Pathways for Mass Spectra Fragmentation of Azulen-1-yl Substituted Six-membered Heterocycles

ALEXANDRU C. RAZUS, LIVIU BIRZAN, OANA LEHADUS, CRISTIAN ENACHE

The splitting in the electrospray ionization spectrometer of several azulene substituted six-membered heterocycles (pyranylium salts, pyridinium salts, and pyridine) was analyzed and some features of fragmentation were evidenced. The splitting fragments were found to be similar for all heterocycles. The alkyl groups substituted at azulene moiety are broken at the same time with the heterocycles decomposition. The \(N^+\)-substituents in pyridinium salts are however lost before other system transformations occur.

Keywords: mass fragmentations, azulene, pyridinium salts, pyranylium salts, pyridines

There has been considerable interest in the mass spectra of charged or uncharged six-membered heterocycles [1] however, no such heterocycles connected with azulene moiety were until now considered from this pint of view. Due to one of the peculiarities of the azulene system, namely its higher reactivity as comparing with the usual aryl moieties, more facile interactions of this group with the positive charged or radical center formed in mass spectrometer is attempted. Since several of our recently published works are directed on the synthesis and characterization of azulenylium pyranylium salts [2] azulenylium pyridines [3] and azulenylium pyridinium salts [4] it was of interest to study systematically the mass spectra of these compounds and the results are reported in this paper.

The used device and fragmentation conditions

Electrospray ionization (ESI) mass spectra were recorded using a VG Analytical 7070 E-HF mass spectrometer at variable potentials with the source temperature fixed at 25°C. The ESI capillary voltage was maintained at 5 kV. Sample solutions in acetone were introduced into the ESI source with a flow rate of 3.3 \(\mu\)L/min via a syringe pump. Nitrogen gas was used as nebulizing and drying gas to improve ionization efficiency. Argon gas, at a pressure of 1 \(\mu\)bar (gauge external to the hexapole collision cell) was used as the collision gas to acquire collision induced dissociation spectra (for pyridines). Collision energy (in the range of 0-50 eV) is indicated in the text. Variations of ion intensities as a function of ionization energy were performed on a VG Fisons Quattro mass spectrometer. The examined pyranylium and pyridinium salts as well as the pyridines were injected at a 10\(^{-3}\) M concentration. When the salts are examined, the ESI-MS in the negative ion mode showed only the presence of the perchlorate anion.

Results and discussion

Since, our preliminary examinations showed that working with ESI procedure better results are obtained for charged azulenic substituted six-membered heterocycles we have used this method for such derivatives. For the pyridines however, which exhibit higher thermal stability, GC-MS method allowed more accurate results. In almost all cases, using GC-MS procedure, at a collision potential less than 15 eV only the protonated molecular peak was recorded for pyridines whereas for pyranylium and pyridinium salts integral ionic peak is present. The last peaks are generally obtained together with the corresponding radical cations with a supplementary unity mass in various mass abundances. Interesting splitting however was observed at higher collision potentials, usually 25-40 eV, or even at accelerating potentials of 70 kV.

We have undertaken here a systematic examination of the relevant fragmentations in mass spectrometer of each heterocycles class in order to find possible relationships between the main splitting routes adopted by different compounds. We have considered the 2,6- or 4,6-diphenyl substituted heterocycles with an azulen-1-yl unsubstituted or substituted group in 4 or 2 positions, respectively (scheme 1).

**Pyranylium salts**

Starting from 4-azulenylium-2,6-diphenyl-pyranylium salts, benzoyl cation, a very stable species, is formed in a retro Diels-Alder fragmentation (scheme 2). The closure of the diradical formed at the splitting of benzoyl cation generates the stable molecule, 2-(azulen-1-yl)naphthalene. This molecule was evidenced in mass spectrum after the elimination of a hydrogen atom and an electron as cation [C\(_{20}\)H\(_{13}\)]\(^+\). Another H\(^+\) loss and an intramolecular attack of azulene moiety lead to the policondensate radical cation that eliminates acetylene molecule. Other reaction route of the cation [C\(_{10}\)H\(_{7}\)]\(^+\) consists in the elimination of molecule C\(_4\)H\(_2\) when the cation Az-C\(_6\)H\(_4\)]\(^+\) is formed. The structure attribution of the charged fragments with low molecular weight is difficult to make. However, for the cations [C\(_{10}\)H\(_{7}\)]\(^+\) and...
[C₆H₅]+ the azulenic and phenyl framework is attempted. The reaction step in which the splitting of these cations takes place is difficult to establish.

