Electron Ionization Mass Spectrometric Studies of 3-(4'-Chlorophenylethyl) isocoumarin and Its 3,4-Dihydroisocoumarin

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Summary: Electron ionization mass spectra of 3-(4'-chlorophenylethyl)isocoumarin (**1**), dihydroisocoumarin (**2**) and keto-acid (**3**) are discussed. The mass spectral fragmentation patterns are assigned with the help of LREIMS.

Introduction

Isocoumarins are a class of organic compounds well known for their biological activities [1]. They have been used as cancer depressants [2], anti-allergic [3] and anti-tumor agents [4]. Synthesis of 7-amino-4-chloro-3-(2''-bromoethoxy) isocoumarin is reported [5] and evaluated as a potent inhibitor of human leukocyte elastase and blood coagulant enzymes [6]. 7-Amino-3-(2''/3''-bromopropoxy)-4-chloroisocoumarin has been used [7], as calpain inhibitor, in the inhibition and treatment of neurodegenaration. Keeping in view the biological activity of this class of compounds, we have synthesized 3-(4'-chlorophenylethyl) isocoumarin (**1**), its 3,4-dihydroisocoumarin (**2**) and keto-acid (**3**). In the present article, we wish to report on electron ionization mass spectrometric studies of 3-(4'-chlorophenylethyl) isocoumarin (**1**), its 3,4-dihydroisocoumarin (**2**) and keto-acid (**3**) derivatives, which will serve as a reference library for this class of compounds.

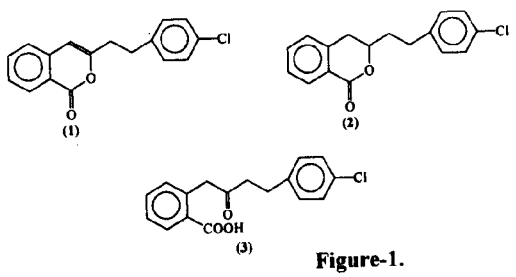


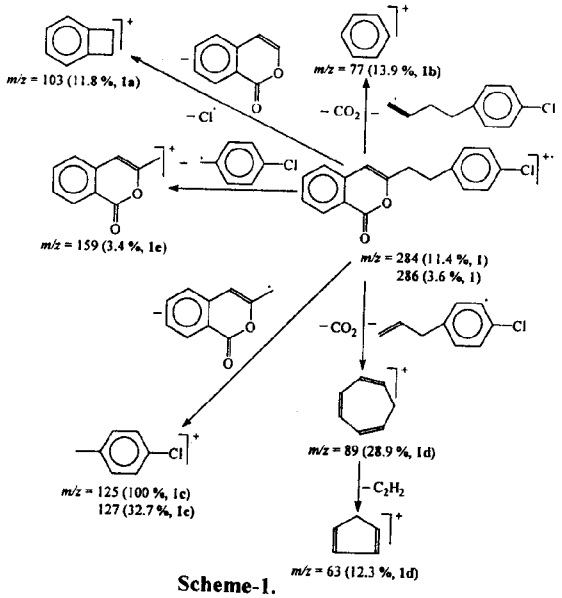
Figure-1.

Results and Discussion

The general fragmentation patterns were designed with the help of LREIMS and are depicted in schemes 1-3.

3- (4'-chlorophenylethyl)isocoumarin (1)

The EIMS of isocoumarin (1) afforded radical cation corresponding to molecular ion with isotopic peaks due to chlorine. The loss of chlorine radical and isocoumarin nucleus gave cation (**1a**) at *m/z* 103. The removal of CO_2 molecule and $C_{10}H_8Cl$ radical gave cation (**1b**) at *m/z* 77. The loss of $C_{10}H_7O_2$ radical gave cation (**1c**) with isotopic peaks, which was the base peak. The removal of CO_2 molecule and C_9H_8Cl radical gave cation (**1d**) at *m/z* 89, which in turn gave cation (**1f**). The loss of C_7H_6Cl radical gave cation (**1e**) at *m/z* 159.



Scheme-1.

