Electron Impact Mass Spectrometry of 2-(2-Pyridyl)-2,3-dihydroxy-5-phenyl-4-pentene

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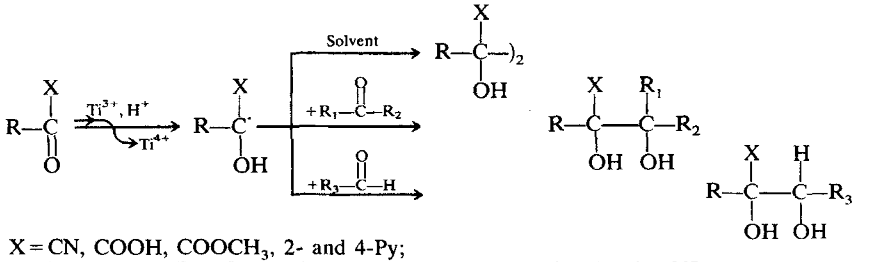
The mass spectrometric behaviour of 2-(2-pyridyl)-2,3-dihydroxy-5-phenyl-4-pentene has been studied with the aid of *B/E*, *B^2/E* linked scans, exact mass measurements, collisionally activated dissociation mass-analysed ion kinetic energy spectra, and labelling experiments. The primary loss of water is proved to involve both hydroxylic hydrogens, thus suggesting the formation of an epoxidic radical ion and the presence of extensive skeletal rearrangements.

INTRODUCTION

For some time we have been carrying out investigations[1] regarding the reducing properties of the species Ti(III) in aqueous acidic solution with respect to carbonyl compounds activated towards reduction by an electron-withdrawing substituent, according to the general scheme shown below (Scheme 1).



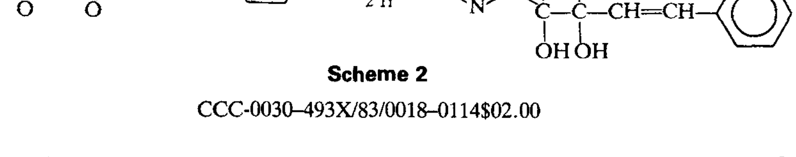
X = CN, COOH, $COOCH_3$, 2- and 4-Py;
R = H, CH_3, Ph; $R_1 = R_2 = CH_3$; $R_3 = CH_3$, Ph, $CH_2{=}CH$, Ph—C≡CH.

Scheme 1

We have also observed[2,3] that an interesting mixed pinacol reaction takes place between the radical intermediate of Scheme 1 and simple ketones and aldehydes affording the corresponding mixed 1,2-diols in very good yields.

In the course of an extension of this study with the scope to further generalize the reaction, we have found[4] that the radical intermediate of Scheme 1 adds selectively to the carbonyl carbon atom of α,β-unsaturated aldehydes providing an exceptionally simple synthesis of useful highly functionalized allylic 1,2-diols.

The title compound, 2-(2-pyridyl)-2,3-dihydroxy-5-phenyl-4-pentene, was obtained easily according to the equation in Scheme 2:



Scheme 2

The mass spectrometric behaviour of diols has been the subject of many papers, and major fragmentation patterns for aliphatic 1,2-diols have been established to occur via cleavage of the glycol carbon–carbon bond.[5,6]

In the case of α,β-unsaturated 1,2-diols this process may occur with hydrogen rearrangements.[5] The spectra of cycloalkane diols permit differentiation of positional isomers since the loss of water occurs more easily from the *cis* than from the *trans* isomer.[7,8] Metastable ion studies have shown that primary water loss from cyclohexane-1,2-diols involves hydrogen scrambling.[9,10] All previous papers on the mass spectrometry of diols, from pioneer studies to recent literature,[11,12] have demonstrated that the loss of water is essentially due to a mechanism involving an hydroxyl group and one hydrogen of the hydrocarbon chain.

In the present paper, the fragmentation of the title compound and an unusual primary water loss from this, involving both the hydroxylic hydrogens and never observed previously, are described and discussed in detail with the aid of *B*/*E*, *B^2*/*E* linked scans,[13] collisionally activated dissociation mass-analysed ion

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kinetic energy (CAD MIKE) spectra[14] and deuterium labelling experiments.

