

Chemistry of Thienopyridines. XIII.  
 Selective Formation of Sulfones in Bi- and Tricyclic Systems.  
 Thieno[2,3-*b*]pyridine 1,1-Dioxide as a Dienophile (1)

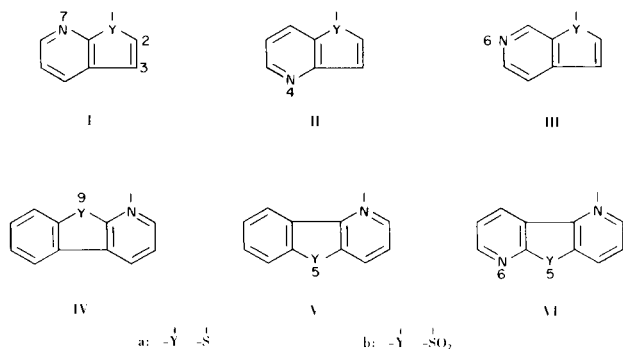
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Bicyclic and tricyclic thienopyridines are converted into sulfones in 13-73% yield by means of acid-hypochlorite. The sulfone thieno[2,3-*b*]pyridine 1,1-oxide (Ib) undergoes Diels-Alder condensation with furan (both *exo* and *endo* products formed), anthracene, and naphthacene. Self-condensation of Ib occurs with elimination of sulfur dioxide to give 8-(3-pyridyl)quinoline (XV). The structure of XV was established by means of pmr and a europium shift reagent. Ultraviolet, pmr, and mass spectral data for various compounds are presented and discussed.

In a preceding paper (3) we described the direct conversion of tricyclic thienopyridines (including Va and VIa) containing a non-terminal thiophene ring into *S*-oxides and *S,S*-dioxides, by means of (a) iodobenzene dichloride in aqueous acetonitrile and (b) excess chlorine in carbon tetrachloride followed by water, respectively. For the bicyclic parent compound thieno[2,3-*b*]pyridine (Ia),

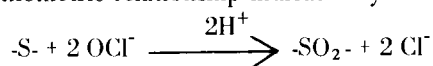


which contains a terminal thiophene ring, chlorination also occurs at C-2 and C-3 to yield a variety of chlorine-bearing products (4). No simple 1-oxide or 1,1-dioxide was obtained from Ia (5). In consideration of the fact that benzo[*b*]thiophene 1,1-dioxide is a well-known stable compound at room temperature, it seemed reasonable to expect that sulfones should also be obtainable in the bicyclic thienopyridine series. The preferred reagent (hydrogen peroxide in glacial acetic acid) for conversion of benzo[*b*]thiophene into its sulfone (6), however, gives exclusive *N*-oxidation with Ia and IIa (3,7). We now report the oxidation of thiophene rings in bicyclic and tricyclic thienopyridine systems to sulfones by means of

sodium hypochlorite-hydrochloric acid.

Limited usage of sodium hypochlorite in basic or aqueous acetic acid solution for *S*-oxidation of dialkyl and diaryl sulfides and sulfoxides has been made previously (8). Treatment of a suspension of thiophene in cold, concentrated hydrochloric acid with aqueous hypochlorite is reported to yield 2,5-dichloro-2,5-dihydrothiophene 1-oxide plus chlorothiophenes (9). However, thiophene is inert toward sodium hypochlorite in basic solution (10).

In our procedure, a solution or suspension of the thienopyridine substrate in dilute hydrochloric acid ( $\leq 1M$ ) was treated at room temperature with aqueous sodium hypochlorite. In general, reagents were used in the stoichiometric relationship indicated by the equation.



The hydrochloric acid served to convert the thienopyridine to its salt and, presumably, also to form hypochlorous acid *in situ*. In fact, omission of the acid halted the reaction completely. However, protonation of the substrate may not be necessary, inasmuch as benzo[*b*]thiophene and dibenzothiophene give sulfones under the same conditions. Yields of bicyclic thienopyridine sulfones (Ib-IIIb) were 13-37%. Yields of the tricyclic sulfones Vb and VIb were 24 and 47% (respectively), closely comparable to those obtained from the aforementioned chlorine-water method (3). In only one case (IVa  $\rightarrow$  IVb) was excess acid-hypochlorite used and this gave a much higher yield (73%) of product. Although we have not sought conditions for obtaining maximal yields, it is apparent that the hypochlorite procedure is the method of choice for conversion of thienopyridine substrates into their sulfones

(11). Use of the *N*-oxide of Ia as substrate gave no reaction.

