Electron Impact Mass Spectrometry of 2-Hydroxymethyl-3,4,5,6,7,8-hexahydro-2*H*-1-benzopyran-5-ones. The Unusual Presence of $[M-H_3O]^+$ Species in the Fragmentation Pattern of 4-Phenyl Derivatives†

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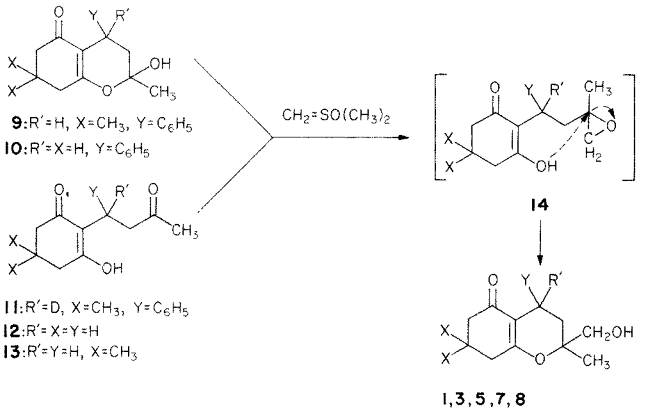
The mass spectrometric behaviour of some 2-hydroxymethyl-3,4,5,6,7,8-hexahydro-2*H*-1-benzopyran-5-ones is described and discussed with the aid of exact mass measurements, linked scans, labelling experiments and low electron energy measurements. The unusual presence of abundant $[M-H_3O]^+$ species in the mass spectra of 4-phenyl substituted compounds is discussed in detail and a mechanism is proposed.

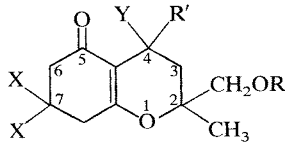
INTRODUCTION

As already reported,[1] 2-hydroxymethyl-3,4,5,6,7,8-hexahydro-2*H*-1-benzopyran-5-ones are easily obtained by reacting dimethylsulfoxonium methylide on 2-hydroxy-3,4,5,6,7,8-hexahydro-2*H*-1-benzopyran-5-ones or on the corresponding 2-(3′-oxoalkyl)-1,3-cyclohexane-1,3-diones, through a methylene transfer reaction (see Scheme 1).



Scheme 1

While mass spectrometry of chromans,[2–4] chromones,[5] homochromones[6] and tetrahydropyran-3-ones[7] has been widely studied, no mass spectrometric investigations have been performed previously on the title compounds. In the present paper the mass spectral behaviour of four 2-hydroxymethyl-3,4,5,6,7,8-hexahydro-2*H*-1-benzopyran-5-ones (**1**, **5**, **7** and **8**) and four deuterated derivatives (**2–4**, **6**) is discussed in detail with the aid of exact mass measurements, linked scans[8] and low electron energy measurements.



1: $R=R'=H$; $Y=C_6H_5$; $X=CH_3$
2: $R=D$; $R'=H$; $Y=C_6H_5$; $X=CH_3$
3: $R=H$; $R'=D$; $Y=C_6H_5$; $X=CH_3$
4: $R=R'=D$; $Y=C_6H_5$; $X=CH_3$
5: $R=R'=H$; $Y=C_6H_5$; $X=H$
6: $R=D$; $R'=H$; $Y=C_6H_5$; $X=H$
7: $R=R'=Y=X=H$
8: $R=R'=Y=H$; $X=CH_3$

EXPERIMENTAL

Mass spectra were run on an Hitachi RMU double focusing instrument operating at 70 eV (80 μA). Samples were introduced directly into the ion source at 200 °C. Linked scans[8] were performed by a Varian 112 S instrument.

Exact mass measurements were obtained with the peak matching technique at 6000 resolution.