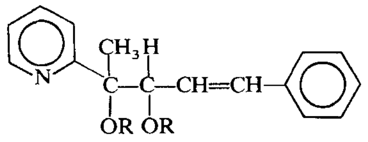
EXPERIMENTAL

The title compound was prepared easily by allowing a solution of 2-acetylpyridine (15 mmol) and cinnamaldehyde (100 mmol) in glacial acetic acid (20 cm^3) with a 15% aqueous acidic solution of $TiCl_3$ (30 mmol, *c.* 30 cm^3) to react for 2 h at room temperature and under nitrogen. After work-up the structure of the two isomers (*threo* and *erythro* mixture) was confirmed by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy:

^{1}H NMR ($CDCl_3$): δ 1.5 and 1.6 (3H, two s, CH_3), 4.45 (1H, d, CH), 4.8 (2H, s, 2OH, D_2O exchanged), 6.0–6.7 (2H, m, CH=CH), 7.2 (5H, m, Ph H), 7.2–7.8 (3H, m, Py H), 8.5 (1H, d, Py α-H); IR (film): 3400 (OH), 1590, 960 (CH=CH out of the plane) cm^{-1}.

All the spectra were obtained on a VG ZAB 2F instrument introducing the sample with the direct electron impact (DEI) technique.[15] The 70 eV electron impact mass spectra were obtained with an electron current of 200 μA and a source temperature of 150 °C. Exact mass measurements were taken with the peak matching technique at 10 000 resolving power (10% valley definition). MIKE spectra were taken in the usual manner with an accelerating voltage of 7 keV. CAD MIKE spectra were obtained using 8 keV ions colliding with air in the second field free region. The deuterium labelled compound was prepared simply by dissolving 10 mg of the title compound in 0.5 cm^3 of CD_3OD and 0.1 cm^3 of D_2O, and leaving the solution to stand for 4 h.

RESULTS AND DISCUSSION



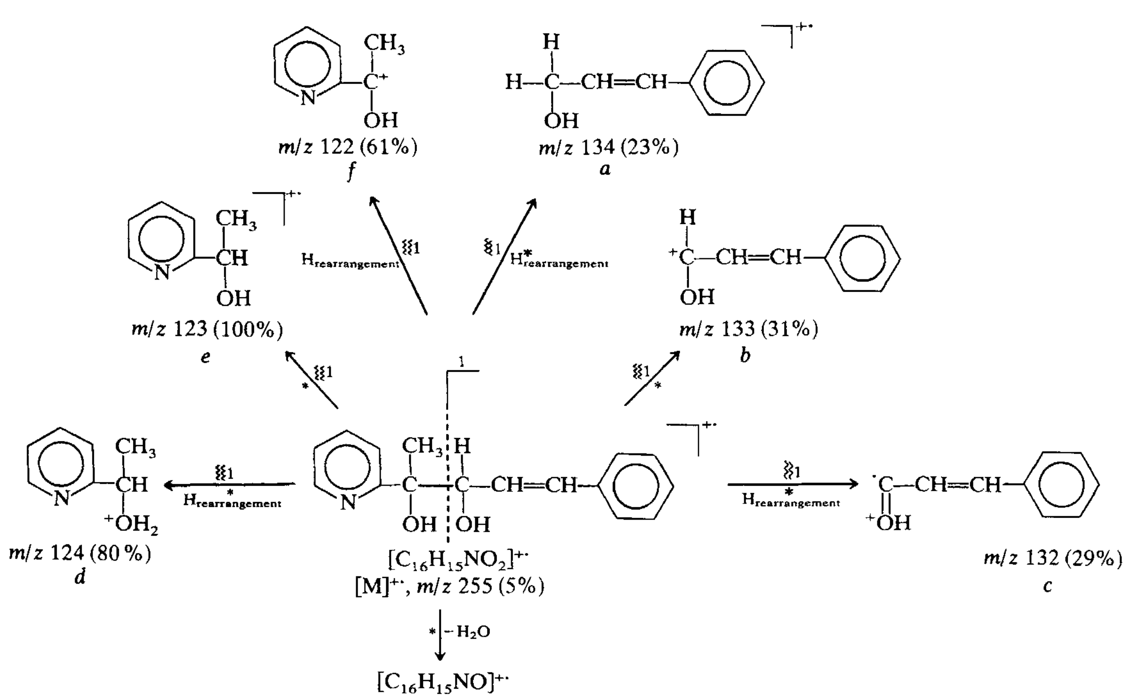
R = H **1**
R = D **2**

The more abundant and interesting peaks for compounds **1** and **2** are reported in Table 1. By means of *B*/*E*, B^2/E linked scans for metastable ion detection and exact mass measurements the fragmentation pattern reported in Scheme 3 was obtained. It shows clearly the usual cleavage of the glycol carbon–carbon bond along with extensive hydrogen rearrangements.

