*Tetrahedron* Vol. 24, pp 6237 to 6258. Pergamon Press 1968 Printed in Great Britain

# STUDIES ON ISOTHIAZOLES—V

## MASS SPECTRA OF 3-PHENYLISOTHIAZOLES

T. NAITO

Bristol-Banyu Research Institute Ltd., Meguro, Tokyo

(*Received in Japan* 26 *April* 1968; *Received in the UK for publication* 27 *May* 1968)

**Abstract**—The mass spectra of twenty-four 3-phenylisothiazoles and three 3-(halophenyl)isothiazoles are reported and discussed. Their common features are the prominent molecular ions and the diagnostic fragment ions arising from cleavages of the N—S or S—C(5) bonds, eliminations of the side chains and fragments from the phenyl ring. The production of M-1 ions is not common in the 5-Me derivatives in contrast with the reported cases of methyl-thiophenes, furans and pyrroles. Several characteristic fragmentation patterns are noted depending upon the nature of substituents at the 4-position: (1) 4-acetoxy-isothiazoles preferentially decompose to give molecular ions of 4-hydroxy derivatives, (2) 4-nonsubstituted and 4-cyano-isothiazoles, though not all, produce the M minus S or M minus SH ions, (3) rearrangements of 4-bromo and 4-cyano groups take place to the phenyl-containing fragment ions, (4) the hydrogen of 4-hydroxy derivatives and the Me group of 4-MeO derivatives migrate to the phenyl containing ions, (5) migration of a hydrogen from the 3-phenyl ring takes place in 4-cyano and 4-hydroxyisothiazoles and (6) methyl esters of 4-carboxylic acids produce M-15 ions regardless of the presence of an adjacent Me group at the 5-position.

MASS spectra of mononuclear 5-membered aromatic heterocycles have been discussed by several workers on thiophenes,[1] furans,[2] thiazoles,[3] oxazoles,[4] isoxazoles,[5] 1,2,4-,[6] 1,2,5-,[7] and 1,3,4-oxadiazoles,[6,8] pyrroles,[9,10] pyrazoles,[10,11] imidazoles[10] and 1,2,4-triazoles,[10] But studies on isothiazoles have not been published.

In connection with another program,[12] we have prepared various 3-phenylisothiazoles by several routes.[13–16] Since the 3-phenylisothiazoles prepared in this laboratory were mostly new compounds and some of them prepared by new cyclization procedures to the isothiazoles ring,[15,16] studies were undertaken to determine whether the mass spectra could be a useful tool for confirmation or identification of 3-phenylisothiazoles structures in the resulting product.

The mass spectra of twenty-four 3-phenylisothiazoles (I–VIII) and three 3-halophenylisothiazoles (IX) listed in Table 1 are shown in Figs 1–11 and in Table 2. The composition of some fragment ions discussed in this paper have been determined by exact mass measurements and are summarized in Table 3. A transition indicated by an asterisk (either in the Figs or the text) is supported by the presence of an appropriate metastable peak. Structures written for fragment ions are only nominal, but are intended to relate the fragmentation process to the structure of the intact molecule.

The common features of the spectra of 3-phenylisothiazoles except for the 4-actoxy derivatives (VII) are that the molecular ion is prominent and the major fragment ions arise from fissions at i to v shown in Scheme 1 or in somewhat modified ways with elimination and rearrangement of the substituents.

SCHEME 1

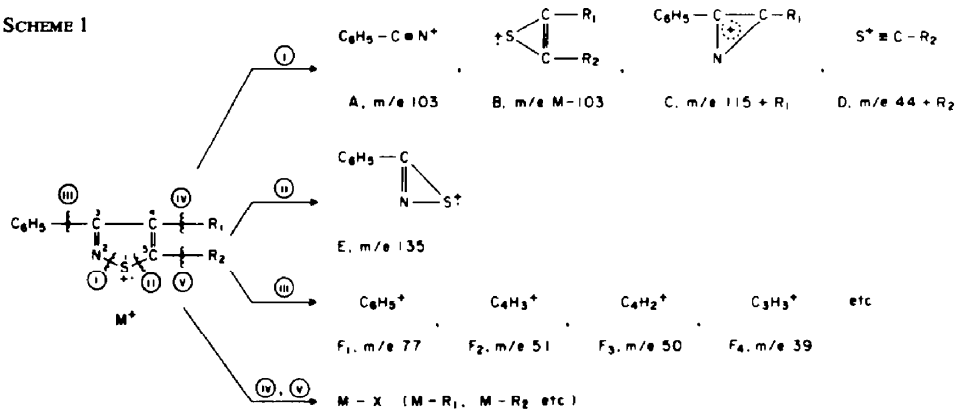
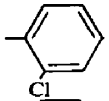
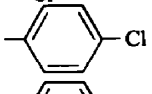
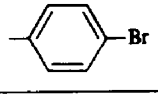



TABLE 1. ISOTHIAZOLES INVESTIGATED

| Compound No. | Substitutions at positions | | |
|---|---|---|---|
| | 3 | 4 | 5 |
| Ia | $C_6H_5$ | H | H |
| Ib | $C_6H_5$ | H | $CH_3$ |
| Ic | $C_6H_5$ | H | Cl |
| IIa | $C_6H_5$ | Br | H |
| IIb | $C_6H_5$ | Br | $CH_3$ |
| IIIa | $C_6H_5$ | CN | H |
| IIIb | $C_6H_5$ | CN | $CH_3$ |
| IIIc | $C_6H_5$ | CN | Cl |
| IVa | $C_6H_5$ | $COOCH_3$ | H |
| IVb | $C_6H_5$ | $COOCH_3$ | $CH_3$ |
| IVc | $C_6H_5$ | $COOCH_3$ | Br |
| Va | $C_6H_5$ | OH | H |
| Vb | $C_6H_5$ | OH | $CH_3$ |
| Vc | $C_6H_5$ | OH | Cl |
| Vd | $C_6H_5$ | OH | CHO |
| VIa | $C_6H_5$ | $OCH_3$ | H |
| VIb | $C_6H_5$ | $OCH_3$ | $CH_3$ |
| VIc | $C_6H_5$ | $OCH_3$ | Cl |
| VIIa | $C_6H_5$ | $OCOCH_3$ | H |
| VIIb | $C_6H_5$ | $OCOCH_3$ | $CH_3$ |
| VIIc | $C_6H_5$ | $OCOCH_3$ | CHO |
| VIIIa | $C_6H_5$ | OD | D |
| VIIIb | $C_6H_5$ | OD | $CH_3$ |
| VIIIc | $C_6H_5$ | OD | Cl |
| IXa |  | CN | $CH_3$ |
| IXb |  | CN | $CH_3$ |
| IXc |  | CN | $CH_3$ |

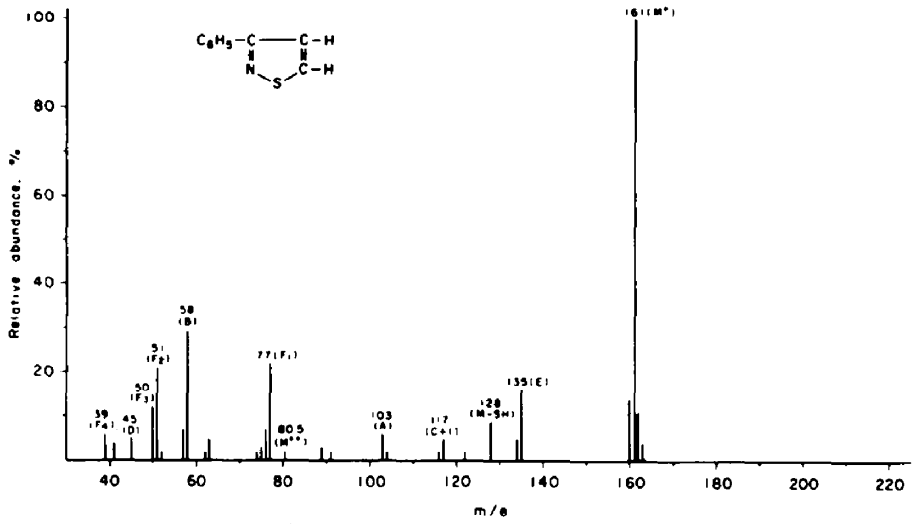



FIG. 1 Mass spectrum of 3-phenylisothiazole (Ia).

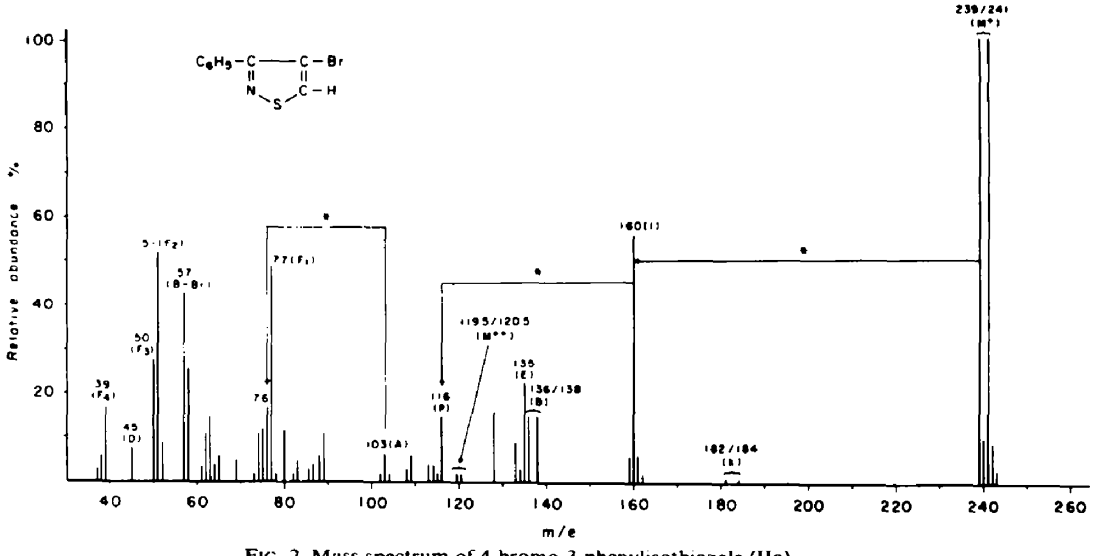
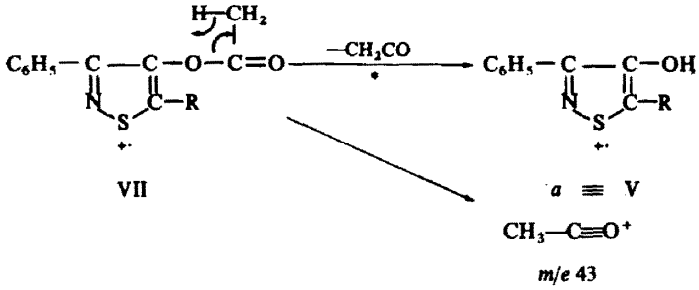


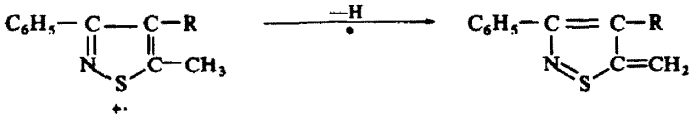

FIG. 2 Mass spectrum of 4-bromo-3-phenylisothiazole (IIa).

