Chemistry of Thienopyridines. XII. Selective Formation of *N*-Oxides, Sulfoxides, and Sulfones in Some Tricyclic Systems (1)

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Direct conversion of [1]benzothieno[3,2-*b*]pyridine (IVa), thieno[3,2-*b*:4,5-*b'*]dipyridine (Va), and thieno[2,3-*b*:4,5-*b'*]dipyridine (VIa) into their sulfoxides was effected by means of an equimolar quantity of iodobenzene dichloride in aqueous acetonitrile. Treatment of IVa-VIa with excess chlorine gas in carbon tetrachloride and then with water gave the corresponding sulfones, IVc-VIc. Hydrogen peroxide in glacial acetic acid converted Va and VIa into di-*N*-oxides, thieno[3,2-*b*]pyridine into its *N*-oxide, and sulfone VIc into an *N*-oxide sulfone (X). Spectral and chemical means of distinguishing amongst the oxide functions are noted, and rationalizations for selectivity in the oxidations are discussed.

Direct conversions of aromatic azines to *N*-oxides and of condensed thiophenes to sulfoxides and sulfones are well known. The presence of both aromatic nitrogen and sulfur atoms in thienopyridines and their polycyclic aromatic homologs poses the problem of effecting such direct oxidations selectively at the two different types of hetero atoms. We have been investigating possible methodology for accomplishing this goal. In an earlier study (5) thieno[2,3-*b*]pyridine (I) was converted into its *N*-oxide by means of 30% hydrogen peroxide in glacial acetic acid at 55°. Likewise, substituted (by means of one or two methyl groups α to the nitrogen atom) thieno[2,3-*c*]- and thieno[3,2-*c*]pyridines gave *N*-oxides when treated with monoperphthalic acid in glacial acetic acid-methanol (6). There are several examples of preferential *S*-oxidation by means of monoperphthalic acid (7), *m*-chloroperbenzoic acid (8,9), and iodobenzene dichloride-water (10) in hydrothienopyridine systems bearing a dihydrothiophene ring and an aromatic pyridine ring. In fact, aqueous pyridine is the recommended solvent in the oxidation of sulfides to sulfoxides by means of iodobenzene dichloride (IBDC) (11). Preliminary study (5) on the conversion of I into 2,3-dichloro-2,3-dihydrothieno[2,3-*b*]pyridine 1-oxide (III) by means of chlorine in chloroform-water has also been described (12). We now report methodology for the direct *S*-oxidation of IVa-VIa to sulfoxides (IVb-VIb) and sulfones (IVc-VIc), as well as extension of the hydrogen peroxide-acetic acid method to *N*-oxidation of II, Va, VIa, and the sulfone VIc.

Treatment of a solution of IVa-VIa in aqueous acetonitrile with an equimolar quantity of IBDC at room temperature gave the crystalline 5-oxides (IVb-VIb) in yields of 17-25% (for analytically pure products). Use of IBDC as a convenient, weighable source of chlorine for the conversion of sulfides into sulfoxides was developed by Italian workers (11), who proposed that a three-step process (Scheme 1) is involved (13). Treatment of I with

SCHEME 1

$$C_6H_5ICl_2 \rightarrow C_6H_5I + Cl_2$$

$$-\overset{|}{S} + Cl_2 \rightleftharpoons -\overset{|}{S}\cdot Cl_2$$

$$-\overset{|}{S}\cdot Cl_2 + H_2O \rightleftharpoons -\overset{|}{S}{=}O + 2HCl$$

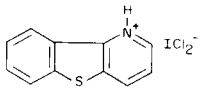
IBDC-water gave a very small yield (< 3%) of III, probably by addition of two moles of chlorine (one to the 2,3-double bond and the other to the sulfur atom) followed by step 3 of the Scheme.

