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PMR AND MASS SPECTRAL STUDIES OF IODO- HYDROXY ACETOPHENONES

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ABSTRACT

Assignments of PMR and mass peaks in case of some tetra- and penta- substituted 2',-hydroxyacetophenones have been made and discussed.

Key words: PMR Spectra, Mass spectral, Hydroxyacetophenone.

INTRODUCTION

Assignment of PMR and mass spectral peaks in case of some substituted acetophenones have been made by number of workers[1-5], but no stress has been given to PMR and Mass spectral studies of tetra and penta substituted (2'/4') hydroxyacetophenones and hence, the PMR and mass study of some 2'/4' hydroxyacetophenones is undertaken.

EXPERIMENTAL

Materials and methods

Substituted 2'- hydroxyacetophenones were prepared and purified by repeated crystallization and then used for spectral analysis.

The isolated hydroxyacetophenones were dissolved in pure $CDC1_3$ and their PMR-spectra were recorded on Gemini-200 MHz spectrometer according to the procedure given in NMR-DOP-13 (HCT, Hyderabad).

The results are given in Table 1. The isolated hydroxyacetophenones were also analysed by VG-7070 H Mass spectrometer using EI - technique at 70 eV (IICT, Hyderabad).

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The spectra were recorded and the results are listed in Table 2.

All hydroxyacetophenones showed the band in between 2.67-2.62 δ ppm due to Ar-CO-CH_3. 3'-iodo, 5'-methyl showed a band at 2.3 δ due to Ar-CH_3. All 2'-hydroxy acetophenones showed a singlet near 13 δ due to Ar-OH. When - OH group is at 4'-position or at 2' and 4' –position, the (-OH) peak appears a singlet at 6.21 δ and at 6.52 δ, respectivly. All these values are in agreement with Silverstein et al.[6] Calculated and observed molecular weights of the comopunds are exactly the same.

Table 1: PMR-Chemical shift in substituted 2'- hydroxyacetophenones

S. No.	Compounnd	Chemical shifts (δ) (ppm.)
1	3'-Iodo-5'-methyl	2 65 (s, 3H, -$COCH_3$), 2.31 (s, 3H, Ar-CH_3), 7.79 (s, 1H, 6 Ar-H), 7.52 (s, 1H, 4Ar-H), 12.96 (s, 1H, Ar-OH)
2	3' -Iodio-5'-chloro	2.67 (s, 3H, -$COCH_3$), 7.52 (s, 1H, 6Ar-H), 7.94 (s, 1H, 4Ar-H), 13.06 (s, 1H, Ar-OH)
3	3'-Chloro-5'-iodo	2.65 (s, 3H, -$COCH_3$), 7.94 (s, 1H, 6Ar-H), 7.93 (s, 1H, 4Ar-H), 12.77 (s, 1H, Ar-OH)
4	3',5'-Dichloro	2.64 (s, 3H, -$COCH_3$), 7.62 (s, 1H, 6Ar-H), 7.61 (s, 1H, 4Ar-H), 12.69 (s, 1H, Ar-OH)
5	3'-Iodo-5'-bromo	2.65 (s, 3H, -$COCH_3$), 7.85 (s, 1H, 6Ar-H), 7.84 (s, 1H, 4Ar-H), 13.06 (s, 1H, Ar-OH)
6	3'-5'-Diiodo	2.67 (s, 3H, -$COCH_3$), 7.29 (s, 1H, 6Ar-H), 7.23 (s, 1H, 4Ar-H), 13.12 (s, 1H, Ar-OH)
7	3'-Iodo-4'-methyl -5'-chloro	2.68 (s, 3H, -$COCH_3$), 2.66 (s, 3H, Ar-CH3), 7.746 (s, 1H, 4Ar-H), 13.23 (s, 1H, Ar-OH)
8	3',5'-Diiodo, 4'-hydroxy	2.59 (s, 3H, -$COCH_3$), 8.11 (s, 1H, 6Ar-H), 6.52 (s, 1H, Ar-H)
9	3',5'-Dibromo, 4'-hydroxy	2.60 (s, 3H, -$COCH_3$), 7.88 (s, 1H, 6Ar-H), 6.52 (s, 1H, 4Ar-H), 13.32 (s, 1H, Ar-OH)
10	3', 5'-Diiodo, 4,-hydroxy	2.56 (s, 3H, -COCH3), 8.30 (s, 2H, 3 and 6Ar-H), 6.21 (s, 1H, Ar-OH)

All the hydroxyacetophenones studied gave strong peaks for the molecular ion and

undergo cleavage at the bond B to the ring to give a respective Ar-C=O$^+$ fragment. This fragment (M - 15) in most of the cases accounts for the base peak. Further, strong peaks are observed in most of the cases at 77 due to phenyl ion, which further looses CH=CH to give the ion $C_4H_3^+$ at m/z 51. All the hydroxyacetophenones gave a strong peak at m/z 43, due to CH_3-C=O$^+$ (Table 2). In some of the cases, this peak is the base peak.