The mass spectra of VII give a quite similar pattern to that of the corresponding 4-hydroxy derivatives (V) except for the molecular ion and an *m/e* 43 ion (Table 2, Figs 9 and 6). This indicates that fragmentations within the 4-acetoxy group occur preferentially to form either an acetyl ion (*m/e* 43) or an M-42 ion (*a*) with loss of a ketene molecule as substantiated by an appropriate metastable peak and that the structure of the *a* ion is consequently the same as that of molecular ion of the corresponding 4-hydroxyisothiazole. The acetoxy derivatives will, therefore, be represented by the hydroxy derivatives in the following discussions.

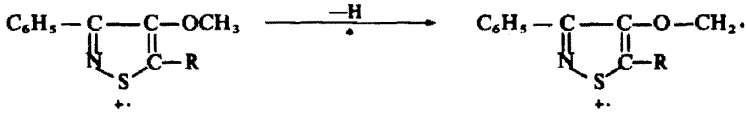



*M Peaks.* As in the cases of biphenyls,[17] phenylthiophenes[1e] and diphenyloxazoles,[4] 3-phenylisothiazoles (I–VI) give pronounced molecular peaks which are the base peak in twelve compounds (I, II, III, IVb, IVc, Vd and VIa) and the second largest peak in the remaining compounds (IVa, Va–c, VIb and IVc). All molecular ions are accompanied with the distinct double charged ion evidenced by the peaks with decimal mass unit of half the molecular ion except for the 4-cyano and 4-methoxycarbonyl derivatives.

*M-X Peaks.* The production of M-1 ions in 3-phenyl-5-methylisothiazoles is not as characteristic as in methyl-thiophenes,[1] furans[2] and pyrroles[9] which have been reported to give very abundant M-1 ion. 3-Phenyl-5-methylisothiazole (Ib) and 4-cyano-3-phenyl-5-methylisothiazole (IIIb) form M-1 ion with an intensity of 14% and 15% to the molecular peak (the base peak), respectively. Such a fragmentation is not observed in three of the other 5-Me derivatives (IIb, IVb and Vb). On the other hand, 4-methoxy-5-methyl-3-phenylisothiazole (VIb) gives M-1 ion, but its relative abundance to the molecular ion (15% of the M ion) is lower than that of the 5-unsubstituted isothiazole (VIa) (33%) and of the 5-chloro derivative (VIc; 20%). This indicates that the M-1 ions of VI arise from loss of an H atom from the 4-MeO group, differing from the cases of Ib and IIIb which produce the M-1 ions by elimination of an H atom from the 5-Me group.




Ib: R = H
IIIb: R = CN




VIa: R = H
VIb: R = $CH_3$
VIc: R = Cl

As shown in Table 4, peaks due to a cleavage of a whole or a part of the 4- or 5-substituent appear in many compounds. In general the side chain fission takes place in a fashion as anticipated with the corresponding benzene derivatives.[18]

4-Bromoisothiazoles (II) exhibit prominent peaks at *m/e* M-Br, 4-MeO derivatives (VI) at *m/e* M—$\dot{C}H_3$ and M—$OCH_2$, 4-cyano derivatives (III) at *m/e* M—HCN, but 4-hydroxy derivatives (V) give only a slight or no M—CO peak probably because of a preferential cleavage of the isothiazole ring. Of 5-halo derivatives, Ic, IIIc and IVc exhibit an intense peak due to elimination of the halogen atom, while Vc and VIc give neither M—Cl nor M—HCl peak.

Mass spectra of methyl 3-phenylisothiazole-4-carboxylates (IV) give unusual peaks which are observed only in esters of aromatic heterocycles with a specific structural requirement. It has been reported that methyl and ethyl esters of pyrroles,[9a] furans[2c] and thiazoles[3] decompose through operation of the ortho-effect,[19] losing an alkyl group from the ester when they have a Me substituent adjacent to the ester group. All of IV, however, exhibit a prominent M-15 peak regardless of the presence of an adjacent Me group, which might probably be due to a fission of the labile N—S bond followed by a concerted cleavage of the Me radical to form M—$CH_3$ ion (*b*) (Scheme 2). This fragmentation process would be supported by an *m/e* 159 peak (*c*, $C_9H_5NS$) present in all the spectra of IV, which might arise from a concerted cleavage initiated by the lability of the N—O bond in *b*. In IVb production of M—$CH_3$ion (*e*) is also possible by the usual ortho-effect of the adjacent Me group and both fragmentations may be operative. The other peak (*f*) which could be formed by the operation of ortho-effect is observed at *m/e* 201 in the spectrum of IVb.

SCHEME 2

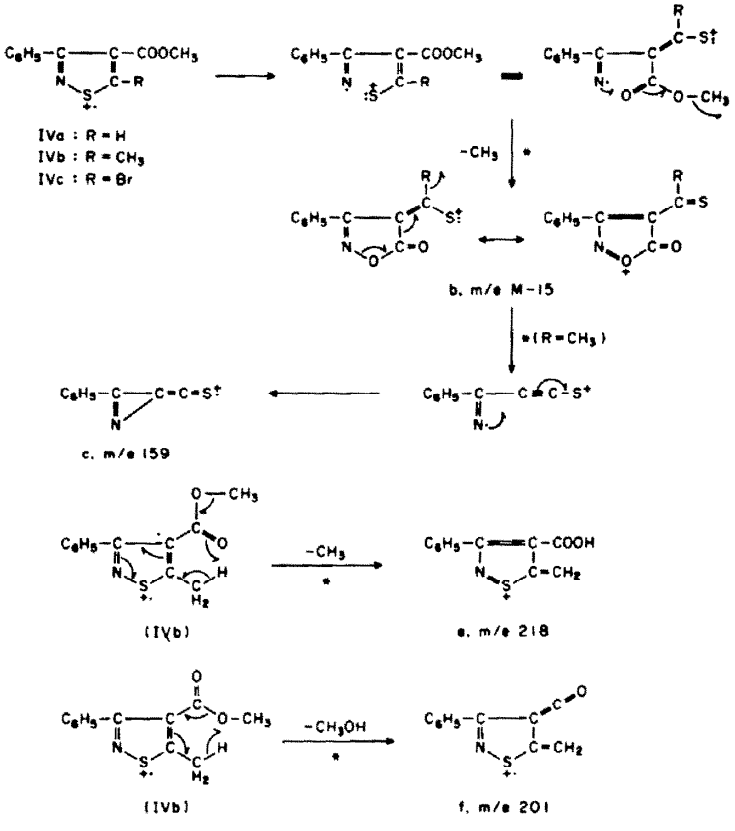


TABLE 2. MASS SPECTRA OF ISOTHIAZOLES*

| Ib | | Ic | | IIb | | IIIa | | IIIc | | IVc | | Vc | | Vd | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) |
| 39 | 12 | 38 | 2 | 37 | 2 | 38 | 3 | 37 | 2 | 39 | 18 | 38 | 2 | 39 | 11 |
| 45 | 9 | 39 | 5 | 38 | 5 | 39 | 7 | 38 | 5 | 41 | 5 | 39 | 6 | 44 | 2 |
| 50 | 7 | 45 | 2 | 39 | 25 | 45 | 10 | 39 | 8 | 43 | 6 | 44 | 6 | 45 | 16 |
| 51 | 18 | 50 | 11 | 45 | 35 | 50 | 15 | 41 | 4 | 45 | 5 | 45 | 11 | 46 | 10 |
| 52 | 2 | 51 | 22 | 50 | 25 | 51 | 29 | 42 | 3 | 50 | 20 | 50 | 15 | 50 | 7 |
| 59 | 6 | 52 | 3 | 51 | 47 | 52 | 5 | 43 | 4 | 51 | 43 | 51 | 28 | 51 | 11 |
| 63 | 4 | 57 | 13 | 52 | 5 | 57 | 3 | 45 | 2 | 52 | 5 | 52 | 6 | 52 | 3 |
| 69 | 2 | 62 | 2 | 59 | 10 | 58 | 13 | 50 | 16 | 55 | 5 | 62 | 3 | 63 | 2 |
| 71 | 18 | 63 | 4 | 62 | 5 | 62 | 2 | 51 | 27 | 57 | 5 | 63 | 5 | 69 | 2 |
| 72 | 19 | 69 | 2 | 63 | 13 | 63 | 4 | 52 | 4 | 58 | 5 | 64 | 3 | 72 | 2 |
| 73 | 2 | 74 | 3 | 64 | 2 | 64 | 2 | 56 | 2 | 59 | 11 | 72 | 12 | 73 | 2 |
| 74 | 3 | 75 | 4 | 65 | 6 | 74 | 4 | 57 | 3 | 63 | 14 | 73 | 4 | 74 | 70 |
| 75 | 3 | 76 | 8 | 69 | 10 | 75 | 6 | 61 | 2 | 65 | 6 | 74 | 6 | 75 | 6 |
| 76 | 6 | 77 | 16 | 70 | 10 | 76 | 12 | 62 | 3 | 69 | 6 | 75 | 9 | 76 | 11 |
| 77 | 22 | 78 | 2 | 71 | 54 | 77 | 23 | 63 | 5 | 74 | 6 | 76 | 21 | 77 | 16 |
| 86·5 | 3 | 79 | 1 | 72 | 15 | 82 | 3 | 64 | 2 | 75 | 11 | 77 | 59 | 78 | 2 |
| 87·5 | 5 | 80 | 6 | 73 | 3 | 83 | 15 | 74 | 5 | 76 | 20 | 78 | 10 | 102 | 6 |
| 91 | 2 | 81 | 0·3 | 74 | 12 | 84 | 2 | 75 | 7 | 77 | 36 | 79 | 34 | 102·5 | 1·5 |
| 103 | 7 | 83 | 2 | 75 | 12 | 91 | 2 | 76 | 14 | 79·5 | 4 | 80 | 7 | 103 | 5 |
| 104 | 3 | 84 | 2 | 76 | 15 | 93 | 2 | 77 | 31 | 84 | 54 | 81 | 12 | 104 | 45 |
| 115 | 3 | 89 | 3 | 77 | 42 | 102 | 4 | 78 | 2 | 85 | 6 | 82 | 3 | 105 | 5 |
| 130 | 2 | 92 | 11 | 78 | 3 | 103 | 11 | 79 | 5 | 87 | 6 | 102 | 4 | 135 | 1·5 |
| 135 | 13 | 94 | 4 | 86·5 | 9 | 104 | 3 | 81 | 2 | 103 | 16 | 103 | 15 | 205($M^+$) | 100 |
| 142 | 16 | 97·5 | 3 | 87 | 9 | 108 | 2 | 82 | 12 | 108 | 4 | 104 | 100 | 206 | 7 |
| 143 | 2 | 98·5 | 1 | 89 | 4 | 114 | 3 | 83 | 3 | 109 | 6 | 105 | 25 | 207 | 3 |
| 147 | 3 | 103 | 6 | 101 | 3 | 129 | 3 | 87 | 2 | 113 | 10 | 105·5 | 5 | | |
| 160 | 8 | 116 | 5 | 102 | 7 | 135 | 22 | 88 | 2 | 114 | 5 | 106 | 2 | | |
| 174 | 14 | 133 | 3 | 103 | 10 | 136 | 2 | 91 | 2 | 115 | 4 | 106·5 | 2 | | |
| 175($M^+$) | 100 | 135 | 5 | 104 | 5 | 140 | 2 | 92 | 7 | 123 | 1 | 108 | 6 | | |
| 176 | 15 | 151 | 2 | 109 | 8 | 142 | 5 | 92·5 | 4 | 125 | 1 | 110 | 2 | | |
| 177 | 6 | 153 | 0·5 | 115 | 3 | 153 | 7 | 93 | 2 | 130 | 4 | 135 | 1·5 | | |

