Chemistry of Thienopyridines. XXIII. Mass Spectra of Some *N*-Oxides, Sulfoxides, and Sulfones (1,2)

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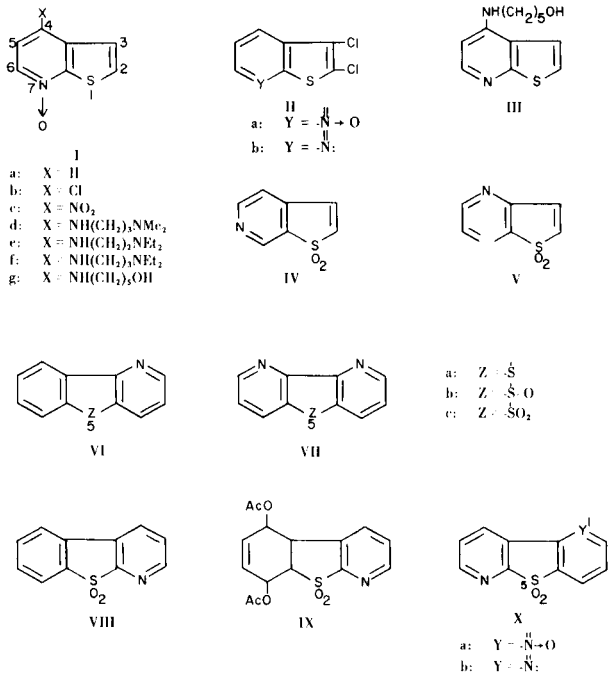
The mass spectral fragmentation patterns of a series of thienopyridine *N*-oxides, *S*-oxides, and *S,S*-dioxides were elaborated as a means of structural determination. Observation of a significant (M-16) peak is diagnostic for the presence of either an *N*-oxide or an *S*-oxide function (indistinguishable from one another by this method) but does not occur for an *S,S*-dioxide function. For a substituted thieno[2,3-*b*]pyridine 7-oxide, structural rearrangement to a pyridone (followed by emission of carbon monoxide or formyl radical) or side-chain fission may be competitive with de-*N*-oxygenation. For two tricyclic parent *S*-oxides, rearrangement and de-*S*-oxygenation are competing initial processes. For parent *S,S*-dioxides structural rearrangement precedes fragmentation, wherein the oxygen is ejected in such forms as sulfur monoxide, carbon monoxide, formyl or cyanate radicals, and ketene.

In previous papers we described selective oxidations of bicyclic and tricyclic thienopyridines to form *N*-oxides, *S*-oxides, and *S,S*-dioxides (5-8). The nature of the oxide function present was established by means of infrared spectra and color tests, of which the former were (in general) more reliable. We now report mass spectral investigations of a number of these compounds as an additional means of distinguishing amongst the three different oxide functions. Distinctions have also been noted in chromatographic characteristics of the compounds (9).

Used in mass spectral investigations were various derivatives (Ib-Ig, IIa) of thieno[2,3-*b*]pyridine 7-oxide (Ia), the deoxo compound III, the bicyclic sulfone IV, the tricyclic sulfoxides VIb and VIIb, the tricyclic sulfones VIc, VIIc, VIII, IX, and Xb, and the *N*-oxide sulfone Xa. Spectra were obtained at 70 eV. The elemental compositions of selected fragmentation ions were ascertained at high resolution. Complete mass spectral data are given in the Experimental section. Typical fragmentation patterns are presented herewith.

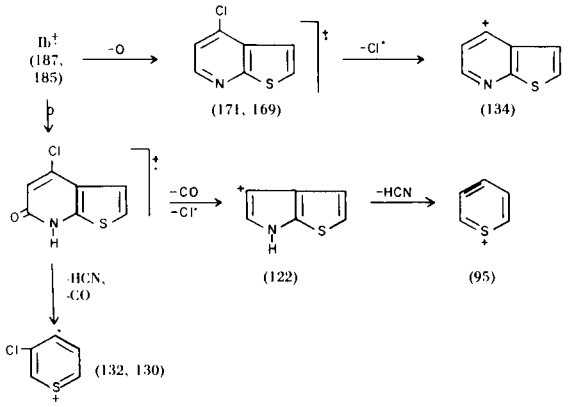
Fragmentation pathways of the *N*-oxides studied fall into three general patterns, *viz.* (a) exclusive initial de-*N*-oxygenation (followed by regular fragmentation of the de-oxo ion), (b) competitive de-*N*-oxygenation and *O*-migration, and (c) competitive de-*N*-oxygenation and side-chain fission. Only the sulfone *N*-oxide Xa (*vide infra*) decomposes according to pattern (a) (10). Chloro-*N*-oxides Ib and IIa decompose as per pattern (b), while nitro derivative Ic and the 4-amino derivatives Id-Ig fragment according to pattern (c).