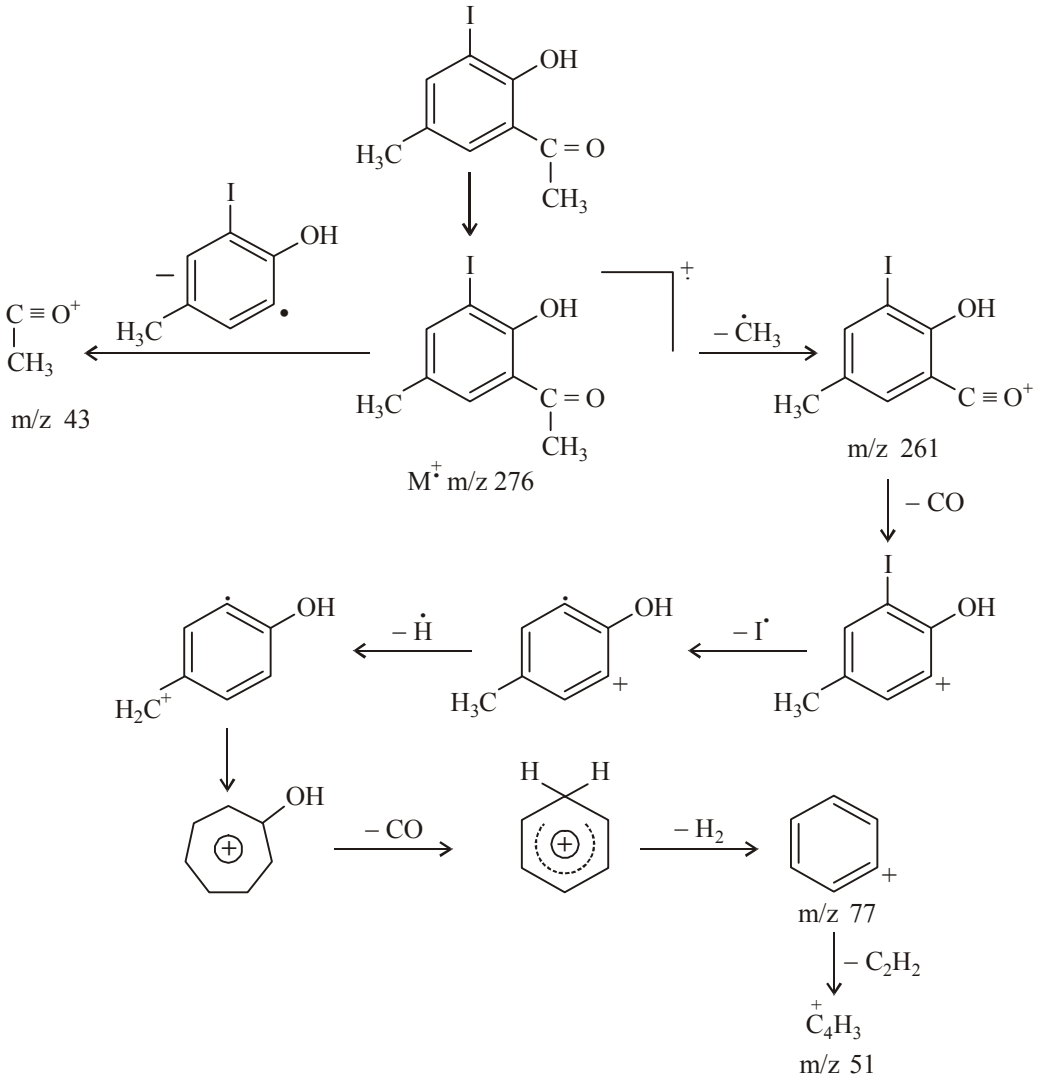

Fig. 1: Mass fragmentation pattern in 5'-methyl-3'-iodo-2'-hydroxyacetophenone

The mass fragmentation patterns of 3'-iodo-5' -methyl- and 3'-iodo-5'-chloro-2'-hydroxyacetophenones are given as the representative cases.