TABLE 2—*continued*

| Ib | | Ic | | IIb | | IIIa | | IIIc | | IVc | | Vc | | Vd | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) |
| | | 159 | 4 | 121 | 3 | 159 | 5 | 94 | 3 | 133 | 5 | 147 | 4 | | |
| | | 160 | 43 | 126 | 3 | 160 | 7 | 102 | 5 | 135 | 8 | 211($M^+$) | 88 | | |
| | | 161 | 5 | 126·5 | 2 | 185 | 7 | 103 | 14 | 137 | 8 | 212 | 12 | | |
| | | 162 | 2 | 127 | 5 | 186($M^+$) | 100 | 108 | 3 | 159 | 20 | 213($M^+$) | 30 | | |
| | | 195($M^+$) | 100 | 127·5 | 2 | 187 | 12 | 110 | 4 | 160 | 6 | 214 | 5 | | |
| | | 196 | 11 | 128 | 5 | 188 | 4 | 114 | 3 | 163 | 68 | 215 | 3 | | |
| | | 197($M^+$) | 33 | 130 | 5 | | | 117 | 11 | 165 | 68 | | | | |
| | | 198 | 3 | 135 | 13 | | | 119 | 4 | 203 | 2 | | | | |
| | | | | 140 | 5 | | | 129 | 3 | 218 | 48 | | | | |
| | | | | 141 | 8 | | | 135 | 12 | 219 | 7 | | | | |
| | | | | 142 | 15 | | | 141 | 3 | 239 | 3 | | | | |
| | | | | 147 | 11 | | | 158 | 3 | 241 | 3 | | | | |
| | | | | 150 | 5 | | | 160 | 4 | 266 | 94 | | | | |
| | | | | 152 | 5 | | | 184 | 12 | 267 | 13 | | | | |
| | | | | 159 | 9 | | | 185 | 47 | 268 | 94 | | | | |
| | | | | 172 | 4 | | | 186 | 7 | 269 | 11 | | | | |
| | | | | 173 | 10 | | | 193 | 1 | 270 | 4 | | | | |
| | | | | 174 | 55 | | | 195 | 0·3 | 282 | 26 | | | | |
| | | | | 175 | 13 | | | 220($M^+$) | 100 | 283 | 3 | | | | |
| | | | | 176 | 2 | | | 221 | 13 | 284 | 26 | | | | |
| | | | | 182 | 1 | | | 222($M^+$) | 35 | 285 | 2 | | | | |
| | | | | 184 | 1 | | | 223 | 5 | 297($M^+$) | 100 | | | | |
| | | | | 220 | 2 | | | | | 298 | 16 | | | | |
| | | | | 222 | 2 | | | | | 299($M^+$) | 100 | | | | |
| | | | | 253($M^+$) | 100 | | | | | 300 | 13 | | | | |
| | | | | 254 | 12 | | | | | 301 | 4 | | | | |
| | | | | 255($M^+$) | 100 | | | | | | | | | | |
| | | | | 256 | 10 | | | | | | | | | | |
| | | | | 257 | 4 | | | | | | | | | | |

TABLE 2—*continued*

| VIb | | VIc | | VIIb | | VIIc | | VIIIa | | VIIIc | | IXa | | IXb | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) |
| 39 | 3 | 39 | 6 | 39 | 4 | 39 | 3 | 39 | 2 | 39 | 3 | 39 | 9 | 39 | 6 |
| 45 | 2 | 41 | 2 | 43 | 77 | 43 | 100 | 45 | 2 | 45 | 2 | 45 | 9 | 45 | 7 |
| 50 | 4 | 43 | 2 | 44 | 2 | 44 | 3 | 46 | 15 | 46 | 6 | 50 | 11 | 50 | 10 |
| 51 | 6 | 44 | 2 | 45 | 2 | 45 | 25 | 47 | 2 | 50 | 6 | 51 | 8 | 51 | 7 |
| 58 | 7 | 45 | 1 | 50 | 6 | 46 | 2 | 48 | 3 | 51 | 13 | 59 | 17 | 59 | 14 |
| 59 | 100 | 50 | 8 | 51 | 8 | 50 | 5 | 50 | 5 | 52 | 3 | 63 | 3 | 63 | 3 |
| 60 | 3 | 51 | 11 | 52 | 2 | 51 | 7 | 51 | 10 | 72 | 4 | 64 | 4 | 64 | 3 |
| 61 | 4 | 52 | 2 | 58 | 12 | 72 | 3 | 52 | 2 | 74 | 2 | 70 | 9 | 70 | 6 |
| 63 | 2 | 58 | 2 | 59 | 63 | 73 | 4 | 75 | 4 | 75 | 3 | 71 | 6 | 71 | 6 |
| 75 | 2 | 59 | 2 | 60 | 14 | 74 | 35 | 76 | 4 | 76 | 6 | 74 | 5 | 72 | 5 |
| 76 | 4 | 63 | 3 | 61 | 4 | 75 | 3 | 77 | 12 | 77 | 17 | 75 | 22 | 73 | 3 |
| 77 | 5 | 65 | 1 | 63 | 2 | 76 | 4 | 78 | 8 | 78 | 10 | 76 | 6 | 74 | 5 |
| 102 | 1·5 | 72 | 4 | 75 | 2 | 77 | 9 | 79 | 2 | 79 | 9 | 96 | 6 | 75 | 20 |
| 102·5 | 1·5 | 74 | 2 | 76 | 7 | 102 | 4 | 89·5 | 0·5 | 81 | 4 | 97 | 7 | 76 | 5 |
| 103 | 3 | 75 | 3 | 77 | 11 | 103 | 3 | 103 | 2 | 103 | 4 | 99 | 7 | 96 | 5 |
| 104 | 3 | 76 | 8 | 78 | 2 | 104 | 31 | 104 | 10 | 104 | 23 | 99·5 | 3 | 97 | 5 |
| 118 | 2 | 77 | 7 | 88 | 20 | 105 | 3 | 105 | 100 | 105 | 100 | 100 | 2 | 98 | 2 |
| 135 | 1 | 79 | 100 | 103 | 4 | 135 | 0·5 | 106 | 6 | 106 | 7 | 102 | 11 | 99 | 6 |
| 144 | 4 | 81 | 35 | 104 | 82 | 205 | 69 | 107 | 3 | 108 | 1 | 111 | 6 | 99·5 | 3 |
| 175 | 2 | 91 | 3 | 105 | 10 | 206 | 9 | 135 | 0·3 | 110 | 0·3 | 113 | 2 | 100 | 2 |
| 190 | 12 | 103 | 6 | 135 | 1·5 | 207 | 4 | 177 | 1 | 201 | 8 | 117 | 2 | 102 | 7 |
| 191 | 2 | 105 | 4 | 191 | 100 | 247($M^+$) | 5 | 178 | 11 | 202 | 35 | 134 | 4 | 111 | 7 |
| 204 | 8 | 107 | 3 | 192 | 13 | | | 179 | 33 | 203 | 7 | 137 | 13 | 113 | 2 |
| 205($M^+$) | 55 | 109 | 1 | 193 | 6 | | | 180 | 4 | 204 | 12 | 138 | 2 | 117 | 2 |
| 206 | 7 | 112·5 | 2 | 233($M^+$) | 17 | | | 181 | 1·5 | 205 | 1 | 139 | 4 | 134 | 2 |
| 207 | 3 | 117 | 2 | 234 | 3 | | | | | | | 140 | 2 | 137 | 12 |
| | | 118 | 4 | | | | | $d_2$ = 73% | | $d_1$ = 80% | | 155 | 2 | 138 | 2 |
| | | 119 | 2 | | | | | | | | | 163 | 3 | 139 | 4 |
| | | 122 | 1·5 | | | | | $d_1$ = 24% | | $d_0$ = 20% | | 165 | 1 | 140 | 2 |
| | | 124 | 0·5 | | | | | | | | | 169 | 15 | 155 | 2 |

TABLE 2—*continued*

| VIb | | VIc | | VIIb | | VIIc | | VIIIa | | VIIIc | | IXa | | IXb | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) | *m/e* | I (%) |
| | | 135 | 3 | | | | | $d_0$ = 3% | | | | 171 | 5 | 163 | 3 |
| | | 145 | 2 | | | | | | | | | 172 | 7 | 165 | 1 |
| | | 159 | 2 | | | | | | | | | 176 | 2 | 169 | 10 |
| | | 160 | 3 | | | | | | | | | 189 | 5 | 171 | 3 |
| | | 162 | 6 | | | | | | | | | 191 | 1·5 | 172 | 5 |
| | | 173 | 2 | | | | | | | | | 198 | 5 | 174 | 2 |
| | | 188 | 1·5 | | | | | | | | | 199 | 22 | 176 | 2 |
| | | 190 | 0·5 | | | | | | | | | 200 | 3 | 189 | 3 |
| | | 195 | 3 | | | | | | | | | 201 | 6 | 191 | 1 |
| | | 197 | 1 | | | | | | | | | 202 | 6 | 198 | 2 |
| | | 210 | 15 | | | | | | | | | 203 | 2 | 199 | 20 |
| | | 212 | 5 | | | | | | | | | 204 | 2 | 200 | 3 |
| | | 224 | 13 | | | | | | | | | 207 | 7 | 201 | 8 |
| | | 225($M^+$) | 65 | | | | | | | | | 209 | 2 | 202 | 7 |
| | | 226 | 12 | | | | | | | | | 233 | 5 | 203 | 3 |
| | | 227($M^+$) | 23 | | | | | | | | | 234($M^+$) | 100 | 204 | 2 |
| | | 228 | 2 | | | | | | | | | 235 | 14 | 207 | 6 |
| | | | | | | | | | | | | 236($M^+$) | 36 | 209 | 2 |
| | | | | | | | | | | | | 237 | 4 | 233 | 7 |
| | | | | | | | | | | | | | | 234($M^+$) | 100 |
| | | | | | | | | | | | | | | 235 | 15 |
| | | | | | | | | | | | | | | 236($M^+$) | 36 |
| | | | | | | | | | | | | | | 237 | 4 |

* All peaks having an abundance greater than 2% of the base peak (arbitrarily 100%) are recorded in the Table. Peaks of lesser abundance are included if they have obvious diagnostic significance or if they are discussed in the text.

