloride in cold methylene chloride. Their cyclization did not go well, and the product Va was not obtained analytically pure. Using essentially the same method but with careful temperature control and slow hydrolysis of the reaction mixture the yield in the cyclization has been improved to as much as 80% and the pro-



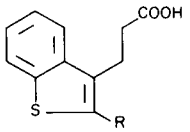

Ia X = S
Ib X = NH



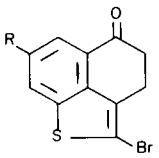

II



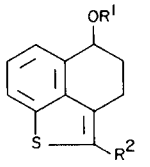

IIIa R = H
IIIb R = $OCH_3$



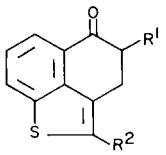

IVa R = H
IVb R = Br



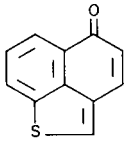

Va R = H
Vb R = Cl



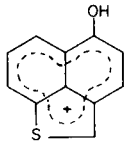

VIa $R^1$ = H, $R^2$ = Br
VIb $R^1$ = $R^2$ = H
VIc $R^1$ = Ac, $R^2$ = H



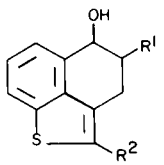

VIIa $R^1$ = $R^2$ = H
VIIb $R^1$ = Br, $R^2$ = H
VIIc $R^1$ = I, $R^2$ = H
VIId $R^1$ = Br, $R^2$ = Br



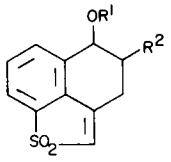

VIII



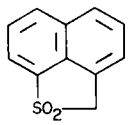

IX



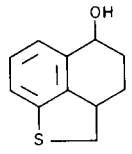
Xa, $R^1$ = Br, $R^2$ = H
Xb, $R^1$ = I, $R^2$ = H
Xc, $R^1$ = $NR^3R^4$, $R^2$ = H
Xd, $R^1$ = Br, $R^2$ = Br



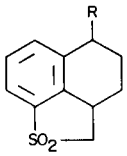
XIa, $R^1$ = $R^2$ = H
XIb, $R^1$ = Ac, $R^2$ = H
XIc, $R^1$ = H, $R^2$ = Br



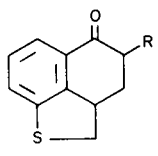
XII



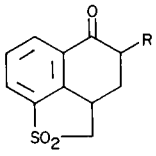
XIII



XIVa, R = H
XIVb, R = OH



XVa, R = H
XVb, R = Br



XVIa, R = H
XVIb, R = Br

duct Va has been obtained analytically pure. The pure product is unstable, however, and readily undergoes acid-catalyzed decomposition with blackening and loss of hydrogen bromide. By contrast, Va appears to be quite stable to base treatment and is unaffected by refluxing with triethylamine in cyclohexane.

The importance of using freshly distilled thionyl chloride to prepare the acid chloride of IVb was illustrated by the finding that impure thionyl chloride gave ring chlorination leading to the isolation of Vb as the cyclization product. The location of the chlorine at C-7 was established by the 100 MHz nmr spectrum. The aromatic region showed only a finely split singlet at δ 7.94. Were the chlorine substituent at C-6 or C-8, the resulting *ortho* protons would be expected to show splitting with a coupling constant on the order of 7-8 Hz (10) (*e.g.*, see nmr of VIIIb, Figure 1).

Several unsuccessful attempts were made to remove the 2-bromo substituent from Va to get VIIa. Aluminum amalgam has been used to dehalogenate thiophenes (11), but when Va was treated with aluminum amalgam, only the carbonyl was reduced giving VIa. Lithium aluminum hydride in tetrahydrofuran has also been used to debrominate thiophenes (12) and reduction of Va by this reagent caused debromination and carbonyl reduction to the alcohol, VIb. The bromo-alcohol VIa was also debrominated to VIb with lithium aluminum hydride in tetrahydrofuran.

The unsubstituted alcohol VIb could now be reoxidized to the unsubstituted ketone VIIa. The instability of Va led us to fear that VIIa might be sensitive. With this in mind, we chose a particularly gentle oxidizing agent, silver carbonate, in our initial efforts to convert VIa to VIIa. A convenient form of silver carbonate in which the reagent is deposited on Celite has been introduced by Fetizon (13). Oxidation of VIb was accomplished by refluxing a benzene solution of the alcohol with the silver carbonate on Celite reagent. The product VIIa was isolated by simple filtration and removal of the solvent from the filtrate. The fears of the instability of VIIa proved to be unfounded further indicating that it is not the ketonic system but rather the labile 2-bromo substituent which accounts for the instability of Va. It was later found that the ketone VIIa could also be prepared by Oppenauer oxidation of the alcohol VIb.

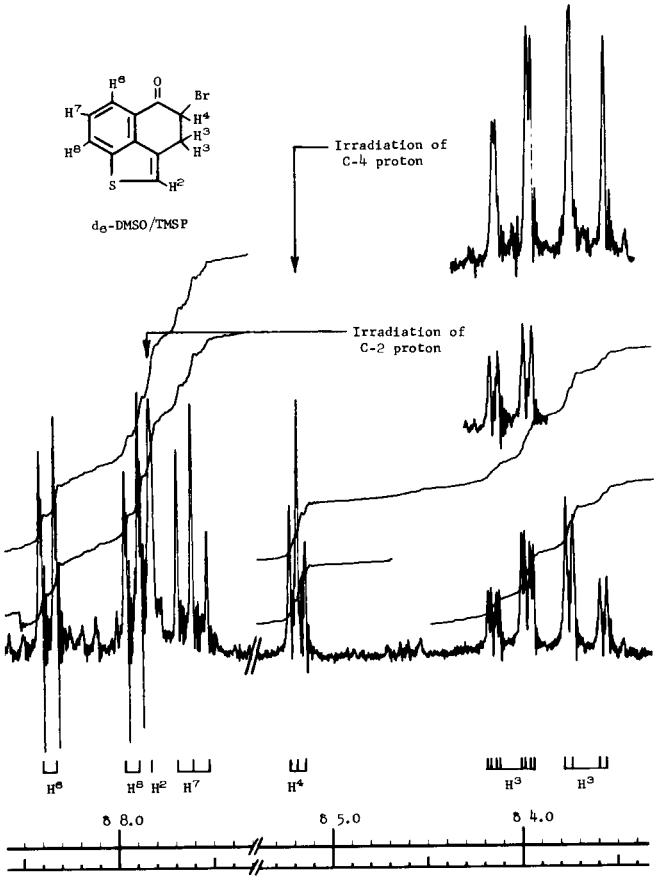



Figure 1 - 100 MHz. NMR Spectrum of VIIb.

