CONDENSED HETEROCYCLES.

41.* MASS SPECTROMETRIC STUDY OF SELENOL(MERCAPTO)ALDIMINES OF BENZO[b]THIOPHENE AND THEIR S,Se-ALKYL DERIVATIVES

B. M. Zolotarev, V. P. Litvinov,
Ya. L. Gol'dfarb, and V. Yu. Mortikov

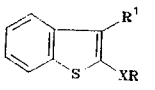
UDC 547.735'739:543.51

The production of imines of 3-selenol(mercapto)-2-benzo[b]thiophenaldehyde and 2-selenol(mercapto)-3-benzo[b]thiophenaldehyde and their S,Se-alkyl derivatives under electron impact was studied. The main distinctions of the decomposition of the molecular ions of selenium-containing compounds from their sulfur analogs, due to the greater strength of the C—S bond in comparison with the C—Se bond, were demonstrated. The different behavior of isomeric 3- and 2-mercaptoaldimines of benzo[b]thiophene was detected.

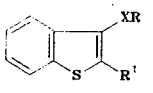
Earlier [2] it was shown that the C—Se bond in α-alkylselenothiophenes is readily cleaved under the action of BuLi, and yet the C—S bond in α-alkylmercaptothiophenes remains unchanged under analogous conditions. This fact is explained by the different strength of two indicated types of bonds. A measure of their strength should find reflection in a study of the mass spectra of compounds of the indicated type [3]. We should emphasize that the cleavage reaction mentioned is observed only for α-derivatives, i.e., at a carbon atom bonded to two functional groups — the heteroatom of the substituent and the ring heteroatom.

The selenol(mercapto)aldimines of the benzo[b]thiophene series, which we recently described [4], are interesting objects from this standpoint, and now it was advisable to use the data of mass spectrometry of compounds of the indicated type as primary criteria.

In the mass spectra of the compounds I-XVIII that we investigated, polyisotopic peaks of the molecular ions are observed, the summary intensity of which for most of the compounds exceeds 20-25% relative to the main peak in the mass spectrum.



IV–VII, XVI–XVIII



I–III, VIII–XV

I—III X=Se; R=CH_3; I R^1=CH=NPh; II R^1=CHO; III R^1=CH(—OCH_2—)$_2$; IV—VII X=Se; IV R=CH_3, R^1=CHO; V R^1=CH=$NC_6H_4CH_3$-*p*; VI R^1=CH=NPh; VII R^1=CH=$NC_{10}H_7$-β; VIII—XV X=S; VIII R=Et, R^1=CH=NPh; IX R=$COCH_3$, R^1=CH=$NC_6H_4NO_2$-*p*; X R^1=CH=$NC_6H_4NO_2$-*p*; XI R^1=CH=NPh; XII R^1=CH=$NC_6H_4OCH_3$-*p*; XIII R^1=CH=$NC_{10}H_7$-β; XIV R=Et, R^1=CHO; XV R=CH_3, R^1=CHO; XVI—XVIII X=S; XVI R^1=CH=$NC_{10}H_7$-β; XVII R^1=CH=$NC_6H_4CH_3$-*p*; XVIII R^1=CH=NPh; V—VII, X—XIII, XVI—XVIII R=H

The presence of ions with m/z 134, 133, and 132 in the mass spectra corresponds to preservation of the charge on the benzo[b]thiophene structural unit, and of ions in the low region of mass numbers, is due mainly to ionization of the fragments R and R^1.

The selenoaldimines V-VII and the alkyl-derivative I are characterized by two main pathways of decomposition of the molecular ions: cleavage of the $C_{(2)}$—Se ($C_{(3)}$—Se) and N—Ar bonds. The joint implementation of these pathways results in an ion with m/z 159 with possible isomeric structures XIX or XX.

*For communication 40, see [1].

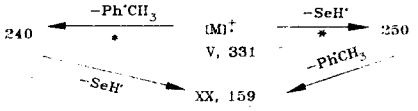
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1057-1061, August, 1984. Original article submitted July 27, 1983.

 0009-3122/84/2008-0858$08.50

XIX,XXI XX,XXII

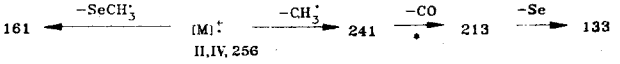
XIX,XX X=NH; XXI,XXII X=O

A characteristic scheme of decomposition of selenoaldimines V-VII is cited on the example of compound V:

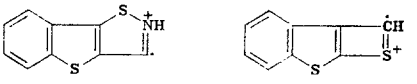


Isomeric 3-methylseleno-2-aldehyde (II) and 2-methylseleno-3-benzo[b]thiophenaldehyde (IV) give virtually the same picture of fragmentation under the action of electron impact, which is evidently explained by the equiprobable elimination of both substituents in the 2- and 3-positions of benzothiophene or by isomerization of the molecular ions with m/z 256 up to their fragmentation to an ion of the same structure.

