

## Mass Spectral Fragmentation Modes of Some Heterocyclically Substituted Chromones-I

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Synthesis of 3-thiocyanatoacetyl chromones, 3-(2-chlorothiazol-4-yl)-2-methylchromones, 3-(2-N-substituted aminothiazol-4-yl)-2-methylchromones and 3-[2-(3,5-disubstituted or 3,4,5-tri-substituted-1*H*-pyrazol-1-yl)-4-thiazolyl]-2-methylchromones have already been published by the author. In this paper mass spectral fragmentation modes of representative compounds are being reported.

**Key Words:** Mass spectra, 6-Chloro-3-thiocyanatoacetyl-2-methylchromones, 6-chloro-3-(2-chlorothiazol-4-yl)-2-methylchromones, 6-chloro-3-(2-N-substituted aminothiazol-4-yl)-2-methylchromones, 6-chloro-3-[2-(3-methyl-5(2-thienyl)-1-*H*-pyrazol-1-yl)-4-thiazolyl]-2-methylchromone.

### INTRODUCTION

Little work has been done on the structural elucidation of heterocyclically substituted chromones using mass spectral technique. Several 3-thiocyanatoacetyl-2-methylchromones, 3-(2-chlorothiazol-4-yl)-2-methylchromones, 3-(2-N-substituted aminothiazol-4-yl)-2-methylchromones and 3-[2-(3,5-disubstituted or 3,4,5-trisubstituted-1*H*-pyrazol-1-yl)-4-thiazolyl]-2-methylchromones have been synthesized by the author<sup>1,2</sup>. Mass spectral fragmentation patterns of representative compound of each type of compounds are being reported in this paper.

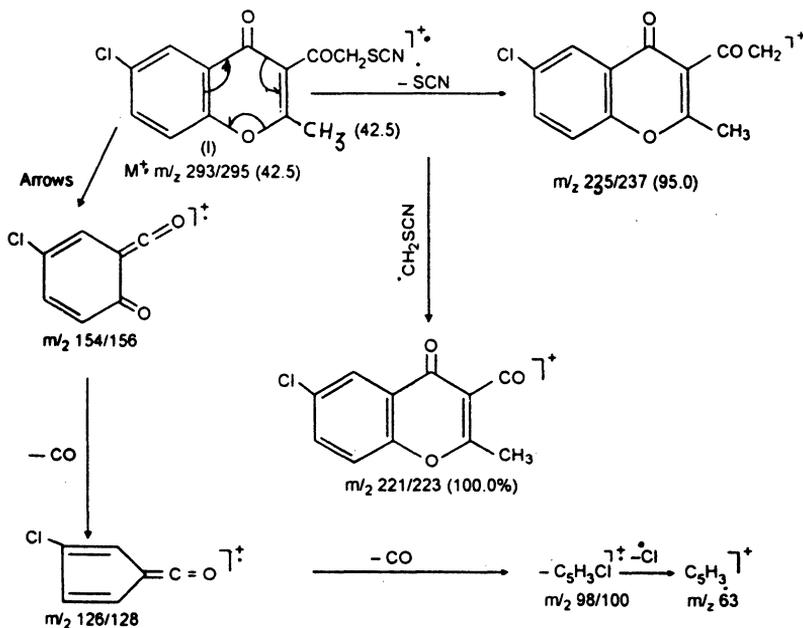
### EXPERIMENTAL

Synthesised compounds were purified by recrystallization in suitable solvent. Purity of compounds was checked by thin-layer chromatography (TLC). Structures of compounds were assigned on the basis of IR and PMR-spectra scanned on Beckmann Spectrophotometer (IR-20) and 90 MHz Perkin-Elmer Spectrometer (R-32), respectively. Mass spectra were recorded on Hitachi RMU-6E spectrometer operating at 70 eV and the figures given in parentheses represent relative intensities corresponding to base peak at 100.

