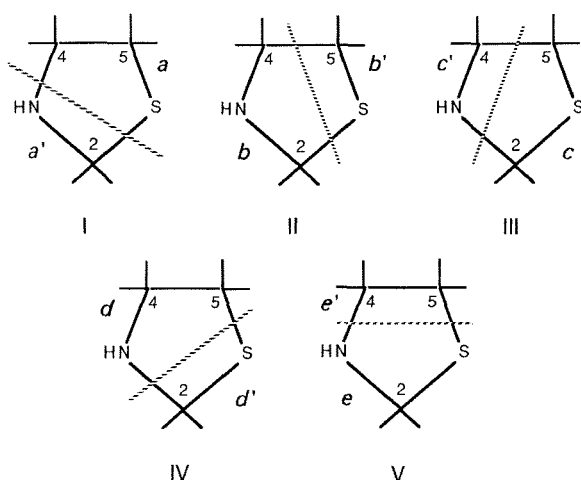


New Mass Spectra

Electron Impact Study of Derivatives of Thiazolidine

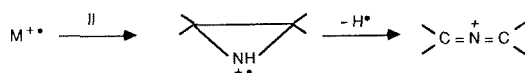
Very few papers report mass spectra of substituted thiazolidines: Vestling and Ogren¹ have analysed some 2-alkylated compounds; Oya and coworkers² have studied some 2-aryl derivatives of 4-thiazolidine carboxylic acid. We here report the fragmentation of 2, 4 or 5-alkyl (or aryl) thiazolidines. These compounds have been analyzed with a Ribermag R10-10 instrument.

All investigated thiazolidines show the molecular ion whose abundance varies in a large intensity range. Loss of S or SH⁺ is only sometimes observed; the base peak may arise from the loss of a substituent to form thiazolidinium ions, its abundance depends on the position of this substituent (2 > 4 > 5) and increases with its bulk.



(Scheme 1)

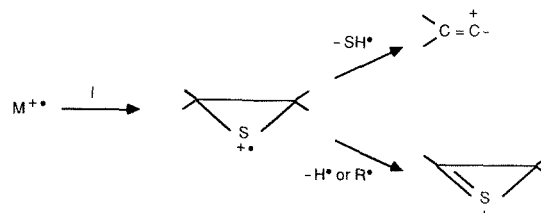
Among the five possible cleavages of the ring, the more abundant is of type II and the immonium ion arising from aziridine often provides the base peak;



(Scheme 2)

the fragmentation of aziridines indeed is well known³ and involves the immonium ion arising from the molecular ion: this one evolves by loss of an H⁺, R⁺ or RCH₂⁺ radical.

The type I process always appears in the spectra:



(Scheme 3)

the thiirane ion is present by the fragments arising from the loss of H⁺, R⁺ or SH⁺: it is a well-known reaction of these sulphur heterocycles.³ The other fragmentations are often of low abundance.

We have recently described⁴ the preparation of the thiazolidines **1**, **8**, **13**, **14**, **15**, **16**, **21**, **22**, **23** and **24**. The following compounds were similarly obtained by reaction of 2R-substituted aziridine with the suitable aldehyde R'CH=O (compound, R, R', yield %, Eb/Torr): **6** and **7**, iPr, Me, 25, 90/18; **9** and **10**, Me, tBu, 54, 83/13; **17** and **18**, Me, Ph, 52, 108/0.6. Other compounds result from the condensation of aminothiols with carbonyl compound (thiazolidine, aminothiols, carbonyl compound, yield %, Eb/Torr): **2**, 1-amino 2-methyl 2-propanethiol, methanal, 92, 65/14; **3** and **4**, 1-amino 2-propanethiol, ethanal, 51, 65/15; **5**, 1-amino 2-propanethiol, acetone, 40, 65/13; **11** and **12**, 1-amino 2-propanethiol, 2,2-dimethylpropanal, 26, 88/13; **19** and **20**, 1-amino 2-propanethiol, benzaldehyde, 38, F = 72 °C. All the compounds give spectral data in agreement with their structure.

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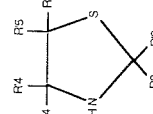
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References

1. M. Vestling and R. Ogren, *J. Heterocycl. Chem.* **12**, 243 (1975).
2. M. Oya, S. Ito, K. Harada, M. Suzuki and A. Tatematsu, *Chem. Pharm. Bull.* **30**, 2705 (1982).
3. Q. Porter, *Mass Spectrometry of Heterocyclic Compounds*, Wiley, New York (1985).
4. D. Barbry and D. Couturier, *Chem. Ber.* **120**, 1073 (1987).

Table I.

Compounds	1	2	3 and 4	5	6 and 7	8	9 and 10	11 and 12	13 and 14	15	16	17 and 18	19 and 20	21 and 22	23 and 24
R2															
R'2															
R4															
R'4															
R5															
R'5															
M ⁺	117(31)	117(78)	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me
[M-S] ⁺			117(57)	131(36)	145(16)	145(7)	159(2)	159(2)	159(12)	165(15)	165(20)	179(43)	179(32)	179(<1)	179(20)
[M-SH] ⁺			85(10)	99(12)											
[M-SH] ⁺			84(11)	98(23)											
[M-R or phenyl] ⁺	102(18)		102(66)	116(28)	102(100) [†]	88(100)	102(100)	102(100)	102(100)	89(16)	136(12)	102(14)	146(12)	136(15)	136(3)
a ⁺	88(2)	88(7)	74(13)	74(11)	102(100) [†]		74(1)			136(8)		74(13)	74(9)		
a ⁺												105(35)	105(4)		
[a-H] ⁺										135(30)	135(19)	104(44)	104(21)	135(40)	135(9)
[a'-H] ⁺										103(11)	103(12)	41(10)	41(10)		103(10)
[a-SH] ⁺	55(29)	55(34)	41(12)	41(16)	69(35)		41(11)		101(12), 59(11) ^{††}	119(71)	43(100)	133(43)	119(27)	133(100)	57(100)
[a-R] ⁺	73(13)	73(10)	59(38)	59(45)	59(22)										
[a'+H] ⁺			44(19)	44(32)	44(32)										
[CH≡S] ⁺	(11)		(22)	(11)	(19)						(14)	106(38)	106(37)		
b ⁺	71(100)	43(100)	57(100)	71(84)	99(20)	99(1)									
b ⁺		75(24)													
[b-H] ⁺	70(23)		56(92)	70(98)	98(21)					118(100)	42(19)	132(100)	118(100)	132(86)	56(37)
[b-R] ⁺	56(16)		42(7)	56(18)	56(11), 84(54)	84(13)				104(10) [†]		118(11)		134(13)	
[b+H] ⁺	72(18)	44(19)	58(40)	72(13)	74(2)						123(13)				
c ⁺															
c ⁺															
[c-R] ⁺															
[c'-R] ⁺															
d ⁺				57(6)	85(71)					104(10) [†]	119(1)		122(2)		
d ⁺															
[d-H] ⁺															
[d'-H] ⁺															
[d-R] ⁺															
[d+H] ⁺				42(15)	70(35)						104(14)		121(11)		
				58(100)											
Benzene fragments															
51															
63															
65															
77															
78															
79															
91															



† Fragmentation of thiazolidines: m/z (abundance %)

†† Indicates several values of m/z for one compound.