Compounds **1** and **5** were obtained by reacting dimethylsulfoxonium methylide on 2-hydroxy-3,4,5,6,7,8-hexahydro-2*H*-1-benzopyran-5-ones **9** and **10**, while compounds **3**, **7** and **8** were obtained by

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Table 1. Partial mass spectra of 1–8

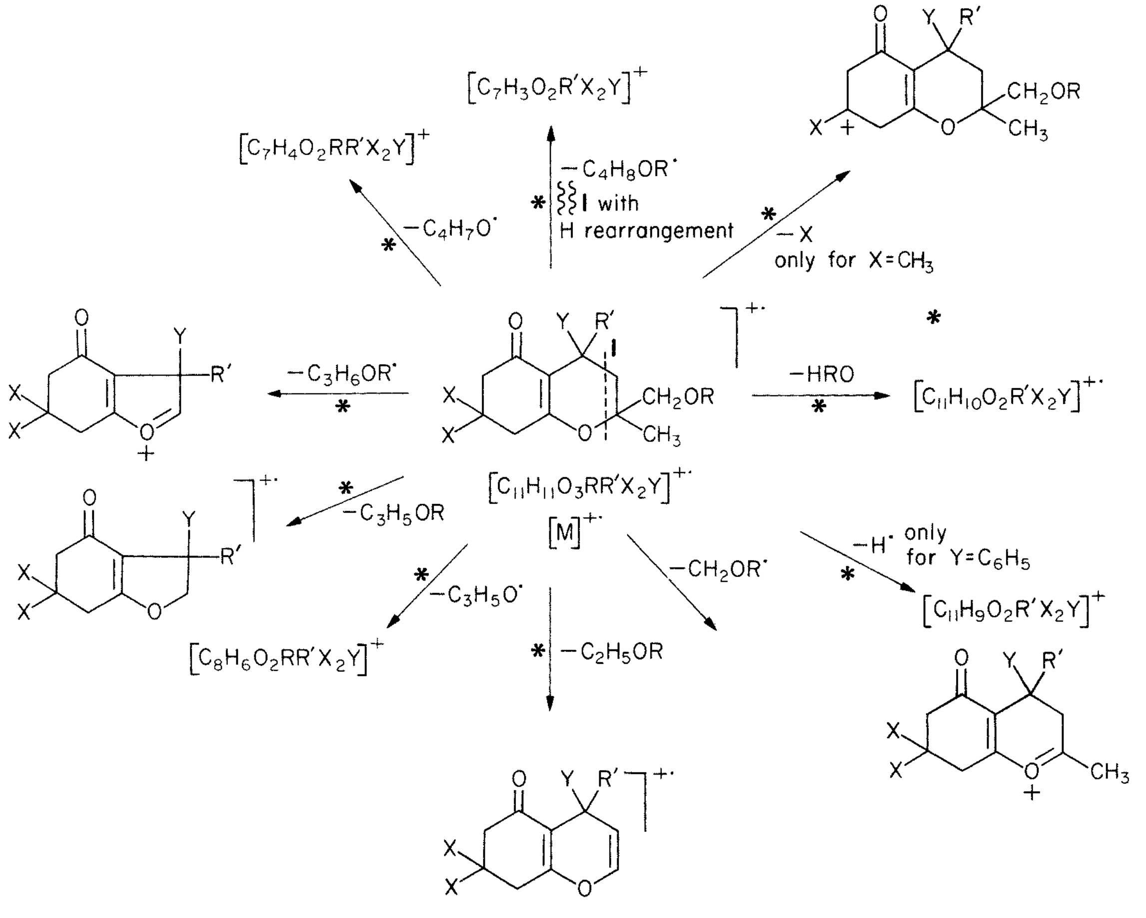
Compounds Ions	**1** *m/z*(int.%)	**2** *m/z*(int.%)	**3** *m/z*(int.%)	**4** *m/z*(int.%)	**5** *m/z*(int.%)	**6** *m/z*(int.%)	**7** *m/z*(int.%)	**8** *m/z*(int.%)
$[M]^{+\cdot}$	300(100)	301(100)	301(100)	302(100)	272(100)	273(100)	196(43)	224(68)
$[M-CH_3]^+$	285(2)	286(2)	286(2)	287(3)	—	—	—	209(5)
$[M-HR\ddot{O}]^{+\cdot}$	282(5)	282(7)	283(5)	283(7)	254(5)	254(6)	178(1)	206(4)
$[M-H_2RO]^+$	281(25)	281(23)	282(22)	282(12)	253(17)	253(17)	—	—
$[M-HRR'O]^{+a}$	—	—	281(4)	281(4)	—	—	—	—
$[M-CH_2OR]^+$	269(15)	269(15)	270(19)	270(18)	241(10)	241(9)	165(40)	193(56)
$[M-C_2H_5RO]^{+\cdot}$	254(9)	254(9)	255(9)	255(9)	226(20)	226(25)	150(7)	178(8)
$[M-C_3H_5O]^+$	243(48)	244(42)	244(40)	245(28)	215(53)	216(54)	139(43)	167(34)
$[M-C_3H_5OR]^{+\cdot}$	242(15)	242(22)	243(15)	243(27)	214(15)	214(24)	138(15)	166(15)
$[M-C_3H_6OR]^+$	241(29)	241(20)	242(20)	242(19)	213(32)	213(26)	137(12)	165(7)
$[M-C_4H_7O]^+$	229(14)	230(10)	230(14)	231(9)	201(22)	202(15)	125(35)	153(17)
$[M-C_4H_8OR^\cdot]^+$	227(17)	227(17)	228(19)	228(17)	199(30)	199(37)	123(20)	151(14)