Having the ketone VIIa, initial plans were to construct the D ring of the lysergic acid analog (Ia) in a manner similar to that used by Kornfeld (14) in his synthesis of lysergic acid (Ib). This would involve introduction of a nitrogen function at C-4 *via* the bromoketone VIIb. Initial attempts to prepare VIIb from VIIa using pyridinium hydrobromide perbromide (15) were unsuccessful giving much bromination at the 2-position. The reagent phenyltrimethylammonium perbromide (PTAB) (16) has been found to be useful for selective *alpha*-bromination of ketones in the presence of reactive aromatic centers (17). Use of PTAB on VIIa gave VIIb cleanly in 82% yield.

The bromoketone VIIb showed a very interesting nmr spectrum (Figure 1) with all of the hydrogens being clearly distinguishable. Spin decoupling results are shown in the upper traces of Figure 1. Particularly interesting is the fact that the C-4 proton is coupled equally with both C-3 protons while the C-2 proton is coupled to only one of the C-3 protons. Examination of Dreiding models in conjunction with this data indicates that the seemingly flexible C ring must exist in a definite fixed conformation. With a fixed axial conformation of the bromine, the C-4 proton bisects the angle between the two C-3 protons, while the C-2 proton is nearly perpendicular to one and parallel to the other C-3 proton. Such a conformation is consistent with the observed coupling data. An equatorial bromine, by contrast, would give a situation where one C-3 proton is parallel to the C-4 proton and perpendicular to the C-2 proton, and *vice versa* for the other C-3 proton.

Attempted introduction of nitrogen at C-4 through reactions of VIIb with secondary and tertiary amines led predominantly to elimination forming VIII. Such elimination is greatly favored by the potential conjugation with both the carbonyl and the aromatic system. The bromoketone VIIb was converted to the iodoketone VIIc, but VIIc gave no improvement with the elimination problem. Compound VIII was also prepared by oxidation of the unsubstituted ketone VIIa with chloranil in refluxing *t*-butanol. The ketone VIII is noticeably basic in that it dissolves in concentrated hydrochloric acid presumably by forming an ionic species such as IX. The nmr spectrum (100 MHz.) of VIII was clearly interpretable. The C-3 and C-4 protons exhibited a pair of doublets (J = 10 Hz.) at δ 6.62 and 7.59 respectively. The C-2 proton showed no observable coupling to H-3 appearing as a singlet at δ 7.87. The C-7 proton (triplet, δ 7.58) exhibited *ortho* coupling J = 8 Hz.) with both the C-6 and C-8 protons (doublets at δ 8.19 and 8.04, respectively), while the C-6 and C-8 protons showed a small *meta* coupling (J = 1 Hz.).

Since the potential for extensive conjugation in VIII greatly favored elimination over substitution with VIIb, it was decided to investigate the results of eliminating some of this potential conjugation. The first efforts were directed toward the carbonyl group. Attempts to prepare the ethylene ketals of VIIa and VIIb yielded only tars, presumably due to decomposition induced by the acid catalyst (*p*-toluenesulfonic acid). Sodium borohydride reduction of VIIb gave the bromo alcohol Xa, but the halogen in Xa proved to be quite resistant to displacement, as expected (18,19). All attempts to aminate Xa were unsuccessful, yielding only starting material or the elimination product VIIa. Compound VIIa can be seen to result from loss of hydrogen bromide from Xa leaving a 4,5-double bond, the enol form of VIIa.

The epoxide formed from Xa could conceivably be treated with an amine to introduce the nitrogen at C-4 forming Xc. Attempts to prepare this epoxide from Xa by base treatment led only to recovery of starting material. The failure to form the epoxide is likely due to improper sterochemistry, *i.e.*, the hydroxy and bromo substituents *cis* to one another. Such a configuration can be rationalized when the preparation of Xa is considered. In the reduction of VIIb, the borohydride would be expected to attack the carbonyl carbon on the less hindered side, *i.e.*, the side opposite the bromine. Such attack would then result in the hydroxyl being formed on the same side as the bromine, the opposite of the situation needed for epoxide formation. If the bromine could be replaced by iodide ion, the resulting iodo alcohol Xb would have the required *trans* sterochemistry for epoxide formation, Unfortunately, the bromo alcohol Xa resisted iodide displacement even with prolonged refluxing in 2-butanone.

Concurrently with this work, the bromo ketone Va was brominated with PTAB to give the dibromo ketone VIId. In this reaction, sodium bicarbonate was added to scavenge the hydrogen bromide formed since Va readily undergoes acid catalyzed decomposition. The product VIId, like Va, was quite unstable, and a satisfactory elemental analysis was not obtained. The structural assignment was based upon the nmr and the fact that VIId was reduced to the dibromo alcohol Xd.

The lack of success with attempts to eliminate the potential carbonyl conjugation led us to examine the other alternative, the conjugation with the aromatic system or, specifically, the 2,2a-double bond. Attempts to directly reduce the 2,3-double bond in benzo[*b*]thiophenes lead to extensive ring cleavage (20). However, the 2,3-double bond can be readily reduced catalytically if the sulfur is first oxidized to the sulfone (21). Not only does this eliminate the catalyst poisoning ability of the sulfur, but it also destroys the aromaticity of the sulfur containing ring rendering the 2,3-double bond a simple conjugated olefin. 2,3-Dihydrobenzo[*b*]thiophene 1,1-dioxide can be reduced to the sulfide with lithium aluminum hydride (22). In some cases it is possible to go directly from the sulfone to 2,3-dihydrobenzo[*b*]thiophene with lithium

aluminum hydride (22).

Oxidation of benzo[*b*]thiophenes to the sulfones is usually accomplished with hydrogen peroxide in acetic acid. Application of this method to VIb resulted in partial acetylation along with the oxidation giving a mixture of XIa and XIb as indicated by the infrared absorption of the product. Treatment of the mixture with methanolic base in an attempt to convert the XIb to XIa resulted in dehydration and bond migration to form XII. The nmr of XII showed only a 2 proton singlet at δ 4.97 and a 6 proton multiplet at δ 7.60-8.30. To avoid the problem of the intermediate mixture of XIa and XIb, the alcohol VIb was acetylated to form VIc prior to the oxidation. The intermediate sulfone XIb was a viscous oil which could not be crystallized. Purification by distillation was not attempted for fear of thermal elimination of acetic acid to form XII. Attempted catalytic hydrogenation of the 2,2a-double bond in XIb using palladium on carbon resulted in no uptake of hydrogen, presumably due to catalyst poisoning by impurities in XIb. The crude XIb was therefore subjected to reduction with lithium aluminum hydride in refluxing tetrahydrofuran giving a low yield of XIII. It was later found that the hydroxy sulfone XIa could be obtained by acid catalyzed transesterfication (methanolic hydrogen chloride) of the mixture obtained from the oxidation of VIb. Catalytic hydrogenation of XIa reduced the 2,2a-double bond but simultaneously removed the hydroxyl group giving XIVa.

The bromo alcohol Xa, on hand from earlier work, was also converted to the sulfone. In this case the oxidation was uncomplicated by acetylation and gave the sulfone XIc in 81% yield.