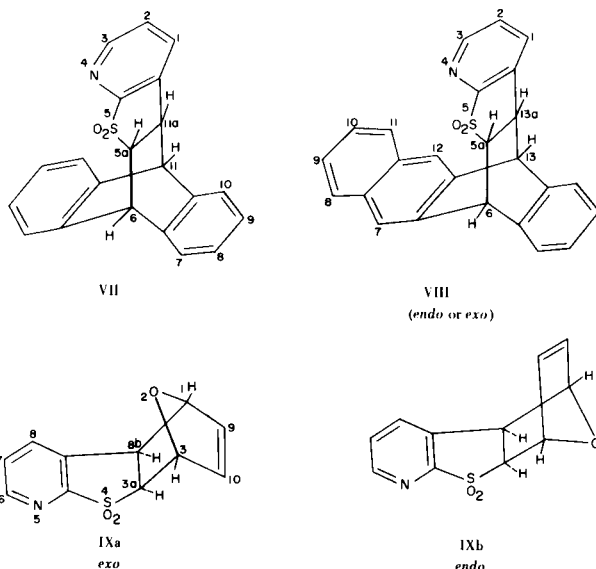
The ultraviolet spectra of sulfones Ib-IIIb show two major regions of absorption - a more intense band (or end absorption) at short wavelength ( $< 215$  nm) and a very broad weaker band at 250-310 nm. In IIb only, the broad band shows some evidence of fine structure. The pmr spectrum of each sulfone (obtained in trideuterioacetonitrile) is similar to that of its parent thiole Ia-IIIa, respectively, (obtained in carbon tetrachloride) (12,13). Coupling constants allow assignment of individual proton signals in the pyridine ring (shifted by -0.2 to +0.5 ppm from those of the parent molecule) of the sulfone. For the thiophene ring protons the coupling constant is larger ( $\Delta J_{2,3} = 0.9$ -1.6 Hz) in the sulfone, though the center of the AB signal is shifted only slightly ( $\Delta\delta = -0.3$  to +0.03 ppm) therein. As in the benzo[*b*]thiophene system (14), the change in  $J_{2,3}$  may be ascribed to a loss in aromaticity of the thiophene ring upon *S*-oxidation. In parents Ia-IIIa the doublet for H-2 falls downfield from that for H-3. As based on the data for benzo[*b*]thiophene 1,1-dioxide (14), however, it seems likely that the signal for H-3 falls downfield from that for H-2 in Ib-IIIb.

Thienopyridine sulfone Ib, like benzo[*b*]thiophene 1,1-dioxide (15), acts as a dienophile in Diels-Alder condensations with typical dienes. Treatment of Ib with anthracene gave adduct VII. That normal addition occurred across the 9,10-positions (rather than the 1,4-positions) of the anthracene ring was apparent from the pmr and ultraviolet spectra of VII. Addition of Ib with naph-

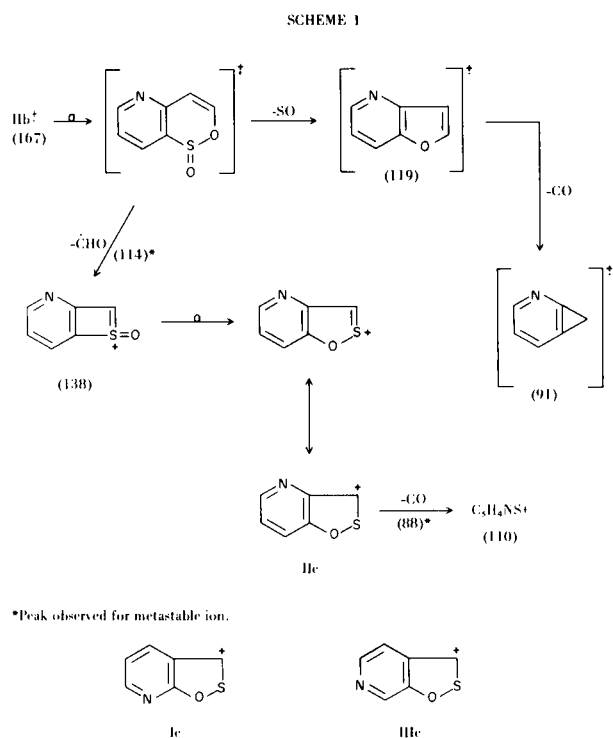
thalene was also observed. Structure VIII depicts the adduct in the presumed *endo* configuration. Refluxing Ib with furan in tetrahydrofuran for an extended period gave two crystalline products. On the basis of pmr spectra, the less soluble one, dec.  $170^\circ$ , was assigned the structure of the *exo*-adduct IXa, while the more soluble one, dec.  $120^\circ$ , appeared to be a 1:1 mixture of IXa and the *endo* isomer IXb. Thus, the pmr spectrum of the  $120^\circ$  product exhibited all of the features shown by that of IXa plus an additional set of partially overlapping analogous features. In the former adduct resonances for H-3a and H-8b occur as a simple AB system, *i.e.* one doublet of doublets, centered at  $\delta$  3.76. In the latter product an additional pattern of two doublets of doublets for these two protons is centered at  $\delta$  4.2. These relationships are analogous to those which have been described in the norbornene system (16) and in the isomeric Diels-Alder adducts of furan with maleic anhydride (17).