Steps 2 and 3 of Scheme 1 are the basis of a reported procedure (14) for the conversion of dibenzothiophene

into dibenzothiophene 5-oxide. A crucial point in this synthesis is the addition of an *equimolar* quantity of dry chlorine gas to a solution of the substrate in carbon tetrachloride at 0°. We found that introduction of *excess* chlorine leads (on hydrolysis with ice-water) to dibenzothiophene 5,5-dioxide, instead of (or in addition to) the 5-oxide. Analogously, action of excess chlorine on IVa-VIa in the same manner gave crystalline sulfones (IVc-VIc) in 24-41% yields. In view of the fact that only 1:1 complexes have been clearly identified from treatment of solutions of organic sulfides in nonpolar solvents with varying (including excess) amounts of chlorine (15) we propose that steps 2 and 3 of Scheme I also apply to sulfone formation. Addition of water to the carbon tetrachloride solution gives the sulfoxide, as an intermediate, which is then converted (through action of the excess chlorine previously added) to the sulfone according to the equation.

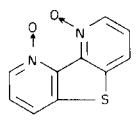
$$\text{-}\overset{|}{S}\text{=O} + Cl_2 + H_2O \rightarrow \text{-}\overset{|}{S}O_2 + 2HCl$$

Oxidation of sulfoxides to sulfones by means of chlorine-water or chlorine-methanol (16) have been reported previously. In fact, treatment of sulfoxide IVb with a limited excess of IBDC in aqueous acetonitrile (reaction time 24 hours) also gave sulfone IVc, albeit by a synthetically less desirable route. On the other hand, treatment of IVa with a large excess of IBDC in the preceding manner gave neither a sulfoxide nor a sulfone. Instead, a yellow, stable solid, $C_{11}H_8Cl_2NIS$, *i.e.* IVa·$HICl_2$, assigned the structure of the salt VII, was formed. Although other azinium iododichlorides have been described (17,18) none of these has been obtained by use of IBDC.

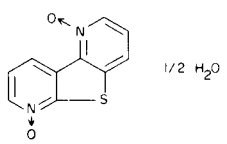


VII

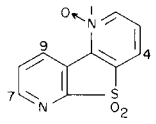
Extension of the hydrogen peroxide-glacial acetic acid method for *N*-oxidation to substrates other than I was also made. Thus, thieno[3,2-*b*]pyridine (II) gave the 4-oxide (isolated as the crystalline monohydrate), Va gave the 1,9-dioxide (VIII), and VIa formed the 1,6-dioxide (isolated as the hemihydrate, IX). Of particular interest, sulfone VIc was converted to an *N*-oxide sulfone, to which structure X (rather than the alternative XI) is assigned (*vide infra*). Compound X may well be the first reported



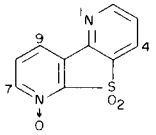
VIII



IX



X



XI

example of a substance which contains both pyridine *N*-oxide and thiophene *S,S*-dioxide functions in the same molecule. Yields on these *N*-oxidations were 22-32%.

Elemental analyses of the products formed give definitive information on the total number of oxygen atoms present (including those which are involved in water of hydration). In general, however, one needs other means to distinguish amongst *N*-oxide, sulfoxide, and sulfone groups *per se*. In this study, both infrared spectral characteristics and confirmatory chemical color tests were used to ascertain the nature of the oxide group(s) present (see Table I) (25). As expected, the unsymmetrical di-*N*-oxide IX showed two moderately strong bands in the N → O stretching region, while the symmetrical di-*N*-oxide VIII exhibited only one band (at 1265 cm^{-1}) in this region. Compound VIII did, however, also have a

TABLE I

Structural Identification of Oxide Functions

Functional Group	Infrared Absorption Band(s), cm^{-1} (a)	Color Test
N-Oxide	1210-1265	Katritzky (b)
Sulfoxide	1040-1050	sulfoxide (c)
Sulfone	1300-1330 (asym.) 1165-1170 (sym.)	none (d)