The reduced alcohol XIII was converted to the ketone XVa by oxidation with silver carbonate or Oppenauer conditions. Attempted bromination of XVa to form XVb using PTAB gave a tar apparently due to intermolecular alkylation of the sulfur by the active halide XVb. It was therefore deemed necessary to maintain the sulfur as the sulfone to prevent such alkylation.

The hydroxy sulfone XIVb was obtained by oxidation of the alcohol XIII with hydrogen peroxide in acetic acid. Oppenauer oxidation of XIVb gave the ketone XVIa. Initial efforts to brominate XVIa to form XVIb even using the specific reagent PTAB went poorly giving mixtures, apparently due to partial bromination *alpha* to the sulfone group.

## EXPERIMENTAL

Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were taken on an Infracord Model 137-B Spectrophotometer and, unless otherwise stated, were measured in potassium bromide mulls. The 60 MHz. spectra were taken on a Varian A-60 insturment, and the 100 MHz. spectra were taken on a Varian HA-100 instrument. Unless otherwise stated, tetramethylsilane (TMS) was used as internal standard. In a few cases, sodium 3-trimethylsilylpropanesulfonate (TMSP) was used as internal standard. In reporting nmr date the following abbreviations are used: s = singlet; d = doublet; t = triplet; q = quartet; and m = multiplet. Ultraviolet spectra were determined in 95% ethanol on a Bausch and Lomb Spectronic 505 Recording Spectrophotometer. Molecular weight determination was in chloroform on a Mechrolab Vapor Pressure Osmometer Model 301A. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana, and Huffman Laboratories, Inc. Wheatridge, Colorado.

3-(2′-Carboxyethyl)benzo[*b*]thiophene (IVa).

To a solution of 37.8 g. (0.70 mole) of sodium methoxide and 112 g. (0.70 mole) of diethyl malonate in 250 ml. of absolute ethanol were added dropwise 109 g. (0.60 mole) of 3-chloromethylbenzo[*b*]thiophene (8). The exothermic reaction required cooling in an ice bath. The mixture was poured into 1 l. of water and the heavy organic layer separated. The aqueous layer was extracted twice with chloroform and the extracts added to the separated organic layer. The combined organic phases were washed with water, dried over magnesium sulfate, and treated with Norit. Evaporation under vacuum yielded an amber oil which was boiled with a solution of 120 g. of sodium hydroxide in 300 ml. of water for 30 minutes. The mixture was diluted with another 200 ml. of water and the clear solution decanted from an insoluble gum (see below). The solution was filtered through a Norit pad and poured into 1 l. of chilled 6 *N* hydrochloric acid yielding 92 g. (62%) of tan precipitate. The precipitate was decarboxylated by heating on a hot plate yielding 75 g. (61%) of IVa. The product was crystallized from benzene (solution treated with Norit) to give white crystals, m.p. 142-144°. Two recrystallizations from benzene gave white crystals, m.p. 146-147° (lit. m.p. 145° (8); 147-148.5° (23)); ir μ 5.94 (aliphatic carboxyl C=O); nmr (60 MHz.) (DMSO-$d_6$) δ 2.70 (2H, t, J = 7 Hz., $CH_2COO$), 3.10 (2H, t, J = 7 Hz., Ar-$CH_2$), 7.10-8.00 (5H, m, aromatics).

*Anal.* Calcd. for $C_{11}H_{10}O_2S$: C, 64.06; H, 4.89; S, 15.55. Found: C, 64.24; H, 4.86; S, 15.37.

Diethyl 2,2-di(3′-benzo[*b*]thenyl)malonate.

The insoluble gum from the above sodium hydroxide hydrolysis would not dissolve even after refluxing in 25% aqueous sodium hydroxide for 18 hours. Crystallization of the gum from 95% ethanol yielded white crystals, m.p. 91-92° (11.0 g., 4%); ir μ 5.80 (aliphatic ester C=O); nmr (100 MHz.) (carbon tetrachloride) δ 0.85 (6H, t, J = 7 Hz., $CH_3$), 3.50 (4H, s, Ar-$CH_2$), 3.76 (4H, q, J = 7 Hz., $COOCH_2$), 7.00-7.70 (10H, m, aromatics).

*Anal.* Calcd. for $C_{25}H_{24}O_4S_2$: C, 66.34; H, 5.35; S, 14.17; Mol. wt., 452. Found: C, 66.22; H, 5.46; S, 14.08; Mol. wt., 466.

2-Bromo-3-(2′-carboxyethyl)benzo[*b*]thiophene (IVb).

A solution of 0.80 g. (3.9 mmoles) of IVa in 15 ml. of glacial acetic acid was heated to 75°, and to this was added slowly a solution of 0.64 g. (4.0 mmoles) of bromine in 10 ml. of glacial acetic acid. The reaction mixture was stirred at 75° for 30 minutes, cooled to room temperature, and poured in 150 ml. of cold water yielding 1.05 g. (95%) of white precipitate, m.p. 113-114.5°. A tenfold increase in reactant quantities gave 88% yield. Two recrystallizations from cyclohexane gave white crystals, m.p. 116-117° (lit. m.p. 117° (4)); ir μ 5.90 (aliphatic carboxyl C=O).

*Anal.* Calcd. for $C_{11}H_9BrO_2S$: C, 46.33; H, 3.18; Br, 28.02. Found: C, 46.08; H, 3.33; Br, 27.72.

2-Bromo-3,4-dihydro-5-oxo-5*H*-naphtho[1,8-*bc*]thiophene (Va).

A solution of 58.0 g. (0.204 mole) of IVb in 200 ml. of freshly distilled thionyl chloride was gently refluxed for 1 hour and the excess thionyl chloride removed by distillation. The residue was dissolved in 1300 ml. of methylene chloride, and the solution was cooled to −5° in an ice-salt bath. To this solution was gradually added with stirring 35.0 g. (0.262 mole) of anhydrous aluminum chloride while keeping the temperature at −5°. The mixture was stirred at −5 to −10° for 3 hours. (A temperature greater than −5° reduces the yield considerably.) The mixture was then hydrolyzed by stirring for 4 hours with 60 g. of sodium sulfate decahydrate crystals still at −5 to −10°. (Slow hydrolysis at low temperature is essential to obtain maximum yield.) The mixture was washed four times with water followed by three washes with 1 *N* sodium bicarbonate. (Thorough water washing before washing with base is essential to avoid emulsions. Thorough base washing is necessary since the product undergoes acid-catalyzed decomposition.) The organic phase was dried over anhydrous magnesium sulfate, treated with Norit, and evaporated under vacuum to an orange solid, which crystallized from cyclohexane, (38.5 g., 71%) m.p. 96-101°. An analytical sample, recrystallized three times from hexane-cyclohexane, gave yellow crystals, m.p. 108-110° dec. (lit. m.p. 105-106°, resolidifying and m.p. 110° dec. (4)); ir $\mu$ 5.98 (aromatic ketone C=O); uv $\lambda$ max (ethanol): m$\mu$ ($\epsilon$) 229 (13,000), 259 (24,000), 312 (6,200). (Reported uv $\lambda$ max (ethanol): m$\mu$ ($\epsilon$) 227 (2360), 257 (2440), 310 (2120), (4).); nmr (100 MHz.) (deuteriochloroform) $\delta$ 2.86 (2H, t, J = 6 Hz., H-4), 3.10 (2H, t, J = 6 Hz., H-3), 7.33 (1H, t, J = 7.5 Hz., H-7), 7.76 (1H, d of d, J = 1, 7.5 Hz., H-8), 7.80 (1H, d of d, J = 1, 7.5 Hz., H-6).