The mass spectra of sulfones Ib, IIb, and IIIb show similar fragmentation patterns. While there is an intense parent ion peak, the most abundant ion ( $m/e$  138) corresponds to the loss of formyl radical from the parent ion. Loss of sulfur monoxide and carbon monoxide are also observed, but (in contrast to the case of benzo[*b*]thiophene 1,1-dioxide) (18) loss of carbon monosulfide is not apparent. Scheme 1 depicts a rationalization of some of the fragmentation processes which occur in IIb. Significantly large peaks occur at  $m/e$  values of 76, 50, and 39. For IIb and IIIb the ion at  $m/e$  110 has an intensity of about 45% of the one at 138. For Ib, however, the 110 peak is very small. It seems likely that instability in the 138 ion is fostered by the resonance forms Ic-IIIc, respectively, where a positive charge resides on a carbon atom attached to the pyridine ring. Such charge should be accommodated more readily at the  $\beta$ -position to the pyridine nitrogen (as in Ic) than at the  $\alpha$ - or  $\gamma$ -positions (as in IIc and IIIc) and make loss of carbon monoxide from Ic less likely than in the other cases.

The mass spectra of adducts VII, VIII, and IXa are dominated by the electron-impact induced retro-Diels-Alder process (19). The parent ion is so unstable that it is barely observed ( $< 3\%$  of the most abundant ion). For VII and VIII (and to a somewhat lesser extent for IXa) fragmentation of this parent ion occurs almost exclusively with transfer of the positive charge to the dienic moiety. Thus in all cases, the most abundant ion peak corresponds to the singly ionized dienic addendum. In addition, for VII and VIII the second most abundant ion is the protonated arene component. Only very minor peaks are found for ionized Ib or its important fragmentation products. These observations are consistent with the expectation that naphthalene, anthracene, and perhaps even furan,



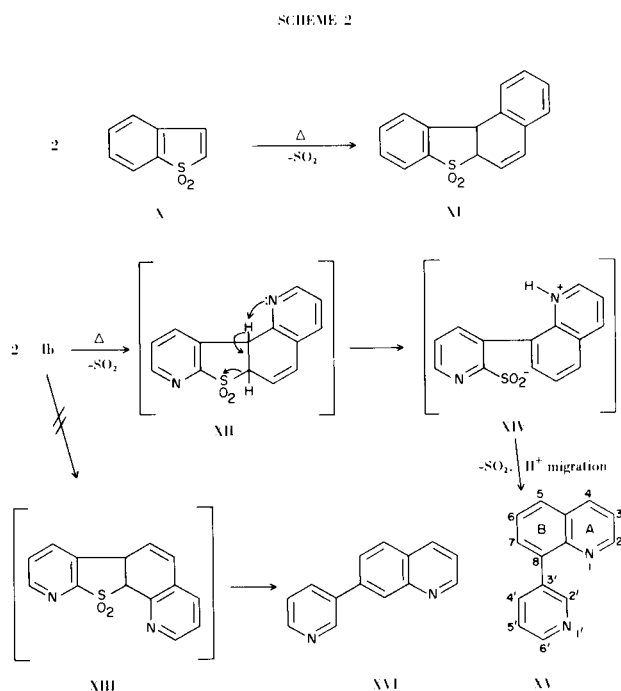
thacene caused loss of color present in the parent hydrocarbon. The high-melting ( $340^\circ$ ) product exhibited ultraviolet absorption similar to that of naphthalene and could



should be more readily ionized than Ib. Only the furan adduct IXa shows an appreciably intense peak ( $m/e$  171) for the loss of sulfur dioxide from the parent ion.

