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Studies on Catechol Esters

Part IV. Mass Spectrometry

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The mass spectrometric behavior of a series of cyclic succinoylcatechols, 3,4-dihydro-1,6-benzodioxocin-2,5-diones (*1*), and the corresponding catechol diacetates, (*3a–c*) has been investigated. It has been found that except for processes due to losses of CO and CO_2 from the molecular ions of *1*, the fragmentation patterns of compounds *1* and *3* under electron impact are essentially of the same type.

Pseudoesters *4* have also been investigated and loss of CO_2 from these compounds has been found to be more dominant than what is observed for the isomeric compounds *1*.

Mass spectrometric analysis of the trimethylsilyl (TMS) derivatives of a series of *o*-hydroxyphenyl acid succinates, *2* (R = 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 succinoylcatechols *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.

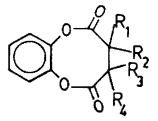
$$R-CO-O-R' \longrightarrow \begin{cases} R^+ \\ (RCO)^+ \\ (COOR')^+ \\ (OR')^+ \end{cases} \qquad (1)$$

In the case of the *o*-hydroxyphenyl acid succinates, *2a–h*, GC/MS analysis of the trimethylsilyl derivatives (TMS-derivatives) (*2a–h*, R = TMS), has also been performed. The TMS derivatives were chosen because no essential

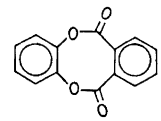
structural information could be obtained when the parent compounds were used, owing to thermal decomposition in the inlet system of the mass spectrometer.

RESULTS AND DISCUSSION

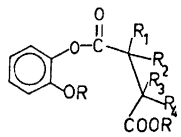
A. Cyclic succinoylcatechols and catechol diacetates. The mass spectral data of the investigated compounds are summarized in Table 1.



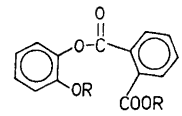
1a $R_{1-4}=H$ *c* $R_{1-4}=Me$
b $R_1=Me$, $R_{2-4}=H$



1d

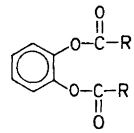


2a $R_{1-4}=H$
b $R_1=Me$, $R_{2-4}=H$
c $R_{1,2}=Me$, $R_{3,4}=H$
d $R_{1,3}=H$, $R_{2,4}=Me$ (D,L)
e $R_{1,3}=H$, $R_{2,4}=Me$ (*meso*)
f $R_{1-3}=Me$, $R_4=H$
g $R_{1-4}=Me$

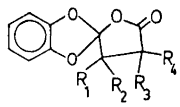


2h

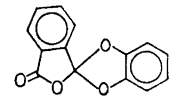
(R = H or TMS)



3a: R = methyl *b*: R = isopropyl *c*: R = *t*-butyl

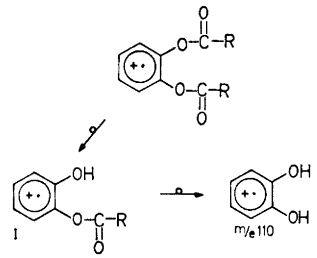


4a $R_{1,3}=Me$, $R_{2,4}=H$ *b* $R_{1-4}=Me$



4c

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



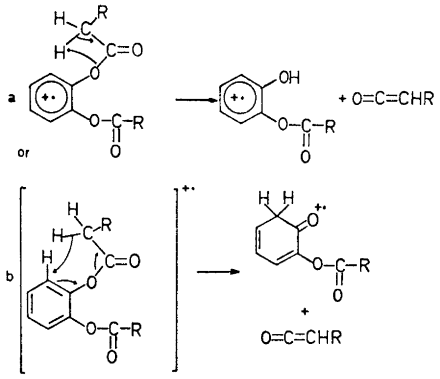
Scheme 1.

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, decomposi-

Table 1. Mass spectra of catechol diesters.

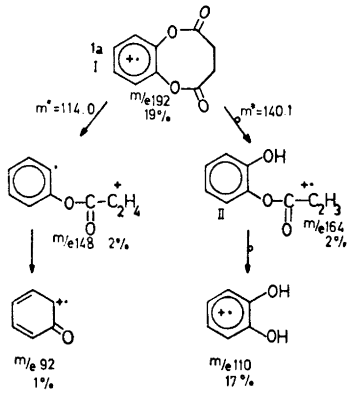
1a: M^+	192 (19), 164 (2), 148 (2), 110 (17), 55 (100).
1b: M^+	206 (10), 178 (1), 162 (0.5), 147 (1), 110 (5), 69 (100).
1c: M^+	248 (14), 220 (0.1), 204 (0.2), 189 (1), 110 (25), 83 (100).
1d: M^+	240 (38), 212 (5), 196 (30), 184 (2), 168 (2), 132 (14), 120 (1), 110 (0.02), 104 (100), 76 (50).
3a: 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).

tion 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.[3]



(2)

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.