Analyses of the fragmentation patterns of Ib (Scheme 1) and IIa (Scheme 2) were aided by reference to published mass spectral data for 3-chlorothieno[2,3-*b*]pyridine, 2,3-dichlorothieno[2,3-*b*]pyridine (IIb) (8), and quinoline 1-oxide (11a). Losses from Ib and IIa of oxygen and chlorine atoms, as well as of carbon monoxide and hydrogen cyanide are readily apparent. Emission of carbon monoxide or formyl radical is taken as evidence

Scheme 1 (a)

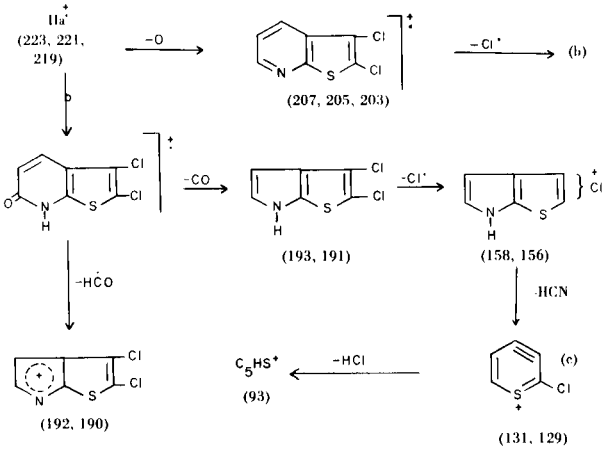
Competitive De-*N*-oxygenation and *O*-Migration in the Mass Spectrum of *N*-Oxide Ib



(a) Includes all peaks of relative abundance > 15% above mass number 94.

Scheme 2 (a)

Competitive De-*N*-oxygenation and *O*-Migration in the Mass Spectrum of *N*-Oxide IIa



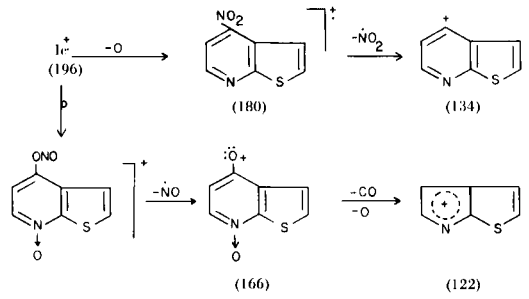
(a) Includes all peaks of relative abundance > 10% above mass number 168, and > 25% above mass number 90. (b) See reference 8 for the fragmentation pattern of 2,3-dichlorothieno[2,3-*b*]pyridine. (c) One possible structure.

for structural rearrangement of the parent compound to a pyridone. Thus, two major competitive pathways (direct loss of oxygen and structural rearrangement) are visualized for initial transformation of the molecular ion. One might expect to find a third competitive pathway that would involve initial loss of a chlorine atom from the parent ion. However, such a route seems unimportant on the basis of the low relative abundance (<5%) of the (M-Cl) peak.

4-Nitrothieno[2,3-*b*]pyridine 7-oxide (Ic) (Scheme 3) shows no clear evidence for rearrangement of the molecular ion into a pyridone. Instead, there is competition in the molecular ion for direct loss of an oxygen atom (presumed to arise from the nitrogen atom at position 7) and transformations in the group at C-4. The latter

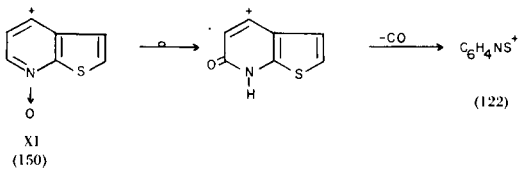
Scheme 3 (a)

Competitive De-*N*-oxygenation and Side-Chain Fission in the Mass Spectrum of *N*-Oxide Ic



(a) Includes all peaks of relative abundance ≥ 10% above mass number 120.

include the well-known rearrangement of the nitro group, followed by emission of a molecule of nitric oxide. Although direct loss of nitrogen dioxide from C-4 is evident it is uncertain whether this process precedes the loss of oxygen from position 7 or follows it (as shown). There is a small peak at mass number 150 which could arise either by de-*N*-oxygenation of the 166 ion or by direct loss of nitrogen dioxide from the molecular ion (to give XI). In the latter case the 122 ion would arise from rearrangement of XI to the pyridone structure, followed by ejection of C-6 in the carbon monoxide fragment, thus:

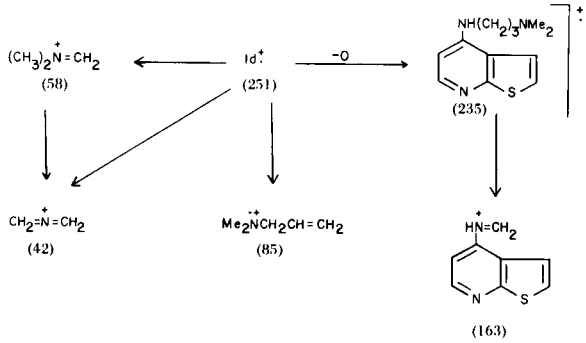


Scheme 3 implies that C-4 is ejected in the carbon monoxide fragment. Isotopic labelling could clarify the the relative extents of these alternative pathways.