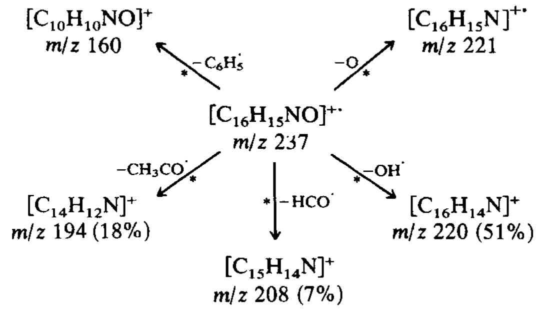
The comparison between the fragmentation pattern of the undeuterated and deuterated compound permits the following conclusions to be drawn which are illustrated in Scheme 3: (i) The hydrogen transferred in the formation of the ionic species at *m*/*z* 134 is not that of the hydroxyl group but probably one of those

Table 1. Fragmentation patterns for compounds 1 and 2

	$[M]^{+\cdot}$	$[M-R_2O]^+$	$[M-R_2O-OH]^+$	$[M-R_2O-HCO]^+$	$[M-R_2O-CH_3CO]^+$	*a*	*b*	*c*	*d*	*e*	*f*
1 *m*/*z* (Rel. int.)	255 (5)	237 (8)	220 (51)	208 (7)	194 (18)	134 (23)	133 (31)	132 (29)	124 (80)	123 (100)	122 (61)
2 *m*/*z* (Rel. int.)	257 (5)	237 (7)	220 (48)	208 (9)	194 (20)	135 (17)	134 (23)	133 (16)	125 (40)	124 (100)	123 (45)