## RESULTS AND DISCUSSION

## Mass spectral fragmentations of 6-Chloro-3-thiocyanatoacetyl-2-methylchromones

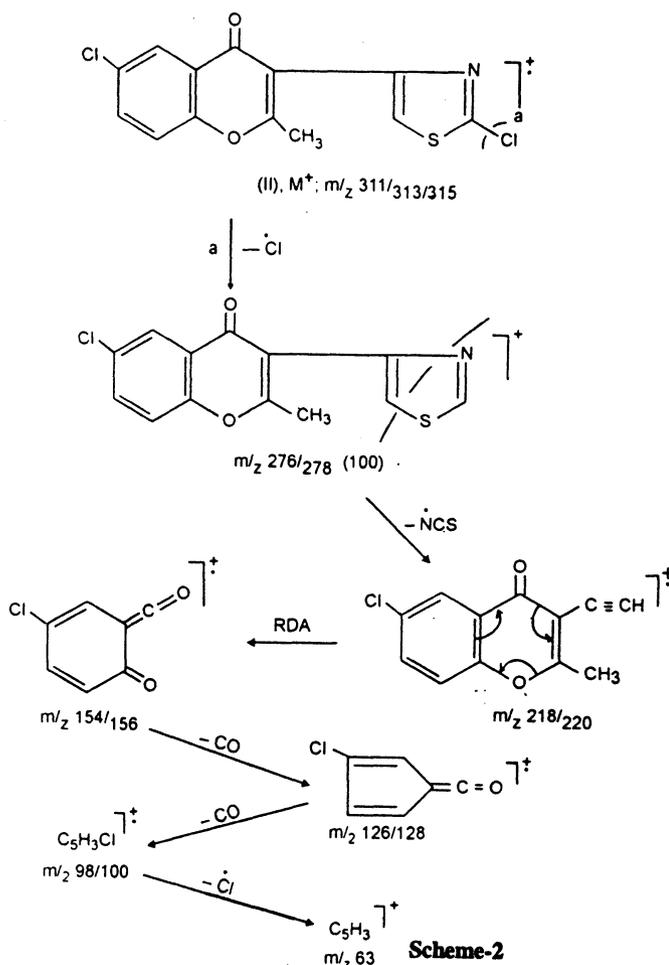
6-Chloro-3-thiocyanatoacetyl-2-methylchromone, I (a typical compound of the series) showed a weak molecular ion peak at  $m/z$  293/295 in its electron impact induced fragmentation.  $M/z$  293/295 peaks were in the ratio 3 : 1 showing the presence of one chlorine atom only (Scheme-1). In addition, it showed the prominent ion peaks analogous to the modes of fragmentation characteristic of chromones<sup>3</sup> and ketones of the type  $\text{RCOCH}_2\text{R}^4$ . Various modes of fragmentation are given in Scheme-1. Presence of chromone ring triggered retro-Diels Alder fragmentation process (arrows) giving rise to well known quinonoid radical ion peak at  $m/z$  154/156. The sequential losses of two carbon monoxide molecules followed by one  $^3\text{Cl}$  were responsible for the ion peaks at  $m/z$  126/128, 98/100 and 63, respectively. Alternatively, the molecular ion underwent  $\alpha$ - and  $\beta$ -cleavages of thiocyanatomethyl ketone side. The  $\beta$ -cleavage involving the elision of SCN radical was responsible for the appearance of an ion at  $m/z$  235/237, whereas the  $\alpha$ -cleavage involving the loss of  $^{\cdot}\text{CH}_2\text{SCN}$  radical gave the acylium ion peak at  $m/z$  221/223, which also formed the base peak as expected.