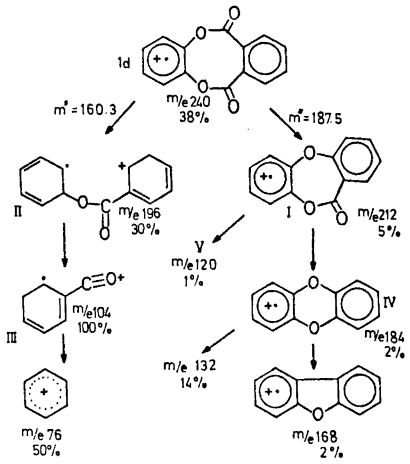


Scheme 2.

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.[4] In the case of compounds *1a*, the processes $M^{+\cdot} \rightarrow (M-CO)^{+\cdot} + CO$ and $M^{+\cdot} \rightarrow (M-CO_2)^{+\cdot} + CO_2$ are accompanied by metastable transitions (Scheme 2). The processes $M^{+\cdot} \rightarrow (M-CO)^{+\cdot} + CO$ and $(M-CO)^{+\cdot} \rightarrow (\text{catechol})^{+\cdot} + RCO$ are assumed to take place *via* a rearrangement analogous to that in eqn. 2.

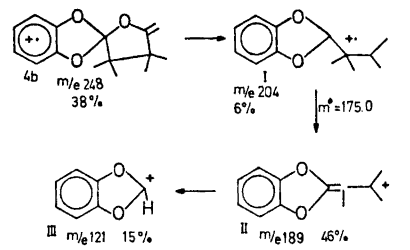
Although compound *1d* gives catechol and phthalic acid after hydrolysis, and also its IR- and NMR-spectra are consistent with the structure *1d*,[1] its mass spectrum does not show more than traces (0.02 %) of the ion at 110 *m/e* (catechol ion). The molecular ion of *1d* is of higher relative intensity (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 [5] and the absence of fragment ions found in the mass spectrum of 3,4-benzocoumarine.[6] 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 *1* sometimes gives the isomeric compounds *4* as sideproducts,[1] and it has been found that also for these compounds (*4*) loss



Scheme 3.

of CO_2 from the molecular ion is an important fragmentation pathway. For compounds *4a* and *b* this process is followed by the transition $(M-CO_2)^{+\cdot} \xrightarrow{m^*} (M-CO_2-Me)^+ + Me\cdot$. Further decomposition of ion II (Scheme 4) gives ion III at *m/e* 121. Other prominent peaks in the mass spectra of compounds *4* are due to the catechol ion and to alkyl cations derived from the succinic acid moiety.



Scheme 4.

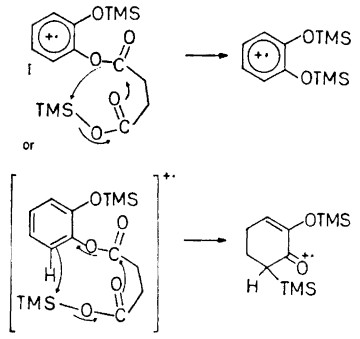
Table 2. Mass spectra of TMS-derivatives of catechol monosuccinates (phthalate).

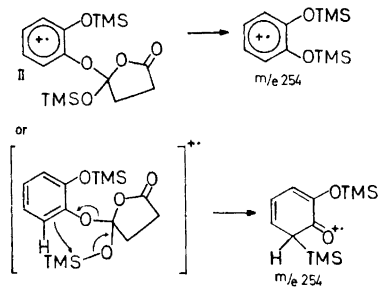
2a: (M−15) 339 (2), 254 (14), 239 (3), 173 (47), 73 (100).
2b: (M−15) 353 (1), 254 (15), 239 (3), 187 (40), 117 (2), 73 (100).
2c: (M−15) 367 (2), 254 (15), 239 (3), 201 (18), 117 (9), 73 (100).
2d: (M−15) 367 (1), 254 (14), 239 (3), 201 (31), 117 (3), 73 (100).
2e: (M−15) 367 (1), 254 (12), 239 (3), 201 (33), 117 (3), 73 (100).
2f: (9.0 eV): (M−15) 381 (0.4), 254 (100), 239 (4), 215 (48), 117 (1), 73 (3).
2g: (7.5 eV) 254 (100), 239 (3), 229 (40), 117 (3), 73 (3).
2g: (9.0 eV): 254 (15), 239 (5), 229 (0.2), 117 (2), 84 (7), 73 (100).
2h: (A)[a]: 254 (6), 239 (2), 221 (22), 117 (1), 100 (17), 73 (100).
2h: (B)[a]: 254 (6), 239 (2), 221 (29), 117 (1), 100 (10), 73 (100).

[a] A and B represent ring and chain tautomeric forms of the compounds.

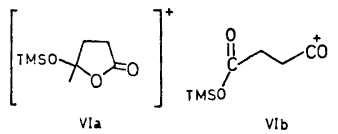
B. TMS-derivatives of o-*hydroxyphenyl acid succinates.* The mass spectral data of compounds *2a–h* are summarized in Table 2.

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]





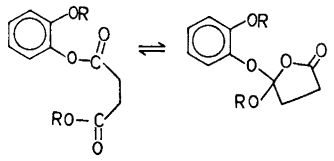
Another common feature in the mass spectra of these compounds are ions for the structure *VIa* or *b*, which for compounds *2f* and *g* (R = TMS) are detectable only at electron beam energies lower than *ca.* 9 eV.



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

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*.



(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]

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