[a] Distinguishable only for compounds **4** and **3**.

reacting the same ylide on 2-(3′-oxoalkyl)-1,3-cyclohexane-1,3-diones **11**, **12** and **13** (Scheme 1). General procedure: a solution of dimethylsulphoxonium methylide was prepared from trimethylsulphonium iodide (9.9 g, 0.045 mol) and NaH (2.2 g, 60% mineral oil dispersion, 0.055 mol) in DMSO (80 cm^3) according to Corey.[9] A solution of the appropriate open chain compound **11**, **12** or cyclic ketal **9**, **10** (0.015 mol) in DMSO (15 cm^3) was added drop-wise over 15 min to the stirred solution of the ylide kept under nitrogen at −5 °C. The pale yellow solution was stirred for 18 h at room temperature and then poured into the ice-water, the pH adjusted to neutral with diluted HCl and extracted with Et_2O (3×100 cm^3). The combined organic layers were washed with water (3×50 cm^3), dried over Na_2SO_4 and evaporated under reduced pressure to give the crude products **1**, **3**, **5**, **7** and **8**, which were crystallized from a convenient solvent.[1]

Spectroscopic methods (infrared and ^1H nuclear magnetic resonance) and elemental analysis confirmed the assigned structures.

The intermediate ketone **11** was synthesized as follows: Deuterobenzaldehyde[10] (**15**) was condensed with



Scheme 2

acetone in alkine medium; the resulting 1- deutero-1-phenyl-1-buten-3-one (**16**) (0.1 mol) was reacted with dimedone (0.1 mol) in absolute ethanol (30 cm^3) and K (0.2 g) according to Stetter.[11] The crude oil resulting from usual work-up was reacted with **13** to give the deutero derivative compound **3**.

Compounds **2**, **4** and **6** were obtained simply by dissolving compounds **1**, **3** and **5** respectively in deutero methanol and D_2O (1:3).

RESULTS AND DISCUSSION

Table 1 reports the *m/z* ratios and the relative abundance of the more important ionic species present in the 70 eV mass spectra of compounds **1–8**. The common fragmentation pattern reported in Scheme 2 was obtained by means of linked scans and exact mass measurements.

The molecular ions of all the compounds examined are very abundant and represent the base peak for the 4-phenyl substituted compounds (**1–6**) (see Table 1).

The primary loss of $CH_3^{\cdot}$ is not present in the fragmentation pattern of compounds **5–7**: this indicates that: (i) the methyl radical lost is definitely one of those in position 7 and (ii) the CH_3 in position 2 is not involved.

Primary losses of $CH_2OR^{\cdot}$ and C_2H_5OR, typical of chromanic system, are also present, giving rise to stable and abundant species. Other important primary decomposition processes are due to losses of $C_3H_5O^{\cdot}$, C_3H_5OR, $C_3H_6OR^{\cdot}$, $C_4H_7O^{\cdot}$ and $C_4H_8OR^{\cdot}$.

A peculiar aspect of the mass spectrometry of compounds **1–6**, substituted in position 4 with a phenyl group, is the unusual presence of $[M-H_3O]^+$ species in their fragmentation pattern.