*Anal.* Calcd. for $C_{11}H_7BrOS$: C, 49.45; H, 2.64; Br. 29.92. Found: C, 49.66; H, 2.63; Br. 30.07.

A fourth recrystallization gave a different crystal form (fine needles) with a lower m.p. (103-104°), but the spectral properties and elemental analysis were unchanged.

The oxime of Va (24) was obtained after three recrystallizations from ethanol as off-white crystals, m.p. 174-175°, (lit., m.p. 183-185° dec. (4)).

*Anal.* Calcd. for $C_{11}H_8BrNOS$: C, 46.83; H, 2.86; S, 11.36. Found: C, 46.55; H, 2.96; S, 11.64.

The 2,4-dinitrophenylhydrazone of Va (25) was obtained after two recrystallizations from benzene-chloroform as a red crystalline powder, m.p. 267° dec.

*Anal.* Calcd. for $C_{17}H_{11}BrN_4O_4S$: C, 45.65; H, 2.48; N, 12.52. Found: C, 45.73; H, 2.55; N, 12.79.

2-Bromo-7-chloro-3,4-dihydro-5-oxo-5*H*-naphtho[1,8-*bc*]thiophene (Vb).

In one attempt to obtain Va, using the foregoing procedure except that crude thionyl chloride was used, an oil was obtained after evaporation of the methylene chloride extracts. The oil was chromatographed on a column of 200 g. of silica gel using benzene then chloroform as elution solvents. The chloroform effluent was collected from 500 to 3,000 ml. and evaporated to yield 1.02 g. (19%) of the product Vb, m.p. 158-180°. No significant amount of other material was recovered from the column. Two recrystallizations of the product from cyclohexane gave 0.60 g. of light yellow needles, m.p. 177-180°; ir $\mu$ 6.00 (aromatic ketone C=O); nmr (100 MHz.) (deuteriochloroform) $\delta$ 2.84 (2H, t, J = 7.5 Hz., H-4), 3.19 (2H, t, J = 7.5 Hz., H-3), 7.94 (2H, finely split s, H-6 and H-8).

*Anal.* Calcd. for $C_{11}H_6BrClOS$: C, 43.80; H, 2.02; Br, 26.50; Cl, 11.81. Found: C, 43.69; H, 2.05; Br, 26.44; Cl, 11.73.

The oxime (24) was recrystallized twice from absolute ethanol to yield fine white needles, m.p. 200-203°.

*Anal.* Calcd. for $C_{11}H_7BrClNOS$: C, 41.72; H, 2.23; S, 10.13. Found: C, 42.12; H, 2.39; S, 10.34.

2-Bromo-5-hydroxy-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene (VIa).

Aluminum amalgam (26) was added to a solution of 3.35 g. (12.6 mmoles) of Va in 200 ml. of gently refluxing ethanol. The mixture was refluxed overnight, filtered, and the filtrate concentrated to a small volume. The solution, on cooling, yielded 1.34 g. (56%) of white crystals, m.p. 146-147° (ir showed no carbonyl absorption). The analytical sample, recrystallized three times from cyclohexane, gave white needles, m.p. 152-153° (27); ir $\mu$ 3.1 (broad, OH).

*Anal.* Calcd. for $C_{11}H_9BrOS$: C, 49.08; H, 3.37; Br, 29.69. Found: C, 49.42; H, 3.31; Br, 29.44.

5-Hydroxy-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene (VIb).

1. From Va.

A solution of 21.6 g. (81.0 mmoles) of Va in 100 ml. of tetrahydrofuran (dried over 5A molecular sieve) was added dropwise to a stirred mixture of 15.0 g. (39.5 mmoles) of lithium aluminum hydride in 400 ml. of tetrahydrofuran (dried as above). The resulting mixture was stirred at room temperature for 22 hours and then hydrolyzed by dropwise addition of 45 ml. of saturated aqueous sodium sulfate. The hydrolyzed mixture was filtered and the filtrate dried over magnesium sulfate. Evaporation of the solvent gave an off-white solid which was crystallized from cyclohexane-hexane to give 11.2 g. (72%) of off-white needles, m.p. 104-107°. An analytical sample was prepared by sublimation (90°, 0.01 mm.) followed by crystallization from cyclohexane, giving white needles, m.p. 110-111°; ir $\mu$ 3.1 (broad, OH); nmr (100 MHz.) (deuteriochloroform) $\delta$ 2.08 (2H, q, J = 6 Hz., H-4), 2.32 (1H, s, OH), 2.80-3.20 (2H, m, H-3), 4.96 (1H, triplet, J = 6 Hz., H-5), 6.97 (1H, s, H-2), 7.28 (2H, d, J = 4 Hz., H-6 and H-8), 7.72 (1H, t, J = 4 Hz., H-7).

*Anal.* Calcd. for $C_{11}H_{10}OS$: C, 69.44; H, 5.30; S, 16.85. Found: C, 69.27; H, 5.38; S, 17.11.

The *p*-nitrobenzoate ester of VIb (28) was obtained after three recrystallizations from 95% ethanol as a light yellow crystalline powder, m.p. 111-112°.

*Anal.* Calcd. for $C_{17}H_{13}NO_4S$: N, 4.28. Found: N, 4.25.

2. From VIa.

To a stirred solution of 1.25 g. (4.65 mmoles) of VIa in 50 ml. in 50 ml. of tetrahydrofuran (dried over 5A molecular sieve) was added 1.0 g. (27 mmoles) of lithium aluminum hydride. The mixture was stirred for 27 hours at room temperature (starting material was present at the end of 3 hours as shown by ir). The mixture was hydrolyzed with water, acidified with 6 *N* hydrochloric acid, and extracted twice with chloroform. The chloroform extracts were dried over magnesium sulfate and evaporated under vacuum to a light yellow oil. The oil was crystallized from cyclohexane to give 0.72 g. (82%) of white crystals, m.p. 107.5-108°. Recrystallization from cyclohexane gave white needles, m.p. 109-110° with infrared spectrum identical to that of the VIb prepared above.

5-Acetoxy-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene (VIc).