(a) In chloroform solvent (19). (b) Boiling with hydrochloric acid and dimethylaniline → blue or violet color (20). (c) Treatment with potassium iodide, hydrochloric acid, and acetic acid → brown color; per the reaction $\text{-}\overset{|}{S}\text{=O} + 2HI \rightarrow \text{-}\overset{|}{S} + H_2O + I_2$ (21). On a preparative scale VIb was also reduced to VIa by this method (22). (d) Feigl (23) proposed a color test for sulfones based on thermal elimination of sulfur dioxide. Since sulfoxides may disproportionate to sulfides and sulfones or be oxidized by *N*-oxides (24), this test seemed of no diagnostic value in the present study.

strong sharp absorption band at 945 cm^{-1}, while none of its congeners Va, Vb, or Vc showed appreciable absorption in this region. Perhaps the 945 band results from the close proximity of the N → O functions in VIII.

In Table II are presented pmr spectra for VIa (see also ref. 26) and three of its oxidation products. In general, the spectra consist of two overlapping sets of signals for the α (H-2, H-7), γ (H-4, H-9), and β (H-3, H-8) protons

TABLE II

PMR Data for Thieno[2,3-*b*:4,5-*b*']dipyridine and Its Oxides

Compound	Solvent	Chemical Shift, in δ						Coupling Constant, in Hz		
		H-2	H-3	H-4	H-7	H-8	H-9	$J_{2,3}$ $J_{7,8}$	$J_{3,4}$ $J_{8,9}$	$J_{2,4}$ $J_{7,9}$
VIa	$CDCl_3$	m (a)	7.51	8.22	m	7.43	m	5	8	1.4
VIb	$CDCl_3$	8.71	7.49	8.46	8.71	7.62	8.36	5	8	1.6
VIc	$CDCl_3$	8.88	7.55	8.52	8.85	7.69	8.22	4.8-5	8	1.5-1.8
VIc	DMSO-d_6	8.94	7.74	8.61	8.86	7.89	8.56	4.5-5	8-9	1.5
X	DMSO-d_6	8.90	m* (b)	8.61	m*	m*	9.30	*ca.* 5	7.5-8	1.5

(a) m = multiplet at 8.6-8.9 ppm. (b) m* = multiplet at 7.6-8.2 ppm.

(listed in general order as one moves toward higher field). Values of the coupling constants permit assignment of individual signals to the three pairs, but do not allow clear distinction within the pairs. Generally, as one increases the degree of oxidation of the substrate (in the order VIa → VIb → VIc → X) there is a small (usually positive) change in chemical shift for each signal. A marked difference is noted, however, in the effects on H-4 and H-9 in going from the sulfone to the *N*-oxide sulfone (in hexadeuteriodimethyl sulfoxide). One signal does not move, while the other is shifted *ca.* +0.7 ppm. This observation is consistent with the structural assignment of X (but not of XI) to the *N*-oxide sulfone. If structure XI were correct, one would expect to find little change in signals for H-2 and H-4, but shifts to *higher* field (if any) in signals for both H-7 and H-9. For structure X, on the other hand, the spatial proximity of the oxygen atom to H-9 should cause the large downfield shift observed (*cf.* $\Delta\delta$ = +0.7 for H-8 in quinoline on *N*-oxidation) (27), with little or no accompanying change for H-2, H-4 and H-7.

Both organic sulfides and tertiary amines form crystalline, isolable addition compounds with halogens by complexation through a non-bonding electron pair on the hetero-atom (15,28-30). Sulfide-chlorine complexes (including ones where the sulfur atom is present in a thiophene ring) hydrolyze readily (Scheme I) to give hydrogen chloride and *S*-oxides (31). In fact, such complexes apparently have a transitory existence even in the presence of an aqueous phase (29). The pyridine-chlorine complex (as an example) is unstable and decomposes rapidly in moist air to regenerate the components (30). When water is present, complexation of chlorine at an azine nitrogen atom probably does not even occur. It is the difference in the effects of water on azine and thiole complexes with chlorine which allow one to accomplish preferential *S*-oxidation in the condensed thienopyridines.