It is reported that at  $220^\circ$  benzo[*b*]thiophene 1,1-dioxide (X) undergoes self-condensation (in a Diels-Alder fashion) plus loss of one molecule of sulfur dioxide to give XI (20). Analogously, heating Ib in refluxing xylene for an extended period gave loss of sulfur dioxide. However, the expected product XII or XIII (Scheme 2) was not obtained. Instead, two molecules of sulfur dioxide were eliminated to form a pyridylquinoline, presumed to be either the 8-(3-pyridyl) isomer XV or the 7-(3-pyridyl) isomer XVI. The melting point of our product ( $108^\circ$ ) and that of its picrate correspond closely to those reported for an authentic sample of XV (21). However, Fischer and van Loo (22) reported the synthesis of a pyridylquinoline (m.p.  $104^\circ$ , no picrate prepared), which may well have the structure of XVI - or of the isomeric 7-(4-pyridyl)quinoline (23). Hence, more definitive structural studies on our product were desirable.

Indication that our amine is XV (rather than XVI) was obtained from its ultraviolet absorption spectrum, which resembles more closely that of 1-phenylnaphthalene than that of 2-phenylnaphthalene (24,25). Conclusive evidence that XV is, indeed, correct was obtained by use of pmr spectrometry and a europium shift reagent, "Eu-Resolve". The results of these experiments are presented in Table I. Observation of the table shows that as one adds increments of Eu-Resolve to a solution of the amine product



(in succession from run 1 to run 4) two protons are shifted downfield markedly and to nearly equal amounts. Moreover, the serious overlapping of signals in the absence of the shift reagent (run 1) is sufficiently well circumvented (run 4) as to allow definitive assignment of the benzenoid protons in ring B. The coupling constants of 1.7, 7, and 8 Hz (respectively) for protons H-5 to H-7 are consistent with structure XV, and not with XVI. Complexing of the europium atom with XV would be expected to be greatest at the sterically less hindered nitrogen atom, N-1'. Nitrogen N-1 appears to be sterically too hindered to permit complexation on it. The expected result is that the  $\alpha$ -protons at C-2' and C-6' should be shifted downfield to the largest extent, and approximately equally. The more remote (from the europium) protons at C-2, C-7, C-4', and C-5' should show lesser shifts, while those at C-3 to C-6 should be the least affected (27). The experimental observations fit this model well. Contrariwise, if our amine were XVI instead, one would expect complexation to occur at both nitrogen atoms - with marked downfield shifts for at least three protons and intermediate amounts of shift for a larger number of others.

Scheme 2 depicts a possible mechanism for the conversion of the hypothetical intermediate XII into amine XV. It is reported (20) that treatment of XI with base causes opening of the hetero ring to give 2-(1-naphthyl)-benzenesulfinate. A similar process might be expected to occur spontaneously in XII, where a basic nitrogen atom is present in the molecule itself. The resultant substituted pyridine-2-sulfonic acid XIV should lose sulfur dioxide

TABLE I  
Proton Magnetic Resonance Data for 8-(3-Pyridyl)quinoline (XV) Plus Eu-Resolve (a)

Run No.	Observed Quantity	H-2	H-3	H-4	H-5	H-6	H-7	H-2'	H-4'	H-5'	H-6'
1 (b)	$\delta$ (ppm)	8.62	7.1-7.92	7.9-8.3	7.1-7.92	7.1-7.92	7.1-7.92	8.93	7.9-8.3	7.1-7.92	8.88
(c)	multiplicity	dd	m	m	m	m	m	bd*	m	m	dd*
	$J$ (Hz)	1.5, 4.8						2.2			1.5, 4.8
2 (d)	$\delta$ (ppm)	8.98	7.43	8.21	7.55-8.09	7.55-8.09	7.55-8.09	10.19	8.47	8.09	9.91
	multiplicity	dd	dd*	dd	m	m	m	d	dt	m	dd
	$J$ (Hz)	1.7, 4	4, 8.2	1.7, 8.2				2	2, 8		2, 5
3	$\delta$ (ppm)	9.14	7.51	8.29	7.5-8.3	7.5-8.3	7.5-8.3	12.03	9.10	8.14	11.75
	multiplicity	dd*	dd*	dd*	m	m	m	d	dt*	dd*	bd
	$J$ (Hz)	1.7, 4	4, 8.2	1.7, 8.2				2	2, 8	5, 8	5
4	$\delta$ (ppm)	9.45	7.70	8.48	8.16	7.92	8.97	15.53	10.28	9.63	15.27
	multiplicity	dd*	dd*	dd	dd	dd*	dd	bs	dt	dd*	bd
(e)	$J$ (Hz)	1.7, 4	4, 8	1.7, 8	1.7, 8	7, 8	1.7, 7		1.7, 7.5	4.5, 7.5	4.5