Compounds Id-Ig undergo both facile de-*N*-oxygenation and side-chain fission on electron impact (Schemes 4 and

Scheme 4 (a)

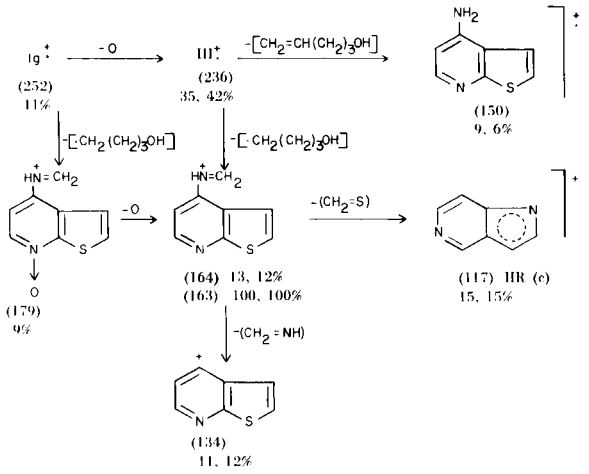
Competitive De-*N*-oxygenation and Side-Chain Fission in the Mass Spectrum of *N*-Oxide Id



(a) Includes all peaks of relative abundance ≥ 8%, except for m/e = 44.

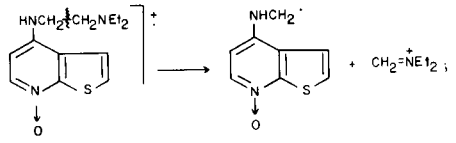
5). In fact, the dialkylaminoalkylamino side chain $[R_2N(CH_2)_nNH\text{-}]$ fragments so readily (by fission *alpha* to a nitrogen atom) that $(R_2N{=}CH_2)^+$ represents the

Scheme 5 (a)
Comparison of Mass Spectral Fragmentation Patterns in III and Its *N*-Oxide Ig (b)



(a) Includes all peaks of relative abundance ≥ 9%. (b) Where two numbers are listed for % relative abundances the first number refers to the Ig series; the second, to the III series. (c) Ion formula confirmed by high resolution.

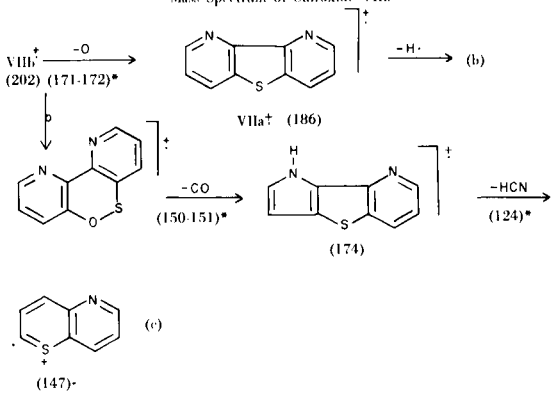
most abundant ion (by far) in the spectrum of each of the compounds Id-If. In Id and If (n = 3) the ions M^+, $(M\text{-}O)^+$, and $(TpNH{=}CH_2)^+$ [where Tp = thienopyridyl] also have appreciable intensities (8-30%). The last of these ions results from α-fission of the side chain with respect to the nitrogen atom attached to the thienopyridine ring (12). For Ie (n = 2), on the other hand, these latter three ions are nearly absent (0-3%). Thus, the overwhelming initial fragmentation process in Ie can be represented by the equation wherein α-cleavage occurs simultaneously with



respect to both nitrogen atoms of the side chain, but where the non-aromatic fragment always assumes the positive charge. In Ig and III (Scheme 5) only one nitrogen atom is present in the ω-hydroxyalkylamino side chain. Again α-fission to the nitrogen atom (plus de-*N*-oxygenation in Ig) occurs readily, but the positively charged fragment observed (most abundant ion in the spectrum) is now $(TpNH{=}CH_2)^+$.

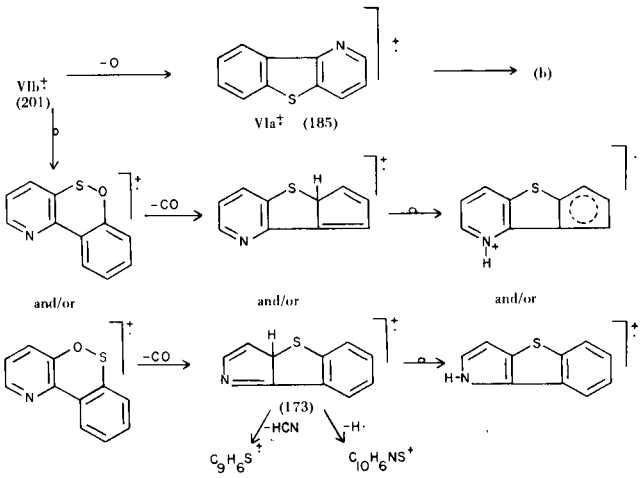
In regard to thienopyridine *S*-oxides, mass spectra have previously been reported only for dihydrobicyclic systems (13). We have now studied the spectra of the two tricyclic aromatic thienopyridine sulfoxides VIb and VIIb (Schemes 6 and 7). The greater symmetry of VIIb permits

