



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 workers¹⁻⁵, 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 CDC1₃ 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-CH₃. 3'-iodo, 5'-methyl showed a band at 2.3 δ due to Ar-CH₃. 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 , respectively. All these values are in agreement with Silverstein et al.⁶ Calculated and observed molecular weights of the compounds are exactly the same.

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

S. No.	Compound	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-CH ₃), 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, -COCH ₃), 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 loses 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 $\text{CH}_3\text{-C=O}^+$ (Table 2). In some of the cases, this peak is the base peak.

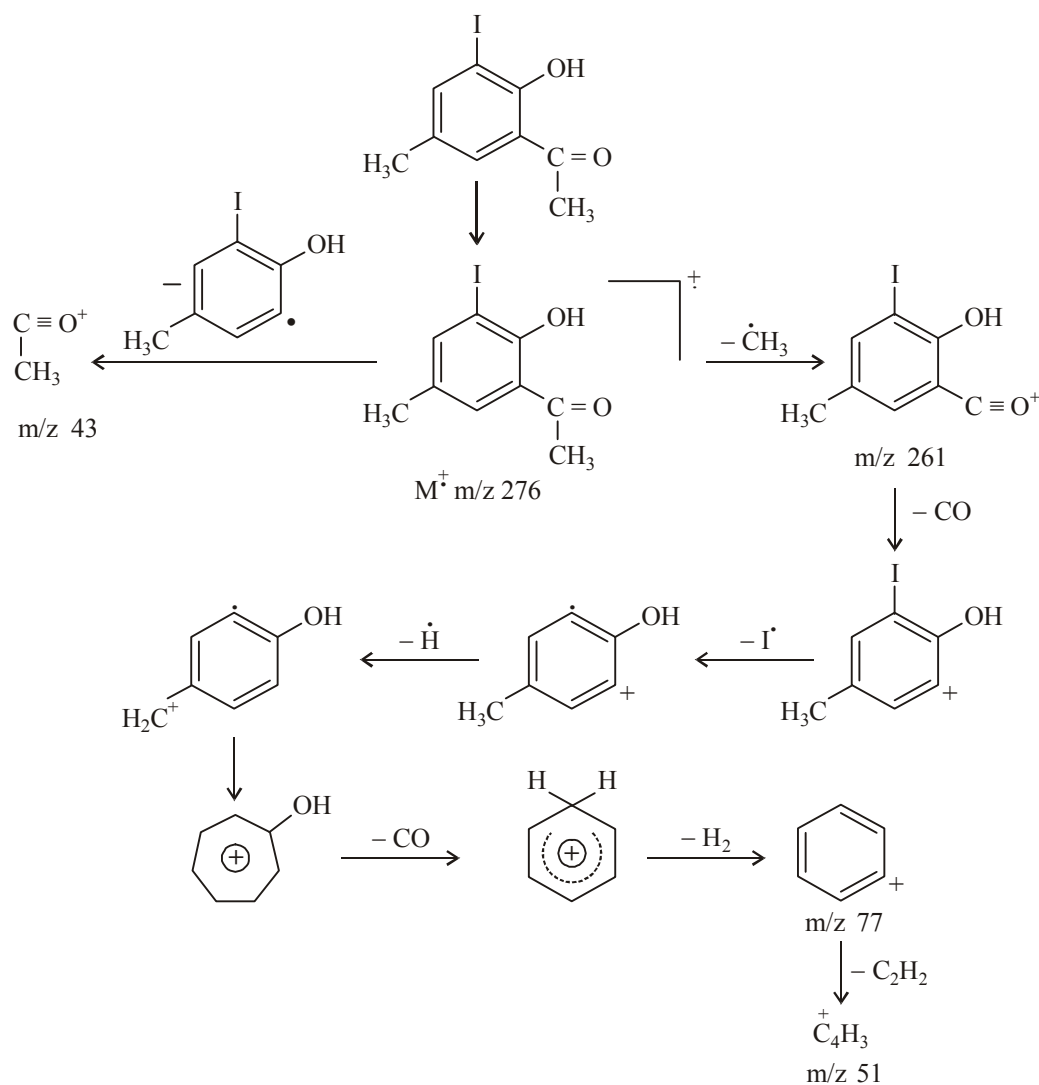


Fig. 1: Mass fragmentation pattern in 5'-methyl-3'-iodo-2'-hydroxyacetophenone

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

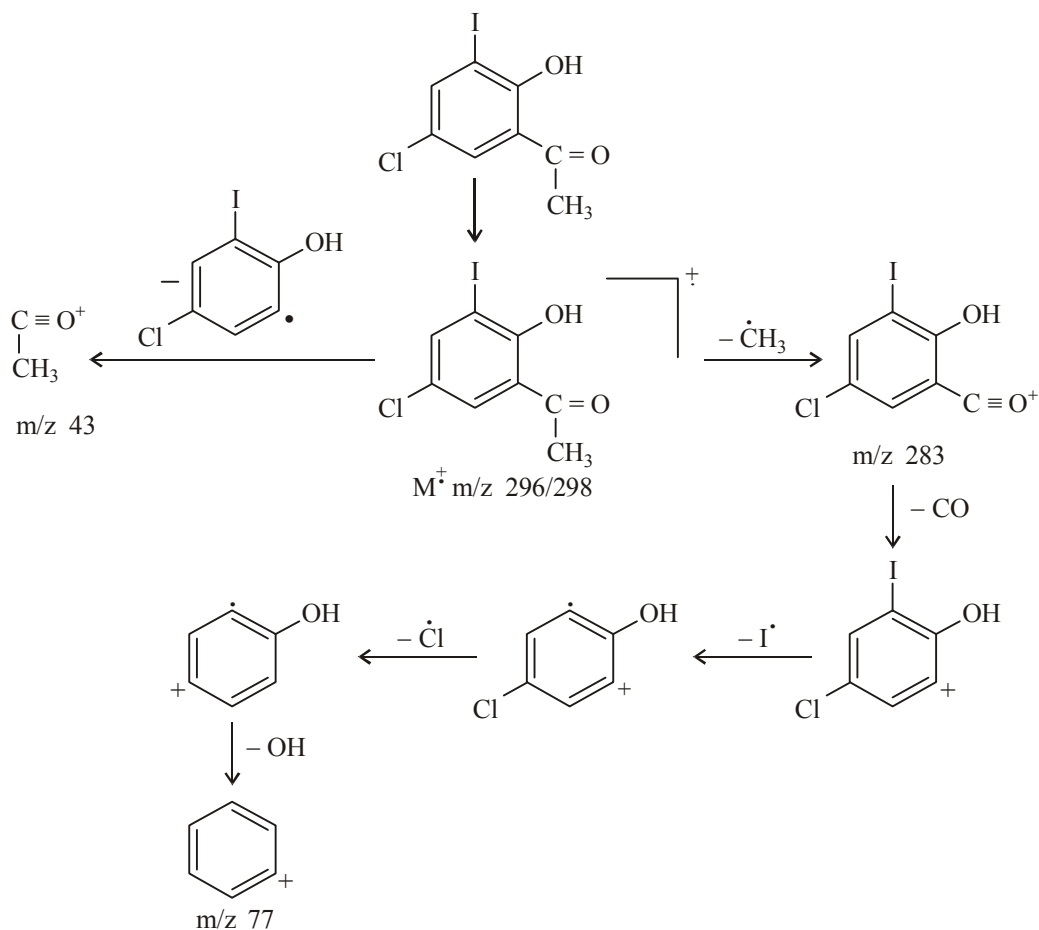


Fig. 2: Mass fragmentation pattern in 5'-chloro-3'-iodo-2'-hydroxyacetophenone

Table 2: Mass fragmentation 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.

ACKNOWLEDGEMENT

The authors are thankful to the Principal, Yeshwant College, Nanded for providing all essential facilities One of the authors (J.K.D) is thankful to U.G.C. for the award of F.I.P. Thanks are also due to Director, I.I.C.T. Hyderabad for providing spectra.

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Revised : 02.11.2009

Accepted : 05.11.2009