Studies on Catechol Esters
Part IV. Mass Spectrometry

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The mass spectrometric behavior of a series of cyclic succinoyl-catechols, 3,4-dihydro-1,6-benzodioxocin-2,5-diones (I), and the corresponding catechol disecates, \(3a-c\) has been investigated. It has been found that except for processes due to losses of \(\text{CO}\) and \(\text{CO}_2\) from the molecular ions of \(I\), the fragmentation patterns of compounds \(I\) and \(3\) under electron impact are essentially of the same type.

Pseudoeaters \(4\) have also been investigated and loss of \(\text{CO}_2\) from these compounds has been found to be more dominant than what is observed for the isomeric compounds \(I\).

Mass spectrometric analysis of the trimethylsilyl (TMS) derivatives of a series of \(o\)-hydroxyphenyl acid succinates, \(2\ (R = \text{TMS})\), has also been performed and a rearrangement involving the TMS group has been observed.

During studies on catechol esters, \(1\), \(i.e.\ 1a-d, 2a-h (R=H)\) and \(4a-c\), mass spectrometry has been used as a routine tool for identification and structure elucidation. In this paper the main features of the mass spectrometric behavior of these compounds are reported. Since the cyclic succinoyl catechols \(1a-d\) were expected to behave differently under electron impact than their non-cyclic analogues, \(3a-c\) (for which a fragmentation pathway close to the usual ester fragmentation pattern \(2\) is predicted; eqn. 1) the mass spectrometry of compounds \(3a-c\) was also investigated.

\[
R-\text{CO}-O-R' \rightarrow \begin{cases} R^+ \\ (\text{RCO})^+ \\ (\text{COOR'})^+ \\ (\text{OR'})^+ \end{cases} \quad (1)
\]

In the case of the \(o\)-hydroxyphenyl acid succinates, \(2a-h\), GC/MS analysis of the trimethylsilyl derivatives (TMS-derivatives) \((2a-h, R=\text{TMS})\), has also been performed. The TMS derivatives were chosen because no essential
structural information could be obtained when the parent compounds were used, owing to thermal decomposition in the inlet system of the mass spectrometer.

RESULTS AND DISCUSSION

A. Cyclic succinoyl catechols and catechol diacetates. The mass spectral data of the investigated compounds are summarized in Table 1.

![Chemical Structures](image)

Compounds 3a–c all display a relatively simple fragmentation pattern with the stepwise loss of the two acyl groups to form the ions shown in Scheme 1. The relative intensities of the molecular ions are usually low, 2–5 %, (see

Table 1) and the intensity of the fragment ions is found to vary with the nature of the alkyl substituent, R, in the acid moiety (see Table 1). In part, decomposition of the molecular ion probably involves a rearrangement of the type proposed in eqn. 2, where the six-membered transition state (eqn. 2b) is believed to be the most probable one.  

\[
\text{Scheme 1.}
\]

\[
\begin{align*}
\text{Table 1. Mass spectra of catechol diesters.} \\
1a: M^+ & 192 (19), 164 (2), 148 (2), 110 (17), 55 (100). \\
1b: M^+ & 206 (10), 178 (1), 162 (0.5), 147 (1), 110 (5), 69 (100). \\
1c: M^+ & 248 (14), 220 (0.1), 204 (0.2), 189 (1), 110 (25), 83 (100). \\
1d: M^+ & 240 (38), 212 (5), 196 (30), 184 (2), 168 (2), 132 (14), 120 (1), 110 (0.02), 104 (100), 76 (50). \\
3a: M^+ & 194 (4), 152 (19), 110 (100), 43 (44). \\
3b: M^+ & 250 (5), 180 (28), 110 (27), 71 (87), 43 (100). \\
3c: M^+ & 278 (2), 194 (5), 110 (19), 85 (28), 57 (100). \\
4a: M^+ & 220 (32), 176 (9), 161 (73), 161^{+} (2), 121 (6), 110 (40), 83 (100). \\
4b: M^+ & 248 (38), 220 (0.1), 204 (6), 189 (46), 161 (3), 121 (15), 110 (25), 83 (100). \\
4c: M^+ & 240 (45), 212 (5), 196 (41), 184 (2), 168 (2), 132 (13), 120 (2), 110 (13), 104 (100), 76 (57). \\
\end{align*}
\]

\[
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\]
Compounds $1a-c$ show the fragmentation pathway depicted in Scheme 2, the relative intensities of the molecular ions being between 10 and 20% of the base peak. The mode of fragmentation of the molecular ion is quite analogous to what is found for compounds $3a-c$, but the relative abundance of ion II (see Scheme 2 and Table 1) is less than for the analogous ion I in Scheme 1.

Scheme 2.

However, the differences in the fragmentation pathways for compounds $1a-d$, compared to $3a-c$, are loss of CO and CO$_2$, which processes are typical for lactones. In the case of compounds $1a$, the processes $M^+ \rightarrow (M-CO)^+ + CO$ and $M^+ \rightarrow (M-CO_2)^+ + CO_2$ are accompanied by metastable transitions (Scheme 2). The processes $M^+ \rightarrow (M-CO)^+ + CO$ and $(M-CO)^+ \rightarrow$ (catechol)$^+ +$ RCO are assumed to take place via a rearrangement analogous to that in eqn. 2.

