Mass Spectrometric Fragmentation of Some Isolated and Fused Heterocyclic Rings with Dibromoquinazoline Moiety

Mounir A. I. Salem\textsuperscript{a}, Mohmoud R. Mahmoud\textsuperscript{a}, El-Said A. Soliman\textsuperscript{a}, Tarik E. Ali\textsuperscript{b} and Ibrahim S. Mabrouk\textsuperscript{a}

\textsuperscript{a}Department of Chemistry, Faculty of Science, Ain Shams University, Abbasia, Cairo, Egypt
\textsuperscript{b}Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt

1. Introduction

Quinazolinones are well known to have biological importance such as antibacterial, antiproliferation, antiinflammatory and fungicidal properties [1-5]. Recently, we performed detailed investigations on the synthesis, spectral properties and biological evaluation of a series of heterocyclic compounds [6-8]. Mass spectrometry was applied to the characterization of the compounds using analysis of metastable ions by the collision induced dissociation technique and exact mass measurements [9-13]. However, to our knowledge, there is no mass spectral fragmentation study for isolated and fused heterocycles with dibromoquinazolines. In continuation of our work on the mass fragmentation mechanisms of the heterocyclic compounds [14-16], a detailed study on a series of related isolated and fused heterocycles with dibromoquinazolines was performed to understand the fragmentation routes of these compounds. Thus, this paper reports a study on the fragmentation mechanisms under electron ionization conditions of some dibromoquinazoline compounds namely \textsuperscript{N}-[1-(6,8-dibromo-4-oxo-3,1-benzoxazin-2-y1)-4-phenyl-buta-1,3-dien-1-yl]benzamide (1 and 2), 6,8-dibromo-2-phenyl-4-[3-phenylprop-2-en-1-y1idene]-1,4-dihydro-10H-[1,2,4]triazino[6,1-b]quinazolin-10-one (3), 6,8-dibromo-4-[3-phenylprop-2-en-1-y1idene]-1,2,5-oxadiazino[3,2-b]quinazolin-10(4H)-one (4), N-[1-(9,11-dibromobenzimidazolo[1,2-c]quinazolin-7-yl)-4-phenylbuta-1,3-dienyl]benzamide (5) and N-[1-(7,9-dibromo-2,3-dihydro-2-thioxo[1,2,4]triazolo[1,5-c]quinazolin-5-yl)-4-phenylbuta-1,3-dienyl]benzamide (6) (Figure 1).

2. Experimental

2.1. Synthesis of the studied compounds

The studied compounds 1-6 were synthesized by treatment of \textsuperscript{N}-[1-(6,8-dibromo-4-oxo-3,1-benoxazin-2-yl)-4-phenyl-buta-1,3-dien-1-yl]benzamide with different types of nitrogen nucleophiles under different conditions as reported in our recent article [17]. All the compounds were characterized by elemental analysis, MS, IR, \textsuperscript{1}H, and \textsuperscript{13}C-NMR spectra.

2.2. Mass spectrometry measurements

Mass spectra were obtained operating under electron impact at 70 eV. Low resolution mass spectra were recorded on a Schimadzu-GC-MS spectrometer, Microanalytical Center, Cairo University, Egypt. The electron ionization ion source kept at 200 \degreeC. The compounds were introduced with a probe which was ballistically heated to 250 \degreeC. The EI mass spectra were obtained over the range of \textit{m/z} 35-650.

3. Results and Discussion

3.1. The detailed fragmentations pathways

For a better understanding of fragmentation routes, the compounds under study were divided into three groups A, B and C according to their substitution patterns.
The mass spectra of compounds 1 and 2 gave the molecular ion peaks at \( m/z \) 633, (M+4, 7%), 631 (M+2, 15%), 629 (M+1, 7%), respectively, which support the presence of two bromine atoms due to recording the molecular ion peaks in the ratio 1:2:1 [18]. Thus, the presence of any fragment ion that contains the two bromine atoms should appear in ratio 1:2:1. The molecular ions (M+) of 1 and 2 undergo fragmentation via elimination of benzoyl radicals at \( m/z \) 105 as the base peaks affording the fragment cation radicals \( m/z \) 525 and 523, respectively, which lose the benzyl radicals producing the fragment cations \( m/z \) 434 and 432, respectively. Also, the fragment ions \( m/z \) 525 and 523 can lose phenyl radicals to give the cations \( m/z \) 448 and 446, respectively. The latter fragment cations remove C\(_2\)H\(_4\) radicals to afford the fragments \( m/z \) 407 and 405, respectively, which were also obtained via removing ethylene radicals from the fragments \( m/z \) 434 and 432, respectively. The fragment ions \( m/z \) 434 and 432 lose the acrylonitrile molecules to yield the dibromoquinazolinone cations \( m/z \) 381 and 379, respectively, which give the dibromobenzimidazole cations \( m/z \) 273 via removing the heterocycles Y followed by loss of carbon monoxide (Figure 2).