The reported orders (32,33) of relative susceptibility to mono-oxidation of functional groups by 30% hydrogen peroxide-glacial acetic acid can now be extended and combined to give: tertiary amine ≥ organic sulphide > azine nitrogen > thiole sulfur > ethylenic bond > arenic bond. These oxidations involve nucleophilic attack by an electron pair (non-bonding for the hetero-atom) of the substrate molecule onto an oxygen atom of the peroxide (33,34). Thus, the order of susceptibility may also be considered an order of nucleophilicity in the peroxide reaction. As expected, incorporation of a nitrogen, sulfur, or carbon atom into an aromatic ring decreases the nucleophilicity of the atom through electron delocalization. For the nitrogen compounds, nucleophilicity toward *N*-oxidation should closely parallel inherent basicity at the nitrogen atom (35), unaltered by appreciable steric effects. Thus, conversion of VIc to X (rather than XI) may be rationalized in terms of the relative electronic effects of the sulfonyl group on the basicities of the nitrogen atoms at positions 1 (*i.e. meta* to the sulfonyl) and 6 (*ortho* to the sulfonyl). It might be noted that selective *N*-oxidation of thienopyridines I and II is not predicted by calculated quantum chemical reactivity indices for π-electron density or superdelocalizability toward electrophilic attack (26,36).

EXPERIMENTAL (37)

Starting Materials.

Thienopyridines I and II (36,38), and tricyclic parent compounds IVa-VIa (26,39) were available from previous studies. Iodobenzene dichloride (IBDC) was prepared by a reported method (40) and stored in a brown bottle under refrigeration.

Preparation of Sulfoxides (IVb-VIb).

To a stirred solution of 3 mmoles of tricyclic compound IVa-VIa in 15-20 ml. of acetonitrile-water (2:1 by vol.) was added (over a period of 15 minutes) a solution of 3 mmoles of iodobenzene dichloride in 15 ml. of acetonitrile. The mixture was stirred 30 minutes longer and extracted with chloroform. Evaporation of the washed (with water), dried extract gave a white or cream-colored residue, which was recrystallized from acetonitrile to analytical purity.

Compound IVa gave [1]benzothieno[3,2-*b*]pyridine 5-oxide (IVb) as needles (17%), m.p. 135-136°; ir 1040 cm^{-1}; pmr (deuteriochloroform) δ 8.74 (broad d, 1, $J_{2,3}$ = 5 Hz, H-2), 7.1-8.5 ppm (m, 6, other protons); greenish brown color in the Katritzky test.

Anal. Calcd. for $C_{11}H_7NOS$: C, 65.7; H, 3.5; N, 7.0; S, 15.9. Found: C, 65.7; H, 3.7; N, 7.0; S, 16.0.

Compound Va gave thieno[3,2-*b*:4,5-*b'*]dipyridine 5-oxide (Vb) as faintly tan plates (25%), m.p. 235-236°; ir 1045 cm^{-1}.

Anal. Calcd. for $C_{10}H_6N_2OS$: C, 59.4; H, 3.0; N, 13.9; S, 15.9. Found: C, 59.1; H, 3.2; N, 13.7; S, 15.9.

Compound VIa gave thieno[2,3-*b*:4,5-*b'*]dipyridine 5-oxide (VIb) as needles (19%), m.p. 175-176°; ir 1050 cm^{-1}; pmr, see Table II.

Anal. Calcd. for $C_{10}H_6N_2OS$: *vide supra.* Found: C, 59.6; H, 3.1; N, 13.9; S, 16.0.

Reduction of VIb to VIa.

A mixture of 1 g. of sulfoxide VIb, 3.3 g. of potassium iodide, 4 ml. of glacial acetic acid, and 1.8 ml. of concentrated hydrochloric acid was heated at 100° for 6 hours. The cooled solution was treated with water and sodium sulfite (to remove iodine color), basified with potassium hydroxide, and extracted with ether. Evaporation of the washed (with water), dried extract gave 0.62 g. (67%) of VIa, identified by direct comparison with an authentic sample.