Treatment of 2.00 g. (10.5 mmoles) of VIb with 1.0 g. of anhydrous sodium acetate in 15 ml. of acetic anhydride at steam bath temperature for 3.5 hours resulted in the formation of VIc (2.16 g., 88%), collected from 111 to 113° at 0.01 mm. A sample for analysis was collected at 112° (0.01 mm.); ir (neat) $\mu$ 5.75 (ester C=O); nmr (60 MHz.) (deuteriochloroform) $\delta$ 2.03 (3H, s, $CH_3$),

2.0-2.3 (2H, m, H-4), 2.8-3.1 (2H, m, H-3), 6.20 (1H, t, J = 5 Hz., H-5), 6.97 (1H, broad s, H-2), 7.2-7.4 (2H, m, aromatics), 7.6-7.8 (1H, m, aromatic).

*Anal.* Calcd. for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21; S, 13.80. Found: C, 67.21; H, 5.41; S, 13.54.

3,4-Dihydro-5-oxo-5*H*-naphtho[1,8-*bc*]thiophene (VIIa).

1. Silver Carbonate Oxidation.

A solution of 2.05 g. (10.8 mmoles) of VIb in 500 ml. of benzene was refluxed in a stream of nitrogen with 52 g. (19 mmoles) of silver carbonate on Celite (13) for 12 hours. The mixture was treated with Norit and filtered. The amber filtrate was evaporated at 75° on a rotary evaporator to an orange oil which crystallized from hexane as orange plates, m.p. 93-95.5° (1.05 g., 52%). A sample was sublimed at 75° (0.01 mm.) and recrystallized twice from hexane to give light yellow crystals, m.p. 99-101°; ir $\mu$ 6.00 (aromatic ketone C=O); uv $\lambda$ max (ethanol): m$\mu$ ($\epsilon$) 212 (15,000), 228 (15,000), 256 (26,000), 332 (5,100); nmr (100 MHz.) (deuteriochloroform) $\delta$ 2.88 (2H, t, J = 8 Hz., H-4), 3.26 (2H, t, J = 8 Hz., H-3), 7.18 (1H, s, H-2), 7.40 (1H, t, J = 8 Hz., H-7), 7.85 (1H, d, J = 8 Hz., H-8), 7.98 (1H, d, J = 8 Hz., H-6).

*Anal.* Calcd. for $C_{11}H_8OS$: C, 70.18; H, 4.28; S, 17.03. Found: C, 70.31; H, 4.33; S, 17;08.

The 2,4-dinitrophenylhydrazone of VIIa (25) was obtained after two recrystallzations from chloroform-benzene as a red crystalline powder, m.p. 281° dec.

*Anal.* Calcd. for $C_{17}H_{12}N_4O_4S$: C, 55.43; H, 3.28; N, 15.21. Found: C, 55.20; H, 3.39; N, 15.38.

2. Oppenauer Oxidation.

A solution of 10.0 g. (52.5 mmoles) of VIb and 12.0 g. (58.8 mmoles) of aluminum isopropoxide in 200 ml. of acetone and 300 ml. of benzene was refluxed for 14 hours. The solution was cooled, washed three times with saturated aqueous sodium potassium tartrate, dried over magnesium sulfate, and evaporated under vacuum leaving a light amber oil which crystallized on cooling. Recrystallization from hexane gave 8.1 g. (80%) of yellow crystals, m.p. 99-101°. The infrared spectrum of this material was identical to that of pure VIIa above.

3. From 4-Bromo-5-hydroxy-3,4-dihydro-5*H*-naphtho[1,8-*bc*]-thiophene (Xa).

To a solution of 0.54 g. of sodium iodide in 50 ml. of absolute ethanol was added 1.0 g. (3.72 mmoles) of Xa, and the mixture was warmed to effect solution. To this was then added 1.00 g. (11.2 mmoles) of 1-methylamino-2-propanol (29), and the solution refluxed under nitrogen for 24 hours. After concentration to a small volume under vacuum, the solution was diluted with 50 ml. of ether, yielding a white precipitate. The mixture was washed with 25 ml. of water, and then extracted with two 25 ml. portions of 1 *N* hydrochloric acid. Evaporation of the dried (magnesium sulfate) ether solution yielded 0.42 g. (60%) of white solid with ir identical to the pure VIIa above.

5-Oxo-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene (VIIa) Tosylhydrazone.

A solution of 1.00 g. (5.3 mmoles) of VIIa in 15 ml. of tetrahydrofuran was added to a solution of 0.98 g. (5.3 mmoles) of *p*-toluenesulfonylhydrazide (30) in 15 ml. of tetrahydrofuran, and several drops of concentrated sulfuric acid were added. The solution was heated on a steam bath for *ca.* 15 minutes and then diluted with chloroform. After washing with 1 *N* aqueous sodium bicarbonate and drying over magnesium sulfate, the solution was evaporated to dryness under vacuum. Two recrystallizations of the residual solid from ethanol gave white needles (0.78 g., 43%), m.p. 192-193° dec.

*Anal.* Calcd. for $C_{18}H_{16}N_2O_2S_2$: C, 60.65; H, 4.52; N, 7.86. Found: C, 60.57; H, 4.58; N, 7.85.

4-Bromo-5-oxo-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene (VIIb).

To a stirred solution of 4.00 g. (10.5 mmoles) of phenyltrimethylammonium tribromide in 40 ml. of tetrahydrofuran under nitrogen was added dropwise over a 10 minute period a solution of 2.0 g. (10.6 mmoles) of VIIa in 25 ml. of tetrahydrofuran. A precipitate began forming immediately and the initially red solution gradually lost its color. After stirring 1 hour the mixture was filtered yielding 2.30 g. (100%) of phenyltrimethylammonium bromide. The filtrate was evaporated to a tan solid which was crystallized from 95% ethanol (solution treated with Norit) yielding yellow crystals, m.p. *ca.* 120° dec. Recrystallization from 95% ethanol gave 2.28 g. (82%) light yellow crystals, m.p. 132-133° dec.: ir $\mu$ 5.95 (C=O); uv $\lambda$ max (ethanol): m$\mu$ ($\epsilon$) 218 (15,000), 259 (19,000), 342 (5,500); nmr (100 MHz.) (DMSO-$d_6$, TMSP) $\delta$ 3.66 (1H, d of d, J = 4, 18 Hz., H-3), 4.06 (1H, d of d of d, J = 2, 4, 18 Hz., H-3), 5.18 (1H, t. J = 4 Ha., H-4), 7.60 (1H, t, J = 8 Hz., H-7), 7.82 (1H, broad s, H-2), 7.92 (1H, d, J = 8 Hz., H-8), 8.37 (1H, d, J = 8 Hz., H-6).

*Anal.* Calcd. for $C_{11}H_7BrOS$: C, 49.45; H, 2.64; Br, 29.91. Found: C, 49.56; H, 2.61; Br, 29.82.

4-Iodo-5-oxo-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene (VIIc).

