CATECHOLIC ION FORMATION FROM 5-SUBSTITUTED 2,2-DIMETHYL-1,3-BENZODIOXOLES MOLECULAR IONS

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Abstract - The presence of catecholic ions in the mass spectra of 5-substituted 2,2-dimethyl-1,3-benzodioxoles is proved to originate from a primary decomposition process analogous to that observed for 2,2-di-substituted 1,3-benzoxathioles.

INTRODUCTION
It is well known that 2,2-disubstituted 1,3-benzodioxoles are easily synthesized by reaction of catechol with ketones\(^1\), as indicated by the following equation.

\[
\text{C}_6\text{H}_6\text{O}_2 + \text{O} = \text{C} \xrightarrow{R_1\text{O}_3} \text{C}_6\text{H}_6\text{O}_2 + \text{H}_2\text{O}
\]

The chemical cleavage of ethereal bond obtained by the action of Grignard reagents on these compounds, leads to a mixture of catechol, alkanes, alkenes and other minor unidentified products\(^2\).

The mass spectrometric behaviour of these compounds has been already studied by Brophy et al.\(^3\) By means of exact mass measurements the composition \(\text{C}_6\text{H}_6\text{O}_2\) was found for ions at \(m/z\) 110 (the most abundant ions in the mass spectra) and metastable analysis indicated that these are formed, at least in part, from the molecular

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ions of the benzodioxoles under study. A similar process has been observed by us for 2,2-disubstituted benzoxathioles. In that case the presence of 2-hydroxybenzethiol ions was proved by collisional activation experiments and an analogy with the chemical degradative processes was also underlined.

In the present paper the mass spectrometric behaviour of six 5-substituted 2,2-dimethyl-1,3-benzodioxoles (1-6) is described and discussed in detail with the aid of B/E and B²/E linked scans and collisional activation experiments for structure investigations.

\[
\begin{align*}
1 & : R=H \text{ (M.W.150)} \\
2 & : R=Br \text{ (M.W.228)} \\
3 & : R=NO_2 \text{ (M.W.195)} \\
4 & : R=CH_3 \text{ (M.W.164)} \\
5 & : R=NH_2 \text{ (M.W.165)} \\
6 & : R=NHCOCH_3 \text{ (M.W.207)}
\end{align*}
\]

**EXPERIMENTAL**

Mass spectra were run on a VG Micromass ZAB-ZF instrument operating at 70 eV (200 \(\mu\)A). Samples were introduced via all glass heated inlet system at 150°C; the source temperature was 200°C. Metastable ions were detected by B/E and B²/E linked scan techniques. Collisional activation (CA) spectra were obtained with 7 keV ions colliding with air in the second field free region. Compounds 1 to 6 were analytically pure samples synthesized as described previously in the literature.

**RESULTS AND DISCUSSION**

The 70 eV mass spectra of compounds 1 to 6 are reported in the table.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (m/z)</th>
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<tbody>
<tr>
<td>1</td>
<td>39(26%), 40(10), 41(24), 43(54), 45(15), 51(14), 52(14), 53(9), 54(9), 55(30), 57(8), 63(15), 64(14), 65(6), 69(8), 76(14), 77(16), 81(6), 82(6), 83(21), 111(5), 112(6), 135(100), 136(9), 150(42), 151(5).</td>
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<tr>
<td>2</td>
<td>39(26%), 41(35), 43(45), 44(38), 51(29), 62(10), 63(38), 79(9), 81(8), 109(7), 188(78), 190(76), 213(100), 215(98), 228(59), 230(57).</td>
</tr>
<tr>
<td>3</td>
<td>39(40%), 40(8), 41(50), 43(37), 51(17), 53(7), 55(9), 62(11), 63(28), 79(9), 81(10), 91(9), 92(12), 93(8), 109(6), 110(5), 111(12), 124(24), 134(51), 155(19), 179(5), 180(100), 181(10), 193(39), 196(4).</td>
</tr>
<tr>
<td>4</td>
<td>39(30%), 40(15), 41(16), 43(44), 51(31), 52(11), 63(6), 65(6), 66(5), 67</td>
</tr>
</tbody>
</table>
As it can be observed, only three intense ions are present, due to $\text{M}^+$, $\text{M}-\text{CH}_3$,$^+$ and $\text{RC}_6\text{H}_5\text{O}_2$,$^+$ species. B/E linked scans show the following fragmentation pattern, valid for compounds 1 to 5 only.

Compound 6 shows a primary loss of ketene giving rise to ions at $m/z$ 165 which undergo a similar fragmentation of the molecular ions of 5.

The process due to $\text{C}_3\text{H}_4$ loss is very favourable, on the contrary to what observed for 2,2-disubstituted 1,3-benzothioles,$^4$ and we have thought interesting to deepen it. First of all it must be underlined that the formation of $\text{RC}_6\text{H}_5\text{O}_2$,$^+$ ions from benzodioxoles in EI conditions is a primary decomposition process involving the hydrogen atoms of both the 2-methyl groups. This is proved by $^{32}$E/E linked scans on these ions (see, for example, figure 1) which indicate the only precursor of these species to be the corresponding molecular ions.

Secondly, the structure of these ions corresponds to that of 4-substituted catechols, as proved by collisional activation experiments (see, for example, fig. 2).
Figure 1. B/E linked scan spectrum of m/z 110 ion originating from M⁺ of compound 1.

Figure 2. Collisional activation spectrum of m/z 110 ion originating from M⁺ of compound 1, identical to that of M⁺ of catechol.

Then we suggest for the formation of these ions the following mechanisms:

Analogously to the 1,3-benzoxathioles, the four center mechanism is suggested by the presence of a wide metastable peak corresponding to this transition in the
MIKE spectra of these compounds. Finally, the primary CH₃⁺ loss leads to a very stable cation. It is to underline how this cation is stable in solution chemistry also, as reported in literature³, giving a good correspondence between the data obtainable by mass spectrometry and those of solution chemistry.

REFERENCES


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