Scheme-1

### Mass spectral fragmentations of 6-chloro-3-(2-chlorothiazol-4-yl)-2-methylchromone

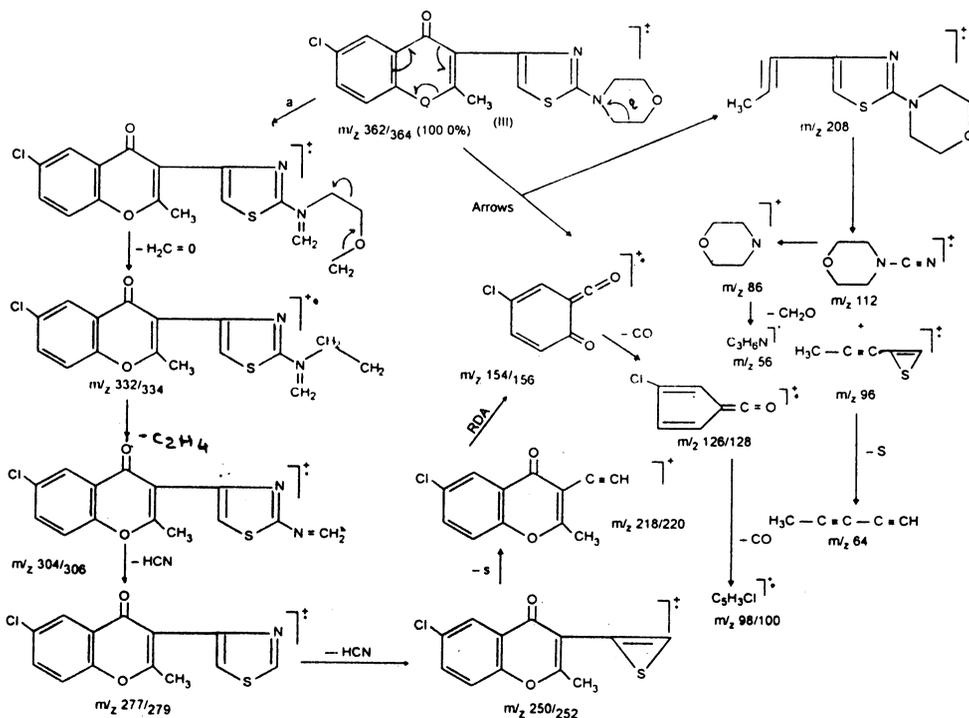
Electron impact induced fragmentation of 6-chloro-3-(2-chlorothiazol-4-yl)-2-methylchromone, **II** (a representative compound) exhibited  $M$ ,  $M+2$ ,  $M+4$  peaks at  $m/z$  311, 313 and 315 with isotopic profile ratio for two chlorine atoms in the molecule. It exhibited prominent peaks analogous to the characteristic modes of fragmentation of chromones<sup>3</sup> and thiazoles<sup>5-7</sup> (Scheme-2). Molecular ion readily lost one chloride radical involving the cleavage of  $C_2-Cl$  of thiazole moiety\* giving rise to ion peaks at  $m/z$  276/278 (base peak). This fragment ion lost  $\dot{N}CS$  radical (58 mass units) to give peaks at  $m/z$  218/220 which may be attributed to 3-ethynylchromone fragment. Chromone ring was responsible for the appearance of quinonoid radical ion at  $m/z$  154/156, further fragmentation of which resulted in the formation of peaks at  $m/z$  126/128, 98/100 and 63 respectively.



\* This view is supported by the fact that the second chlorine atom is retained in the fragment ions at  $m/z$  218/220, 154/156, 126/128 and 98/100.