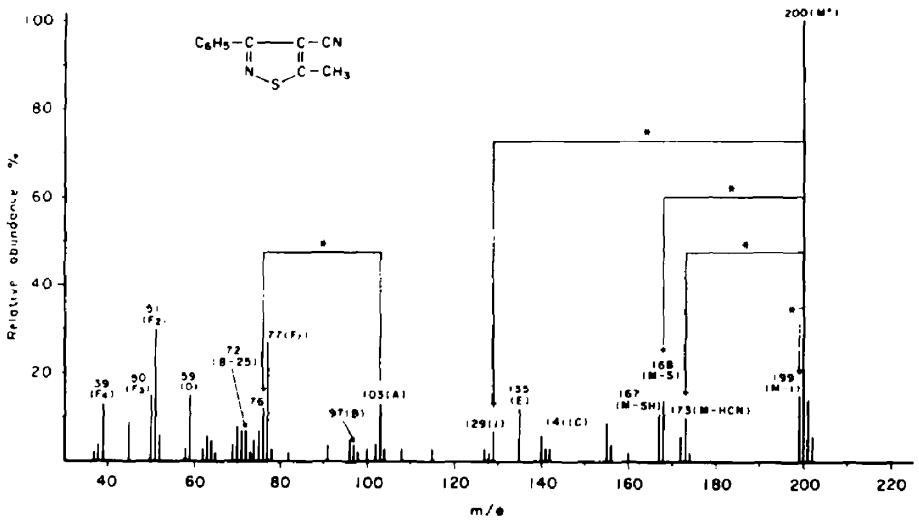



FIG. 3 Mass spectrum of 4-cyano-5-methyl-3-phenylisothiazole (IIIb).

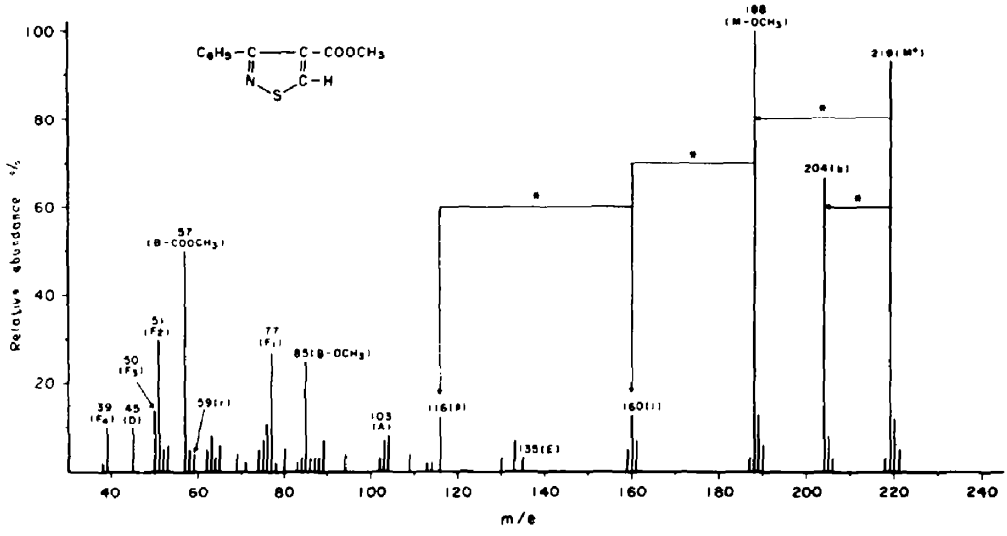



FIG. 4 Mass spectrum of 4-methoxycarbonyl -3-phenylisothiazole (IVa).

Distinct M-33 peaks are observed in Ia (Fig. 1), Ib and IIIa at *m/e* 128 (9% of the base peak), *m/e* 142 (16%) and *m/e* 153 (7%), respectively. High resolution measurement of the M-33 peak of Ib establishes that this peak is exclusively due to loss of the SH group from the molecular ion. The mass spectrum of IIIb (Fig. 3) demonstrates both M—S and M—SH peaks. and the halogeno analogs (IX) also give such fragments in pairs due to the isotopic abundance (Fig. 11). Such M—SH or M—S skeletal rearrangement ions have been reported for many open-chain sulfides and disulfides,[20] but for only a few sulphur-containing heterocyclic compounds.[1e]

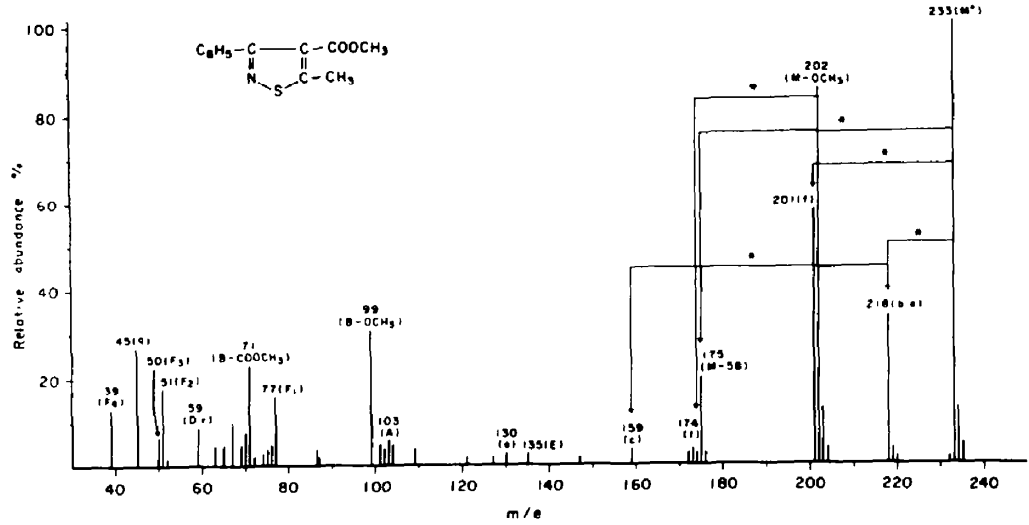



FIG. 5 Mass spectrum of 4-methoxycarbonyl-5-methyl-3-phenylisothiazole (IVb).

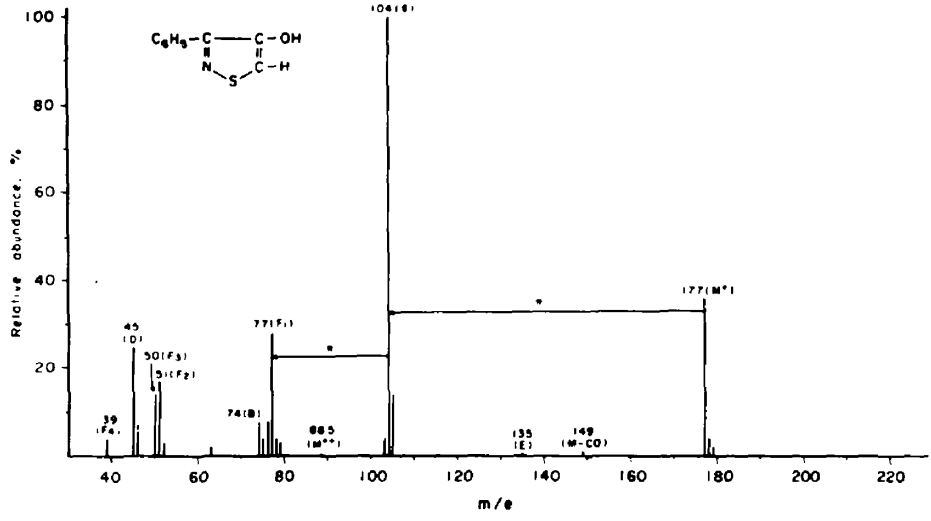
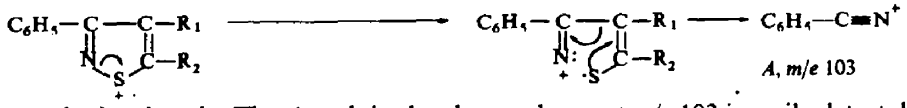



FIG. 6 Mass spectrum of 4-hydroxy-3-phenylisothiazole (Va).



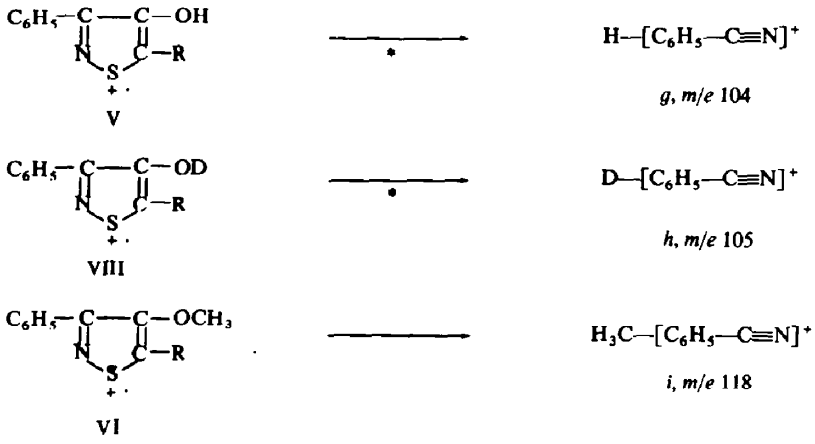

*A and related peaks.* The *A* peak in the above scheme at *m/e* 103 is easily detectable in the 4-substituted isothiazoles, II and III, which contain no H atom in the substituent, and in the 4-unsubstituted derivatives (I). The introduction of a hydrogen-containing substituent in the 4-position (IV, V and VI) increases the relative abundance of a peak which is higher by one mass unit (*A* + 1, *m/e* 104), and especially the