Analogously to the selenoaldimines, alkylselenoaldehydes are characterized by elimination of an alkylseleno group and the formation of an ion (m/z 161) with possible isomeric structures XXI and XXII, as well as the formation of an ion with m/z 213, which permits us to represent the scheme of decomposition of compounds II and IV below:

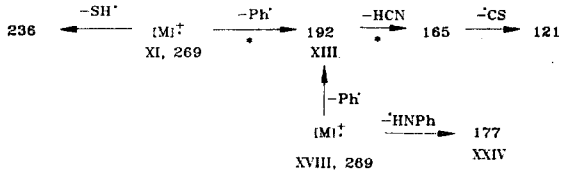


In contrast to selenolaldimines, mercaptoaldimines X-XIII, XVI-XVIII and their S-derivatives VIII and IX are characterized in all cases by the formation of ions retaining the sulfur atom. Moreover, 3-mercaptoaldimines X-XIII are characterized by the formation of the ion XXIII with m/z 192, while 2-mercaptoaldimines XVI-XVIII are characterized by the formation of the ion XXIV with m/z 177:

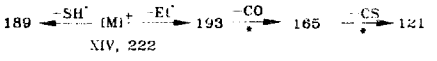


XXIII, 192 XXIV, 177

The peaks of these ions have a rather high intensity (20-50%) or close to the maximum intensity. The scheme of the presumed fragmentation of these compounds is presented on the examples of XI and XVIII:



The alkylmercaptoaldehydes XIV and XV are characterized by the formation of an ion with m/z 193 — an oxygen analog of the ion XXIII retaining a sulfur atom, in contrast to their selenium analogs. Subsequent fragmentation of this ion is presented on the example of XIV:



As was shown by a comparison of the data of mass spectra of selenolaldimines, for example, VI or VII, with the spectra of mercaptoaldimines with analogous substituents at the nitrogen atom, for example, XVI, or, correspondingly XVIII, the summary intensity of the peaks of the ions containing both selenium and sulfur atoms in the spectra of selenolaldimines VI and VII is 13.2 and 6.6%, respectively, relative to the total ionic current. At the same time, the summary intensity of the peaks of the ions containing two sulfur atoms is equal to 46 and 33% for mercaptoaldimines XVIII and XVI, respectively.

Thus, these data indicate a predominent cleavage of the C—Se bond in ions of the investigated ions in comparison with the C—S bond, which agrees with the data obtained earlier [2].

EXPERIMENTAL

The mass spectra were recorded on a Varian MAT CH-6 mass spectrometer (Federal Republic of Germany) with direct introduction of the sample into the ion source. Temperature of the

ionization chamber 180°C, ionizing voltage 70 eV, emission current 100 μA. The temperature of heating of the samples was varied depending on their volatility, from 25 to 140°C. The gross formula of the ions was obtained from the intensity ratio of the isotope peak for Se and S. For graphic representation, the text cites the nominal masses of the ions, on the basis of the main isotopes ^{80}Se and ^{32}S. Ions with an intensity of less than 5% (except for molecular ions and close to them, as well as those mentioned in the discussion) are excluded.

Selenol(mercapto)aldehydes and their derivatives were produced according to the procedures that we described earlier [4].

MASS SPECTRA

(3-Methylseleno-2-benzo[b]thenylidene)phenylamine (I). *M* 331. *m/z* (%): 331 (1), 332 (1), 331 (5), 330 (0,8), 329 (3), 328 (1), 327 (1), 318 (11), 317 (7), 316 (43), 315 (5), 314 (22), 313 (9), 312 (9), 240 (6), 239 (15), 238 (20), 237 (13), 236 (51), 235 (16), 234 (7), 213 (11), 211 (6), 208 (9), 169 (7), 165 (8), 161 (5), 160 (10), 159 (67), 157 (5), 147 (6), 146 (5), 145 (7), 134 (7), 133 (4), 132 (8), 93 (8), 89 (12), 78 (21), 77 (100), 52 (10), 51 (63), 50 (15); W_M=1,9%.