Scheme 6 (a)
Competitive De-*S*-oxygenation and *O*-Migration in the Mass Spectrum of Sulfoxide VIIb



(a) Includes all peaks of relative abundance ≥ 8% above mass number 82. (b) See reference 1 for the fragmentation pattern of thieno[3,2-*b*;4,5-*b*']-dipyridine, VIIa. (c) One possible structure.

Scheme 7 (a)
Competitive De-*S*-oxygenation and *O*-Migration in the Mass Spectrum of Sulfoxide VIb



(a) Includes all peaks of relative abundance > 10% above mass number 39. (b) See reference 1 for the fragmentation pattern of [1]benzothieno[3,2-*b*]pyridine, VIa.

a simpler interpretation of its spectrum. However, in both cases one has competitive loss of oxygen either as an atom *per se*, or as carbon monoxide after initial structural rearrangement. Ejections of a hydrogen atom and of hydrogen cyanide are also observed. The spectrum of VIIb is especially informative since it shows metastable ion peaks for three of these transformations. A metastable peak for loss of hydrogen from the intermediate ion $VIIa^+$ was also noted previously (1).

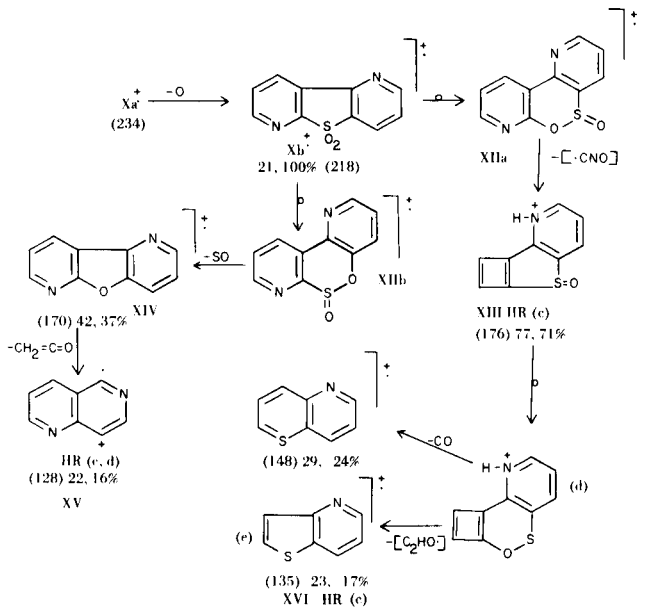
Comparison of Schemes 1 and 2 for chloro-substituted thienopyridine *N*-oxides with Schemes 6 and 7 shows remarkable similarities in major fragmentation pathways (where chlorine and hydrogen atoms play analogous roles) for these structurally different compounds. Bryce and Maxwell (14,15) originally proposed that *N*-oxide func-

tions can be diagnosed by the presence of an intense (M-16) peak in the mass spectrum of the molecule. It is now clear that the Bryce-Maxwell criterion cannot be used to distinguish between an *N*-oxide and an *S*-oxide function in a molecule which contains both nitrogen and sulfur atoms (16). The significant loss of an oxygen atom from the molecular ion (as found for VIb and VIIb) is also noted in the compounds dibenzo[*b*,*d*]thiophene 5-oxide (17) and phenanthro[4,5-*bcd*]thiophene 4-oxide (18), each of which contains an internally catenated thiophene *S*-oxide ring.

In contrast to the preceding cases it seems clear that one can distinguish by mass spectrometry between an *S*,*S*-dioxide function and a combination of two *S*- or *N*-oxide functions in the same molecule. Compound Xa, which is an *N*,*S*,*S*-trioxide, illustrates this point; since its spectrum (Scheme 8) is clearly inconsistent with an

Scheme 8 (a)

The Mass Spectrum of Trioxide Xa--Exclusive Initial De-*N*-oxygenation Followed by Competitive Rearrangement-Fragmentation (b)