TABLE 3. EXACT MASS MEASUREMENTS IN THE SPECTRA OF 3-PHENYLISOTHIAZOLES

| Compound No. | Fragment ion | Composition | Exact mass (*m/e*) | |
|---|---|---|---|---|
| | | | Calcd. | Obsd. |
| Ib | B | $C_3H_4S$ | 72·003 | 72·003 |
| | A | $C_7H_5N$ | 103·042 | 103·044 |
| | o | $C_9H_8N$ | 130·066 | 130·064 |
| | E | $C_7H_5NS$ | 135·014 | 135·012 |
| | M-SH | $C_{10}H_8N$ | 142·066 | 142·065 |
| IIIb | B-25 | $C_3H_4S$ | 72·003 | 72·003 |
| | j | $C_8H_5N_2$ | 129·045 | 129·048 |
| | E | $C_7H_5NS$ | 135·014 | 135·012 |
| | M-SH | $C_{11}H_7N_2$ | 167·061 | 167·059 |
| | M-S | $C_{11}H_8N_2$ | 168·069 | 168·068 |
| IVa | r | $C_2H_3O_2$ (59%) | 59·013 | 59·017 |
| | — | $CNO_2$ (37%) | 58·993 | 58·997 |
| | — | CHNS (4%) | 58·983 | 58·978 |
| | p | $C_8H_6N$ | 116·050 | 116·050 |
| | E | $C_7H_5S$ | 135·014 | 135·017 |
| | c | $C_9H_5NS$ | 159·014 | 159·016 |
| | l | $C_9H_6NS$ | 160·022 | 160·024 |
| IVb | o | $C_9H_8N$ | 130·066 | 130·066 |
| | c | $C_9H_5NS$ | 159·014 | 159·017 |
| | l | $C_{10}H_8NS$ | 174·038 | 174·040 |
| | M-58 | $C_{10}H_9NS$ | 175·046 | 175·049 |
| IVc | r | $C_2H_3O_2$ (46%) | 59·013 | 59·017 |
| | — | $CNO_2$ (42%) | 58·993 | 58·999 |
| | — | CHNS (12%) | 58·983 | 58·982 |
| | B-Br-$OCH_3$ | $C_3OS$ | 83·967 | 83·966 |
| | B-$COOCH_3$ | $C_2{}^{79}BrS$ (90%) | 134·890 | 134·891 |
| | E | $C_7H_5NS$ (10%) | 135·017 | 135·016 |
| | c | $C_9H_5NS$ | 159·014 | 159·014 |
| Va | B | $C_2H_2OS$ | 73·983 | 73·982 |
| Vb | B | $C_3H_4OS$ | 87·998 | 87·997 |
| VIa | D | CHS | 45·980 | 45·980 |
| | A + l | $C_7H_6N$ | 104·050 | 104·051 |
| | i | $C_8H_8N$ | 118·066 | 118·066 |

peak is quite predominant in compounds V (Table 5). The additional hydrogen of the *m/e* 104 ion in V (g, $C_7H_6N$) has been established to have originated from the 4-OH group by analysing the mass spectra of VIII (deuterio analogues of V), in which the prominent peak shifts to *m/e* 105 (*h*) (Fig. 10).

On the analogy of hydrogen migration from the 4-OH group of V, the 4-MeO derivatives (VI) exhibit an *m/e* 118 ion (*i*) corresponding to the migration of a Me group to the *A* ion moiety, the abundance of which being 5% (VIa, Fig. 8), 3% (VIb) and 4% (VIc) relative to the base peak. The elemental composition of the *i* ion was established as $C_8H_8N$ by the accurate mass measurement of the *m/e* 118 ion in VIa.



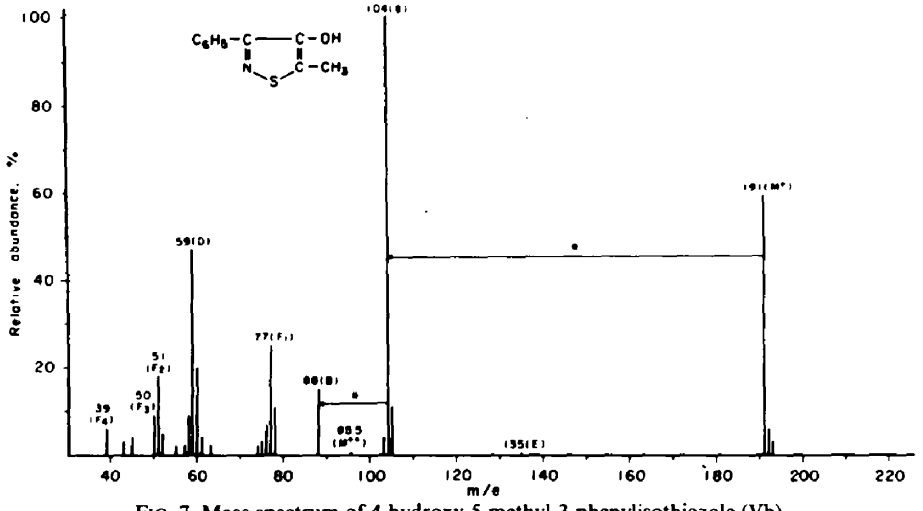




FIG. 7 Mass spectrum of 4-hydroxy-5-methyl-3-phenylisothiazole (Vb).

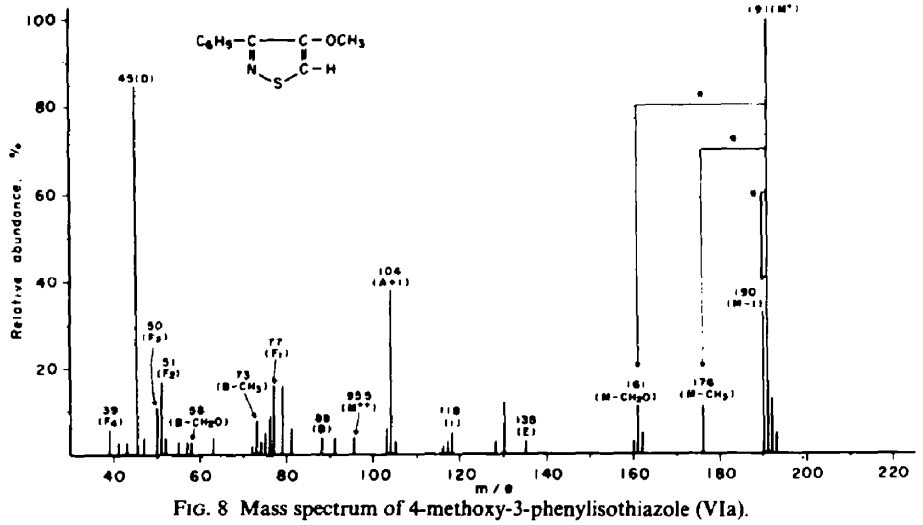
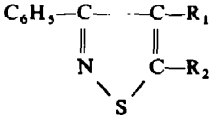



FIG. 8 Mass spectrum of 4-methoxy-3-phenylisothiazole (VIa).

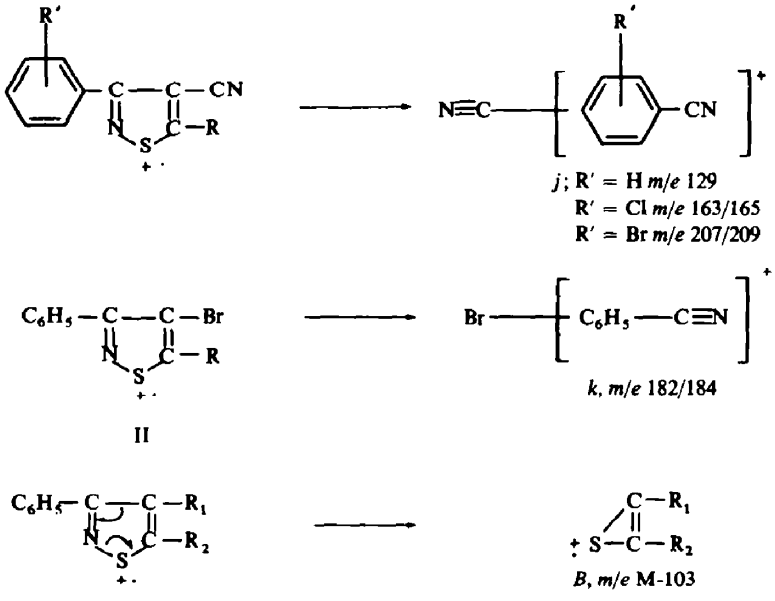
TABLE 4. M-X AND B-X IONS SPECTRA OF 3-PHENYLISOTHIAZOLES (I–VI)



| Compound No. | $R_1$ | X mu | a: $R_2$ = H | | b: $R_2$ = $CH_3$ | | c: $R_2$ = Cl | |
|---|---|---|---|---|---|---|---|---|
| | | | M-X *m/e* (I, %) | B-X *m/e* (I, %) | M-X *m/e* (I, %) | B-X *m/e* (I, %) | M-X *m/e* (I, %) | B-X *m/e* (I, %) |
| I | H | 1(H) | — | — | 174(14) | 71(18) | — | — |
| | | 15($CH_3$) | — | — | 160(8) | — | — | — |
| | | 33(SH) | 128(9) | — | 142(16) | — | — | — |
| | | 33/37(Cl) | — | — | — | — | 160(43) | 57(13) |
| II | Br | 79/81(Br) | 160(56) | 57(43) | 174(55) | 71(54) | | |
| III | CN | 1(H) | — | — | 199(15) | 96(5) | — | — |
| | | 25(CN—H) | — | 58(13) | — | 72(7) | — | 92(94(7/3) |
| | | 27(HCN) | 159(5) | — | 173(10) | 70(8) | — | — |
| | | 32(S) | — | — | 168(14) | — | — | — |
| | | 33(SH) | 153(7) | — | 167(11) | — | — | — |
| | | 35/37(Cl) | — | — | — | — | 185(47) | 82(12) |
| IV* | $COOCH_3$ | 15($CH_3$) | 204(67) | — | 218(34) | — | 282/284(26/26) | — |
| | | 31($OCH_3$) | 188(10) | 85(25) | 702(85) | 99(31) | 266/268(94/94) | 163/165(68/68) |
| | | 32($CH_3OH$) | — | — | 201(58) | — | — | — |
| | | 58 | — | — | 175(20) | — | 239/241(3/3) | — |
| | | 59($COOCH_3$) | 160(13) | 57(50) | — | 71(23) | — | 135/137(8/8) |
| | | 79/81(Br) | — | — | — | — | 218(48) | 115(4) |
| V | OH | 28(CO) | 149(2) | — | — | — | — | — |
| VI | $OCH_3$ | 1(H) | 190(33) | — | 204(8) | — | 224/226(13/12) | — |
| | | 15($CH_3$) | 176(11) | 73(8) | 190(12) | — | 210/212(15/5) | 107/109(3/1) |
| | | 30($CH_2O$) | 161(11) | 58(3) | 175(2) | — | 195/197(3/1) | — |

* IVc: $R_2$ = Br

Recently, rearrangement ions due to cyano group migration have been reported in β-phenyl-α,β-unsaturated nitriles[21] and isohexyl cyanide.[22] The mass spectra of 3-phenyl-4-cyanoisothiazoles (III) exhibit similar interesting peaks which involve a rearrangement of the cyano group to the *A* ion moiety (A + CN). The rearrangement ion affords a weak but distinct peak (3–7% of the base peak) at *m/e* 129 (*j*, R′ = H), which is established as $C_8H_5N_2$ by high resolution measurement of IIIb. The introduction of a chlorine atom to *ortho*- or *para*-position of the phenyl ring (IXa, IXb) makes the *m/e* 129 ion shift to *m/e* 163/165 (*j*, R′ = Cl) with the characteristic isotopic abundances (ca. 3:1) of $^{35}Cl$ and $^{37}Cl$. Also, the *p*-bromo derivative (IXc, Fig. 11) gives the rearrangement peak at *m/e* 207/209 (*j* R′ = Br) in the ratio of about 1:1. Similarly, migration of Br atom to the *A* ion is seen in the 4-bromoisothiazoles (II) giving a pair of isotopic peaks at *m/e* 182/184 (*k*), although the intensity is small (1–2% of the base peak). On the other hand, migration of the MeO group does not in 4-methoxycabonyl derivatives (IV), being different from β-phenyl-α, β-unsaturated esters.[21]




*B and related peaks.* The *B* ion shown in the above scheme is characteristic of all the 3-phenylisothiazoles studied in the present paper with exceptions of 4-methoxycarbonyl derivatives IVa–c (IVa and IVb give a peak at *m/e* M-103 but with a different elemental composition from the *B* ion; see, the next section). The relative abundance to the base peak varies in a range of 1 to 29% and the 5-Me derivatives show a weaker peak than do the corresponding 5-unsubstituted ones (Table 5). The isotope peaks are, of course, seen in the compounds having halogens in their substituents at the 4 or 5 position.