3-Methylseleno-2-benzo[b]thiophenaldehyde (II). *M* 256. *m/z* (%): 258 (7), 257 (4), 256 (34), 255 (3), 254 (17), 253 (7), 252 (6), 243 (8), 242 (5), 241 (38), 240 (5), 239 (21), 238 (8), 237 (8), 215 (13), 214 (8), 213 (57), 212 (12), 211 (28), 210 (13), 209 (12), 175 (26), 171 (8), 170 (6), 169 (41), 168 (11), 167 (23), 166 (12), 165 (11), 162 (6), 161 (46), 160 (9), 148 (6), 147 (45), 145 (9), 134 (11), 133 (30), 132 (54), 121 (32), 120 (5), 106 (11), 105 (6), 103 (7), 102 (8), 101 (17), 98 (32), 90 (9), 89 (100), 88 (15), 87 (15), 82 (16), 81 (7), 77 (13), 75 (25), 74 (12), 69 (34), 63 (35), 62 (17), 51 (14), 50 (10), 45 (11), 39 (19); W_M=6,8%.

1,4-Dioxalane of 3-methylseleno-2-benzo[b]thiophenaldehyde (III). *M* 300. *m/z* (%): 302 (15), 301 (9), 300 (55), 299 (8), 298 (29), 297 (14), 296 (11), 287 (24), 286 (15), 285 (100), 284 (9), 283 (49), 282 (18), 281 (18), 257 (13), 256 (8), 255 (27), 254 (5), 253 (13), 243 (7), 242 (6), 241 (29), 240 (14), 239 (18), 238 (13), 237 (9), 228 (8), 227 (8), 226 (7), 225 (17), 223 (8), 215 (15), 214 (10), 213 (66), 212 (19), 211 (33), 210 (17), 209 (15), 206 (10), 205 (61), 204 (71), 175 (9), 171 (6), 169 (33), 168 (10), 167 (17), 166 (10), 165 (9), 162 (13), 161 (65), 160 (41), 148 (15), 147 (99), 146 (14), 145 (50), 134 (25), 133 (25), 132 (44), 121 (30), 120 (7), 115 (15), 103 (11), 102 (15), 101 (21), 95 (5), 93 (17), 89 (51), 88 (7), 87 (7), 77 (13), 75 (18), 73 (30), 69 (23), 63 (17), 51 (7), 45 (48), 39 (9); W_M=7,9%.

2-Methylseleno-3-benzo[b]thiophenaldehyde (IV). *M* 256. *m/z* (%): 258 (11), 257 (6), 256 (48), 255 (5), 254 (24), 253 (10), 252 (9), 243 (11), 242 (7), 241 (49), 240 (8), 239 (25), 238 (12), 237 (11), 215 (14), 214 (9), 213 (60), 21⁹ (15), 211 (33), 210 (15), 209 (14), 175 (17), 171 (8), 170 (6), 169 (49), 168 (18), 167 (29), 166 (16), 165 (15), 163 (7), 162 (10), 161 (82), 160 (9), 147 (36), 145 (8), 134 (13), 133 (40), 132 (67), 121 (44), 119 (14), 117 (21), 108 (7), 106 (12), 101 (22), 95 (7), 94 (6), 93 (36), 90 (9), 89 (100), 88 (15), 87 (18), 82 (18), 77 (20), 75 (29), 69 (40), 63 (40), 62 (22), 51 (20), 50 (13), 45 (18), 39 (27); W_M=8,1%.

(2-Selenol-3-benzo[b]thenylidene)-p-methylphenylamine (V). *M* 331. *m/z* (%): 333 (12), 332 (11), 331 (61), 330 (14), 329 (28), 328 (11), 327 (11), 252 (6), 251 (18), 250 (65), 249 (11), 248 (7), 242 (9), 241 (5), 240 (32), 239 (7), 238 (23), 237 (9), 236 (19), 235 (12), 227 (5), 225 (23), 223 (14), 222 (5), 221 (10), 161 (7), 160 (20), 159 (84), 146 (5), 145 (29), 135 (5), 134 (23), 133 (7), 132 (9), 118 (12), 102 (7), 101 (12), 93 (5), 92 (11), 91 (100), 90 (15), 89 (40), 78 (11), 77 (18), 65 (84), 63 (16), 51 (21), 41 (18), 39 (28); W_M=14,5%.

