

## Mass Spectral Fragmentation Pattern of 2,3-dihydrothieno[2,3-b] Quinoline-S-Oxide and its Benzo(h) Derivative upon Electron Impact

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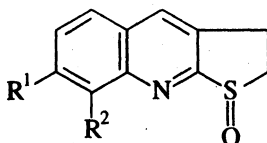
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A mass spectral study of 2,3-dihydrothieno(2,3-b)quinoline-S-oxide and its benzo(h) derivative is reported. In the spectra, the molecular ion which appears as the base peak fragments by the loss of CH<sub>3</sub>, O, OH, H<sub>2</sub>O, CO, CHO, SH, CHS, SO and SOH species. Rearrangement of molecular ion to a cyclic sulphenate structure which initiates the loss of CO, CHO, SH and CHS was suggested. A highly abundant peak appears at M-74 and it is accounted.

**Key Words:** Mass spectral fragmentation, 2,3-Dihydrothieno-[2,3-b] quinoline-S-oxide, Benzo(h) derivative, Electron impact.

### INTRODUCTION

We have recently reported<sup>1</sup> an improved synthesis of thieno[2,3-b]quinolines starting from 3-(2'-hydroxy-ethyl)quinolin-2(1H)ones<sup>2</sup> via 2,3-dihydrothieno(2,3-b)quinoline-S-oxides (1). In this paper, we wish to present the outcome of our study on the mass spectral fragmentation of 2,3-dihydrothieno (2,3-b)quinoline-S-oxide (1a) and its benzo(h) derivative (1b).



1a

1b

R <sub>1</sub>	R <sub>2</sub>
H	H
—CH=CH—CH=CH—	

### RESULTS AND DISCUSSION

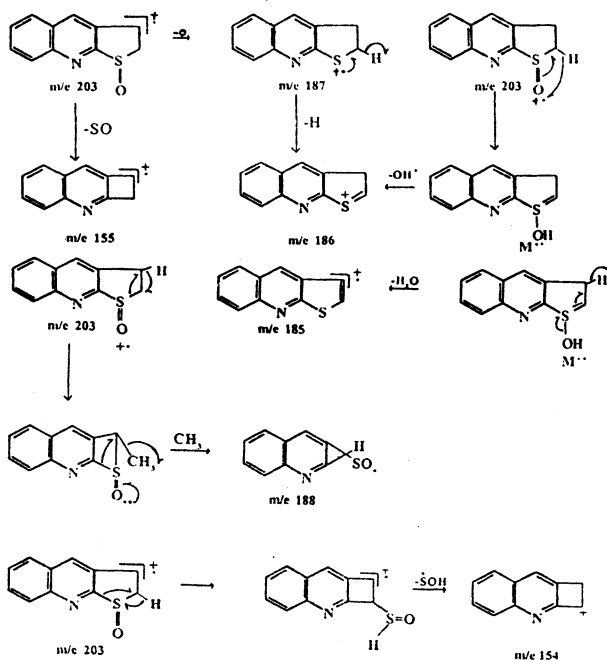
Mass spectra of the compounds 1a and 1b are reported in Tables 1 and 2. Structures written for the fragment ions are nominal only, but are intended to relate the fragmentation processes to the structure of the intact molecule (Schemes 1-3).

TABLE-1

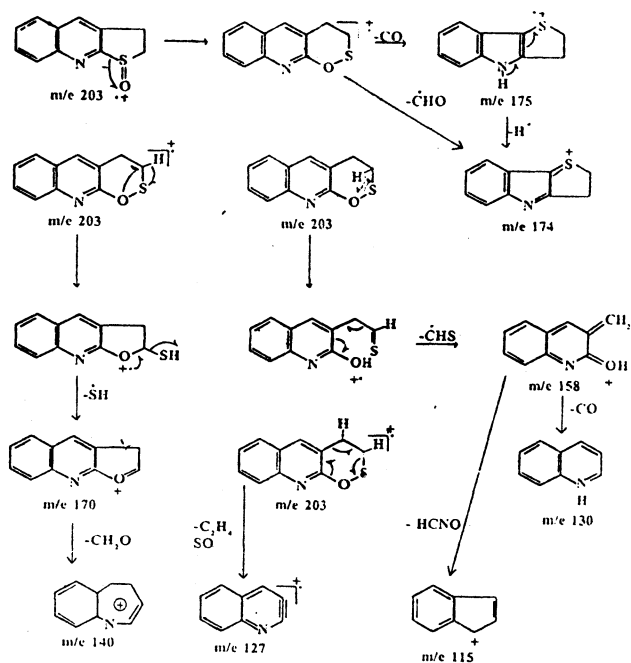
(PRINCIPAL FRAGMENTS M/Z (REL.INT%))