A warm solution of 1.00 g. (3.75 mmoles) of VIIb in 30 ml. of acetone was added to a stirred solution of 0.56 g. (3.75 mmoles) of sodium iodide in 10 ml. of acetone. The mixture darkened immediately, and sodium bromide began to precipitate. After stirring overnight and warming to redissolve the precipitated product, the mixture was filtered yielding 0.32 g. (84%) of sodium bromide. The filtrate was treated with Norit, concentrated, cooled, and the product recrystallized from cyclohexane-benzene as yellow crystals 0.93 g. (79%) melting at 110°; ir $\mu$ 5.98 (C=O); uv $\lambda$ max: m$\mu$ ($\epsilon$) 212 (17,000), 229 (17,000), 259 (15,000), 351 (5,700).

*Anal.* Calcd. for $C_{11}H_7IOS$: C, 42.05; H, 2.25; I, 40.40. Found: C, 41.99; H, 2.27; I, 40.10.

2,4-Dibromo-5-oxo-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene (VIId).

To a stirred solution of 1.18 g. (4.41 mmoles) of Va in 30 ml. of tetrahydrofuran containing 0.37 g. (4.4 mmoles) of powdered sodium bicarbonate was added dropwise over a 10 minute period a solution of 1.65 g. (4.41 mmoles) of phenyltrimethylammonium tribromide in 30 ml. of tetrahydrofuran. The mixture was stirred for 10 minutes after the addition, and the solids (sodium bromide and phenyltrimethylammonium bromide) were prepared by filtration and washed with fresh tetrahydrofuran (1.33 g., 95%). The filtrate and washings were treated with anhydrous sodium carbonate and Norit. Removal of the solvent at 75° under vacuum, and crystallization from hexane-cyclohexane gave yellow crystals, 1.06 g., m.p. 127-131°. A second crop (0.14 g., m.p. 127-129°) was obtained by concentrating the mother liquor, giving a total crude yield of 1.20 g. Two recrystallizations from hexane-cyclohexane gave 1.00 g. (65%) of yellow crystals, m.p. 133-134° dec.; ir $\mu$ 5.95 (C=O); uv $\lambda$ max: m$\mu$ ($\epsilon$) 229 (13,000), 263 (20,000), 323 (6,000); nmr (100 MHz.) (deuteriochloroform) $\delta$ 3.66 (2H, d of d, J = 2,4, Hz., H-3), 4.89 (1H, t, J = 4 Hz., H-4), 7.48 (1H, t, J = 7 Hz., H-7), 7.94 (2H, d, J = 7 Hz., H-6 and H-8). The product was unstable, and a satisfactory analysis was not obtained.

*Anal.* Calcd. for $C_{11}H_6Br_2OS$: C, 38.18; H, 1.75; Br, 46.19. Found: C, 37.75; H, 1.87; Br, 47.06.

5-Oxo-5*H*-naphtho[1,8-*bc*]thiophene (VIII).

1. Oxidation of VIIa.

To a mixture of 5.74 g. (53.2 mmoles) of practical grade chloranil in 150 ml. of *t*-butanol was added 1.0 g. (5.32 mmoles) of VIIa and the mixture refluxed for 3 hours. After cooling to room temperature, the mixture was filtered to remove excess chloranil and the solvent removed under vacuum. The residue was dissolved in chloroform and the solution washed three times with water, four times with 5% aqueous sodium hydroxide (until the purple color in the aqueous phase disappeared), and again twice with water. After drying (magnesium sulfate), the chloroform was removed to yeild a solid which crystallized twice from cyclohexane as a yellow crystalline powder (0.54 g., 54%), m.p. 157.5-158.5°; ir $\mu$ 6.13 (conjugated ketone C=O); uv $\lambda$ max: m$\mu$ ($\epsilon$) 229 (12,000), 250 (14,000), 313 (6,600); nmr (100 MHz.) (deuteriochloroform) $\delta$ 6.62 (1H, d, J = 10 Hz., H-3), 7.58 (1H, t, J = 8Hz., H-7), 7.59 (1H, d, J = 10 Hz., H-4), 7.87 (1H, s, H-2), 8.04 (1H, d of d, J = 1, 8 Hz., H-8), 8.19 (1H, d of d, J = 1, 8 Hz., H-6).

*Anal.* Calcd. for $C_{11}H_6OS$: C, 70.94; H, 3.25; S, 17.22. Found: C, 70.69; H, 3.38; S, 17.24.

2. Dehydrohalogenation of VIIb.

A solution of 9.5 g. (35.6 mmoles) of VIIb and 10.0 g. (99 mmoles) of triethylamine in 100 ml. of benzene was refluxed for 12 hours. The reaction mixture was washed twice with 1 *N* hydrochloric acid, once with water, and treated with Norit. After drying over magnesium sulfate, the solution was evaporated under vacuum; crystallization from benzene-cyclohexane gave 5.2 g. (78%) of yellow crystals, m.p. 153-155°, with spectral properties identical to the above VIII.

5-Hydroxy-4-bromo-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene (Xa).

A solution of 4.50 g. (16.9 mmoles) of VIIb and 0.40 g. (9.6 mmoles) of sodium borohydride in 100 ml. of tetrahydrofuran containing 5 ml. of water was stirred at room temperature for 1.5 hours. The solution was poured into 250 ml. of water and extracted twice with ether. The ether extracts were dried over magnesium sulfate and evaporated to a white solid which, after two recrystallizations from cyclohexane-benzene, gave fine white needles (3.9 g., 85%), m.p. 160-161.5° dec.; ir $\mu$ 2.95 (broad, OH); nmr (100 MHz.) (DMSO-$d_6$, TMSP) $\delta$ 3.30-3.75 (2H, m, H-3), 4.75-4.95 (1H, broad m, H-4), 5.10-5.25 (1H, broad d, J = 4 Hz., H-5), 4.5-6.0 (1H, very broad s, OH), 7.35-7.95 (4H, m, aromatics). The H-3, H-4, and H-5 assignments were confirmed by spin decoupling.

*Anal.* Calcd. for $C_{11}H_9BrOS$: C, 49.08; H, 3.37; Br, 29.69. Found: C, 48.97; H, 3.28; Br, 29.93.

2,4-Dibromo-5-hydroxy-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene (Xd).

A solution of 0.89 g. (2.6 mmoles) of VIId and 0.10 g. (2.6 mmoles) of sodium borohydride in 30 ml. of tetrahydrofuran and 1 ml. of water was stirred at room temperature for 2 hours. The solution assumed a red color with the addition of the borohydride, but this gradually faded to a faint violet. The solution was poured into three volumes of water, and extracted with two 50 ml. portions of ether. The ether extracts were dried over anhydrous sodium sulfate and evaporated to a white solid (0.88 g.) which was recrystallized three times from 95% ethanol to give 0.57 g. (64%) of white needles, m.p. 185-187° dec.; ir $\mu$ 2.89 (OH); nmr (60 MHz.) (DMSO-$d_6$, TMSP) $\delta$ 3.30-3.50 (2H, m, H-3), 4.70-5.00 (1H, m, H-4), 5.10 (1H, broad d, J = 2.5 Hz., H-5), 7.30-7.80 (3H, m, aromatics). The OH proton absorption was obscured by a solvent water peak at $\delta$ 3.70.