(2-Selenol-3-benzo[b]thenylidene)phenylamine (VI). *M* 317. *m/z* (%): 319 (7), 318 (6), 317 (29), 316 (5), 315 (13), 314 (7), 313 (6), 242 (4), 241 (2), 240 (17), 239 (2), 238 (10), 237 (10), 236 (40), 235 (6), 225 (12), 223 (6), 213 (5), 208 (5), 161 (3), 160 (12), 159 (43), 145 (15), 134 (16), 133 (5), 132 (5), 121 (5), 104 (9), 102 (5), 101 (7), 93 (9), 89 (18), 78 (18), 77 (100), 76 (5), 75 (8), 52 (10), 51 (45), 50 (8), 39 (16); W_M= =12,7%.

(2-Selenol-3-benzo[b]thenylidene)-β-naphthylamine (VII). *M* 367. *m/z* (%): 370 (2), 369 (4), 368 (4), 367 (11), 366 (2), 365 (5), 364 (3), 363 (3), 288 (5), 287 (10), 286 (36), 285 (5), 240 (7), 238 (4), 236 (2), 160 (7), 159 (28), 145 (14), 144 (18), 143 (96), 142 (7), 134 (12), 132 (7), 128 (25), 127 (52), 126 (13), 117 (8), 116 (40), 115 (100), 114 (12), 113 (7), 102 (10), 101 (16), 90 (5), 89 (26), 77 (10), 76 (6), 75 (8), 65 (12), 63 (24), 51 (14), 39 (20); W_M=4,7%.

(3-Ethylmercapto-2-benzo[b]thenylidene)phenylamine (VIII). *M* 297. *m/z* (%): 299 (0,2), 298 (0,6), 297 (2), 270 (11), 269 (17), 268 (87), 240 (8), 236 (13), 235 (21), 234 (6), 208 (9), 207 (11), 206 (18), 205 (99), 204 (43), 203 (6), 192 (8), 191 (18), 190 (38), 172 (17), 171 (9), 166 (6), 165 (40), 164 (6), 161 (6), 160 (5), 159 (20), 147 (6), 146 (17), 134 (15), 122 (7), 121 (48), 120 (21), 115 (9), 109 (12), 89 (12), 78 (8), 77 (100), 69 (12), 51 (60), 50 (6), 45 (7), 39 (7); W_M=0,32%.

(3-Acetylmercapto-2-benzo[b]thenylidene)p-nitrophenylamine (IV). *M* 356. *m/z* (%): 358 (0,5), 357 (0,8), 356 (3,2), 314 (11), 313 (24), 268 (5), 267 (20), 266 (6), 193 (3), 192 (18), 191 (8), 190 (8), 165 (6), 159 (6), 134 (4), 121 (14), 120 (9), 108 (23), 77 (6), 76 (11), 75 (6), 69 (5), 65 (8), 64 (7), 63 (8), 51 (6), 50 (8), 45 (5), 43 (100), 42 (5); $W_M = 1.1\%$.

(3-Mercapto-2-benzo[b]thenylidene)-p-nitrophenylamine (X). *M* 314. *m/z* (%): 316 (6), 315 (9), 314 (43), 313 (4), 298 (5), 268 (6), 267 (12), 266 (6), 252 (6), 251 (7), 240 (12), 236 (16), 235 (17), 234 (10), 224 (6), 223 (13), 222 (5), 209 (6), 208 (9), 194 (10), 193 (13), 192 (100), 191 (14), 190 (14), 166 (7), 165 (19), 164 (6), 159 (23), 146 (11), 145 (9), 138 (20), 134 (21), 133 (8), 132 (9), 122 (10), 121 (41), 120 (29), 109 (13), 108 (87), 101 (13), 93 (12), 92 (35), 90 (9), 89 (23), 80 (43), 78 (9), 77 (39), 76 (27), 75 (20), 74 (13), 69 (25), 66 (12), 65 (87), 64 (20), 63 (43), 62 (12), 53 (15), 52 (24), 51 (29), 50 (38), 41 (17), 39 (39); $W_M = 4.6\%$.

(3-Mercapto-2-benzo[b]thenylidene)phenylamine (XI). *M* 269. *m/z* (%): 271 (10), 270 (22), 269 (100), 268 (29), 253 (6), 240 (5), 236 (24), 235 (8), 194 (9), 193 (13), 192 (85), 191 (14), 190 (8), 166 (8), 165 (33), 160 (8), 159 (41), 134 (15), 122 (6), 121 (44), 120 (19), 109 (7), 108 (13), 90 (9), 89 (17), 78 (10), 77 (80), 76 (8), 75 (10), 69 (18), 51 (69), 39 (26); $W_M = 17\%$.