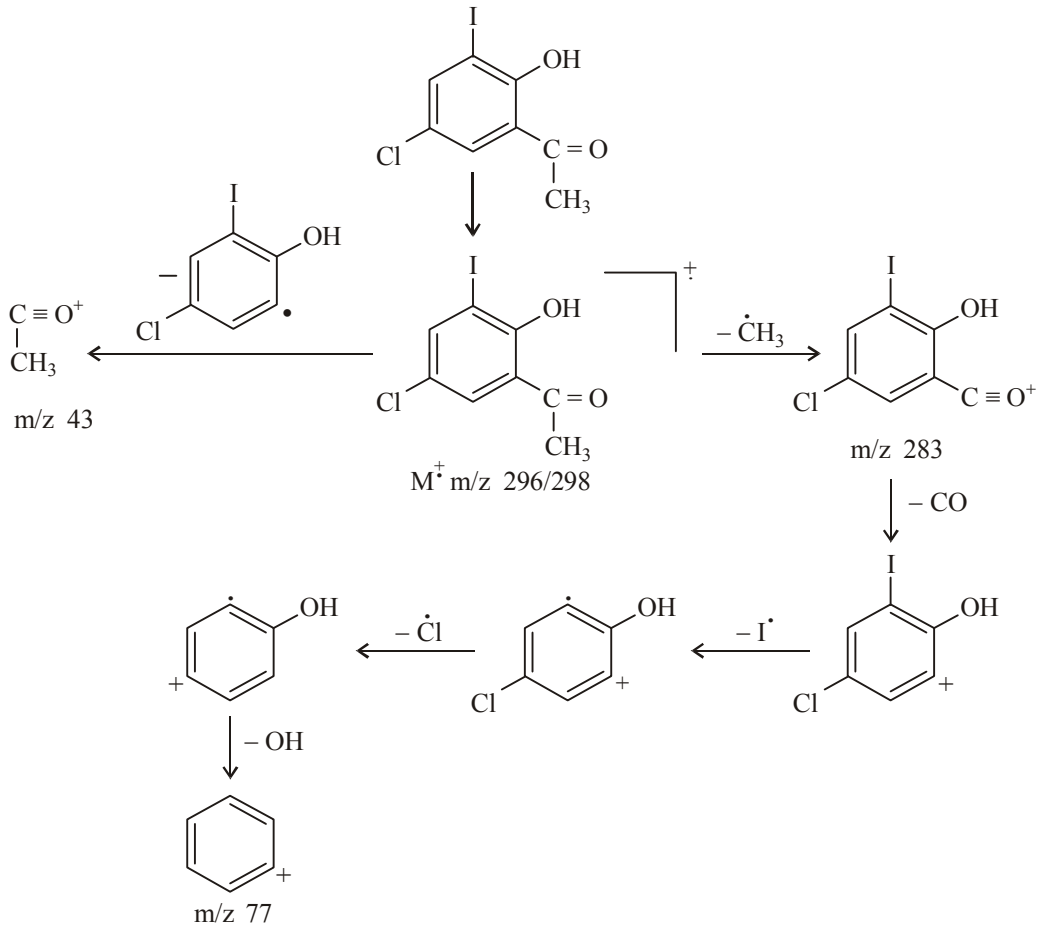

Fig. 2: Mass fragmentation pattern in 5'-chloro-3'-iodo-2'-hydroxyacetophenone

Table 2: Mass fagmentation values (m/z values) of substituted 2'-hydroxyacetophenone

S. No.	Compound	Mol. Wt (Calc.)	m/z Value
1	3'-Iodo-5'-methyl	276	276, 261, 106, 77, 51, 43.
2	3'-Iodo-5'-chlorol	296	296, 281, 126, 77, 63, 43.
3	3'-Iodo-5'-iodo	296	296, 281, 225, 126, 126, 62, 43.
4	3', 5'-Dichloro	206	206, 204, 191, 189, 133, 97, 63, 43.

Cont…

S. No.	Compound	Mol. Wt (Calc.)	m/z Value
5	3'-Iodo-5'-bromo	341	340, 325, 170, 78, 63, 43.
6	3', 5'-Diiodo	388	388, 373, 218, 91, 43.
7	3'-Iodo-4'-methyl- 5'-chloro	310	310, 295, 140, 112, 77, 43.
8	3'5'-Diodo, 4'-hydroxy	404	404, 389, 278, 263, 43
9	3',5'-Dibromo, 4'-hydroxy	310	310, 389, 278, 263, 43
10	3'5'-Diiodo, 4'-hydroxy	388	388, 373, 345, 218, 91, 43.

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