Interestingly enough, the *B* peaks of 4-OH derivatives, Vb and Vc, do not change position in the corresponding deuterium-labeled compounds, VIIIb and VIIIc, and the *B* peak of Va shifts to higher position only by one mass unit in the di-deuterio compound, VIIIa. This might suggest that the *B* ions arise from a fragmentation

TABLE 5. RELATIVE ABUNDANCES OF A, A + 1, B, D and E PEAKS OF 3-PHENYLISOTHIAZOLES. (I–VI).

| Compound No. | A | A + 1 | B | D | | | E |
|---|---|---|---|---|---|---|---|
| | *m/e* 103 (%) | *m/e* 104 (%) | *m/e* M-103 (%) | *m/e* 45 (%) | *m/e* 59 (%) | *m/e* 79/81 (%) | *m/e* 135 (%) |
| Ia | 6 | 2 | 29 | 5 | — | — | 16 |
| Ib | 7 | 3 | 19 | 9 | 6 | — | 13 |
| Ic | 6 | — | 11/4 | 2 | — | 1/0·3 | 5 |
| IIa | 9 | 2 | 15/15 | 8 | — | — | 26 |
| IIb | 10 | 5 | 5/5 | 35 | 10 | — | 13 |
| IIIa | 11 | 3 | 15 | 10 | — | — | 22 |
| IIIb | 13 | 3 | 4 | 9 | 15 | — | 12 |
| IIIc | 14 | — | 11/4 | 2 | — | 5/2 | 12 |
| IVa | 7 | 8 | [b] | 10 | 4[a] | — | 3 |
| IVb | 6 | 5 | [c] | 27 | 9[a] | — | 3 |
| IVc | 16 | — | — | 5 | 11[a] | 1/1 (*m/e* 123/125) | 8 |
| Va | 4 | 100 | 8 | 25 | — | — | 0·5 |
| Vb | 4 | 100 | 15 | 4 | 47 | — | 0·5 |
| Vc | 15 | 100 | 6/2 | 11 | — | 34/12 | 1·5 |
| Vd | 5 | 45 | 6 | 16 | — | 70 (*m/e* 74) | 1·5 |
| VIa | 6 | 38 | 4 | 85 | — | — | 3 |
| VIb | 3 | 3 | 1·5 | 2 | 100 | — | 1 |
| VIc | 6 | — | 1·5/0·5 | 1 | — | 100/35 | 3 |

[a] These include methoxycarbonyl ion, *r*.
[b] A peak due to *p* is observed at the same position.
[c] A peak due to *o* is observed at the same position.

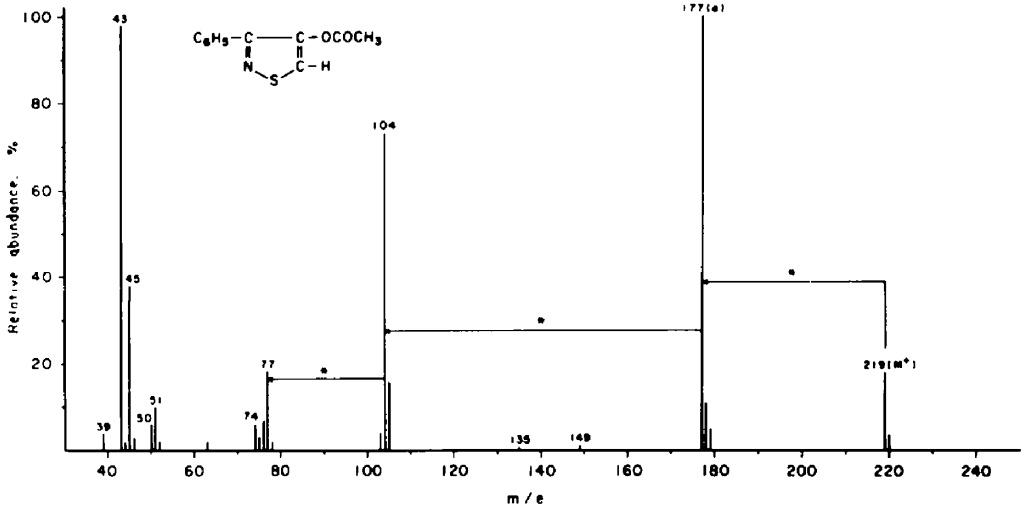
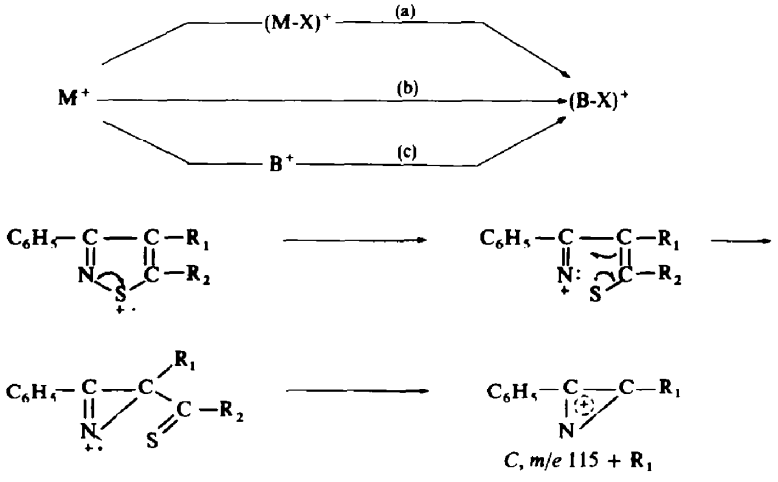



FIG. 9 Mass spectrum of 4-acetoxy-3-phenylisothiazole (VIIa).

process through both an elimination of the hydrogen in the 4-OH group and an addition of a hydrogen from the 3-phenyl ring. Similar behavior is observed in the spectra of 4-cyano derivatives (III), which afford *B*-25 ions indicating an elimination of the cyano group from the *B* ions and an addition of an H atom (Table 4). A support for this discussion is that a distinct *B*-25 peak appears even in IIIc which has no hydrogen atom except for those on the phenyl ring.

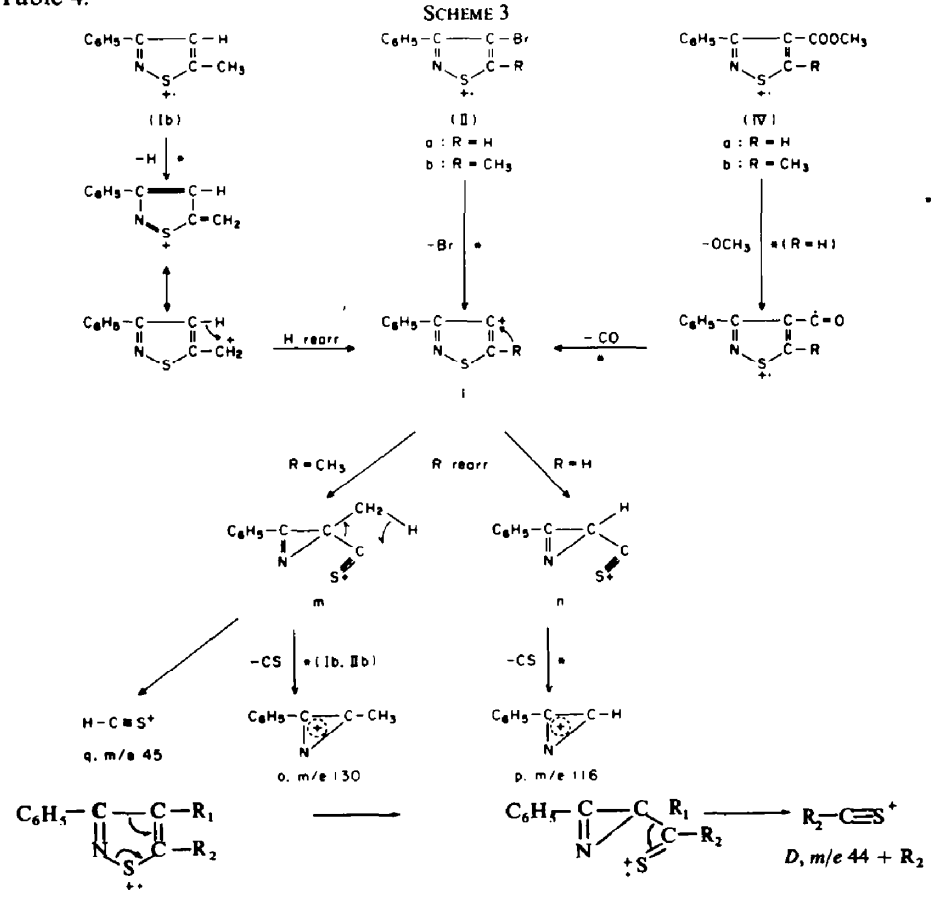
Most compounds exhibit B-X species corresponding to the loss of a whole or a part of 4- and 5-substituents from the *B* ions (Table 4). The eliminating groups, with an exception of *B*-25 ions described above, are the same as those encountered in the production of the M-X ions from the molecular ions. The B-X ions may, therefore, be produced by either one of or combination of the following routes: (a) fragmentation of the M-X ion in a similar way to that of the corresponding M ion to the *B* ion, (b) direct formation from the M ion, (c) elimination of the X group from the *B* ion. The actual process to the B-X ion, however, can not be determined because of a lack of the metastable peak.