Preparation of Sulfones (IVc-VIc).

Into a solution of 0.15-0.35 g. of tricyclic compound IVa-VIa in 25 ml. of carbon tetrachloride at 0° was bubbled dry chlorine gas for 30-60 minutes. The solution was then stirred vigorously with 50-100 ml. of ice-cold water for 30 minutes. Filtration of the mixture gave the solid sulfone, which was washed with water, dried in air, and recrystallized from acetonitrile to analytical purity.

Compound IVa gave [1]benzothieno[3,2-*b*]pyridine 5,5-dioxide (IVc) as needles (24%), m.p. 229-230°; ir 1170 and 1315 cm^{-1}; negative sulfoxide test; pmr (deuteriochloroform) δ 8.94 (d of d, 1, $J_{2,3}$ = 5 Hz, $J_{2,4}$ = 1.5 Hz, H-2), 8.53 (d of d, 1, $J_{3,4}$ = 7.5 Hz, H-4), 7.6-8.3 ppm (m, 5, other protons).

Anal. Calcd. for $C_{11}H_7NO_2S$: C, 60.8; H, 3.3; N, 6.5; S, 14.8. Found: C, 61.0; H, 3.6; N, 6.2; S, 14.8.

Compound Va gave thieno[3,2-*b*:4,5-*b'*]dipyridine 5,5-dioxide (Vc) as needles (30%), m.p. 287-288°; ir 1165 and 1300 cm^{-1}; pmr (deuteriochloroform) δ 8.9-9.4 (m, 2, H-2 and H-8), 8.28 (d of d, 2, $J_{2,4} = J_{6,8}$ = 1.2 Hz, $J_{3,4} = J_{6,7}$ = 8 Hz, H-4 and H-6), 7.64 ppm (d of d, 2, $J_{2,3} = J_{7,8}$ = 5 Hz, H-3 and H-7).

Anal. Calcd. for $C_{10}H_6N_2O_2S$: C, 55.0; H, 2.8; N, 12.8; S, 14.7. Found: C, 55.2; H, 2.7; N, 12.8; S, 14.6.

Compound VIa gave thieno[2,3-*b*:4,5-*b'*]dipyridine 5,5-dioxide (VIc) as fine needles (41%), m.p. 222-223°; ir 1165 and 1330 cm^{-1}; negative sulfoxide test (light yellow color); pmr, see Table II.

Anal. Calcd. for $C_{10}H_6N_2O_2S$: *vide supra.* Found: C, 55.1; H, 2.8; N, 12.8; S, 14.3.

Thieno[3,2-*b*]pyridine 4-Oxide Monohydrate.

A mixture of 0.15 mole of II, 32 ml. of 30% hydrogen peroxide, and 32 ml. of glacial acetic acid was converted to the *N*-oxide in the manner used with I (5,41). Crystallization from aqueous acetone-cyclohexane gave 8.2 g. (32%) of product, m.p. 79-83°, changed to 79-80° on distillation at 180° (0.3 mm) plus further recrystallization (obtained as faintly tan needles); ir 1260 cm^{-1}.

Anal. Calcd. for $C_7H_7NO_2S$: C, 49.7; H, 4.2; N, 8.3; S, 19.0. Found: C, 49.8; H, 3.9; N, 8.3; S, 18.9.

Thieno[2,3-*b*:4,5-*b'*]dipyridine 1,6-Dioxide Hemihydrate (IX).

A mixture of 0.33 g. of VIa, 1.2 ml. of glacial acetic acid, and 0.4 ml. of 30% hydrogen peroxide was heated at 65-70° for 24 hours. Two or three times, water (2-5 ml.) was added and the mixture was evaporated *in vacuo* (41). The residue was neutralized with saturated, aqueous sodium bicarbonate and extracted with chloroform. Evaporation of the washed (with water), dried extract and recrystallization of the residue from chloroform-cyclohexane gave fine, yellow needles (92 mg., 22%), m.p. 224-225°; positive Katritzky test; ir 1210 and 1250 cm^{-1} (two nonequivalent N → O groups).

