Asian Journal of Chemistry Vol. 16, Nos. 3–4 (2004), 1819–1823

Mass Spectral Fragmentation Modes of Some Heterocyclically Substituted Chromones-II

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Results of synthesis and medicinal activities of 6-(2-amino or substituted aminothiazol-4-yl)-2,3-dimethylchromones, 3-(7-methyl-5*H*-thiazolo[3,2-a] pyrimidin-5-one-3-yl)-2-methylchromones and 3-(2*H*-1,4-benzothiazin-3-yl)-2-methylchromones have been communicated by the author in other communications. This paper reveals mass spectral fragmentations of these compounds.

Key Words: Mass spectra, 6-(2-Amino or substituted aminothiazol-4-yl)-2,3-dimethylchromones, 3-(7-Methyl-5*H*-thiazolo[3,2-a]pyrimidin-5-one-3-yl)-2-methylchromones, 3-(2*H*-1,4-Benzothiazin-3-yl)-2-methyl chromones.

INTRODUCTION

In continuation of the program to synthesise, biologically screen and study the spectral characteristics of heterocyclically substituted chromones[1-10], this paper reveals mass spectral fragmentation modes of 6-(2-amino or N-substituted aminothiazol-4-yl)-2,3-dimethylchromones, 3-(7-methyl-5*H*-thiazolo[3,2-a]pyrimidin-5-one-3-yl)-2-methylchromones and 3-(2*H*-1,4-benzothiazin-3-yl)-2-methylchromones.

EXPERIMENTAL

Synthesised compounds were purified by recrystallization in suitable solvents. Purity of the compounds was checked by TLC on silica gel plates. Structures of the compounds were assigned on the basis of IR and PMR-spectral data scanned on Beckmann spectrophotometer (IR-20) and 90 MHz Perkin-Elmer (R-32) machine, respectively. Mass spectra were recorded on Hitachi RMU-6E spectrometer at 70 eV. Figures given in parentheses represent relative intensities corresponding to base peak at 100.

RESULTS AND DISCUSSION

Mass spectral fragmentations of 6-(2-amino or N-substituted aminothiazol-4-yl)-2,3-dimethylchromones

Electron impact induced fragmentation of 6-(2-methylaminothiazol-4-yl)-2,3-dimethylchromone (1) showed fragmentations in agreement with the structure

assigned to it. The mass spectrum showed the molecular ion peak at m/z 286 (base peak) as expected. This exhibited prominent fragmentations characteristic of chromones[11] and thiazoles[11] ring systems as depicted in **Chart-1**. Molecular ion $M^{+\bullet}$ underwent fragmentations by three alternate modes, followed by further fragmentations of fragment ions: (a) elision of CO giving rise to ion peak at m/z 258; (b) a retro Diels-Alder fragmentation giving rise to peak at m/z 232. Loss of CH_3NHCN from this (path b) gave thierene ion peak at m/z 176; sequential losses of sulphur and two molecules of CO resulted in ion peaks at m/z 144, 116 and 88, respectively; (c) elision of CH_3NHCN from $M^{+\bullet}$ (path a) showed up as thierene radical ion at m/z 230 which lost S to give rise to an ion peak at m/z 198. Presence of chromone ring in the radical ions at m/z 230 and 198 also triggered retro Diels-Alder process forming peaks at m/z 176 and 144, respectively.