*C and related peaks.* The *C* ion shown above is not characteristic of the 3-phenylisothiazole, though the 3-substituted 5-methylisoxazole have been reported[5] to exhibit distinct peaks due to the similar fragmentation. Only three compounds (Ic, IIIb and IIIc) give this peak with a relative abundance of 3–5% to the base peak. The corresponding 5-hydrogen derivatives (Ia and IIIa) give *C* + 1 peak which is probably produced by a similar fragmentation process with a hydrogen rearrangement. In contrast to the above, 3-phenyl-5-methylisothiazole (Ib) does not give the *C* peak but an *m/e* 130 peak which comes from the M-1 ion as evidenced by an appropriate metastable ion. As shown in Scheme 3, one plausible process to the *m/e* 130 ion, though by no means the sole one, can be visualized by the migration of 4-hydrogen to 5-substituent (the electron deficient site) to form an intermediate ion *l* (R = $CH_3$) followed by Me migration to the electron deficient 4-position (*l* → *m*) and elimination of CS group (*m* → *o*). The similar *m/e* 130 peak (*o*) is observed in the

mass spectrum of IIb, which gives the M-Br ion formulated as *l* (R = $CH_3$) in Scheme 3. Also the corresponding 5-hydrogen analog (IIa) exhibits an *m/e* 116 peak (*p*) which is interpretable by the migration of the 5-hydrogen to the positively charged 4-position in *l* (R = H). Spectra of IVa and IVb also afford *m/e* 116 and 130 peaks, respectively. Exact mass measurement show that these peaks are not due to the *B* ions, but *p* and *q* ions, which can be similarly explained by the production through the same intermediate ion, *l*, corresponding to M—$COOCH_3$ ions. The fragmentation process may be supported by the fact that the mass spectra of Ib, IIb and IVb exhibit a more pronounced peak at *m/e* 45 (*q*) which is rationalized by invoking four membered transition state (see, arrow in *m*) rather than the *D* peak at *m/e* 59 as shown in Table 4.

SCHEME 3




*D Peaks.* The *D* ion gives useful information on the 5-substituent because the mass number depends merely upon the substituent. The relative abundance, however, is affected by the 4-substituent. The *D* peak of VI is the bas epeak or the second largest (85% of the base peak), compounds V afford a intense peak (25–70%) and the other a smaller one (4–17%).

5-Methyl-3-phenylisothiazoles, Ib, IIb, IIIb, IVb, Vb and VIb, have the *D* peak at *m/e* 59 (44 + $CH_3$). As shown in Table 5, the methoxycarbonylisothiazoles exhibit an *m/e* 59 peak not only in the 5-Me derivative (IVb), but also in the 5-unsubstituted

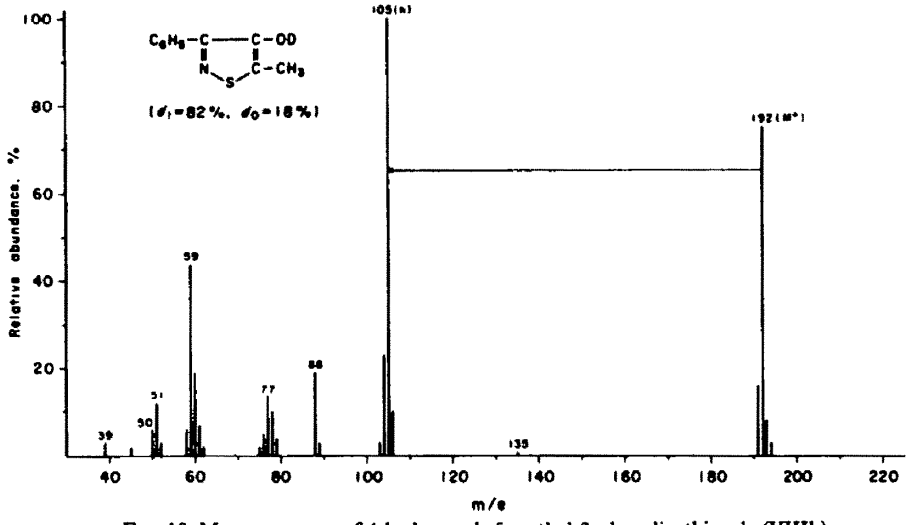
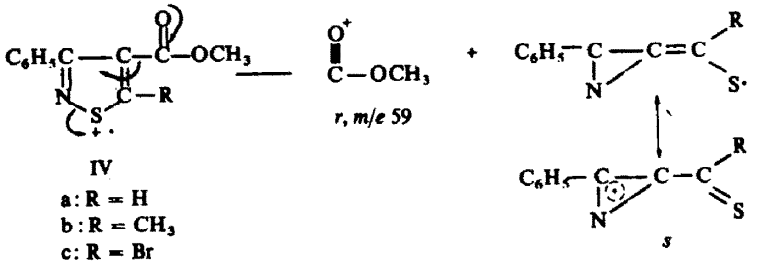



FIG. 10 Mass spectrum of 4-hydroxy-$d_1$-5-methyl-3-phenylisothiazole (VIIIb).

(IVa) and 5-chloro (IVc) derivatives This suggests the production of methoxycarbonyl ion (*r*), which can be illustrated reasonably by concerted bond cleavages due to the lability of the N—S bond and a resonance stabilization of the eliminating radical (*s*).

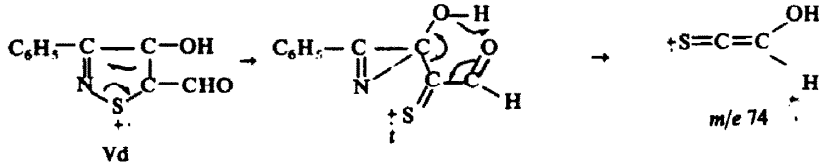


IV
a: R = H
b: R = $CH_3$
c: R = Br

*r*, *m/e* 59

*s*

The 5-chloro derivatives (Ic, IIIc, Vc and VIc) produce peaks at *m/e* 79/81 (44 + Cl) and the 5-bromo derivative (IVc) at *m/e* 123/125 (44 + Br) with the respective isotopic abundances. The 5-formyl derivative (Vd) affords a prominent peak at *m/e* 74 which is higher by one mass unit than the expected (44 + CHO) ion and may form through a 6-membered transition state (*t*).



Vd

*t*

*m/e* 74

The 5-unsubstituted derivatives produce an *m/e* peak (44 + H). However it is also observed in mass spectra of other compounds (Table 5), especially in the 5-Me derivatives (Ib, IIb and IVb) in which the *m/e* 45 ion is more abundant than the *m/e* 59 ion because of the reason described above. The *m/e* 45 ion can not, therefore, be a diagnostic peak for the 5-unsubstituted 3-phenylisothiazoles.

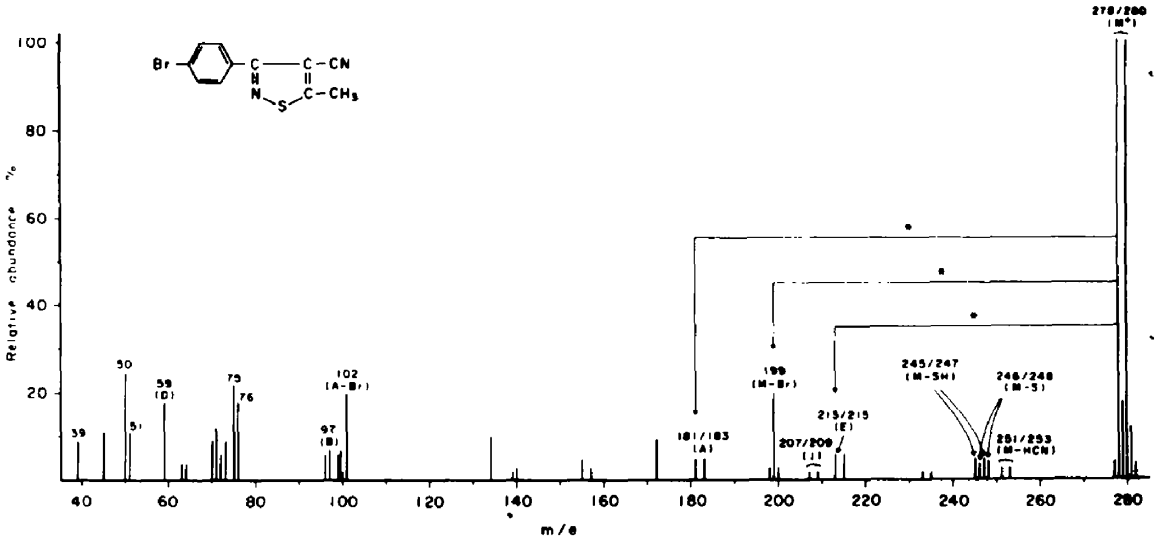
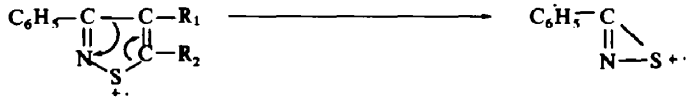



FIG. 11 Mass spectrum of 3-(p-bromophenyl)-4-cyano-5-methylisothiazole (IXc).



*E*, *m/e* 135

*E Peaks.* The *E* peak at *m/e* 135 is rather strong in I, II and III (12–28% of the base peak), while it is weak in IV, V and VI (0·5–3%). However, it can be easily detected even in the latters, because no prominant peak appears around *m/e* 135. The high resolution spectra of Ib and IIIb establish that this peak contains a sole ion with an elemental composition of $C_7H_5NS$. Of the fragment ions produced by ring fission where the fragmentations are interpretable, this is the only ion which contains both nitrogen and sulfur atoms. As might be expected for the fragmentation process, the chlorophenyl derivatives (IXa and IXb) afford a doublet at *m/e* 169/171 in the ratio 3:1 and the bromo analogue (IXc) at *m/e* 213/215 in the ratio 1:1.