(a) Runs 1-4 have increasing ratios of Eu-Resolve:XV. (b) Solvent used in run 1 only, deuteriochloroform. No europium was added. (c) Letter b indicates broadened. Starred multiplicities are partially obscured by overlapping of signals. (d) In runs 2-4 the solvent was deuteriochloroform-carbon tetrachloride. (e) Assignments of signals for H-5 and H-7 are based on the differences in  $J$  values (26).

readily (28), especially during the prolonged heating of the reaction mixture.

Amine XV is obtainable from thieno[2,3-*b*]pyridine (Ia) in a yield of 9% for the two steps reported here, or of 3% overall for four steps from thiophene (12). British workers (21) did not report yields for the final steps in their two synthetic routes to XV. However, each of their routes involves a difficult separation of isomers from the Gomberg-Bachmann reaction of a diazonium compound (from 8-aminoquinoline or from 2-nitroaniline) (29) on pyridine. Hence, it seems likely that our indirect route to XV is synthetically preferable.

#### EXPERIMENTAL (30)

##### Starting Materials and General Procedure for Sulfones.

Mallinckrodt aqueous sodium hypochlorite solution was filtered and titrated *versus* standardized sodium sulfite (with potassium iodide-starch as indicator). The total oxidizing titre of the solution was ascribed to the presence of sodium hypochlorite *per se* (0.33-0.55 *M*). The thienopyridine substrates used (1.40 mmoles) were available from previous studies (12,13,31,32). Hydrochloric acid was 0.25-1 *M*. Unless otherwise noted, the reactants were used in the molar ratio of 1:2:2 for substrate:acid:hypochlorite.

To a vigorously stirred mixture of thienopyridine and hydrochloric acid at room temperature was added (dropwise, over a period of 10-60 minutes) the hypochlorite solution. This mixture was stirred for 0.5-7 hours longer, whereupon it normally showed a negative starch-iodide test and a  $\text{pH} > 7$ . If the starch-iodide test remained positive, the solution was treated with sodium sulfite to remove unreacted oxidizing agents. If the solution was acidic, it was neutralized with sodium bicarbonate. A chloroform extract of the mixture was dried (magnesium sulfate) and evaporated to a small volume (or to dryness) to obtain solid, crude sulfone.

##### Thieno[2,3-*b*]pyridine 1,1-Dioxide (Ib).

This compound, m.p. 145-146.5° (37%) was recrystallized from chloroform to give prisms, m.p. 152.5-153.5°;  $\nu$  1330 and 1165  $\text{cm}^{-1}$ ; pmr (trideuterioacetonitrile)  $\delta$  7.02 (d, 1,  $J_{2,3} = 7.5$  Hz, H-2), 7.52 (d, 1, H-3) which overlaps 7.59 (d of d, 1,  $J_{5,6} = 5$  Hz,  $J_{4,5} = 8$  Hz, H-5), 7.94 (d of d, 1,  $J_{4,6} = 1.5$  Hz, H-4), 8.66 ppm (d of d, 1, H-6); uv max. (absolute ethanol) 268 nm ( $\log \epsilon = 3.70$ ); uv min. 246 (3.49); mass spectrum,  $m/e$  (relative abundance) 167 (75), 138 (100), 119 (63), 91 (36), 76 (53), 50 (29).

*Anal.* Calcd. for  $\text{C}_7\text{H}_5\text{NO}_2\text{S}$ : C, 50.3; H, 3.0; N, 8.4; S, 19.2. Found: C, 50.1; H, 3.1; N, 8.2; S, 19.2.