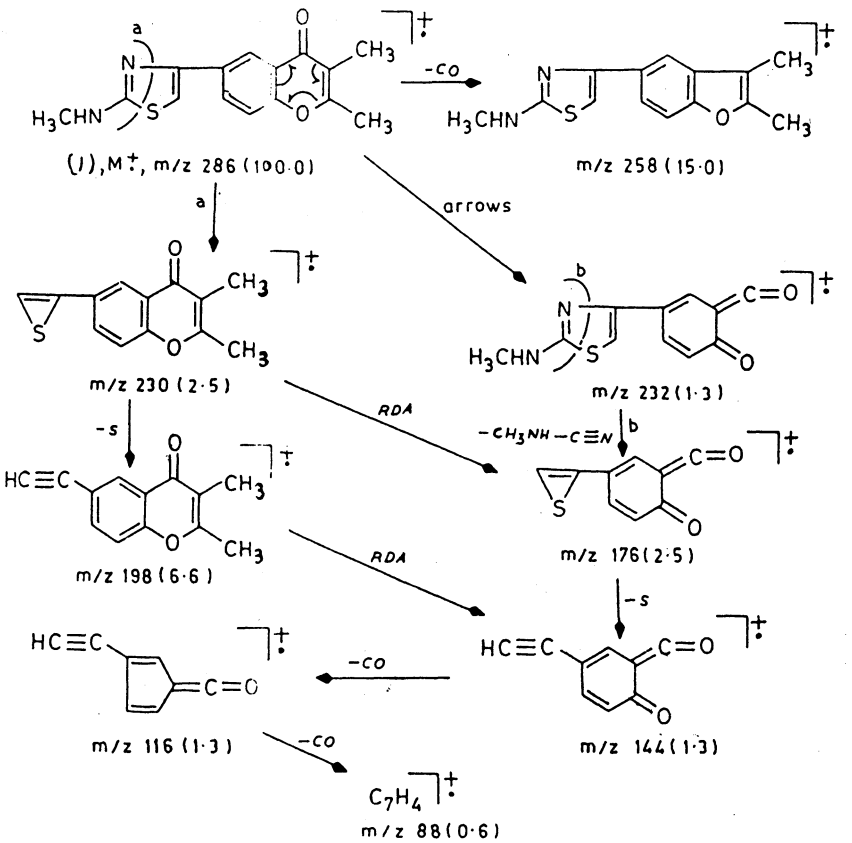
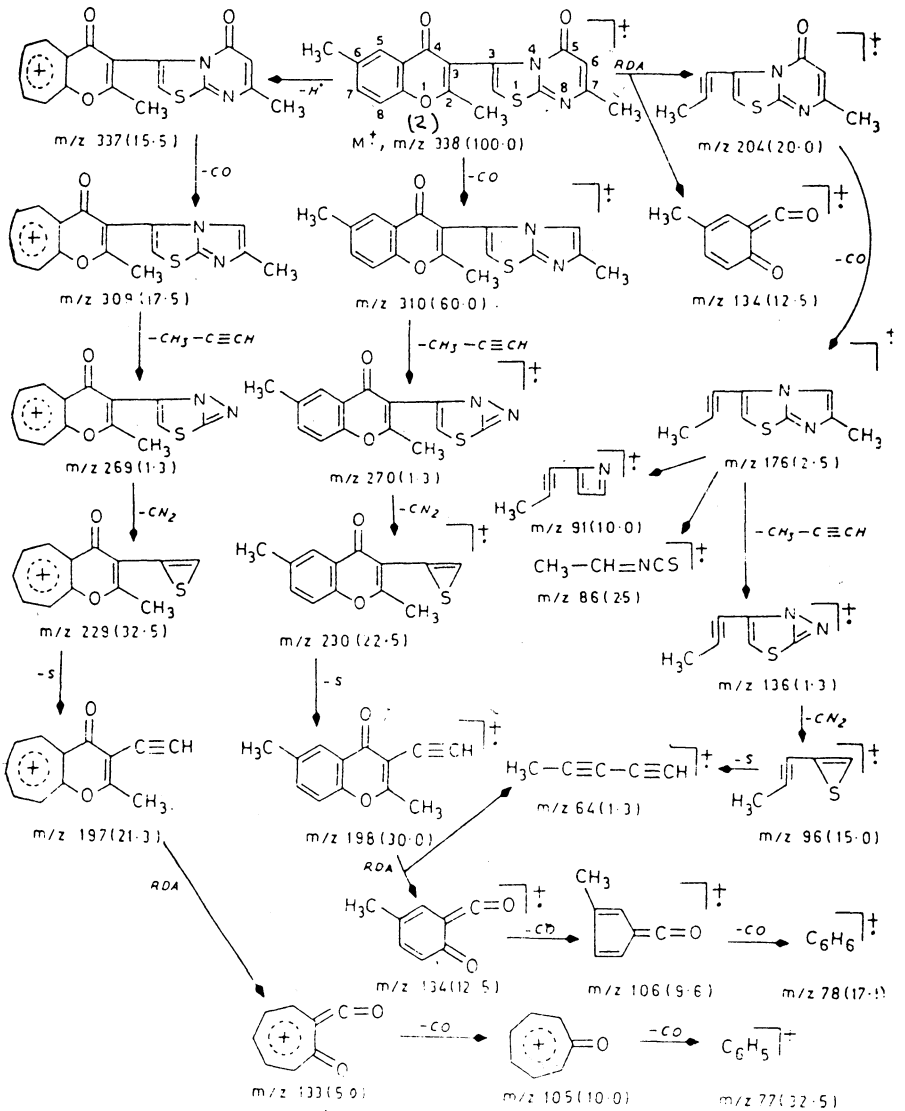