*F Peaks.* The fragment ions due to 3-phenyl ring are present as usual[23] at *m/e* 77, 76, 75, 65, 64, 63, 52, 51, 50 and 39. In most compounds in this study, ions of *m/e* 77, 51, 50 and 39 are relatively abundant. Besides a direct formation from the molecular ion, the phenyl ion may arise from cleavage of some fragment ions. Mass spectra of V exhibit a metastable ion at *m/e* 57·0, indicative of a decomposition of the 104 ion to the *m/e* 77 ion by elimination of HCN molecule. The presence of the metastable ions in Ic, IIa, and IIIb shows that the *A* ion decomposes to the *m/e* 76 ion similar to the fragmentation of benzonitrile.[18]

## EXPERIMENTAL

*Materials.* Preparation of compounds Ia, b,[13] IIa, b,[13] IIIa, b,[13,16] IIIc,[16] Va–d,[15] VIa–c,[15] VIIa–c,[15] and IXa–c[13] have been described in the preceding papers of this series. Compound Ic was prepared by the procedure of Goerdeler and Pohland,[24] m.p. 46–47° (lit., m.p. 46°). Compounds IVa–c were prepared by treatment of the corresponding 4-carboxylic acids[13] with diazomethane in ether; IVa, m.p. 85–87° (from

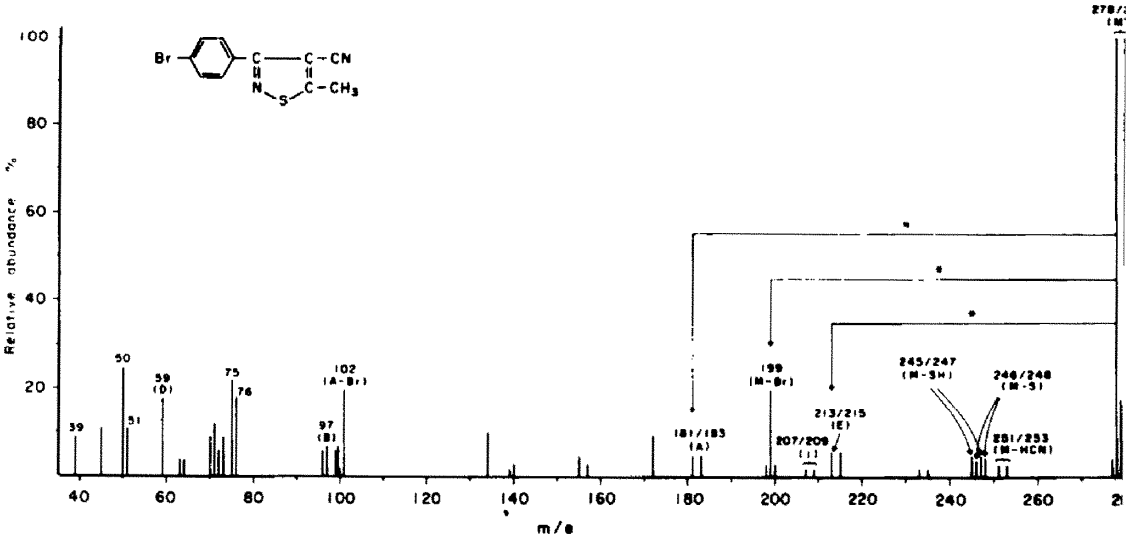
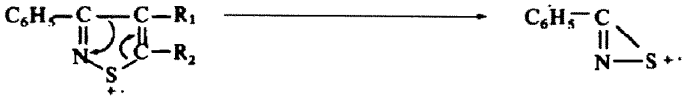



FIG. 11 Mass spectrum of 3-(p-bromophenyl)-4-cyano-5-methylisothiazole (IXc).




*E*, *m/e* 135

*E Peaks.* The *E* peak at *m/e* 135 is rather strong in I, II and III (12–28% of the base peak), while it is weak in IV, V and VI (0·5–3%). However, it can be easily detected even in the latters, because no prominant peak appears around *m/e* 135. The high resolution spectra of Ib and IIIb establish that this peak contains a sole ion with an elemental composition of $C_7H_5NS$. Of the fragment ions produced by ring fission where the fragmentations are interpretable, this is the only ion which contains both nitrogen and sulfur atoms. As might be expected for the fragmentation process, the chlorophenyl derivatives (IXa and IXb) afford a doublet at *m/e* 169/171 in the ratio 3:1 and the bromo analogue (IXc) at *m/e* 213/215 in the ratio 1:1.

*F Peaks.* The fragment ions due to 3-phenyl ring are present as usual[23] at *m/e* 77, 76, 75, 65, 64, 63, 52, 51, 50 and 39. In most compounds in this study, ions of *m/e* 77, 51, 50 and 39 are relatively abundant. Besides a direct formation from the molecular ion, the phenyl ion may arise from cleavage of some fragment ions. Mass spectra of V exhibit a metastable ion at *m/e* 57·0, indicative of a decomposition of the 104 ion to the *m/e* 77 ion by elimination of HCN molecule. The presence of the metastable ions in Ic, IIa, and IIIb shows that the *A* ion decomposes to the *m/e* 76 ion similar to the fragmentation of benzonitrile.[18]

## EXPERIMENTAL

*Materials.* Preparation of compounds Ia, b,[13] IIa, b,[13] IIIa, b,[13,16] IIIc,[16] Va–d,[15] VIa–c,[15] VIIa–c,[15] and IXa–c[13] have been described in the preceding papers of this series. Compound Ic was prepared by the procedure of Goerdeler and Pohland,[24] m.p. 46–47° (lit., m.p. 46°). Compounds IVa–c were prepared by treatment of the corresponding 4-carboxylic acids[13] with diazomethane in ether; IVa, m.p. 85–87° (from

ether). (Found: C, 60·08; H, 4·30; N, 6·09. Calc. for $C_{11}H_9NO_2S$: C, 60·25; H, 4·14; N, 6·39%). IVb, b.p. 135°/0·1 mm. (Found: C, 61·90; H, 4·76; N, 5·58. Calc. for $C_{12}H_{11}NO_2S$: C, 61·78; H, 4·75; N, 6·00%). IVc gave a single peak by vapour-phase chromatography (SE-30; 178°; retention time, 13·1 min). The spectra of the deuterated VIIIa–c were obtained by introducing the corresponding hydroxy derivatives (Va–c) into the spectrometer in the presence of $D_2O$.[25]

*Mass spectra.* The low-resolution mass spectra were run with a Hitachi RMU-6 spectrometer. The chamber voltage was either 70 V or 80 V and the electron multiplier voltage 1500 V or 2000 V. Samples were introduced into the ion chamber through a heated inlet system operating at 80–120°.

Exact mass measurements were performed either against reference masses in the spectrum of perfluorokerosene with a Japan Electron Optics JMS-01S mass spectrometer (compounds Ib, IIIb and VIa) or a CEC-21-110B mass spectrometer (compounds IVa and IVc), or against ions of previously established composition in the spectrum of an appropriate compound with a Hitachi RMU-6E mass spectrometer (compounds IVa, IVb, Va and Vb).

*Acknowledgement*—The author wishes to express his thanks to professor S. Hishida of Nihon University for measurements of low resolution mass spectra and to Professor A. Tatematsu of Meijo University, Government Chemical Industrial Research Institute of Tokyo, Japan Electron Optics Laboratory Co. Ltd. and Hitachi Ltd. for exact mass measurements.

## REFERENCES

1 [a] I. W. Kinney, Jr., and G. L. Cook, *Analyt. Chem.* **24**, 1391 (1952);
[b] V. Hanuš and V. Čermák, *Coll. Czech. Chem. Commun.* **24**, 1602 (1959);
[c] R. Grigg, H. J. Jakobsen, S.-O. Lawesson, M. V. Sargent, G. Schroll and D. H. Williams, *J. Chem. Soc* (B), 331 (1966);
[d] T. Nishiwaki, *Tetrahedron* **23**, 2979 (1967);
[e] J. H. Bowie, R. G. Cooks, S.-O. Lawesson and C. Nolde, *J. Chem. Soc.* (B), 616 (1967).
2 [a] J. Collin, *Bull. Soc. Chim. Belg.* **69**, 449, 575 (1960);
[b] R. I. Reed and W. K. Reid, *J. Chem. Soc.* 5933 (1963);
[c] R. Grigg, M. V. Sargent and D. H. Williams, *Tetrahedron* **21**, 3441 (1965);
[d] K. Heyns, R. Stute and H. Scharmann, *Ibid.*, **22**, 2223 (1966).
3 G. M. Clarke, T. Grigg and D. H. Williams, *J. Chem. Soc.* (B), 339 (1966).
4 [a] W. D. Crow, J. H. Hodgkin and J. S. Shannon, *Austral. J. Chem.* **18**, 1433 (1965);
[b] J. H. Bowie, P. F. Donaghne, H. J. Rodda, R. G. Cooks and D. H. Williams, *Org. Mass Spec.* **1**, 13 (1968).
5 M. Ohashi, H. Kamachi, H. Kakisawa, A. Tatematsu, H. Yoshizumi and H. Nakata, *Tetrahedron Letters* 379 (1968).
6 J. L. Cotter, *J. Chem. Soc.* 5491 (1964).
7 [a] H. E. Ungnade and E. D. Loughran, *J. Heterocyclic Chem.* **1**, 61 (1964);
[b] R. A. Olofson and J. S. Michelman, *J. Org. Chem.* **30**, 1854 (1965).
8 J. L. Cotter, *J. Chem. Soc.* 6842 (1965).
9 [a] H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman and J. M. Wilson, *J. Chem. Soc.* 1949 (1964);
[b] A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams and C. Djerassi, *J. Am. Chem. Soc.* **87**, 805 (1965).
10 A. L. Jennings, Jr. and J. E. Boggs, *J. Org. Chem.* **29**, 2065 (1964).
11 T. Nishiwaki, *J. Chem. Soc.* (B) 885 (1967).
12 T. Naito, S. Nakagawa, K. Takahashi, K. Kasai, K. Fujisawa and H. Kawaguchi, to be published.
13 T. Naito, S. Nakagawa and K. Takahashi, *Chem. Pharm. Bull. Tokyo* **16**, 159 (1968).
14 T. Naito, S. Nakagawa and K. Takahashi, *Ibid.* **16**, 168 (1968).
15 T. Naito, S. Nakagawa, J. Okumura, K. Takahashi and K. Kasai, *Bull. Chem. Soc. Japan* **41**, 959 (1968).
16 T. Naito, S. Nakagawa, J. Okumura, K. Takahashi, K. Masuko and Y. Narita. *Ibid.* **41**, 965 (1968).
17 Catalog of Mass Spectral Data, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburg, Pa., spectrum Nos. 613, 906, 907 and 908.
18 H. Budzikiewicz, C. Djerassi, D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds* p. 162–212. Holden-Day, San Francisco (1964).
19 F. W. McLafferty and R. S. Gohlke, *Analyt. Chem.* **31**, 2076 (1959).

[20] Summarized in an excellent review of P. Brown and C. Djerassi, *Angew. Chem.* (Intern. Ed. Engl.) **6**, 477 (1967).
[21] D. H. Williams, R. G. Cooks, J. H. Bowie, P. Maden, G. Schroll and S.-O. Lawesson, *Tetrahedron* **23** 3173 (6967).
[22] R. Beugelmans, D. H. Williams, H. Budzikiewicz and C. Djerassi, *J. Am. Chem. Soc.* **86**, 1386 (1964).
[23] F. W. McLafferty, *Interpretation of Mass Spectra, An Introduction* p. 57. Benjamin, New York (1966).
[24] J. Goerdeler and H. W. Pohland, *Chem. Ber.* **94**, 2950 (1961).
[25] J. S. Shannon, *Austral. J. Chem.* **15**, 265 (1962).