The molecular ions of compounds 3 and 4 appeared at 550 (M+4, 5%), 548 (M+2, 10%), 546 (M+5, 5%) and 475 (M+4, 3%), 473 (M+2, 6%), 471 (M+, 3%), respectively. The molecular fragment ions at \( m/z \) 546 and 471 eliminate phenyl acetylene molecules producing the cation radicals \( m/z \) 444 and 369, respectively. The latter two fragments undergo two fragmentation routes. Firstly, they can remove ethylene molecules to give the fragments \( m/z \) 418 and 343, respectively, which lose R radicals leading to the formation of the cations \( m/z \) 341 and 342, respectively. The fragments \( m/z \) 341 and 342 underwent further decomposition of the 5-membered rings to yield the ions at \( m/z \) 301. The second route is removing of RCN molecules to afford the base peaks at \( m/z \) 341 and 342, respectively. The base peaks underwent decomposition of the 4-membered ring via loss of CH=\( \text{C}=\text{O} \) or CH\(_2\)CN to give the cations \( m/z \) 301. The latter fragments \( m/z \) 301 lose CO, 1/2N\(_2\) and CN radicals to yield the fragments 273, 258 and 232, respectively (Figure 3).

The molecular ion peaks of compound 5 were recorded at \( m/z \) 626 (M+4, 5%), 624 (M+2, 10%) and 622 (M+5, 5%). The molecular ion (M+) was fragmented via elimination of benzooyl radical as a base peak at \( m/z \) 105 to form the fragment \( m/z \) 518. The fragmentation pathway of the fragment \( m/z \) 518 involves the loss of PhC\(_2\)H\(_2\) radical, followed by CH\(_2\)CN to give the fragment ions \( m/z \) 415 and 374, respectively. The latter fragment \( m/z \) 374 undergoes further decomposition with acceptance two hydrogen radicals into the peaks at \( m/z \) 259 and 117 in moderate intensities. The fragment \( m/z \) 274 undergoes loss of HCN and 1/2N\(_2\) radical to give the cation radical \( m/z \) 76, while the fragment \( m/z \) 259 loses CN radical to give the dibromophenyl cation \( m/z \) 233 (Figure 4).

The molecular ion peaks of compound 6 appeared at 609 (M+4, 5%), 607 (M+2, 10%) and 605 (M+, 5%). The molecular ion (M+) eliminates benzooyl radical as a base peak at \( m/z \) 105 to form the fragment ion \( m/z \) 501 which loses PhC\(_2\)H\(_2\) radical and CH\(_2\)CN to give the fragments \( m/z \) 398 and 357, respectively. The latter fragment \( m/z \) 357 undergoes decomposition via loss of CS and 1/2N\(_2\) with acceptance of hydrogen radical to produce the moderately stable ion \( m/z \) 300, which eliminates CN radical, HCN and 1/2N\(_2\) radical to afford the fragment is \( m/z \) 274 and 233, respectively (Figure 5).

4. Conclusions

1. The [M\(^+\)] ion of all compounds are low intensities (relative abundances 3–7%) due to easily breaking of side chains.
2. Each fragment contains the two bromine atoms appeared in ratio 1:2:1 as in the molecular ion peaks M+4, M+2 and M+, respectively.
3. Compounds 1, 2, 5 and 6 gave the benzooyl radical \( m/z \) 105 as the base peak due to its easily elimination.
4. Compounds of each group take nearly the same fragmentation routes to give the corresponding fragments in similar relative abundance.
5. The fragments obtained from compounds 1–6 are produced by elimination of side functional groups followed by fragmentation of the heterocycle ring attached to the dibromoquinazoline ring.
Figure 2: Mass fragmentation pattern of compounds 1 and 2

Figure 3: Mass fragmentation pattern of compounds 3 and 4
Figure 4: Mass fragmentation pattern of compound 5

Figure 5: Mass fragmentation pattern of compound 6
5. References


