MASS-SPECTROSCOPIC STUDY OF DIHYDRO-8H-PYRANO(THIOPYRANO)[4',3':4,5]THIENO-[2,3-d]URACIL DERIVATIVES

R. G. Mirzoyan, K. E. Basentsyan,
P. B. Terent'ev, A. Sh. Oganisyan,
and A. S. Noravyan

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When a saturated six-membered oxygen- or sulfur-containing heteroring is present in the thienouracil molecule, retrodiene decomposition of the uracil ring takes place in all cases in later stages of the fragmentation. Under the influence of electron impact the more saturated heteroring undergoes fragmentation first with ejection of CHO and SH radicals, respectively, or fragmentation proceeds via a retrodiene mechanism. This is probably associated with the primary localization of the positive charge in it in the molecular ion.

The mass-spectrometric fragmentation of uracil derivatives involves first and foremost retrodiene fragmentation of the heteroring and the elimination of an HNCO (RNCO) molecule [1]. Retrodiene fragmentation of the heteroring is also characteristic for many derivatives of saturated six-membered heterocycles that are annelated with aromatic or heteroaromatic rings [2]. The dihydro-8H-pyrano(thiopyrano)[4',3':4,5]thieno[2,3-d]uracil derivatives (I-VIII) that we recently synthesized [3] include various saturated heterorings that are condensed with the electron-rich thiophene ring. In this connection, continuing our study of the processes involved in the dissociative ionization of pyrimidine derivatives [4], we decided to ascertain which of the heterorings will first undergo fragmentation under the influence of electron impact.

It follows from an analysis of the mass spectra of I-VIII that the molecular ions of these heterocycles are quite stable (see Tables 1 and 2); their stabilities are somewhat higher in the case of thiopyrano derivatives V-VIII. The transition from unsubstituted (in the uracil fragment) I and II to their N-phenyl-substituted derivatives (III, IV) in the series of dihydropyran derivatives increases the resistance of the molecules to electron impact appreciably, whereas in the thiopyran-substituted series the introduction of a phenyl ring has almost no effect on the W_M value. An increase in the size of R^2 (transition from CH_3 to C_2H_5) always leads to a decrease in the stabilities of the molecular ions. All of these data make it possible to conclude that the positive charge in the molecular ions of I-IV is localized primarily in the region of the electron-rich thiophene ring, whereas in the case of thio compounds V-VIII it is also partially located on the sulfur atom of the thiopyran ring.

In fact, it follows from the scheme of the fragmentation of these compounds that the primary processes of dissociative ionization are characterized above all by retrodiene fragmentation of the pyran (thiopyran) ring with the formation, as a rule, of an intense F_1 ion peak (Table 1). On the other hand, elimination from the molecular ion of primarily the larger R^2 grouping to give an F_2 ion is also observed; in the case of thio derivatives V-VIII the relative intensities of the F_2 ion peaks increase appreciably. Primary retrodiene fragmentation of the uracil part of the molecule virtually does not occur. Low-intensity peaks of $[M-C_6H_5NCO]^+$ ions, the percentage of which in the total ion current does not exceed 1-2%, are observed in the mass spectra only in the case of N-phenyl derivatives (III, IV, VII, and VIII). At the same time, this fragmentation process is most likely in the second stage of the fragmentation, i.e., after the formation of the F_1 (F_3) ion. An analysis of the high-

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TABLE 1. Intensities of the Peaks of the Characteristic Ions in the Mass Spectra of I-VIII (Σ_{100}%)

Compound	W_M	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8
I	15,5	42,1	1,2	11,7	1,7	1,2	1,9	—	—
II	9,3	36,9	5,7	10,3	1,5	0,7	1,8	—	—
III	28,6	23,1	0,9	13,9	1,1	1,4	2,9	—	—
IV	23,5	28,2	4,4	11,3	0,6	0,6	1,1	—	—
V	26,8	15,4	2,3	4,6	—	12,5	1,2	16,5	6,0
VI	24,1	12,8	10,0	2,7	—	10,0	0,9	13,7	2,5
VII	24,3	5,0	1,5	7,5	—	9,9	1,3	16,9	6,9
VIII	21,8	4,5	4,5	6,6	—	8,0	1,5	15,6	4,0