**Mass spectrum of 1a:** 205(5), 204(13), 203(100), 202(7), 188(12), 187(43), 186(87), 185(8), 184(3), 175(4), 174(6), 170(14), 160(4), 159(4), 158(15), 155(9), 154(30), 153(6), 152(6), 143(4), 142(8), 141(7), 140(17), 130(15), 129(78), 128(20), 127(22), 126(7), 125(4), 117(4), 116(6), 115(17), 114(11), 113(8); 103(5), 102(13), 101(12), 100(4), 99(3), 93(3), 90(3), 89(8), 88(6), 87(6), 79(3), 78(4), 75(15), 76(9), 75(22), 74(7), 69(4), 65(3), 64(10), 63(17), 62(6).

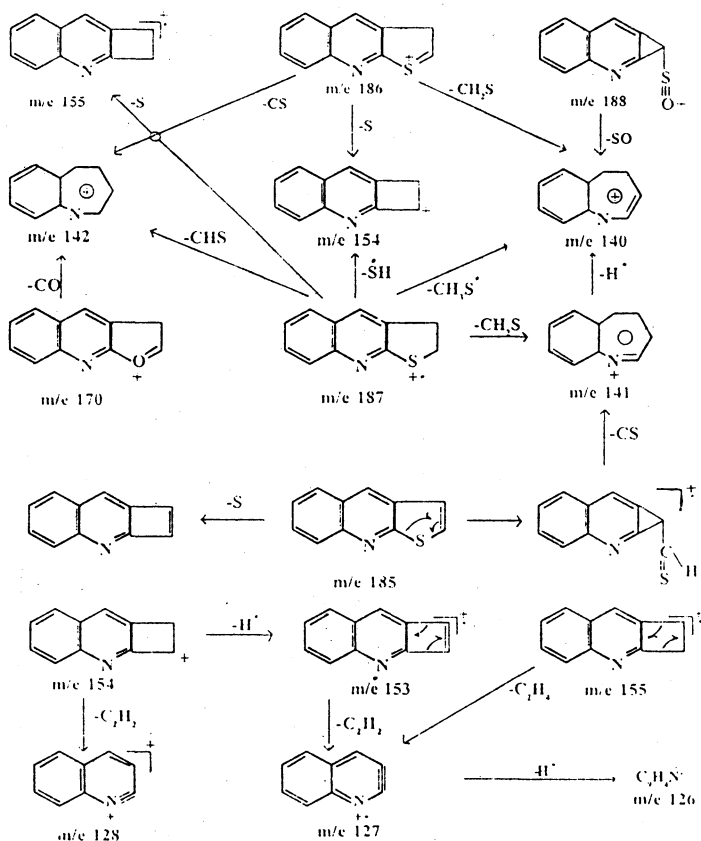
**Mass spectrum of 1b:** 255(8), 254(24), 253(100), 252(3), 238(9), 237(31), 236(50), 235(10), 234(3), 225(9), 224(9), 220(6), 211(4), 210(3), 209(3), 208(5), 205(5), 204(14), 203(9), 202(4), 201(3), 197(11), 196(3), 193(12), 192(6), 191(7), 190(13), 180(13), 179(56), 178(15), 177(10), 176(11), 175(4), 171(3), 167(3), 166(4), 165(7), 164(7), 163(9), 153(5), 152(8), 151(12), 150(7), 140(5), 139(8), 127(5), 126(4), 118(8), 117(4), 105(4), 104(3), 102(5), 101(3).



Scheme-1



Scheme-2



Scheme-3

**Mass spectrum of 2,3-dihydrothieno(2,3-b)quinoline-S-oxide (1a):** The formations of  $(M-1)^+$  and  $M^{++}$  ions are noted in 1a. The formations of the ions corresponding to (M-16), (M-17), (M-33), (M-45), (M-48) and (M-49) suggest the loss of O,  $\text{OH}^\bullet$ ,  $\text{SH}^\bullet$ ,  $\text{CHS}^\bullet$ , SO and SOH respectively from the molecular ion (Schemes I and II) as expected of a cyclic sulfoxide<sup>3,4</sup>. A rearrangement of molecular ion to a cyclic sulfenate structures<sup>5,6</sup> followed by its disintegration could be assumed to account for the ions corresponding to (M-CO), (M-CHO), (M-SH) and (M-CHS).

The compound 1b undergoes fragmentation in a pattern very similar to the parent sulfoxide 1a. The list of transitions which are supported by meta-stable peaks in the mass spectrum of this compound is given in Table-2. A comparative account of relative abundance of characteristic peaks in the mass spectra of 1a and 1b is given in Table-3.