Sulfone Ib was also prepared by a modification of the general procedure wherein the hydrochloric acid was replaced by an equivalent amount of 0.4 *M* sulfuric acid (33), yield 48%, m.p. 141-144°. On the other hand, addition of hypochlorite solution to a solution of Ia in aqueous tetrahydrofuran gave no reaction.

##### Thieno[3,2-*b*]pyridine 1,1-Dioxide (IIb).

The product, m.p. 132-135° (34%), was recrystallized from methylene dichloride to give prisms, m.p. 149.5-150.5°;  $\nu$  1320 and 1165  $\text{cm}^{-1}$ ; pmr (trideuterioacetonitrile)  $\delta$  7.30 (AB system, 2,  $\Delta\delta = 15$  Hz,  $J = 7$  Hz, H-2 and H-3) which overlaps 7.48 (d of d, 1,  $J_{5,6} = 5$  Hz,  $J_{6,7} = 7-8$  Hz, H-6), 8.11 (d of d, 1,  $J_{5,7} = 1.5$  Hz, H-7), 8.72 ppm (d of d, 1, H-5); uv max. (absolute ethanol) 213 nm ( $\log \epsilon = 4.31$ ), 276 (3.54), 284 (3.54), 294 (3.39, shoulder);

mass spectrum, *m/e* (relative abundance) 167 (73), 138 (100), 119 (31), 110 (49), 91 (31), 83 (22), 76 (51), 75 (30), 74 (30), 51 (25), 50 (61), 39 (43).

*Anal.* Calcd. for  $C_7H_5NO_2S$ : *vide supra*. Found: C, 50.4; H, 3.1; N, 8.3; S, 19.3.

#### Thieno[2,3-*c*]pyridine 1,1-Dioxide (IIIb).

The crude yield of IIIb was 13%, m.p. 172-175°, raised to 186-186.5° by sublimation of 90-120° (3 mm.) and recrystallization from chloroform as sticky needles; *ir* 1330 and 1165  $cm^{-1}$ ; *pmr* (trideuterioacetonitrile)  $\delta$  7.03 (d, 1,  $J_{2,3} = 7$  Hz, probably H-2), 7.44 (broadened d, 1, probably H-3) which overlaps 7.51 (d of pseudotriplets,  $J_{4,5} = 5$  Hz,  $J_{4,7} \cong 1$  Hz, H-4), 8.83 (d, 1, H-5) which overlaps 8.92 ppm (broadened d, H-7); *uv* max. (absolute ethanol) 279 nm ( $\log \epsilon = 3.19$ ); *uv* min. 248 (3.14); mass spectrum, *m/e* (relative abundance) 167 (92), 138 (100), 110 (44), 76 (21), 50 (38).

*Anal.* Calcd. for  $C_7H_5NO_2S$ : *vide supra*. Found: C, 50.2; H, 3.1; N, 8.4; S, 19.1.

#### [1]Benzothieno[2,3-*b*]pyridine 5,5-Dioxide (IVb).

In this case the molar ratio of components used was 1:2.4:2.4 and the reaction was stirred for 15 hours after admixture was complete; yield of IVb 73%, m.p. 247-249.5°; converted to prisms (m.p. 253.5-255°) on recrystallization from acetonitrile-acetone plus sublimation at 155-190° (2 mm.); *ir* 1320 and 1175  $cm^{-1}$ ; *pmr* (hexadeuteriodimethyl sulfoxide)  $\delta$  7.6-8.3 (m, 5, H-3 plus H-5 to H-8), 8.5-8.8 ppm (m, 2, H-2 and H-4).

*Anal.* Calcd. for  $C_{11}H_7NO_2S$ : C, 60.8; H, 3.3; N, 6.5; S, 14.8. Found: C, 60.7; H, 3.1; N, 6.3; S, 14.7.

