Electron impact mass spectrometry of some thienopyrimidone derivatives

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Abstract. The electron impact mass spectra of some previously synthesized thienopyrimidones have been recorded and the identity of various ions in the mass spectra established.

1. Introduction

Many thienopyrimidone derivatives show diverse pharmacological activities including antibacterial/antiviral [1–3], analgesic/antiinflammatory [4–6] and antiallergic activities [7]. Our interest in the synthesis, biological and spectroscopic properties of heterocyclic compounds [8,9], prompted us to investigate the electron impact mass spectra of some thienopyrimidones previously prepared in our laboratories [10,11] (Table 1).

Table 1
Thienopyrimidone derivatives

Compounds	Ar	Formula	M
I	C ₆ H ₅	C ₁₈ H ₁₇ N ₃ OS	323
II	<i>p</i> -CH ₃ -C ₆ H ₄	C ₁₉ H ₁₉ N ₃ OS	337
III	<i>p</i> -OH-C ₆ H ₄	C ₁₈ H ₁₇ N ₃ O ₂ S	339
IV	<i>p</i> -F-C ₆ H ₄	C ₁₈ H ₁₆ FN ₃ OS	341
V	<i>p</i> -Cl-C ₆ H ₄	C ₁₈ H ₁₆ ClN ₃ OS	357
VI	<i>p</i> -NO ₂ -C ₆ H ₄	C ₁₈ H ₁₆ N ₄ O ₃ S	368
VII	C ₁₀ H ₇	C ₂₂ H ₁₉ N ₃ OS	383

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2. Results and discussion

Principal peaks in the EI mass spectra of the compounds **I–VII** are presented in Tables 2 and 3. The isotopic fragment $M + 2$ denote the presence of sulfur atom in all the compounds and chlorine atom for the compound **V**, and are in agreement with the proposed structures.

The main features of the spectra from molecular ions are summarized in Scheme 1. In this series of compounds there are two possibilities to form the base peak at $m/z = 220$ from molecular ions either by loss of a neutral molecule ArCN due to cleavage of a bond α to the $\text{N}=\text{C}$ double bond or by subsequent elimination of aryl and nitrile radicals. In both cases an hydrogen atom migration occurs. The high stability of the base peak probably arises from a prototropic rearrangement in the pyrimidine ring as shown below:

Other important peaks arising from molecular ions are those represented by A, B and C fragments. Formation of these fragments involves an α -cleavage of the $\text{N}=\text{C}$ double bond yielding A and B. A rup-

Table 2
Principal fragments and intensities from molecular ions

Compounds	M^+	m/z (%)		A	B	C
		246	220			
I	323 (40)	4	100	77 (37)	103 (114)	90 (17)
II	337 (16)	2	100	91 (27)	117 (7)	104 (22)
III	339 (17)	1	100	93 (6)	119 (7)	106 (15)
IV	341 (40)	3	100	95 (37)	121 (15)	108 (31)
V	357 (41)	3	100	111 (19)	137 (7)	124 (13)
VI	368 (37)	4	100	122 (12)	148 (5)	135 (22)
VII	373 (23)	2	100	127 (34)	153 (25)	140 (12)

Table 3
Principal fragments and intensities from the base peak

Compounds	m/z (%)								
	205	192	177	164	149	136	108	104	76
I	17	74	14	6	5	3	5	12	7
II	18	83	3	6	5	4	6	22	4
III	17	73	3	11	5	7	5	15	13
IV	20	83	20	10	2	5	32	3	4
V	15	72	17	9	7	4	5	2	6
VI	22	93	32	22	16	9	1	6	16
VII	13	57	6	5	3	3	3	1	3

Scheme 1.

ture from N=C double bond itself accounting for the C fragment. All of the compounds also show the ion $m/z = 246$ though of very low intensity.

The main ions formed from the base peak are obtained from four possible pathways with similar fragmentation pattern nearly always with loss of a neutral molecule.

Although paths 1 and 2 in Scheme 2 show the same peaks at $m/z = 192$, $m/z = 164$ and $m/z = 136$, they are structurally different. Basically, in two paths the different losses of 28 mass units correspond to the same way of elimination of the neutral molecules CO, C₂H₄ and N₂. Thus, through path 1 the ion at $m/z = 192$ can be formed from the base peak by loss of ethene molecule. A further elimination of carbene monoxide leads to the ion at $m/z = 164$. This ion by loss of C₂H₄ moiety yields the ion at $m/z = 136$ which then eliminates a nitrogen molecule to afford the ion at $m/z = 108$.

On the other hand, through path 2, the same peaks are obtained by the successive loss of the neutral molecules CO [12], C₂H₄, N₂ and C₂H₄. The presence of an ion at $m/z = 104$ is a result of the loss of a sulfur atom.

In path 3 the base peak loses 15 mass units which corresponds to the loss of a NH fragment to give the ion at $m/z = 205$. This ion by two subsequent eliminations of 28 mass units (CO and/or C₂H₄) must give the peaks at $m/z = 177$ and $m/z = 149$. Or else, the former can be formed through path 4 by direct loss of neutral molecule HNCO [12] from the base peak. Beside, this ion can give the same fragment at $m/z = 136$ (path 2) by loss of an acetonitrile molecule. A similar fragmentation from ion at $m/z = 149$ affords a peak at $m/z = 108$ which can form the ion of $m/z = 76$ by loss a sulfur atom.

Scheme 2.

3. Experimental

Electron impact mass spectra were recorded using a VG Autospec Q instrument operating at 70 eV ionizing energy. Samples were introduced by using a direct inlet system with a source temperature of 180 °C.

4. Conclusion

The fragmentation pathways for thienopyrimidones studied show the principal characteristic such as the same base peak at $m/z = 220$ for all the compounds, a common fragmentation pattern with an elimination of neutral molecules CO, C₂H₄, N₂, CH₃CN and, finally, the M + 2 isotope peak mainly due to the presence of sulfur atom.

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