**Mechanism of formation of (M-74) peaks:** It is of interest to note that the M-74 peaks in the mass spectra of both 1a and 1b appear with high abundance, *viz.*, 78% and 56% respectively. The formation of M-74 ion may be suggested as initiated by the rearrangement of  $M^{++}$  to the intermediate 2 followed by the elimination of  $\text{C}_2\text{H}_2$  and SO. Such types of rearrangement during thermolysis in sulfoxide<sup>7</sup> and selenoxide<sup>8</sup> have been recorded in the literature. The formation of

(M-74)<sup>+</sup> directly from the molecular ion is evidenced by the appearance of the metastable ion (M\*) in the spectrum of 1b at m/e 126.5 (Table-3) which corresponds to the transition m/z 253 → 179.

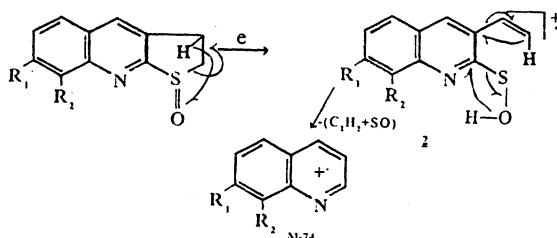


TABLE-2

LIST OF TRANSITIONS SUPPORTED BY METASTABLE PEAKS IN THE MASS SPECTRUM OF 1b

Initial ion	Fragment expelled	Transition	M*	
			Found	Calculated
M <sup>++</sup>	CH <sub>3</sub> <sup>+</sup>	253-238	224.0	224.0
M <sup>++</sup>	OH <sup>+</sup>	253-236	220.5	220.2
M <sup>++</sup>	CO	253-225	200.1	200.1
M <sup>++</sup>	SH	253-220	191.3	191.3
M <sup>++</sup>	SOH	253-204	164.0	164.4
M <sup>++</sup>	C <sub>2</sub> H <sub>2</sub> + SO	253-179	126.5	126.8
(M-O) <sup>++</sup>	H	237-236	235.1	235.1
(M-O) <sup>++</sup>	S	237-205	177.4	177.4
(M-O) <sup>++</sup>	SH	237-204	175.5	175.6
(M-OH) <sup>++</sup>	H	236-235	234.1	234.1
(M-OH) <sup>++</sup>	S	236-204	176.1	176.1
(M-H <sub>2</sub> O) <sup>++</sup>	S	235-203	175.3	175.3
(M-CO) <sup>++</sup>	H	225-224	223.2	222.9
(M-SH) <sup>++</sup>	CH <sub>2</sub> O	220-190	162.0	161.9
(M-SOH) <sup>++</sup>	H	204-203	202.0	202.0
(M-O-CH <sub>2</sub> S) <sup>++</sup>	H	191-190	189.0	189.0
(M-C <sub>2</sub> H <sub>2</sub> SO) <sup>++</sup>	H	179-178	177.0	177.0
(M-C <sub>2</sub> H <sub>4</sub> -SO) <sup>++</sup>	H	177-176	175.0	175.0
(M-O-CS-HCN) <sup>++</sup>	H	166-165	164.0	164.0
(M-O-CS-HCN) <sup>++</sup>	C <sub>2</sub> H <sub>2</sub>	166-140	117.5	118.0
(M-CHS-HCN) <sup>++</sup>	C <sub>2</sub> H <sub>2</sub>	165-139	117.0	117.0
(M-C <sub>2</sub> H <sub>2</sub> -SO-HCN) <sup>++</sup>	H	152-151	150.0	150.1

TABLE-3  
COMPARATIVE ACCOUNT OF THE CHARACTERISTIC PEAKS IN THE MASS  
SPECTRA OF **1a** AND **1b**

Compound	Peaks/Relative abundance (%)						
	M <sup>+</sup> *	M-1	M-15	M-16	M-17	M-18	M-28
<b>1a</b>	100	7	12	43	87	8	4
<b>1b</b>	100	3	9	31	50	10	9

Compound	Peaks/Relative abundance (%)						
	M-29	M-33	M-45	M-48	M-49	M-74	M-76
<b>1a</b>	6	14	50	9	30	78	22
<b>1b</b>	9	6	5	5	14	56	10

### EXPERIMENTAL

The spectra were determined by direct insertion of the sample into the ion source of an Hitachi-Perkin-Elmer RMU-6E mass spectrometer. The energy of the electron beam was 70 eV. The compounds used in the study were of analytical purity and both of them have been reported previously<sup>1</sup>. The compounds **1a** and **1b** were obtained by the S-oxidation of the corresponding 2,3-dihydrothieno (2,3-b) quinoline<sup>1</sup> with NaIO<sub>4</sub>/ethanol.

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