### Mass spectral fragmentations of 6-chloro-3-[2-(4-morpholinyl)thiazol-4-yl]-2-methylchromone

Mass spectrum of 6-chloro-3-[2-(4-morpholinyl)thiazol-4-yl]-2-methylchromone, III (a representative compound) showed molecular ion peaks at  $m/z$  362/364 in the ratio of 3 : 1 showing isotopic profile for one chlorine atom. Molecular ion showed fragmentations characteristic of chromone<sup>3</sup>, thiazole<sup>3-7</sup> and morpholine<sup>3,4</sup> ring systems. These modes of fragmentation are depicted in Scheme-3. Expected retro Diels-Alder fragmentation gave peaks at  $m/z$  154/156 and  $m/z$  208. The former peak was ascribed to well known quinonoid radical ion. Two sequential losses of carbon monoxide molecules followed by loss of  $^{\bullet}\text{Cl}$  were responsible for the ion peaks at  $m/z$  126/128, 98/100 and 63, respectively. The peak at  $m/z$  208 underwent further fragmentation by the elision of morpholino cyanide radical ion appearing at  $m/z$  112. Loss of cyanide from this was responsible for the appearance of prominent peak at  $m/z$  86, which eliminated  $\text{CH}_2\text{O}$  to give another peak at  $m/z$  56. The other fragment ion obtained from the splitting of the fragment at  $m/z$  208 was the thierene radical ion appearing at  $m/z$  96. Loss of S from this was responsible for the appearance of ion peak at  $m/z$  64.

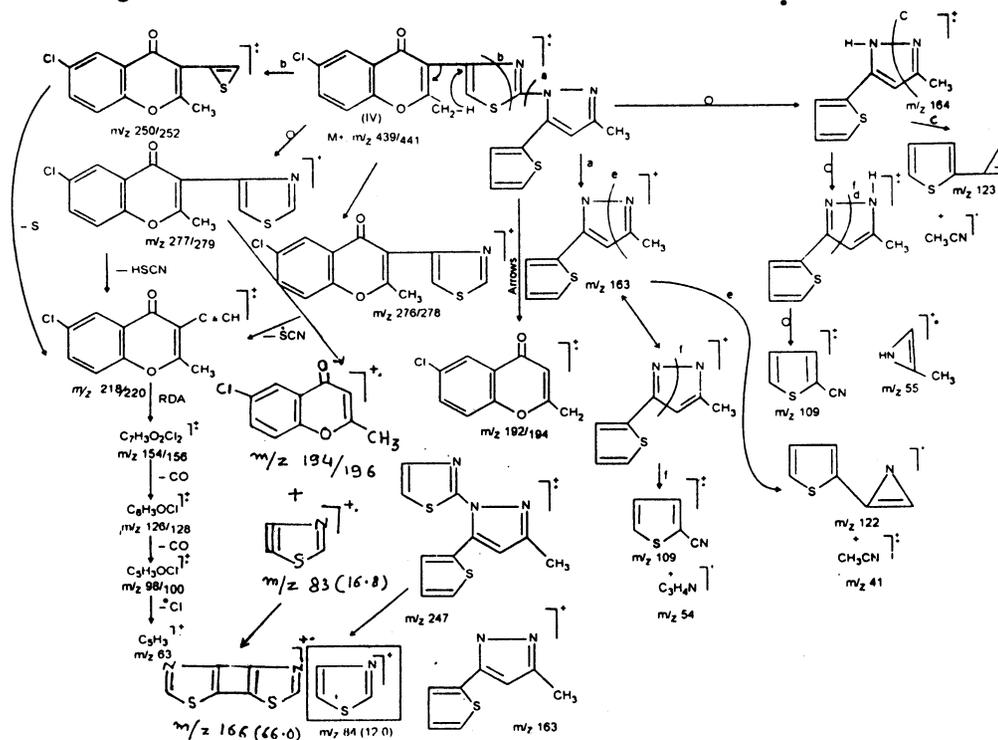


Scheme-3

In addition to above types of fragmentations, the molecular ion ( $m/z$  362/364) underwent  $\beta$ -cleavage (path a) to afford an isomeric radical ion which lost a molecule of  $\text{CH}_2\text{O}$  (30 mass units) to give an ion peak at  $m/z$  332/334. Loss of  $\text{C}_2\text{H}_4$  from this afforded the ion peak at  $m/z$  304/306 which eliminated  $\text{HCN}$  yielding the thiazolyl chromone ion peak at  $m/z$  277/279. This thiazolyl chromone fragment lost another molecule of  $\text{HCN}$  affording the thierene radical ion at  $m/z$  250/252. Elision of sulphur from  $m/z$  250/252 fragment gave the 3-ethynyl-chromone ion peaks at  $m/z$  218/220. The retro Diels-Alder cleavage of this ion afforded quinonoid ion at  $m/z$  154/156.