These ions are very abundant in the 70 eV mass spectra with respect to the $[M-H_2O]^{+\cdot}$ species (in Table 1, the relative abundances of these last are uncorrected for the isotopic contribution of the $[M-H_3O]^+$ species).

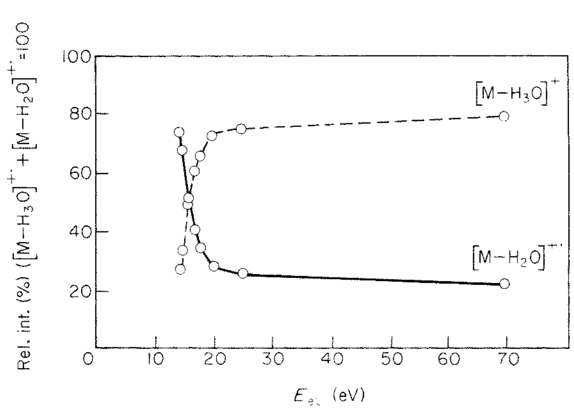


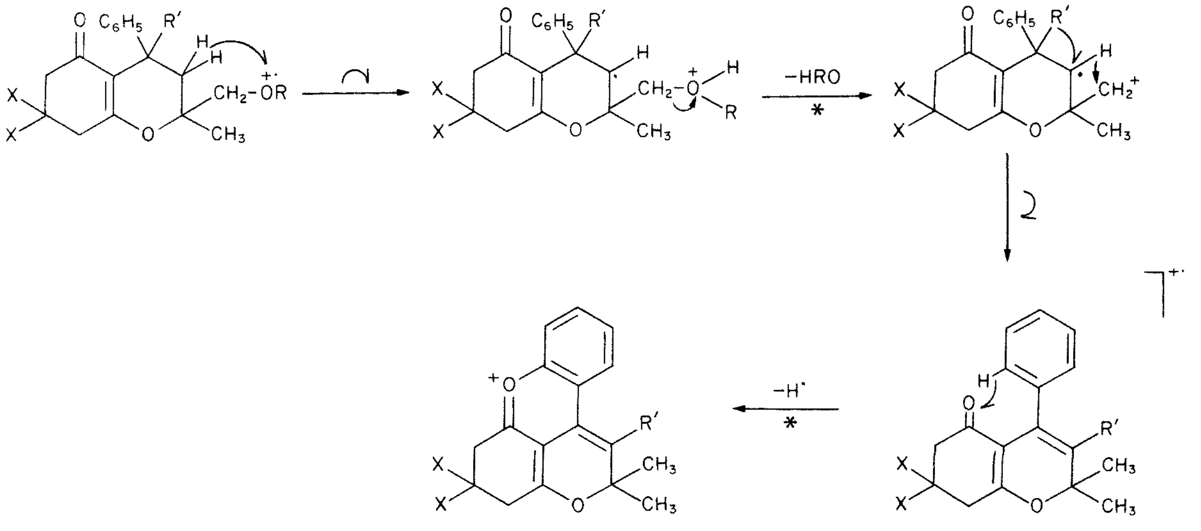
Figure 1. Relative abundances of $[M-H_3O]^{+\cdot}$ and $[M-H_3O]^{+\cdot}$ as a function of ionizing energy.

By means of linked scans the following pathways for the formation of $[M-H_3O]^+$ ions have been elucidated:

$$\begin{tikzcd}
 & {[M-H_2O]^{+\cdot}} \arrow[dr, "*"] & \\
{[M]^{+\cdot}} \arrow[ur, "*"] \arrow[rr, bend right, "*"'] & & {[M-H_3O]^+}
\end{tikzcd}$$

i.e. these species may originate either from a primary decomposition process or through sequential losses of H_2O and $H^{\cdot}$.

On the other hand the plots of rel. ab. vs E_{el} (see Fig. 1) for $[M-H_3O]^+$ and $[M-H_2O]^{+\cdot}$ species show clearly that the formation of the former is a high energy process to take place subsequent to the H_2O primary loss. By the comparison of the mass spectrometric behaviour of the deuterated compounds and the compounds **7** and **8**, for which the position 4 is not substituted with a phenyl group, we assume the mechanism for the formation of $[M-H_3O]^+$ to be as reported in Scheme 3.



Scheme 3

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