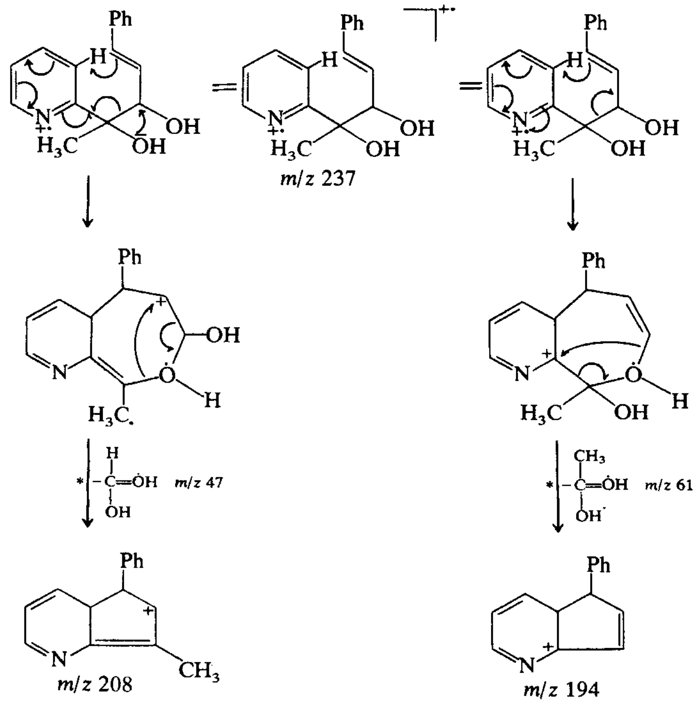
Scheme 3



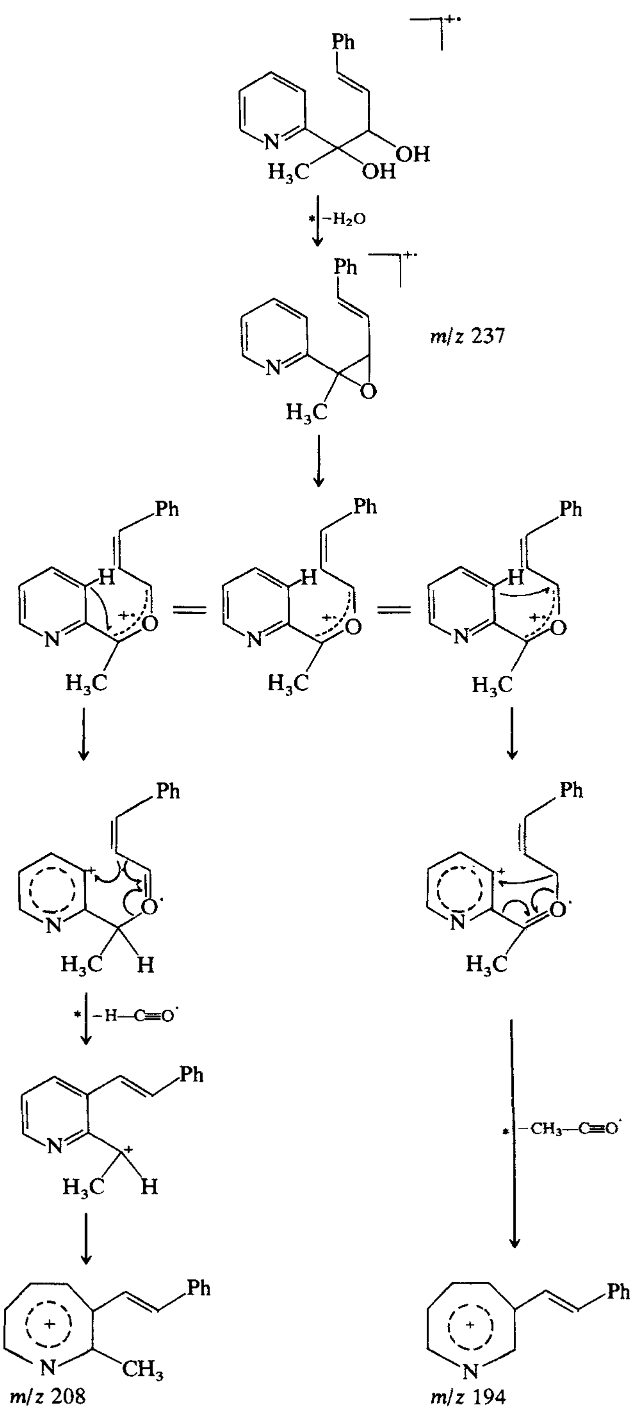
Scheme 4

of the methyl group; in fact, for compound **2** the peak due to this species shifts to *m/z* 135 and not at *m/z* 136. (ii) The hydrogen loss in the formation of radical ions at *m/z* 132 is not that of the hydroxyl group: were it not so, in the mass spectrum of compound **2** this peak would have remained at *m/z* 132 and not appeared at *m/z* 133. (iii) The same behaviour is also observed for the ion clusters at *m/z* 122, 123, and 124. While this fact may be reasonable when we consider the ions at *m/z* 122 and 123, it seems quite surprising for ions at *m/z* 124 to ascertain that the double hydrogen transfer does not involve the other hydroxylic hydrogen. CAD MIKE experiments regarding ionic species at *m/z* 123 confirm that its structure corresponds to 2-(2-pyridyl)ethanol. (iv) The primary loss of water for compound **1** gives rise to $[C_{16}H_{15}NO]^{+\cdot}$, the *m/z* 237 species. The same composition is also found for compound **2**: this finding demonstrates for the title 1,2-diol studied that the loss of water originates from one hydroxyl group together with the hydrogen of the other hydroxyl group, and not according to the usual mechanism reported in the literature. The CAD MIKE spectrum of the ionic species at *m/z* 237 suggests the fragmentation pattern reported in Scheme 4. The oxygen loss, to which corresponds a peak with a large energy release, supports the presence of an epoxidic radical ion structure, while the hydroxyl loss seems to contrast this. Again the $HCO^{\cdot}$ and $CH_3CO^{\cdot}$ losses indicate the presence of extensive skeletal rearrangements.

For these reasons we believe that the radical ions at *m/z* 237 represent a set of different molecular structures which could be related to the presence of a diastereomeric mixture of the title compound. Hence



Scheme 5



Scheme 6

we propose two different fragmentation patterns for the formation of ions at *m*/*z* 208 and 194 in Schemes 5 and 6 which both seem reasonable to explain the experimental results given. Additional work is presently being undertaken.

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