Anal. Calcd. for $C_{10}H_6N_2O_2S \cdot \frac{1}{2}H_2O$: C, 52.9; H, 3.1; N, 12.3; S, 14.1; molecular weight, 227. Found: C, 52.7; H, 2.6; N, 12.4; S, 14.1; molecular weight (ebullioscopic, in benzene at 37°) 230.

Thieno[3,2-*b*:4,5-*b'*]dipyridine 1,9-Dioxide (VIII).

In the manner used to synthesize IX (except that the reaction temperature was 50-55°), Va was oxidized to VIII, obtained as yellow-brown prisms from chloroform (28%), m.p. 203-204° dec.; ir (chloroform) 945 and 1265 cm^{-1}; ir (nujol) 945 and 1280 cm^{-1}; positive Katritzky test, negative sulfoxide test.

Anal. Calcd. for $C_{10}H_6N_2O_2S$: C, 55.0; H, 2.8; N, 12.8; S, 14.7. Found: C, 54.9; H, 2.9; N, 13.0; S, 14.6.

Thieno[2,3-*b*:4,5-*b'*]dipyridine 1,5,5-Trioxide (X).

A mixture of 0.26 g. of sulfone VIc, 0.6 ml. of glacial acetic acid, and 0.1 ml. of 30% hydrogen peroxide was heated at 60-65° for 24 hours and processed further as in the preparation of IX. Crystallization of the product from acetonitrile gave yellow rosettes (80 mg., 30%) of X, m.p. 274-275°; ir 1165, 1220, and 1325 cm^{-1}; positive Katritzky test (light violet color), negative sulfoxide test; pmr, see Table II.

Anal. Calcd. for $C_{10}H_6N_2O_3S$: C, 51.3; H, 2.6; N, 12.0; S, 13.7. Found: C, 51.2; H, 2.3; N, 12.1; S, 13.9.

[1]Benzothieno[3,2-*b*]pyridinium Iododichloride (VII).

To a stirred solution of 1.8 g. (0.01 mole) of IVa in 60 ml. of acetonitrile-water (2:1) was added (over a period of 30 minutes) a solution of 15.5 g. (0.056 mole) of IBDC in 100 ml. of acetonitrile. Stirring was continued for 24 hours and the mixture was extracted with chloroform. Evaporation of the extract gave a solid which was crystallized from chloroform and sublimed at 60° (0.15 mm.) to give VII as yellow crystals (1.2 g., 31%), m.p. 174-175°; positive tests for iodine and chlorine after sodium fusion; forms iodine vapors on combustion; pmr (hexadeuteriodimethyl sulfoxide) aromatic protons only.

Anal. Calcd. for $C_{11}H_8Cl_2INS$: C, 34.4; H, 2.1; Cl, 18.5; N, 3.7; S, 8.4. Found: C, 34.6; H, 2.2; Cl, 18.8; N, 3.6; S, 8.5.

After standing on the shelf for three years the remainder of the preceding sample had partially decomposed, as evidenced by the following data. Only part of the sample melted (sharply) at 174-175°. The ultraviolet spectrum in 95% ethanol was nearly identical with that of the parent compound IVa (42). The mass spectrum (70 eV, 100°), on the other hand, showed the presence of the IVa moiety [m/e 185 (IVa parent ion, most abundant) and 92.5 (IVa^{++})], iodine (127 and 254), chlorine (35 and 37, in ratio of 3:1), hydrogen chloride (36 and 38, same ratio), and iodine chloride (162 and 164, ratio of 2.8:1).

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(42) Enhanced absorption at 227 nm due to the presence of the iododichloride ion was not apparent (ref. 18). However, both IVa and its protonated ion absorb strongly in this region.