Chart-1

Mass spectral fragmentations of 3-(7-methyl-5H-thiazolo[3,2-a]pyrimidin-5-one-3-yl)-2-methylchromones

Modes of fragmentation of molecular ion ($M^{+\bullet}$), m/z 338, of 3-(7-methyl-5*H*-thiazolo[3,2-a]pyrimidin-5-one-3-yl)-2,6-dimethylchromone **(2)** are depicted in **Chart-2.**



(a) Presence of thiazolopyrimidone moiety triggered the expected loss of elements of carbon monoxide generating a radical ion at m/z 310. Subsequent elision of methylacetylene afforded a radical ion at m/z 270. Elision of CN_2 from this produced thierene radical ion at m/z 230. As expected, the loss of sulphur

from m/z 230 gave the 3-ethynylchromone radical ion appearing at m/z 198. The presence of chromone ring triggered retro Diels-Alder process which is characteristic of mass spectral fragmentation of chromones, yielding the quinonoid radical ion at m/z 134. The elision of CH_3—C≡C—C≡CH from m/z 198 fragment is established by the appearance of a radical ion at m/z 64. Sequential losses of two molecules of carbon monoxide from m/z 134 fragment resulted in the formation of radical ions at m/z 106 and 78, respectively.

(b) The presence of C_6—CH_3 (of chromone) triggered the elimination of hydrogen radical forming a prominent ion peak at m/z 337 [$M^{+\bullet}$-1] which may be assigned to the typical tropylium ion structure. The mode of fragmentation of [$M^{+\bullet}$-1] is exactly similar to that of molecular ion as evident by the appearance of ionic peaks at m/z 309, 269, 229, 197 and 133 which may be ascribed to the sequential losses of CO, CH_3—C≡C—CH, CN_2, S and CH_3—C≡C—C≡CH, respectively. Sequential losses of two molecules of carbon monoxide from the ion peak at m/z 133 gave rise to peaks at m/z 105 and m/z 77, respectively.

It may be worth mentioning that [$M^{+\bullet}$-1] ion is also expected to arise by the loss of hydrogen from C_7—CH_3 of thiazolopyrimidone moiety. The fact that this loss is not taking place is evidenced by the observation that molecular ion undergoes RDA process forming radical ion at m/z 134 and the corresponding acetylene radical ion at m/z 204. There was not seen a peak at m/z 203 which would normally arise by the RDA type cleavage of [$M^{+\bullet}$-1]. The radical ion at m/z 204 eliminates CO giving another radical ion at m/z 176. Elision of methylacetylene from it gave radical ion m/z 136 which eliminates CN_2 to form the corresponding thierene radical ion at m/z 96. Elision of sulphur from this resulted in the radical ion at m/z 64. Alternatively, the fragment at m/z 176 undergoes the expected elision of CH_3CHNCS (also appearing at m/z 86) to form azetidine radical ion at m/z 91.

