in 10 ml of alcohol. To the resulting clear solution was added with vigorous stirring and cooling a solution of 0.4 g (10 mmoles) of NaOH in 1 ml of water. The solid which separated was filtered off and washed with 2 ml of alcohol.

Compounds (IXa-c) and (XIIb-e) were obtained similarly.

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ELECTRON IMPACT MASS SPECTRA OF 2-HYDRAZONO-1,3-THIAZOLIDIN-4-ONE DERIVATIVES

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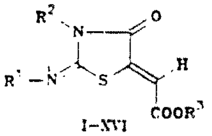
Mass fragmentation of 2-hydrazono-1,3-thiazolidin-4-ones is dominated by two processes, namely cleavage of the hydrazone fragment with accompanying proton transfer from the latter to the thiazolidine ring, and cleavage of a hydrazone imide residue.

The reaction of thiourea with dimethyl acetylenedicarboxylate is known to result in the formation of 1,3-thiazine derivatives [1, 2]. The structures of these products have been established based on analysis of their high-resolution mass spectra [2]. It was later demonstrated [3, 4] that the compounds consist of 2-imino-1,3-thiazolidin-4-ones. In the present paper we have studied the mass spectra of newly synthesized 2-hydrazono-1,3-thiazolidin-4-ones I-XVI [5].



I–XVI

I—IX R¹=Me₂N, X, XI R¹=PhNH, XII, XIII R¹=PhEtN, XIV—XVI R¹=(CH₂)₅N; I, II R²=H, III, IV, X, XII—XV R²=Me, V R²=*t*-Bu, VI, XI, XVI R²=CH₂CH=CH₂, VII, VIII R²=Ph, IX R²=CH₂Ph; I, III, V—VII, IX, XII, XIV R³=H, II, IV, VIII, X, XI, XIII, XV, XVI R³=Me

Formation of the highly conjugated system involving three exocyclic double bonds in the thiazolidine ring in compounds I-XVI increases the stability of these molecules with respect to electron impact and hinders their fragmentation via ring decomposition. The maximum intensity peaks in the mass spectra of most of these compounds are their respective molecular ion peaks (Table 1). Ring decay or decomposition occurs via the formation of fragments A and B (pathway *a* in scheme), whose corresponding peaks have either medium or low intensity. This type of fragmentation (cleavage of fragment A) accompanied by formation of a $[C_5H_4O_3S]^+$ ion is characteristic of all 2-imino-5-methoxycarbonylmethylene-1,3-thiazolidin-4-

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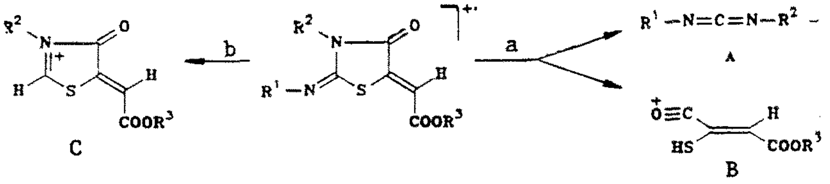
TABLE 1. Characteristic Peaks in the Mass Spectra of 2-Hydrazono-1,3-thiazolidin-4-ones I-XVI