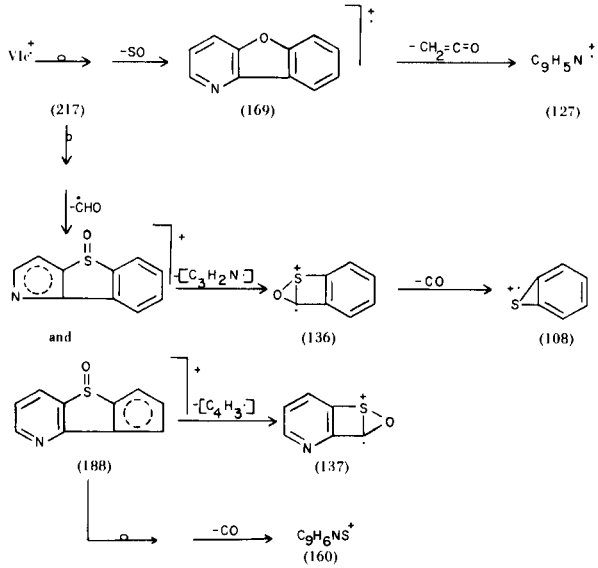
(a) Includes all peaks of relative abundance ≥ 20% for Xa and ≥ 15% for Xb. (b) Where two numbers are listed for % relative abundances the first number refers to the Xa series; the second, to the Xb series. (c) Ion formula confirmed by high resolution. (d) One possible structure. (e) See reference 1 for the fragmentation pattern of thieno[3,2-*b*]pyridine.

alternative *N*,*N*′,*S*-trioxide formulation. Most significantly, only one of the three oxygen atoms is lost as such from the molecular ion. Thus, the relative abundance of the (M-16) peak is 21%, while those of (M-32) and (M-48) peaks are negligibly small (< 2%). Moreover, the single oxygen atom is lost so readily that the mass spectrum of Xa is closely approximated by that of the derived sulfone Xb, plus a parent peak for Xa. It is apparent, therefore, that the first fragmentation process in every molecule of Xa must be the loss of the *N*-oxygen.

Sulfone Xb does not lose an oxygen atom *per se*.

Scheme 9 (a)

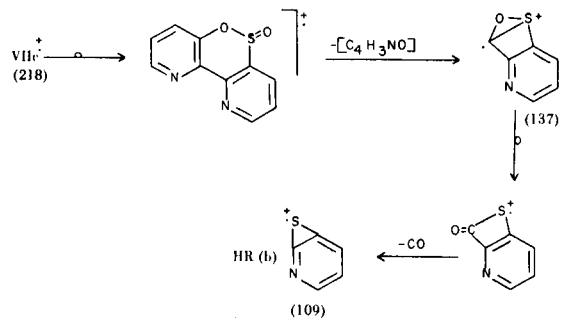
Competitive Rearrangement-Fragmentation Pathways in the Mass Spectrum of Sulfone VIc



(a) Includes all peaks of relative abundance ≥ 10% above mass number 75.

Scheme 10 (a)

Rearrangement-Fragmentation Pathway in the Mass Spectrum of Sulfone VIIc



(a) Includes all peaks of relative abundance ≥ 10% above mass number 76.
(b) Ion formula confirmed by high resolution.

Instead, it presumably rearranges to the cyclic sulfite ion, XIIa, which can undergo fragmentation either by loss of the cyanate radical to give XIII (as depicted in Scheme 8) or by loss of sulfur monoxide to give XIV. Ion XIV could also arise by way of XIIb, isomeric with XIIa. The final oxygen atom to leave the parent molecule Xb is emitted in the form of carbon monoxide, ketene, or a C_2HO radical. While emissions of CO and SO molecules are easy to rationalize, the other three ejecta are less frequently postulated. For this reason the compositional formulas of the daughter ions XIII, XV, and XVI were ascertained by high resolution mass spectrometry. On this basis it was possible to suggest plausible structural formulas for the various ions in Scheme 8.

Schemes 9 and 10 show the fragmentation pathways for the sulfones VIc and VIIc. As for sulfone Xb one finds losses of carbon monoxide (or formyl radical),

sulfur monoxide, and ketene, but no direct loss of an oxygen atom. Again, emissions of unusual, multiatomic fragments are apparent. It is clear that the mass spectra are inconsistent with the presence of two monoxide functions in the parent molecules. Hence, one must have a sulfone structure. As in the case of the dibenzo[*b,d*]-thiophene and phenanthro[4,5-*bcd*]thiophene systems (11b,18), the mass spectra of the sulfoxides and sulfones in systems VI and VII are markedly different.

The mass spectrum of sulfone IV (prepared by hypochlorous acid oxidation of thieno[3,2-*c*]pyridine) closely resembles that of V, published previously (*cf.* Scheme 1, reference 5). In fact, the main difference between the two spectra is that the intensities of all important peaks in IV (except the most abundant one at mass number 138) are lower than those of the corresponding peaks in V.

Sulfone IX results from Diels-Alder condensation of thieno[2,3-*b*]pyridine 1,1-dioxide with *trans,trans*-1,4-diacetoxy-1,3-butadiene. The most abundant ion in its mass spectrum is Ac^+, while the molecular ion has a very low intensity. As expected, there are losses of acetic acid (as well as ketene) and sulfur dioxide. The peak at m/e 217 $(M\text{-}2HOAc)^{\ddagger}$ is assigned the structure of $VIII^{\ddagger}$. Correspondingly, the spectrum shows small peaks at the five mass numbers which are most abundant in the fragmentation scheme of VIII (*vide infra*). Surprisingly, significant peaks occur at mass numbers 170, 171, and 172 (formulas $C_{11}H_{8\text{-}10}NO$).