(3-Mercapto-2-benzo[b]thenylidene)-p-methoxyphenylamine (XII). *M* 299. *m/z* (%): 301 (11), 300 (20), 299 (100), 298 (17), 284 (15), 283 (7), 268 (7), 266 (14), 257 (5), 256 (18), 255 (13), 254 (6), 240 (8), 224 (28), 223 (34), 222 (17), 193 (10), 192 (50), 191 (28), 190 (24), 177 (30), 166 (13), 165 (30), 159 (40), 134 (20), 133 (9), 121 (48), 120 (22), 108 (36), 93 (9), 92 (40), 80 (36), 78 (14), 77 (42), 69 (17), 65 (24), 64 (40), 63 (30), 53 (16), 52 (17), 51 (14), 39 (24); $W_M = 13.1\%$.

(3-Mercapto-2-benzo[b]thenylidene)-β-naphthylamine (XIII). *M* 319. *m/z* (%): 321 (11), 320 (26), 319 (100), 318 (26), 303 (7), 287 (13), 286 (49), 285 (9), 193 (6), 192 (37), 191 (14), 165 (18), 160 (6), 159 (28), 143 (32), 128 (38), 127 (64), 126 (18), 121 (22), 120 (8), 116 (6), 115 (25), 114 (5), 101 (12), 89 (10), 77 (28), 51 (8), 39 (8); $W_M = 21.2\%$.

3-Ethylmercapto-2-benzo[b]thiophenaldehyde (XIV). *M* 222. *m/z* (%): 224 (3), 223 (4), 222 (25), 205 (6), 195 (5), 194 (6), 193 (42), 189 (25), 166 (17), 165 (30), 164 (7), 161 (15), 160 (10), 134 (14), 132 (13), 123 (5), 122 (10), 121 (100), 120 (25), 94 (10), 93 (17), 89 (22), 77 (29), 69 (27), 63 (17), 51 (10), 45 (10), 39 (19); $W_M = 6.1\%$.

3-Ethylmercapto-2-benzo[b]thiophenaldehyde (XV). *M* 208. *m/z* (%): 210 (6), 209 (7), 208 (48), 207 (3), 194 (5), 193 (39), 191 (11), 179 (7), 177 (7), 176 (5), 175 (36), 174 (12), 167 (5), 166 (7), 165 (52), 164 (11), 149 (5), 147 (30), 146 (10), 135 (14), 134 (19), 133 (9), 132 (25), 122 (13), 121 (100), 120 (42), 119 (9), 94 (13), 93 (37), 90 (6), 89 (50), 82 (19), 81 (10), 77 (25), 69 (48), 63 (33), 62 (15), 51 (10), 45 (37), 39 (25); $W_M = 6.9\%$.

(2-Mercapto-3-benzo[b]thenylidene-β-naphthylamine (XVI). *M* 319. *m/z* (%): 321 (4), 320 (9), 319 (39), 318 (5), 287 (5), 286 (23), 192 (11), 191 (7), 179 (11), 178 (13), 177 (100), 165 (9), 160 (9), 159 (21), 128 (22), 127 (51), 126 (20), 121 (24), 120 (11), 116 (7), 115 (32), 114 (7), 102 (9), 101 (26), 90 (5), 89 (21), 78 (8), 77 (36), 76 (6), 75 (13), 69 (6), 63 (13), 51 (14), 39 (8); $W_M = 8.2\%$.

(2-Mercapto-3-benzo[b]thenylidene)-p-methylphenylamine (XVII). *M* 283. *m/z* (%): 285 (8), 284 (16), 283 (65), 282 (8), 250 (11), 192 (22), 191 (7), 179 (9), 178 (13), 177 (100), 159 (18), 148 (10), 147 (52), 146 (25), 145 (16), 132 (15), 121 (20), 120 (11), 102 (21), 101 (15), 91 (20), 89 (26), 77 (18), 69 (15), 65 (25), 63 (13), 51 (13), 39 (20); $W_M = 14.7\%$.

(2-Mercapto-3-benzo[b]thenylidene)phenylamine (XVIII). *M* 269. *m/z* (%): 271 (10), 270 (18), 269 (93), 268 (13), 236 (13), 193 (6), 192 (33), 191 (7), 190 (6), 179 (11), 178 (16), 177 (100), 159 (20), 133 (7), 121 (22), 120 (11), 119 (16), 118 (9), 117 (18), 102 (9), 101 (11), 93 (13), 89 (16), 78 (7), 77 (60), 76 (7), 69 (9), 64 (18), 51 (53), 45 (25), 39 (22); $W_M = 17.7\%$.

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