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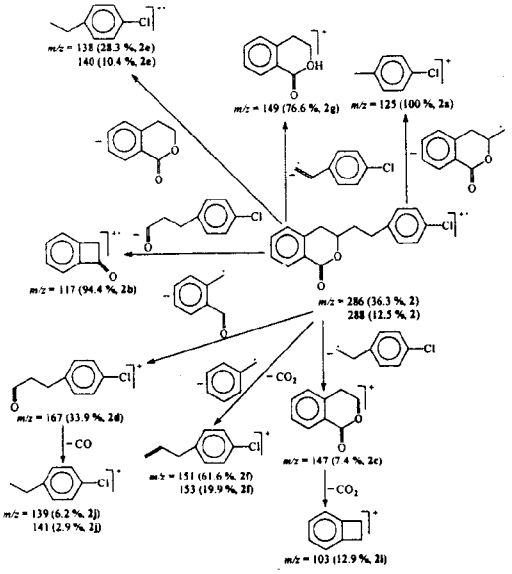
(dl)-3-(4'-chlorophenylethyl)-3,4-dihydroisocoumarin (2)

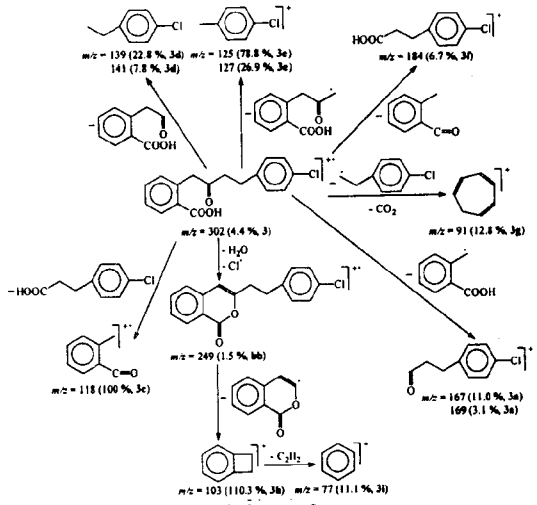
The EIMS of 3,4-dihydroisocoumarin (**2**) afforded the radical cation corresponding to the molecular ion with isotopic peaks. The loss of $C_{10}H_9O_2$ radical gave cation (**2a**) at *m/z* 125, which was the base peak. The removal of C_9H_8OCl neutral afforded radical cation (**2b**) at *m/z* 117. The loss of C_8H_8Cl radical gave cation (**2c**) at *m/z* 147, which yield cation (**2i**) after loss of CO_2 molecule. The removal of C_8H_6O radical occurred at *m/z* 167 of cation (**2d**), which in turn gave cation (**2j**) after loss of CO_2 molecule. The loss of 3,4-dihydroisocoumarin nucleus gave radical cation (**2e**) with isotopic peaks. The loss of CO_2 molecule and C_7H_6 radical gave cation (**2f**) with isotopic peaks. Cation (**2g**) appeared after a loss of fragment C_8H_6Cl at *m/z* 149.



Scheme-2.

2-[2'-Oxo-4'-(4'-chlorophenyl)butyl]benzoic acid (3)

The radical cation observed for keto-acid (**3**) corresponding to molecular ion, was of considerably lower intensity. The loss of $C_8H_7O_2$ radical from molecular ion gave cation (**3a**), with isotopic peaks. The loss of H_2O molecule and chlorine radical gave cation (**3b**), which in turn gave cation (**3h**) at *m/z* 103. Cation (**3h**) gave cation (**3i**) after the loss of C_2H_2 fragment. The loss of $C_9H_9O_2Cl$ radical gave cation (**3c**), which was the base peak. The loss of $C_9H_7O_3$ radical gave cation (**3d**) with isotopic peaks and the loss of $C_{10}H_9O_3$ radical gave cation (**3e**). The rearranged cation (**3f**) was obtained after the loss of C_8H_6O radical. The characteristic cation (**3g**) was furnished after the loss of C_8H_8Cl radical and CO_2 molecule.



Scheme-3.

Experimental

All the compounds were prepared according to the literature procedure [8] and were characterized by IR, ^{1}H-NMR and high resolution mass spectral data. The EIMS were recorded on Mat-311 instrument with an accelerating voltage of 3kV and ionization energy of 70eV. The temperature of the ion source was maintained at 250 °C with the inlet temperature being 110 °C.

Conclusion

Isocoumarin (**1**) appeared as the molecular ion peak. The base peak was observed at *m/z* 125. Both the molecular ion peak and base peak showed isotopic peaks due to chlorine. Other characteristic peaks were at *m/z* 103 and 89. Dihydroisocoumarin (**2**) also appeared as the molecular ion peak and the base peak was at *m/z* 125 as in the isocoumarin (**1**). Other important fragments were observed at *m/z* 167, 151, 147, 139 and 117. Molecular ion peak for keto-acid (**3**) was of very low intensity. The base peak of keto-acid (**3**) was at *m/z* 118. Other characteristic peaks for (**3**) were at *m/z* 248, 184, 167, 139 and 125, respectively.

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