The spectrum of sulfone VIII shows similarities to that of Xb. It is proposed that the molecular ion rearranges to two isomeric cyclic sulfite ions which variously eject carbon monoxide, sulfur monoxide, cyanate radical, and hydrogen cyanide.

EXPERIMENTAL (19)

Starting Materials.

Unless otherwise noted, samples of substrates used were available from previous studies or were made by reported methods (5-8). Crystalline samples were either analytically pure or had melting ranges ≤ 1.5°; for [1]benzothieno[2,3-*b*]pyridine 9,9-dioxide (VIII) (20), uv max (absolute ethanol): 227 nm (log ε 4.42), 268 (4.24), 275 (4.25), 287 (3.95) shoulder; for VIc, uv max (absolute ethanol): 224 nm (log ε 4.56), 232 (4.58), 278 (4.11), 287 (4.06) shoulder; for Xb, uv max (absolute ethanol) 218 nm (log ε 4.44), 286 (3.96), 294 (3.92) shoulder, 303 (3.83) shoulder.

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

By the general procedure described previously (5) a mixture of 0.93 g. (6.9 mmoles) of thieno[3,2-*c*]pyridine (21) and 25 ml. (6.8 mmoles) of 0.27 *M* sulfuric acid (used instead of hydrochloric acid) was treated with 11.2 ml. (13.4 mmoles) of 1.2 *M* sodium hypochlorite solution. The mixture was stirred for 21 hours and processed as before to give 72 mg. (6%) of brown product, m.p. 168.5-171.5°. Recrystallization from hexane-dichloromethane gave light-brown prisms of IV, m.p. 174-175°; ir (chloroform): 1155, 1320, and 1325 cm^{-1}; pmr (hexadeuterioacetone): (22) δ 7.20 (d, 1, $J_{2,3}$ = 7 Hz, H-2), 7.72 (dd, 1, $J_{3,7}$ = 0.8 Hz, H-3), 7.80 (dm, 1, $J_{6,7}$ = 5 Hz, $J_{4,7}$ = 1 Hz, H-7), 8.88 (broad s, 1, H-4), 8.94 ppm (d, 1, H-6); mass spectrum, m/e (relative abundance): (23) 167 (54) $M^{\ddagger}$, 138 (100) $[M\text{-}\dot{C}HO]^+$, 119 (13) $[M\text{-}SO]^{\ddagger}$, 114* [167 → 138], 110 (26) $C_5H_4NS^+$, 88* [138 → 110], 83 (17), 76 (24), 75 (21), 74 (21), 64 (15), 63 (14), 50 (42), 47 (19).

Anal. Calcd. for $C_7H_5NO_2S$: C, 50.3; H, 3.0; N, 8.4. Found: C, 50.0; H, 2.9; N, 8.5.

6,9-Diacetoxy-5a,6,9,9a-tetrahydro[1]benzothieno[2,3-*b*]pyridine 5,5-Dioxide (IX).

A mixture of 1.67 g. (10 mmoles) of thieno[2,3-*b*]pyridine 1,1-dioxide (5), 1.7 g. (10 mmoles) of *trans,trans*-1,4-diacetoxy-1,3-butadiene (24), and 25 ml. of xylene was refluxed for 48 hours. The cold mixture was poured into 150 ml. of hexane. The resultant precipitate was collected by filtration, washed with hexane, and recrystallized from acetone-acetonitrile to give 867 mg. (26%) of grayish needles, m.p. 191-192.5°. Recrystallization from chloroform-carbon tetrachloride produced white globules, m.p. 189-190.5°; ir (chloroform): 1740 (carbonyl), 1330, and 1160 cm^{-1} (sulfone); pmr (hexadeuteriodimethyl sulfoxide): (25) δ 8.74 (dd, 1, $J_{2,3}$ = 5 Hz, $J_{1,3}$ = 1.5 Hz, H-3), 8.05 (dd, 1, $J_{1,2}$ = 8 Hz, H-1), 7.68 (dd, 1, H-2), 5.7-6.5 (m, 4, H-6 to H-9), 4.43 (pseudopentet, 2, J = 7 Hz, H-5a and H-9a), 2.13 and 1.70 ppm (2 s, 2 methyl groups); pmr (deuteriochloroform plus $Eu(dpm)_3$): (26) δ 8.94 (H-3), 8.52 (H-1), 7.56 (H-2), 6.4-7.2 (H-6 to H-9), 5.12 and 4.71 (2 pseudotriplets, J = 7-8 Hz, H-5a and H-9a), 3.18 and 3.04 ppm (2 methyl groups); mass spectrum, m/e (relative abundance): (23) 337 (3) $M^{\ddagger}$, 295 (17) $[M\text{-}(CH_2{=}C{=}O)]^{\ddagger}$, 235 (14) $[M\text{-}(CH_2{=}C{=}O + HOAc)]^{\ddagger}$, 231 (10), 217 (12) $[M\text{-}2\ HOAc]^{\ddagger}$, 188 (13), 172 (30) $(C_{11}H_{10}NO^+$, HR), 171 (26) $(C_{11}H_9NO^{\ddagger}$, HR), 170 (21) $(C_{11}H_8NO^+$, HR), 168 (17), 146 (11), 143 (14), 142 (14), 45 (10) CHS^+, 43 (100) Ac^+, 39 (10) $C_3H_3^+$.