Although compound $1d$ gives catechol and phthalic acid after hydrolysis, and also its IR- and NMR-spectra are consistent with the structure $1d$, its mass spectrum does not show more than traces (0.02%) of the ion at 110 m/e (catechol ion). The molecular ion of $1d$ is of higher relative intensity (38%) than is found for compounds $1a-c$, reflecting increased stability from an additional aromatic ring. The fragmentation pathway for compound $1d$ is seen in Scheme 3, where the ion III (104 m/e) is responsible for the base peak in the spectrum. This ion may be formed via loss of a phenol type fragment from ion II (Scheme 3), which is supposed to have the open structure seen in the scheme. This conclusion is based on the similarity in fragmentation between this ion and phenyl benzoate and the absence of fragment ions found in the mass spectrum of 3,4-benzocoumarine. Loss of CO from the molecular ion (metastable transition) may give the ring-closed ion I (Scheme 3) which in turn loses CO to give ion IV. Ion V may in the same way be derived from ion I by loss of a phenol-like fragment.

The synthesis of compounds $I$ sometimes gives the isomeric compounds $4$ as sideproducts, and it has been found that also for these compounds (4) loss

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of CO$_2$ from the molecular ion is an important fragmentation pathway. For
compounds 4a and b this process is followed by the transition (M−CO$_2$)$^+$→
M$^\ast$ (M−CO$_2$−Me)$^+$ + Me$. Further decomposition of ion II (Scheme 4)
gives ion III at m/e 121. Other prominent peaks in the mass spectra of com-
ounds 4 are due to the catechol ion and to alkyl cations derived from the
succinic acid moiety.

Scheme 4.

Table 2. Mass spectra of TMS-derivatives of catechol monosuccinates (phthalate).

<table>
<thead>
<tr>
<th>Compound</th>
<th>M (Da)</th>
<th>M+1 (Da)</th>
<th>M+2 (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>339</td>
<td>353</td>
<td>367</td>
</tr>
<tr>
<td>2b</td>
<td>353</td>
<td>377</td>
<td>391</td>
</tr>
<tr>
<td>2c</td>
<td>367</td>
<td>391</td>
<td>405</td>
</tr>
<tr>
<td>2d</td>
<td>367</td>
<td>391</td>
<td>405</td>
</tr>
<tr>
<td>2e</td>
<td>367</td>
<td>391</td>
<td>405</td>
</tr>
</tbody>
</table>

Scheme 3.
B. TMS-derivatives of o-hydroxyphenyl acid succinates. The mass spectral data of compounds 2a–h are summarized in Table 2.

The main feature of the mass spectrometric behavior of this class of compounds is a rearrangement involving the trimethylsilyl group. This rearrangement may take place either via the open chain form I (eqn. 3) or via the ring form II (eqn. 4) of the silyl derivative. Similar rearrangements have often been observed in the mass spectroscopy of silyl derivatives.\(^7\)

\[
\begin{align*}
&\text{I} \quad \text{or} \quad \text{II} \\
&\begin{array}{c}
\text{OTMS} \\
\text{TMS}
\end{array} \\
&\begin{array}{c}
\text{OTMS} \\
\text{TMS}
\end{array} \\
&\begin{array}{c}
\text{OTMS} \\
\text{TMS}
\end{array} \\
&\begin{array}{c}
\text{OTMS} \\
\text{TMS}
\end{array}
\end{align*}
\]

Another common feature in the mass spectra of these compounds are ions for the structure \(VIa\) or \(b\), which for compounds 2f and g (R = TMS) are detectable only at electron beam energies lower than ca. 9 eV.

\[
\begin{align*}
&\text{VIa} \\
&\begin{array}{c}
\text{TMSO} \\
\text{OTMS} \\
\text{TMSO}
\end{array} \\
&\begin{array}{c}
\text{TMSO} \\
\text{OTMS} \\
\text{TMSO}
\end{array} \\
&\begin{array}{c}
\text{TMSO} \\
\text{OTMS} \\
\text{TMSO}
\end{array}
\end{align*}
\]

Moreover, these two compounds do not show any (M – 15) peak at 70 eV and only traces of this peak are observed when lower ionization energies are used (i.e. 7.5 and 9.0 eV).

These findings may be interpreted in terms of the existence of ring-chain tautomerism in the compounds 2f and g (R = H). Since the gem-dimethyl

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effect will operate strongly in these compounds by stabilizing the ring tautomer in a ring-chain tautomeric equilibrium (eqn. 5), one may not exclude the operation of such a mechanism in compounds 2f and g.

\[
\begin{align*}
\text{OR} & \iff \text{OR} \\
R & \text{O} & \text{O} \\
\end{align*}
\]

(5)

Thus, silylation of such a tautomeric mixture will result in the two TMS derivatives I and II (eqns. 3 and 4), which may hardly undergo further tautomerisation without general catalysis. During the GC/MS analysis of compound 2h (R=TMS), two peaks, which gave almost the same mass spectra, were recognized in the gas chromatogram. Since phthaloyl derivatives are known to undergo ring-chain tautomerism,8 the two peaks observed in the gas chromatogram of 2h (R=TMS) may most probably be due to the ring and chain forms of 2h.

Moreover, the ring tautomer II in eqn. 4, with a six-membered transition state, ought to rearrange with much a higher rate than the chain tautomer I in eqn. 3, which for 2f and g (R=TMS) will make the expelling of a fragment of the type VIa less probable. This is also in agreement with what is observed in the mass spectra of compounds 2f and g (R=TMS).

EXPERIMENTAL

Mass spectra were recorded using an LKB 9000 instrument (at 70 eV, if not otherwise stated).

The preparation of the compounds investigated has previously been described.1

Acknowledgements. This investigation was supported by grants from the Matematisk Naturvetenskapliga Fakulteten, University of Lund, and from the Kungl. Fysiografiska Sällskapet, Lund.

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Received December 2, 1971.

Acta Chem. Scand. 26 (1972) No. 7