*Anal.* Calcd. for $C_{11}H_8Br_2OS$: C, 37.96; H, 2.32; Br, 45.92. Found: C, 37.96; H, 2.50; Br, 46.13.

5-Hydroxy-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene 1,1-Dioxide (XIa).

A solution of 2.50 g. (13.1 mmoles) of VIb in 15 ml. of glacial acetic acid containing 7.5 ml. (87 mmoles) of 30% hydrogen peroxide was held at a temperature of 50° for 13 hours. The solution was cooled in an ice bath, ice was added, and the solution was neutralized with 40% aqueous sodium hydroxide slowly enough to maintain the cold temperature. The resulting mixture of liquid and gummy precipitate was extracted twice with chloroform, dried over magnesium sulfate and evaporated under vacuum to a light amber oil. The mixture was dissolved in 50 ml. of methanol, 20 ml. of 3% methanolic hydrogen chloride was added, and the resulting solution stirred at room temperature for 19 hours. The solution was diluted with chloroform and washed twice with 1 *N* sodium bicarbonate. After drying over magnesium sulfate, the chloroform solution was evaporated, and the amber oil was crystallized three times from benzene to give 1.02 g. (35%) of white crystals, m.p. 125-126°; ir $\mu$ 2.94 (OH), 7.76, 8.62 ($SO_2$); nmr (100 MHz.) (DMSO-$d_6$) $\delta$ 1.65-2.30 (2H, m, H-4), 2.70-2.97 (2H, m, H-3), 4.65-4.90 (1H, m, H-5), 5.65 (1H, d, J = 6 Hz., OH), 6.90 (1H, finely split s, H-2), 7.45-7.80 (3H, m, H-6, H-7, and H-8).

*Anal.* Calcd. for $C_{11}H_{10}O_3S$: C, 59.43; H, 4.53; S, 14.42. Found: C, 59.47; H, 4.57; S, 14.67.

The *p*-nitrobenzoate ester of XIa (28) was obtained as a white crystalline powder after three recrystallizations from 95% ethanol, m.p. 191-192°.

*Anal.* Calcd. for $C_{17}H_{13}NO_6S$: N, 3.90. Found: 3.88.

4-Bromo-5-hydroxy-3,4-dihydro-5*H*-naphtho[1,8-*bc*]thiophene 1,1-Dioxide (XIc).

A 2.80 g. (10.4 mmoles) quantity of Xa was dissolved by warming in 50 ml. of glacial acetic acid. To this was added 8.0 ml. (93 mmoles) of 30% hydrogen peroxide and the resulting solution kept at 50° for 12 hours. The solution was cooled and poured into 150 ml. of saturated aqueous sodium chloride yielding 2.06 g. of white precipitate. Chloroform extraction of the aqueous solution afforded an additional 0.47 g., for a crude yield of 2.53 g. Two recrystallizations from ethanol gave 2.10 g. of white crystals (78%), m.p. 130° dec.; ir $\mu$ 2.87 (OH), 7.74, 8.53 ($SO_2$); nmr (100 MHz.) (DMSO-$d_6$) $\delta$ 3.29 (1H, d of d, J = 5, 17 Hz., H-3), 3.62 (1H, d of t, J = 2, 17 Hz., H-3), 4.87 (1H, q, J = 3 Hz., H-4), 5.07 (1H, d, J = 3 Hz., H-5), 5.60 (1H, broad s, OH), 7.06 (1H, broad s, H-2), 7.50-7.80 (3H, m, aromatics). The material was quite unstable even when pure and decomposed within a few days in spite of protection from light and air.

*Anal.* Calcd. for $C_{11}H_9BrO_3S$: C, 43.87; H, 3.01; Br, 26.54. Found: C, 43.92; H, 3.20; Br, 26.51.

2*H*-Naphtho[1,8-*bc*]thiophene 1,1-Dioxide (XII).

A solution of 2.50 g. (13.1 mmoles) of VIb was oxidized with 7.5 ml. (87 mmoles) of 30% hydrogen peroxide as described for the preparation of XIa, except that base was used. The residue from the chloroform extract was dissolved in 50 ml. of methanol and 20 ml. of 1 *N* methanolic sodium hydroxide was added giving a dark solution. (Identical results were obtained with 1 *N* methanolic sodium methoxide.) Upon standing at room temperature

for 16 hours, 0.94 g. of tan needles were deposited, m.p. 195-197°. Dilution of the liquid with half saturated aqueous sodium chloride, extraction of the solution with chloroform, and evaporation of the extracts after drying over magnesium sulfate gave 0.59 g. of yellow solid, m.p. 193-195°, with infrared spectrum identical to the needles. The combined material was sublimed (180°, 0.01 mm.) giving a white solid, which recrystallized from 95% ethanol as white needles (1.26 g., 47%), m.p. 198.5-199.5°. Resublimation followed by recrystallization did not raise the melting point; ir $\mu$ 7.77, 8.95 ($SO_2$); uv $\lambda$ max: m$\mu$ ($\epsilon$) 227 (38,000), 294 (5,600), 324 (1,400); nmr (100 MHz.) (DMSO-$d_6$, TMSP) $\delta$ 4.97 (2H, s, H-2), 7.60-8.30 (6H, m, aromatics).

*Anal.* Calcd. for $C_{11}H_8O_2S$: C, 64.68; H, 3.95; S, 15.70. Found: C, 64.58; H, 4.00; S, 15.59.

5-Hydroxy-2,2a,3,4-tetrahydro-5*H*-naphtho[1,8-*bc*]thiophene (XIII).

A solution of 1.60 g. (6.90 mmoles) of VIc in 15 ml. of glacial acetic acid containing 3.5 ml. (41 mmoles) of 30% hydrogen peroxide was heated at 55° for 11 hours. The mixture was diluted with water and extracted twice with chloroform. The extracts were washed three times with water and twice with 1 *N* sodium bicarbonate. After drying over magnesium sulfate, the chloroform extracts were evaporated under vacuum to a light yellow oil. The oil, dissolved in 50 ml. of tetrahydrofuran, was refluxed for 24 hours with 2.0 g. (53 mmoles) of lithium aluminum hydride. The mixture was hydrolyzed with 6 ml. of saturated aqueous sodium sulfate, filtered, and the filtrate evaporated to a light amber-liquid. Distillation of the liquid under vacuum gave a low yield of material boiling at *ca.* 110° (0.01 mm.) which solidified in the receiver to a yellow solid. Sublimation at 105° (0.02 mm.) gave a white crystalline solid, m.p. 123-126°; ir $\mu$ 3.00 (OH); nmr (100 MHz.) (deuteriochloroform) complex series of multiplets between $\delta$ 1.5 and 5.1 integrating for 9 protons, $\delta$ 6.9-7.4 (3H, m, aromatics).

