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# MASS SPECTRAL STUDIES OF 2-ARYL-1,2-DIHYDROPYRIDINES*

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The mass spectral studies of 1,4-dihydropyridines have shown two major pathways for the fragmentation to be prominent.[1,2] The molecular ion by loss of a radical from the 4-position gave the stable pyridinium ion. The second decomposition route was initiated by loss of a radical from the 1-substituent of the molecular ion. With 1,4,4-trimethyl-1,4-dihydropyridine, the fragmentation of the molecular ion to the pyridinium ion, requiring the loss of a methyl radical, occurred in overwhelming preference to the loss of a hydrogen from the 1-alkyl substituent.[1,2]

A series of 2-aryl-1-alkyl-5-substituted-1,2-dihydropyridines (1)[3], has been investigated in the mass spectrometer as a means of comparing the mode of fragmentation of 1,2- and 1,4-dihydropyridines. Fragmentation of the molecular ion of the dihydropyridine to a pyridinium ion could occur by loss of either a hydrogen atom or an aryl radical. A comparison of the importance of these two routes was possible.

The mass spectra of the 1,2-dihydropyridines all exhibited molecular ions (2). The molecular ion readily fragmented to form a pyridinium ion by loss of a neutral fragment from the $sp^3$ carbon at position 2. In every case the preferred route was the loss of the aryl radical to form 3 (see Table 1). This fragmentation route was supported by detectable metastable ions.

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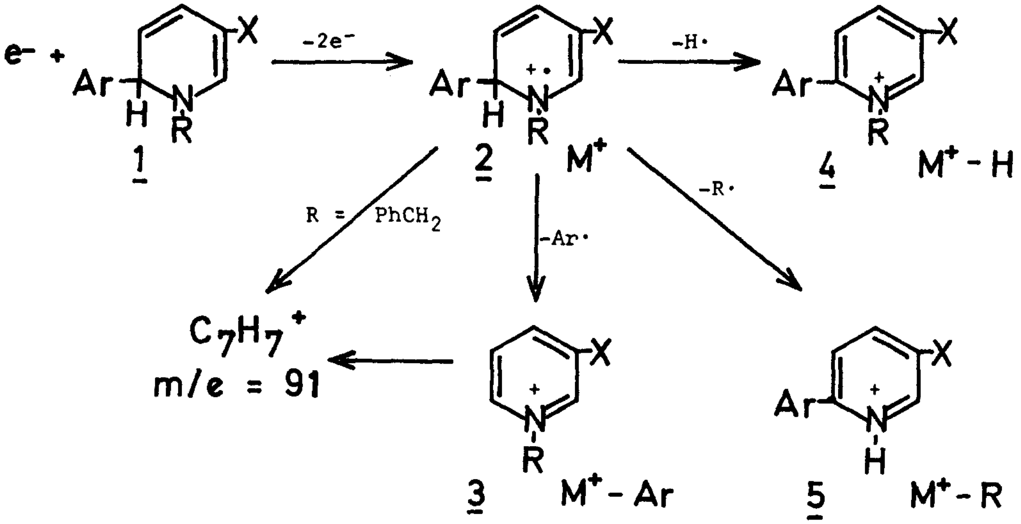

The 1-methyl derivatives (I-IV and VIII) showed little tendency to lose the N-methyl to form 5; however, the 1-benzyl derivatives (V-VII) gave large peaks at m/e = 91 due to the benzyl or tropilium ion as well as a fragment corresponding to $(M-R)^+$ 5. The $C_7H_7^+$ particle probably forms by fragmentation of the $M^+$-Ar ion, for in the spectrum of V a metastable ion was detected at m/e = 42.4.

The proposed fragments received further structural support, for the 6-monodeuterated derivative of V (VI) gave a mass spectrum with the major fragments at one larger mass with the exception of the ion at m/e = 91 which was unchanged in the spectrum of VI.

A change of the 5-substituent from the cyano to the methoxycarbonyl substituent in VIII caused little change in the course of the fragmentation. The most prominent peak resulted from the loss of the 2-aryl group from the molecular ion. A fragment of 7% relative intensity was evident at $(M^+-31)$ suggesting the loss of $OCH_3$ from the ester function, but otherwise the patterns were similar.

Thus it is clear that the primary fragmentation pathway for 1-methyl or 1-benzyl-2-aryl-1,2-dihydropyridines 1 in the mass spectrometer is the loss of the 2-aryl group from the molecular ion rather than loss of the hydrogen from the 2-position. The formation of the 1-substituted pyridinium ion provides the overwhelming route for fragmentation of the molecular ion.

These results are similar to those observed with the 1,4-dihydropyridines. Since the formation of the pyridinium ion occurs by the loss of the radical from the $sp^3$ hybrid carbon of the dihydropyridine, mass spectrometry provides a very valuable means for determining the structures of partially reduced pyridines. The difference in mass between the parent peak and the first major fragment represents the mass of the group attached to the reduced position. This technique thus provides a means for detecting any rearrangement of the double bonds of dihydropyridines and should provide a powerful tool for studying the orientation of nucleophilic addition to pyridinium ions.

## References

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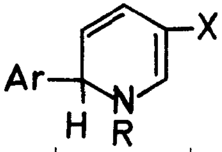
TABLE 1

Major Fragment in the Mass Spectra[a] of



| Sub. | X | R | Ar | $M^+$<br>%(m/e) | $M^+$-H<br>%(m/e) | $M^+$-Ar<br>%(m/e) | $M^+$-R<br>%(m/e) | m/e=91<br>% |
|---|---|---|---|---|---|---|---|---|
| I | CN | $CH_3$ | Ph | 15(196) | 17(195) | 100(119) | 1(181) | 2 |
| II 3-$CH_3$ | CN | $CH_3$ | Ph | 11(210) | 4(209) | 100(133) | 5(195) | 3 |
| III | CN | $CH_3$ | o-$CH_3C_6H_4$ | 6(210) | 5(209) | 100(119) | 1(195) | 4 |
| IV | CN | $CH_3$ | p-$CH_3C_6H_4$ | 18(210) | 25(209) | 100(119) | 8(195) | 8 |
| V | CN | $PhCH_2$ | Ph | 67(272) | 3(271) | 100(195)[c] | 27(181)[d] | 67[b] |
| VII | CN | $PhCH_2$ | p-$CH_3C_6H_4$ | 39(286) | 2(285) | 88(195)[e] | f | 100[b] |
| VIII | $COOCH_3$ | $CH_3$ | Ph | 12(229) | 10(228) | 100(152) | 2(214) | 2 |

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[a] The spectra were determined using an Hitachi Perkin-Elmer RMU-6E mass spectrometer with a direct inlet for the sample and an ionizing voltage of 80 ev.

[b] This ion is probably formed by fragmentation of ($M^+$-Ar) ion as well as from $M^+$, for a metastable ion is shown at 42.4 corresponding to the fragmentation of 195 to 91.

[c] Metastable ion at 139.9.

[d] Metastable ion at 120.5.

[e] Metastable ion at 133.0.

[f] For compound VII, $M^+$-Ar corresponds also to $M^+$-R.