Anal. Calcd. for $C_{15}H_{15}NO_6S$: C, 53.4; H, 4.5; N, 4.2. Found: C, 53.1; H, 4.5; N, 4.3.

Mass Spectra.

Mass spectra were determined by means of a CEC model 21-110 double-focusing mass spectrometer, operated at 70 eV. Metastable peaks observed are designated by an asterisk. The ion formulas of selected fragments, designated by HR, were determined by high resolution spectrometry. Complete data for the relative abundances of the molecular ions plus all fragments of relative intensities ≥ 10% (unless otherwise designated) above mass number 38 are given herewith, as m/e (relative abundance).

4-Chlorothieno[2,3-*b*]pyridine 7-Oxide (Ib): 187 (37) $M^{\ddagger}$, 186 (11), 185 (100) $M^{\ddagger}$, 171 (11), 169 (29), 156 (12), 134 (24), 132 (11), 130 (24), 122 (69), 95 (58), 94 (16), 93 (26), 75 (16), 74 (15), 69 (17), 63 (22), 62 (12), 61 (11), 50 (12), 45 (30) [See Scheme 1].

4-Nitrothieno[2,3-*b*]pyridine 7-Oxide (Ic): 197 (10), 196 (100) $M^{\ddagger}$, 180 (10), 166 (30), 134 (16), 122 (10), 120 (10), 94 (13), 93 (12), 63 (16), 45 (18) [See Scheme 3].

4-(γ-Dimethylaminopropylamino)thieno[2,3-*b*]pyridine 7-Oxide (Id) (27): 251 (26) $M^{\ddagger}$, 235 (16), 163 (8), 85 (8), 58 (100), 44 (8), 42 (12) [See Scheme 4].

4-(γ-Diethylaminoethylamino)thieno[2,3-*b*] pyridine 7-Oxide (Ie) (28): 265 (4) $M^{\ddagger}$, 249 (1) $[M\text{-}O]^{\ddagger}$, 87 (7) $Et_2NMe^{\ddagger}$, 86 (100) $Et_2NCH_2^+$, 58 (5) $EtNMe^+$.

4-(γ-Diethylaminopropylamino)thieno[2,3-*b*]pyridine 7-Oxide

(If): 279 (24) M^+, 263 (14) $[M\text{-}O]^+$, 163 (10) (*cf.* Scheme 5), 86 (100) $Et_2N{=}CH_2{}^+$, 72 (23) Et_2N^+, 58 (18) $EtNMe^+$.

4-(ε-Hydroxypentylamino)thieno[2,3-*b*]pyridine 7-Oxide (Ig): See Scheme 5.

2,3-Dichlorothieno[2,3-*b*]pyridine 7-Oxide (IIa) (29): 223 (15) M^+, 221 (68) M^+, 219 (100) M^+, 207 (11), 205 (49), 203 (72), 193 (16), 192 (16), 191 (25), 190 (21), 168 (28), 164 (23), 158 (31), 156 (84), 131 (28), 129 (64), 119 (23), 97 (21), 94 (23), 93 (45), 84 (21), 79 (34), 74 (27), 69 (40), 61 (25) [See Scheme 2].

4-(ε-Hydroxypentylamino)thieno[2,3-*b*]pyridine (III): See Scheme 5.

[1]Benzothieno[3,2-*b*]pyridine 5-Oxide (VIb): 202 (13), 201 (100) M^+, 185 (47), 173 (33), 172 (12), 146 (11), 39 (17) [See Scheme 7].

[1]Benzothieno[3,2-*b*]pyridine 5,5-Dioxide (VIc): 218 (13), 217 (100), M^+, 188 (11), 169 (15), 160 (12), 137 (11), 136 (67), 127 (10), 108 (11), 75 (10), 63 (10), 50 (11), 39 (20) [See Scheme 9].

Thieno[3,2-*b*:4,5-*b'*]dipyridine 5-Oxide (VIIb) (27): 203 (13), 202 (100) M^+, 201 (8), 186 (26), 174 (31), 171-172* (202 → 186), 150-151* (202 → 174), 147 (16), 124* (174 → 147), 82 (10), 39 (27) [See Scheme 6];

Thieno[3,2-*b*:4,5-*b'*]dipyridine 5,5-Dioxide (VIIc): 219 (13), 218 (100), M^+, 137 (46), 109 (83) (HR), 76 (11), 50 (14), 39 (19) [See Scheme 10].