#### Other Sulfones Prepared by Means of Acid-Hypochlorite.

[1]Benzothieno[3,2-*b*]pyridine 5,5-dioxide (Vb) was obtained as crystals from acetonitrile, yield 24%, m.p. 221-222.5°; reported (3) 24%, 229-230°. Thieno[2,3-*b*:4,5-*b'*]dipyridine 5,5-dioxide (VIb) formed needles from acetonitrile, yield 47%, m.p. 220-221.5°; reported (3) 41%, 222-223°. Compounds Vb and VIb were identified by comparison of *ir* and *pmr* spectra with samples prepared from excess chlorine, carbon tetrachloride, and water (3). Benzo[*b*]thiophene 1,1-dioxide was obtained in 26% yield, m.p. 130-132°, raised to 135.5-137° on recrystallization from chloroform-carbon tetrachloride, identified by *ir* and *pmr* spectra; reported (6) 95%, m.p. 142-143°. Oxidation of dibenzothiophene was conducted in tetrahydrofuran - 1 *M* hydrochloric acid (2:1 by vol.) to increase solubility of the substrate. There were obtained dibenzothiophene 5,5-dioxide (47%), m.p. 226.5-229.5°; identified by mixture m.p. with an authentic sample; plus impure dibenzothiophene 5-oxide (14%), m.p. 175-177°, positive sulfoxide test (34), *ir* 1030  $cm^{-1}$  (S=O).

#### *Cis*-6,11-(1,2-Benzo)-5a,6,11,11a-tetrahydro[1]naphtho[2,3-*b*]thieno[2,3-*b*]pyridine 5,5-Dioxide (VII).

A mixture of 0.84 g. (5 mmoles) of sulfone Ib, 1.78 g. (10 mmoles) of anthracene, and 15 ml. of xylene was refluxed for 44 hours. The cooled mixture was diluted with hexane and filtered. The precipitate was leached with acetone-benzene (1:1) to leave crude VII. The residue was chromatographed on Brinkman neutral alumina. Benzene caused elution of unreacted anthracene and then chloroform plus ethyl acetate eluted additional VII, total yield 0.78 g. (45%) of light gray powder, m.p. 257-260°. Recrystallization from tetrahydrofuran-acetone gave fine white needles, m.p. 263.5-264.5°; *ir* 1320 and 1155  $cm^{-1}$ ; *pmr* (hexadeuteriodimethyl sulfoxide)  $\delta$  3.86 (d of d, 1,  $J_{5a,11a} = 9$  Hz,  $J_{11,11a} = 2.5$  Hz, H-11a), 4.33 (d of d, 1,  $J_{5a,6} = 3.5$  Hz,

H-5a), 5.06 (d, 1, H-11) which overlaps 5.15 (d, 1, H-6), 6.8-7.8 (m, 9, H-2 plus benzo ring protons), 8.2-8.6 ppm (m, 2, H-1 and H-3); *uv* max. (absolute ethanol) 264 nm ( $\log \epsilon = 3.70$ ), 271 (3.70), 278 (3.51, shoulder); *uv* min. 243 (3.43); mass spectrum, *m/e* (relative abundance) 345 (1,  $M^+$ ), 179 (17, anthracene- $H^+$ ), 178 (100, anthracene $^+$ ).

*Anal.* Calcd. for  $C_{21}H_{15}NO_2S$ : C, 73.0; H, 4.4; N, 4.1; S, 9.3. Found: C, 72.8; H, 4.7; N, 3.8; S, 9.0.

#### *Cis*-6,13-(1,2-Benzo)-5a,6,13,13a-tetrahydro[1]anthro[2,3-*b*]thieno[2,3-*b*]pyridine 5,5-Dioxide (VIII).

A mixture of 0.84 g. (5 mmoles) of sulfone Ib, 1.14 g. (5 mmoles) of naphthalene (Aldrich), and 25 ml. of xylene was treated as in the preparation of VII. The crude precipitate was sublimed at 260-300° (0.5 mm.) to give 0.58 g. (29%) of cream-colored needles, m.p. 326-328°, raised to 340-341° dec. on further sublimation; *ir* (potassium bromide) 1300 and 1150  $cm^{-1}$ ; *uv* max. (95% ethanol) 231 nm ( $\log \epsilon = 5.04$ ), 258 (4.34, shoulder), 265 (4.39), 274 (4.34, shoulder); mass spectrum, *m/e* (relative abundance) 395 (2,  $M^+$ ), 229 (22, naphthalene- $H^+$ ), 228 (100, naphthalene $^+$ ).

*Anal.* Calcd. for  $C_{25}H_{17}NO_2S$ : C, 75.9; H, 4.3; N, 3.5; S, 8.1. Found: C, 76.0; H, 4.4; N, 3.4; S, 8.2.