*Anal.* Calcd. for $C_{11}H_{12}OS$: C, 68.71; H, 6.29; S, 16.68. Found: C, 68.55; H, 6.33; S, 16.42.

The *p*-nitrobenzoate ester of XIII (28) was obtained after three recrystallizations from 95% ethanol as yellow needles, m.p. 168-170°.

*Anal.* Calcd. for $C_{17}H_{15}NO_4S$: N, 4.25. Found: N, 4.17.

2,2a,3,4-Tetrahydro-5*H*-naphtho[1,8-*bc*]thiophene 1,1-Dioxide (XIVa).

A solution of 222 mg. (1.000 mmoles) of XIa in 30 ml. of 95% ethanol containing 30 mg. of 10% palladium on carbon was hydrogenated on a Parr apparatus for 4 hours (starting pressure 38 p.s.i.). At the end of this period, chloroform was added to dissolve the precipitated product, the catalyst was removed by filtration, and the filtrate was evaporated to give about 200 mg. of white solid (essentially quantitative yield), m.p. 164-165°. The solid was sublimed (150°, 0.01 mm.) and recrystallized from 95% ethanol to give 140 mg. of white needles, m.p. 165-166.5°; ir $\mu$ 7.70, 8.91 (sulfur dioxide).

*Anal.* Calcd. for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; S, 15.39. Found: C, 63.27; H, 5.77; S, 15.37.

5-Hydroxy-2,2a,3,4-tetrahydro-5*H*-naphtho[1,8-*bc*]thiophene 1,1-Dioxide (XIVb).

A solution of 1.00 g. (5.22 mmoles) of XIII in 15 ml. of glacial acetic acid was heated to 50°. To this was added 4.0 ml. (46 mmoles) of 30% hydrogen peroxide, and the resulting solution was held at 50° for 12 hours, poured over 20 g. of ice and slowly made basic with 6 *N* sodium hydroxide with cooling in an ice bath. The mixture was then extracted three times with chloroform, dried over magnesium sulfate, and evaporated to a light yellow oil which slowly crystallized. Two recrystallizations from benzene gave 0.96 g. (82%) of white crystals, m.p. 138-139°; ir $\mu$ 2.95 (OH), 7.81, 8.87 (sulfur dioxide); nmr (100 MHz.) (DMSO-$d_6$) $\delta$ 1.69 (2H, q, J = 10 Hz., H-3), 1.90-2.40 (2H, m, H-4), 3.10-3.85 (3H, m, H-2 and H-2'), 4.53-4.83 (1H, m, H-5), 5.55 (1H, d, J = 6 Hz., OH), 7.33-7.78 (3H, m, H-6, H-7, and H-8).

*Anal.* Calcd. for $C_{11}H_{12}O_3S$: C, 58.90; H, 5.35; S, 14.30. Found: C, 58.88; H, 5.41; S, 14.05.

The *p*-nitrobenzoate ester of XIVb (28) was obtained after two recrystallizations (one treatment with Norit) from 95% ethanol as an off-white crystalline powder, m.p. 209-210.5°.

*Anal.* Calcd. for $C_{17}H_{15}NO_6S$: N, 3.88. Found: N, 3.71.

5-Oxo-2,2a,3,4-tetrahydro-5*H*-naphtho[1,8-*bc*]thiophene (XVa).

1. Silver Carbonate Oxidation.

A solution of 200 mg. (1.04 mmoles) of XIII in 50 ml. of benzene was refluxed under nitrogen with 5.0 g. (17 mmoles) of silver carbonate on Celite (13) for 12 hours. The mixture was cooled, filtered, and evaporated under vacuum to yield 191 mg. of brown solid, m.p. 96-103°. The solid was sublimed (110°, 0.20 mm.) and two recrystallizations from hexane gave 158 mg. (80%) light yellow needles, m.p. 104-106°; ir $\mu$ 5.95 (C=O), uv $\lambda$ max (ethanol): m$\mu$ ($\epsilon$) 207 (10,000), 245 (18,000), 345 (2,900).

*Anal.* Calcd. for $C_{11}H_{10}OS$: C, 69.44; H, 5.30; S, 16.85. Found: C, 69.29; H, 5.21; S, 16.73.

The 2,4-dinitrophenylhydrazone of XVa (25) gave a red crystalline solid upon recrystallization from benzene-chloroform, m.p. 285° dec.

*Anal.* Calcd. for $C_{17}H_{14}N_4O_4S$: C, 55.13; H, 3.81. Found: C, 55.11; H, 3.64.

2. Oppenauer Oxidation.

A solution of 300 mg. (1.56 mmoles) of XIII and 480 mg. (1.95 mmoles) of aluminum *t*-butoxide in 15 ml. of acetone and 25 ml. of benzene was refluxed under nitrogen for 12 hours. The reaction mixture was cooled to room temperature and washed twice with an equal volume of saturated aqueous sodium potassium tartrate. The organic phase was dried over magnesium sulfate and evaporated under vacuum to give 298 mg. of light yellow solid. Crystallization from hexane gave 227 mg. (77%) of light yellow plates melting at 103-106° with infrared absorption identical to that of pure XVa prepared above.

5-Oxo-2,2a,3,4-tetrahydro-5*H*-naphtho[1,8-*bc*]thiophene 1,1-Dioxide (XVIa).

A solution of 516 mg. (2.30 mmoles) of XIVb and 700 mg. (2.85 mmoles) of aluminum *t*-butoxide in 40 ml. of acetone and 60 ml. of benzene was refluxed for 14 hours. The reaction mixture was cooled, and washed twice with saturated aqueous sodium potassium tartrate, dried (magnesium sulfate), concentrated to a small volume and the product allowed to crystallize. Three crystallizations from benzene gave 316 mg. (62%) of white crystals, m.p. 185-187°; ir $\mu$ 5.92 (C=O), 7.66, 8.89 ($SO_2$); nmr (100 MHz.) (DMSO-$d_6$) $\delta$ 1.60-4.00 (7H, m, aliphatic), 7.40-8.10 (3H, m, aromatic).

*Anal.* Calcd. for $C_{11}H_{10}O_3S$: C, 59.43; H, 4.53; S, 14.42. Found: C, 59.62; H, 4.84; S, 14.19.

The 2,4-dinitrophenylhydrazone of XVIa (25) was obtained after recrystallization from benzene-chloroform as an orange crystalline powder, m.p. 290° dec.

*Anal.* Calcd. for $C_{17}H_{14}N_4O_6S$: C, 50.74; H, 3.51. Found: C, 50.73; H, 3.63.

Acknowledgment.

We are indebted to Mr. A. Dinner for the determination of the 100 MHz. nmr spectra and to Mr. G. Sutton for technical assistance.

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Received September 29, 1969 Bloomington, Indiana 47401