Compound	m/z (I, %)				
	M	A	B	C	others (> 10%)
I	215 (100)	85 (28)	131 (1)	158 (19)	214 (13) $[M-R^2]^+$, 171 (13) $[M-R^1]^+$, 58 (22), 45 (16), 44 (34), 43 (62) 42 (34)
II	229 (100)	85 (21)	145 (17)	172 (21)	228 (10) $[M-R^2]^+$, 73 (14), 58 (17), 57 (17), 55 (13), 45 (24), 44 (28), 43 (52), 42 (21), 41 (13)
III	229 (100)	—	—	172 (65)	58 (11), 57 (11), 56 (22), 43 (39), 42 (26)
IV	243 (100)	99 (20)	145 (16)	186 (72)	212 (10) $[M-OR^3]^+$, 85 (16), 71 (10), 69 (16), 58 (24), 56 (37), 43 (63), 42 (29)
V	271 (100)	—	—	214 (12)	217 (30), 216 (13), 212 (12), 173 (66), 158 (17), 85 (18), 84 (12), 59 (17), 58 (17), 57 (17), 56 (17), 46 (13), 45 (22), 44 (78), 43 (83), 42 (33), 41 (17)
VI	255 (100)	—	—	198 (17)	240 (11), 214 (19) $[M-R^2]^+$, 211 (21) $[M-R^1]^+$, 197 (14), 85 (15), 84 (56), 81 (23), 59 (14), 58 (11), 45 (37), 44 (53), 43 (67), 42 (58), 41 (58)
VII	291 (100)	161 (13)	—	234 (36)	118 (24), 104 (25), 77 (27), 58 (27), 43 (57), 42 (13)
VIII	305 (100)	161 (24)	145 (13)	248 (43)	118 (24), 104 (13), 91 (11), 77 (32), 58 (27), 43 (47)
IX	305 (45)	—	—	—	214 (11) $[M-R^2]^+$, 91 (100), 65 (11), 44 (11)
X	291 (100)	147 (6)	—	—	259 (14) $[M-R^3OH]^+$, 105 (36), 92 (22), 77 (55), 65 (14)
XI	317 (100)	—	145 (3)	212 (8)	225 (24) $[M-R^1]^+$, 105 (26), 93 (18), 77 (55)
XII	305 (60)	—	—	172 (3)	290 (41), $[M-R^2]^+$, 105 (70), 104 (23), 91 (26), 77 (100)
XIII	319 (61)	—	—	186 (3)	304 (41) $[M-R^2]^+$, 105 (63), 104 (19), 91 (24), 77 (100)
XIV	269 (100)	—	—	172 (3)	214 (10), 213 (10), 84 (10), 55 (21), 42 (39)
XV	283 (100)	—	145 (5)	186 (3)	242 (10), 228 (13), 227 (10), 85 (16), 55 (26), 42 (42)
XVI	309 (100)	—	—	212 (5)	268 (14), 254 (19), 227 (28), 225 (21), 211 (19), 124 (19), 117 (14), 85 (24), 84 (83), 81 (52), 69 (17), 59 (14), 56 (17), 55 (69), 42 (57), 41 (76)

ones [6]. The nature of the substituents R^2 and R^3 does not have a significant effect on the pathway for this process, with the exception of compound IX; the principal peak in the spectrum of the latter is due to the R^2 substituent, namely benzyl cation (m/e 91). Only a few of the compounds studied herein give rise to $[M - OR^3]^+$ or $[M - R^2]^+$ ions upon decomposition (see Table 1).



Fragmentation of the 2-dimethylhydrazonothiazolidines I-VIII occurs similarly. The appearance of $[M - C_2H_5N_2]^+$ ion peaks in their mass spectra (high resolution; see Experimental) is probably due to migration of a hydrogen atom from a carbon in the dimethylamino group to a ring carbon atom, resulting in the formation of a stable immonium ion C.

As the structure of the R^1 radical is changed, for instance in the transition from dimethylamine to piperidine, the contributions of decay processes of the cyclic system (ions A and B) decrease, along with the formation of ion C. Fragmentation of the 2-phenylhydrazonothiazolidines X-XIII proceeds via charge retention both on the hydrazone residue, with formation of the C_6H_5–N^+=N ion, as well as on the phenyl group (m/e 77 ion).

The available data lead us to conclude that the general principles governing the fragmentation of 2-hydrazono- and 2-imino-1,3-thiazolidin-4-one-5-methylenecarboxylic acids can be interpreted in terms of their electronic structure characteristics, including delocalization of electron density in the NCN fragment of the conjugated system [7] and donor-acceptor interaction between the sulfur atom and the carbonyl oxygen atom in the carboxyl group [8], which facilitate cleavage along the S–$C_{(2)}$ and $N_{(3)}$–$C_{(4)}$ bonds.

EXPERIMENTAL

Mass spectra were measured on an MS-50 spectrometer (AEI) at an ionizing electron energy of 70 eV, and at an ionization temperature of 200°C.

High-Resolution Mass Spectrum of Compounds VIII. $C_{14}H_{15}N_3O_3S$, exp. 305.0816; calc. 305.0834. $C_{12}H_{10}NO_3S$, exp. 248.0379; calc. 248.0382.

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