[1]Benzothieno[2,3-*b*]pyridine 9,9-Dioxide (VIII): 218 (15), 217 (100) M^+, 188 (12) $[M\text{-}\dot{C}HO]^+$, 185 (13), 169 (38) $[M\text{-}SO]^+$, 162 (33) $[M\text{-}(CO + HCN)]^+$, 161 (19) $[M\text{-}(\dot{C}HO + HCN)]^+$, 147 (47) ($C_9H_7S^+$, HR), 134 (16), 127 (39) $[M\text{-}(SO_2CN)]^+$, 112 (11), 76 (16), 75 (15), 74 (15), 63 (41), 51 (14), 50 (17), 39 (15).

Thieno[2,3-*b*:4,5-*b'*]dipyridine 1,5,5-Trioxide (Xa): 234 (21) M^+, 219 (14), 218 (100), 176 (77), 170 (42), 161 (11), 154 (12), 153 (12), 148 (29), 135 (23), 128 (22), 127 (13), 109 (12), 100 (13), 77 (15), 76 (15), 75 (13), 51 (12), 50 (19), 39 (19) [See Scheme 8].

Thieno[2,3-*b*:4,5-*b'*]dipyridine 5,5-Dioxide (Xb): 219 (11), 218 (100) M^+, 176 (71) (HR), 170 (37), 154 (11), 148 (24), 135 (17) (HR), 128 (16) (HR), 77 (10), 76 (10), 50 (13), 39 (13) [See Scheme 8].

REFERENCES AND NOTES

(1) For Paper XXI see L. H. Klemm and S. Rottschaefer, *J. Heterocyclic Chem.*, **12**, 865 (1975).

(2) For Paper XXII see S. Alunni, S. Clementi and L. H. Klemm, *J. Chem. Soc., Perkin II*, submitted.

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(5) L. H. Klemm and R. E. Merrill, *J. Heterocyclic Chem.*, **9**, 293 (1972).

(6) L. H. Klemm, S. B. Mathur, R. Zell and R. E. Merrill, *ibid.*, **8**, 931 (1971).

(7) L. H. Klemm, I. T. Barnish and R. Zell, *ibid.*, 7, 81 (1970).

(8) L. H. Klemm, R. E. Merrill, F. H. W. Lee and C. E. Klopfenstein, *ibid.*, **11**, 205 (1974).

(9) Unpublished data from this laboratory. See reference 8 for some preliminary results and literature references.

(10) Some parent bicyclic thienopyridine *N*-oxides (*e.g.* Ia) fail to exhibit a molecular ion peak [unpublished observations by Steve K. Nelson of this laboratory].

(11) Q. N. Porter and J. Baldas, "Mass Spectrometry of Heterocyclic Compounds", Wiley-Interscience, New York, N.Y., 1971 (a) pp. 409-410, (b) pp. 273-276.

(12) For a discussion of α-fission in amines see H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, Inc., San Francisco, California, 1967, Chapter 8.

(13) L. H. Klemm, R. E. Merrill and F. H. W. Lee, *J. Heterocyclic Chem.*, **11**, 535 (1974).

(14) T. A. Bryce and J. R. Maxwell, *Chem. Commun.*, 206 (1965).

(15) A. R. Katritzky and J. M. Lagowski, "Chemistry of the Heterocyclic *N*-Oxides", Academic Press, New York, N.Y., 1971, pp. 17-18.

(16) One can, of course, still use ir spectra and color tests to distinguish between *N*-oxides and *S*-oxides (6).

(17) J. Heiss, K. P. Zeller and B. Zeeh, *Tetrahedron*, **24**, 3255 (1968).

(18) L. H. Klemm, D. R. McCoy and D. R. Olson, *J. Heterocyclic Chem.*, 7, 1347 (1970).

(19) Infrared spectra were obtained by means of a Beckman IR-5A or IR-7 spectrometer; pmr spectra, by means of a Varian XL-100-12 spectrometer; and ultraviolet spectra, by means of a Cary model 15 spectrometer.

(20) In reference 5 compound VIII was incorrectly listed as the "5,5-dioxide".

(21) F. Eloy and A. Deryckere, *Bull. Soc. Chim. Belges*, 79, 301 (1970).

(22) Using a reference signal at 2.05 δ for pentadeuterioacetone as a standard.

(23) See paragraph on Mass Spectra (*vide infra*).

(24) R. M. Carlson and R. K. Hill, *Organic Syntheses*, **50**, 24 (1970).

(25) Using a reference signal at 2.50 δ for pentadeuteriodimethyl sulfoxide as a standard [L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd Ed., Pergamon Press, New York, N.Y., 1969, p. 177].

(26) Tris(dipivalomethanato)europium (III).

(27) For all peaks of relative abundance ≥ 8%.

(28) For all peaks of relative abundance ≥ 4%, plus the peak at (M-16).

(29) For all peaks of relative abundance > 10% and mass number > 168, and of relative abundance > 20% and mass number > 38.