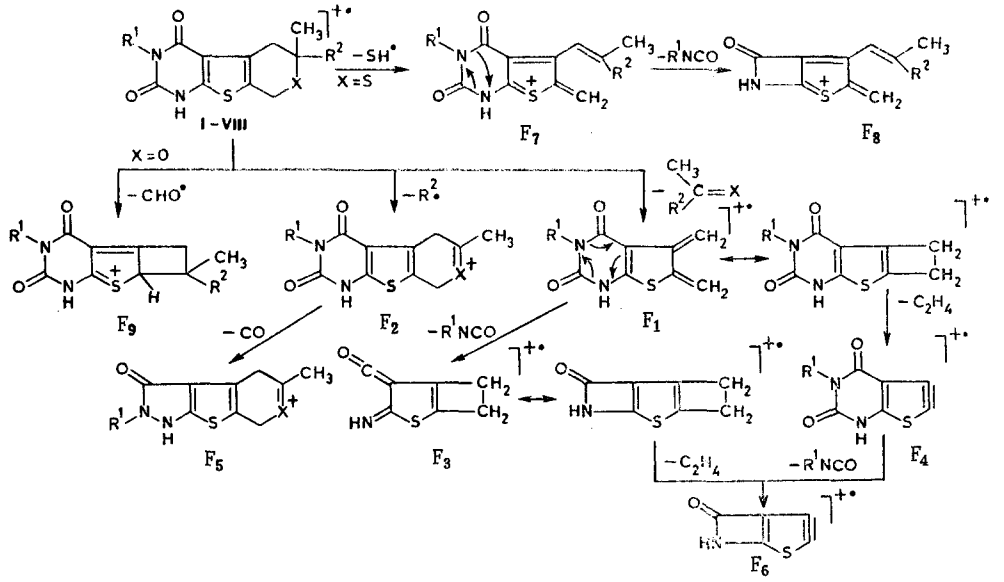
TABLE 2. Mass Spectra of I-VIII*

Compound	m/z (relative intensities, %)
I	252 (30), 237 (3), 223 (6), 209 (3), 194 (100), 181 (4), 166 (4), 151 (28), 138 (2), 123 (5), 122 (4)
II	266 (20), 251 (2), 237 (16), 209 (2), 194 (100), 166 (4), 151 (28), 138 (3), 125 (3), 123 (5), 122 (3)
III	328 (90), 299 (13), 285 (6), 270 (100), 242 (5), 223 (6), 209 (6), 194 (8), 151 (60), 123 (13), 119 (20)
IV	342 (61), 313 (16), 285 (2), 271 (44), 270 (100), 257 (2), 242 (2), 178 (3), 151 (40), 123 (4), 119 (9)
V	268 (100), 253 (11), 235 (77), 225 (63), 194 (77), 192 (30), 182 (6), 164 (6), 151 (23), 123 (6), 122 (4)
VI	282 (100), 267 (2), 253 (54), 249 (73), 225 (54), 206 (13), 194 (68), 182 (5), 151 (15), 123 (5), 122 (4)
VII	344 (100), 329 (9), 311 (89), 270 (29), 225 (9), 208 (6), 192 (40), 182 (7), 151 (43), 123 (8), 119 (20)
VIII	358 (85), 329 (27), 325 (100), 301 (49), 270 (27), 208 (9), 206 (24), 182 (7), 151 (39), 123 (9), 119 (21)

*The molecular-ion peaks and the 10 most intense ion peaks are presented. The peaks of the isotope ions are not presented.

resolution mass spectra of I confirmed the elementary compositions of the F_1-F_9 ions. At the same time, it follows from this analysis that another pathway in the fragmentation of the F_1 ion in the case of pyrano-substituted compounds is the loss of a molecule of C_2H_4 (but not CO), which leads to the F_4 ion, which possibly includes a dehydrothiophene fragment. In the case of thiopyran derivatives this ion is not formed, which is possibly associated with the lower internal energy of the F_1 ions formed in this case.

In addition to the principal fragmentation pathways worked out above, low-intensity peaks of $[M-CHO]^+$ ions, which are probably formed as a result of fragmentation of the pyran ring, are also characteristic for the mass spectra of oxygen-containing I-IV. Such ions are completely absent in the mass spectra of V-VIII, and consequently their formation is not associated with fragmentation of the uracil residue. Moreover, the thiopyran derivatives under the influence of electron impact, like most of the sulfur derivatives, readily lose a sulfhydryl radical (with the formation of an F_7 ion), after which retrodiene fragmentation of the uracil ring (to give the F_8 ion) occurs again.



I—IV X=O, V—VIII X=S; I, V R^1=H, R^2=CH_3; II, VI R^1=H, R^2=C_2H_5; III, VII R^1=C_6H_5, R^2=CH_3; IV, VIII R^1=C_6H_5, R^2=C_2H_5

The ions discussed above constitute from 60 to 85% of the total ion current, which indicates the high selectivity of the fragmentation of the investigated compounds.

Thus, when two annelated [with the aromatic (heteroaromatic) ring] hydrogenated heterorings are presented in the molecule, the more saturated ring first undergoes retrodiene fragmentation; this is apparently associated with primary localization in it of the positive charge in the molecular ion.

EXPERIMENTAL

The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the ionization region at an ionizing voltage of 50 eV and at an input temperature that was 15-20°C below the melting points of the samples. The high-resolution mass spectrum of I was obtained with a Jeol JMS-01-SG-2 spectrometer.

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