#### *Cis*-1,3-Etheno-1,3,3a,8b-tetrahydro[1]furo[3,4-*b*]thieno[2,3-*b*]pyridine 4,4-Dioxide (IX).

A solution of 0.67 g. (4 mmoles) of sulfone Ib in 15 ml. of furan and 15 ml. of tetrahydrofuran was stirred and refluxed for 10 days, while a precipitate was formed. Filtration of the cooled mixture gave 287 mg. (31%) of crude *exo* adduct IXa, m.p. ca. 165° dec. An analytical sample was prepared by recrystallization from ethanol-acetone and drying *in vacuo* at 25°: faintly tan prisms, m.p. ca. 170° dec.; *ir* 1325 and 1165  $cm^{-1}$ ; *pmr* (hexadeuteriodimethyl sulfoxide)  $\delta$  3.76 (AB system, 2,  $\Delta\delta = 18$  Hz,  $J = 7$  Hz, H-3a and H-8b), 5.12 and 5.45 (2d, 1 each,  $J_{1,9} = J_{3,10} = 1.5$  Hz, H-1 and H-3), 6.56 and 6.71 (2 d of d, 1 each,  $J_{9,10} = 6$  Hz, H-9 and H-10), 7.75 (2 overlapping d of d, 1,  $J_{6,7} = 4.5$  Hz,  $J_{7,8} = 8$  Hz, H-7), 8.27 (d of d, 1,  $J_{6,8} = 1.5$  Hz, H-8), 8.75 ppm (d of d, 1, H-6); *uv* max. (absolute ethanol) 263 nm ( $\log \epsilon = 3.58$ , shoulder), 268 (3.61), 275 (3.48, shoulder); *uv* min. 238 (2.90); mass spectrum, *m/e* (relative abundance) 171 [ $22(M-SO_2)^+$ ], 68 (100, furan $^+$ ), 39 (23,  $C_3H_3^+$ ).

*Anal.* Calcd. for  $C_{11}H_9NO_3S$ : C, 56.2; H, 3.9; N, 6.0; S, 13.6. Found: C, 56.2; H, 3.7; N, 5.9; S, 13.7.

Evaporation of the filtrate from isolation of IXa gave 473 mg. (50%) of slightly tan powder, a 1:1 mixture of IXa and *endo* adduct IXb, m.p. ca. 130° dec. An analytical sample formed white globules, m.p. ca. 120° dec.; *ir* 1320 and 1155  $cm^{-1}$ ; *pmr* (hexadeuteriodimethyl sulfoxide) same as for IXa plus the following:  $\delta$  4.05 (d of d, 1,  $J_{3a,8b} \cong 9$  Hz,  $J_{1,8b} = 4.5$  Hz, H-8b), 4.35 (d of d, 1,  $J_{3,3a} = 4.7$  Hz, H-3a), ca. 5.52 (partially obscured m, H-1), 5.97 (d of d, 1,  $J_{9,10} = 6$  Hz,  $J_{1,9} = 1.5$  Hz, H-9), 6.42 (d of d, 1,  $J_{3,10} = 1.5$  Hz, H-10), ca. 7.2 (observed m, H-7), ca. 8.08 (d of d, 1,  $J_{7,8} = 8$  Hz,  $J_{6,8} = 1.5$  Hz, H-8), ca. 8.68 (partially obscured d of d, H-6); *uv*, superimposable on that of IXa.

*Anal.* Found: C, 56.0; H, 3.9; N, 5.7; S, 13.5.

#### 8-(3-Pyridyl)quinoline (XV).

A solution of 0.84 g. of sulfone Ib in 10 ml. of xylene was refluxed for 50 hours while a stream of nitrogen gas was bubbled through it. The cooled mixture was diluted with hexane, filtered, and evaporated slowly to form 131 mg. (25%) of light brown crystals, m.p. 107.5-109°, [lit. 111-112° (21)]; *uv* max. (absolute

ethanol) at 219 nm ( $\log \epsilon = 4.50$ ), 288 (3.92), 313 (3.68, shoulder); mass spectrum, parent ion at  $m/e$  206.

The picrate of XV formed canary yellow crystals from acetone, m.p. 223-224°; lit. 224-226° (21).

*Anal.* Calcd. for  $C_{20}H_{13}N_5O_7$ : N, 16.1. Found: N, 15.8.

A sample of pyridylquinoline XV in deuteriochloroform-carbon tetrachloride was treated with incremental amounts of tris(dipivalomethanato)europium(III) (Alfa Inorganics) and allowed to stand at room temperature for hours or days until the solution became clear and gave a sharp pmr spectrum. Data are recorded as runs 2-4 in Table I.

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