### Mass spectral fragmentations of 6-chloro-3-[2-(3-methyl-5-(2-thienyl)-1H-pyrazol-1-yl)-4-thiazolyl]-2-methylchromones

Mass spectrum of 6-chloro-3-[2-(3-methyl-5-(2-thienyl)-1H-pyrazol-1-yl)-4-thiazolyl]-2-methylchromone, IV (a representative compound of the series) showed molecular ion ( $M^+$ ) at  $m/z$  439/441 showing a typical isotopic profile characteristic of one chlorine atom. The fragmentation of molecular ion was accompanied by several modes of splitting which are in agreement with the fragmentation patterns of chromone<sup>3</sup>, thiazole<sup>3-7</sup> and pyrazole<sup>8-12</sup> moieties. Major fragmentations are indicated in Scheme-4.



Scheme-4

\*Ion peak at  $m/z$  154/156 may arise from a retro Diels-Alder fragmentation of molecular ion or the fragment ions at  $m/z$  250/252, 277/279, 276/278 and 194/196.

Most interesting fragmentation of molecular ion involved its cleavage along path 'a' giving rise to ion at  $m/z$  277/279, 276/278, 164 and 16, whereas the first and the third peaks could be ascribed to the formation of thiazolyl chromone and pyrazole radical ions by picking up hydrogen, the second and fourth peaks could have arisen by a simple cleavage. Loss of HSCN from radical ion at  $m/z$  276 and 278 gives rise to ethynyl radical ion appearing at  $m/z$  218/220 which undergoes the well known retro Diels-Alder fragmentation to give ion peaks at  $m/z$  154/156\*. Sequential losses of two molecules of carbon monoxide followed by elision of chlorine radical generated peaks at  $m/z$  126/128, 98/100 and 63, respectively. As expected, the pyrazole ion appearing at  $m/z$  164 underwent further splitting (Path-c) to give an ion at  $m/z$  123 which is ascribed to ionized aziridinylium thiophene. In a competitive process, the radical ion at  $m/z$  164 may have undergone rearrangement followed by splitting along path-d to give to 2-cyanothiophene radical ion at  $m/z$  109 along with 2-methylaziridine radical ion at  $m/z$  55. Similar type of cleavage (path-e and path-f) of radical ion at  $m/z$  163 are responsible for the appearance of ion peaks at  $m/z$  122, 41, 109 and 54, respectively.

The second mode of fragmentation of molecular ion may involve cleavage along path-b forming the thierene radical ion at  $m/z$  250/252 Elision of sulphur from this gave rise to radical ion at  $m/z$  218/220. Cleavage of bond between C of thiazole and N of pyrazole from molecular ion gave peaks at  $m/z$  247 and 192/194. Presence of thiazole ring in the compound is also confirmed by the appearance of a peak at  $m/z$  84 obtained by the cleavage of  $m/z$  247 fragment.

An important feature of mass spectra of compound IV is that  $m/z$  277/279 fragment breaks up to give chromone fragment and a benzyne type fragment of thiazole at  $m/z$  194/196 and  $m/z$  83, respectively. As benzyne are very reactive it easily dimerizes to dibenzyne of thiazole appearing as a prominent peak at  $m/z$  166.

Noteworthy features of mass spectrum of 6-chloro-3-[2-(3-methyl-5-(2-thienyl)-1H-pyrazol-1-yl)-4-thiazolyl]-2-methylchromone are the appearance of rare fragments at  $m/z$  84 and  $m/z$  83 that clearly indicates presence of thiazole ring in the compound. Benzyne type fragment that appears at  $m/z$  83 is being reported for the first time in thiazole.

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