Mass spectral fragmentations of 3-(2*H*-1,4-benzothiazin-3-yl-2-methylchromones

3-(2*H*-1,4-benzothiazin-3-yl)-6-chloro-2-methylchromone **(3)**, a typical compound of the series showed molecular ion peak at m/z 341/343 with isotopic profile for one chlorine atom. Molecular ion ($M^{+\bullet}$) underwent fragmentations characteristic of chromones[11] and benzothiazines[12] **(Chart-3)** which are as follows:

(a) It underwent loss of sulphur forming radical ion at m/z 309/311. Hydrogen transfer followed by cleavage of resultant indole generated aziridine radical ion at m/z 91 along with 2-ethynylchromone radical ion at 218/220. The RDA of the latter resulted in the well known quinonoid radical ion at m/z 154/156 and fragment at m/z 64.

(b) The molecular ion after the loss of SH must have resulted in the formation of peak at m/z 308/310.

(c) $M^{+\bullet}$ underwent rearrangement to isomeric radical ion which cleaved into 3-ethynylchromone, m/z 218/220 radical ion and other fragment at m/z 123. The latter fragment lost CS to give a fragment at m/z 79.

(d) RDA of $M^{+\bullet}$ produced radical ion at m/z 154/156 and 187. Quinonoid peak

at m/z 154/156 lost subsequently two molecules of CO and one molecule of Cl in the usual way. m/z 187 fragment lost S to give m/z 155, peak rearrangement of which followed by cleavage resulted in m/z 91 and 64 fragments.

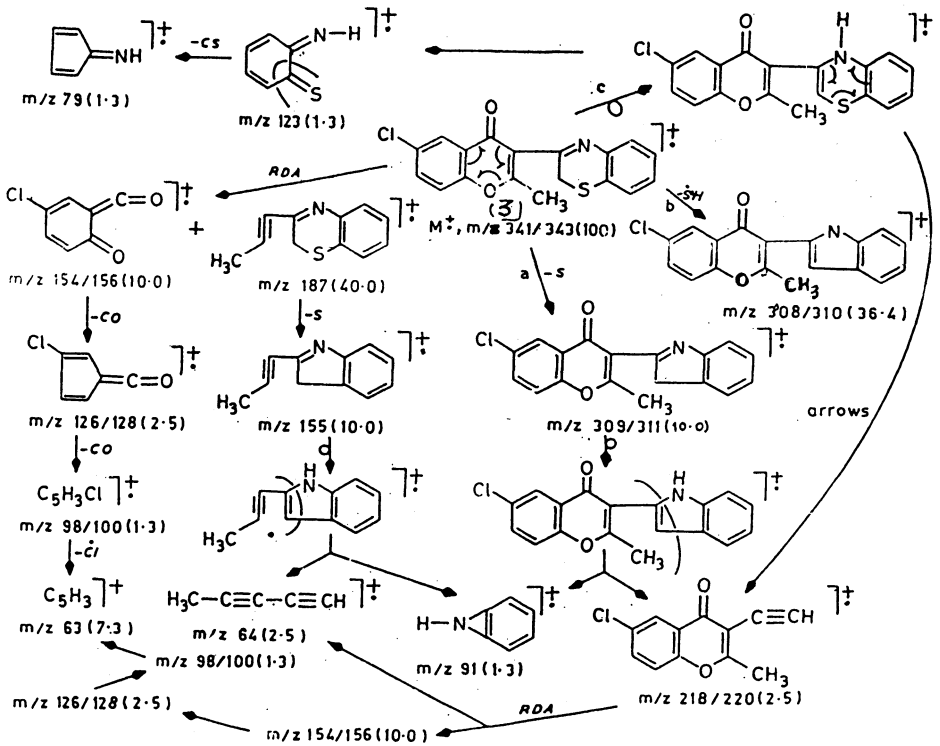


Chart-3

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(*Received*: 13 March 2004; *Accepted*: 10 June 2004) AJC-3448