Next we shall examine the pyranylium salts with azulen-1-yl in 2-position and with phenyls in 4- and 6-position. In this case, as an alternative to the benzoyl splitting, the elimination of corresponding azulene-carbonyl fragment can be observed. As can be shown from scheme 4, the splitting of fragment remained after the AzCO⁺ elimination is similar with those described in scheme 3. Thus, 2-phenynaphthalene and fluorene cations are present in the mass spectrum of 2-(azulene-1-yl)-4,6-diphenyl-pyranylium cation. The peaks for azulenyl and phenyl fragmentations are also observed.

The elimination of benzoyl cation is much more interesting because, as results from scheme 5, in this case the azulene moiety is implied in the internal ring closure. The stabilization of positive charge as tropylium cation and the presence of unpaired electron at the five-membered azulene ring assure the stability of the condensed radical cation [C₃₀H₂₂O⁺]. The proposed subsequent fragmentations in scheme 5 are based on the peaks present in the mass spectrum and on the fragmentation route already examined for other compounds that contain azulene or tropylium moieties [5,6]. The abundance of the characteristic fragments at
the elimination of PhCO+ or AzCO+ was not very different therefore the two splitting routes occur with similar probability.

The previous analyzed signals in mass spectra of 4-(azulene-1-yl)-2,6-diphenyl-piranilium cations with alkylated azulene moiety (scheme 3) indicates a competition between the splitting of benzoyl cation and azulene dealkylation. If we consider the fragmentation of the isomer with 4,6,8-trimethylazulene-1-yl in position 2, together with the previous splits azulene-carbonyl cation can be also eliminated. At the azulene-carbonyl elimination more of the fragments encountered in Scheme 3 (m = 401, 402, 386, 385, 384, 371, 343, 297, 295, 290, 280, 265, 264, 197) are present also in spectrum of compound with alkylated azulene in 2-position. That is in accordance with the same fragmentation routes for both isomeric pyranylium cations at the azulene-carbonyl cation splitting. The same is valuable for the splitting of benzoyl cation for the two isomeric pyranylium salts.

**Pyridinium salts**

For the pyridinium salts the splitting of the substituent at the quaternized nitrogen with the generation of a new pyridinium salt protonated at this atom necessitates the lower fragmentation energy. Obviously, there is a great difference between the splitting aptitudes of the nitrogen-carbon bond depending on the nature of the substituent. As can be seen from the scheme 6, the abundance of the molecular ion decrease in series Ph > Me > Bn > nBu > iPr in agreement with the stability of the eliminated fragments. It is interesting to observe that the major fragment for benzyl elimination is the stable tropylium cation with $m = 91$.

The fragmentation of the ion with $m = 358$ follows a route similar to that for the pyranylium cation. Of course, as is described in scheme 7, the elimination of benzoyl cation is replaced by the elimination of phenyl and one molecule of hydrocyanic acid.
Pyridines

In ESI procedure, the protonation of neutral molecules generates the recorded molecular ion. Thus, it is not surprising that there were no significant differences in mass spectra of pyridines and the corresponding pyridinium salts with different substituents at quaternary nitrogen after the substituent splitting. The most of the fragment signals are present in both mass spectra with several differences in the abundance of the obtained fragments. This is mainly due to the higher collision energy needed for the fragmentation of the more stable pyridines.

Conclusion

There were no significant differences between the fragmentations of the examined six-membered heterocycles with azulen-1-yl moiety at 4- or 2-position. The first step consists in the splitting of stable PhCO+ AzCO+ for pyranylium salts. For pyridinium salts the dealkylation of quaternary nitrogen and its protonation generates the same protonated pyridines as in mass spectra of pyridines as such. At the splitting of Az or Ph and HCN the same fragment was obtained as in the case of pyranylium primary splitting. The subsequent behaviour of this fragment in mass spectrometer is similar for all analyzed heterocycles. When alkyl groups are substituted at azulene moiety, a concurrence between their elimination and the above discussed splitting can occur. The splitting of N-substituent in the pyridinium salts is governed by the stability of formed species after the bond breaking.

References


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