Electron Impact Mass Spectrometry of Some New Macrocyclic Tetraesters

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The electron impact mass spectrometric behaviour of a new class of macrocyclic tetraesters is reported and discussed in detail with the aid of linked scans, exact mass measurements and collisionally activated decomposition mass analyzed ion kinetic energy spectra.

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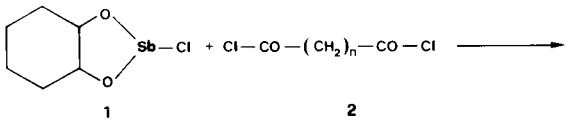
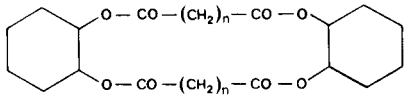
Introduction.

As already reported in this Journal, macrocyclic tetraesters can easily be obtained by reaction of 2-chloro-1,3,2-dioxacyclohexanestibolane with diacyl chlorides [1] (Scheme 1).

Scheme 1





trans	cis
3) n = 1	8) n = 1
4) n = 3	9) n = 3
5) n = 5	10) n = 5
6) n = 7	11) n = 7
7) n = 8	12) n = 8

Although there are various methods of preparing macrocyclic esters, we have preferred to use the method mentioned in Scheme 1, because it allows us to obtain the dimeric macrocycles **3-12** rapidly and conveniently.

Depending on whether *trans* or *cis* isomers are used as reacting species, different stereoisomeric products are obtained. More exactly: by reaction of *trans*-2-chloro-1,3,2-dioxacyclohexanestibolane (**1**) and diacyl chloride **2**, *trans-syn-trans* and *trans-anti-trans* macrocyclic tetraesters are obtained. Analogously, by reaction of the compound *cis*-**1** and **2**, *cis-syn-cis* and *cis-anti-cis* macrocyclic tetraesters are obtained. Unfortunately, so far it has been impossible for us to separate *syn* from *anti* species, but experiments are in progress in this respect.

In any case, performing the reaction with *trans*- or *cis*-2-chloro-1,3,2-dioxacyclohexanestibolane, two different sets of compounds are obtained, *i.e.* *trans*-dicyclohexo[*b,i*]-1,4,8,11-tetraoxacyclotetradecane-5,7,12,14-tetraone (**3**), *trans*-dicyclohexo[*b,k*]-1,4,10,13-tetraoxacyclooctadecane-5,9,14,18-tetraone (**4**), *trans*-dicyclohexo[*b,m*]-1,4,12,15-tetraoxacyclodocosane-5,11,16,22-tetraone (**5**), *trans*-dicyclohexo[*b,o*]-1,4,14,17-tetraoxacyclohexacosane-5,13,18,26-tetraone (**6**), *trans*-dicyclohexo[*b,p*]-1,4,15,18-tetraoxacyclooctacosane-5,14,19,28-tetraone (**7**), and *cis*-dicyclohexo[*b,i*]-1,4,8,11-tetraoxacyclotetradecane-5,7,12,14-tetraone (**8**), *cis*-dicyclohexo[*b,k*]-1,4,10,13-tetraoxacyclooctadecane-5,9,14,18-tetraone (**9**), *cis*-dicyclohexo[*b,m*]-1,4,12,15-tetraoxacyclodocosane-5,11,16,22-tetraone (**10**), *cis*-dicyclohexo[*b,o*]-1,4,14,17-tetraoxacyclohexacosane-5,13,18,26-tetraone (**11**), *cis*-dicyclohexo[*b,p*]-1,4,15,18-tetraoxacyclooctacosane-5,14,19,28-tetraone (**12**).

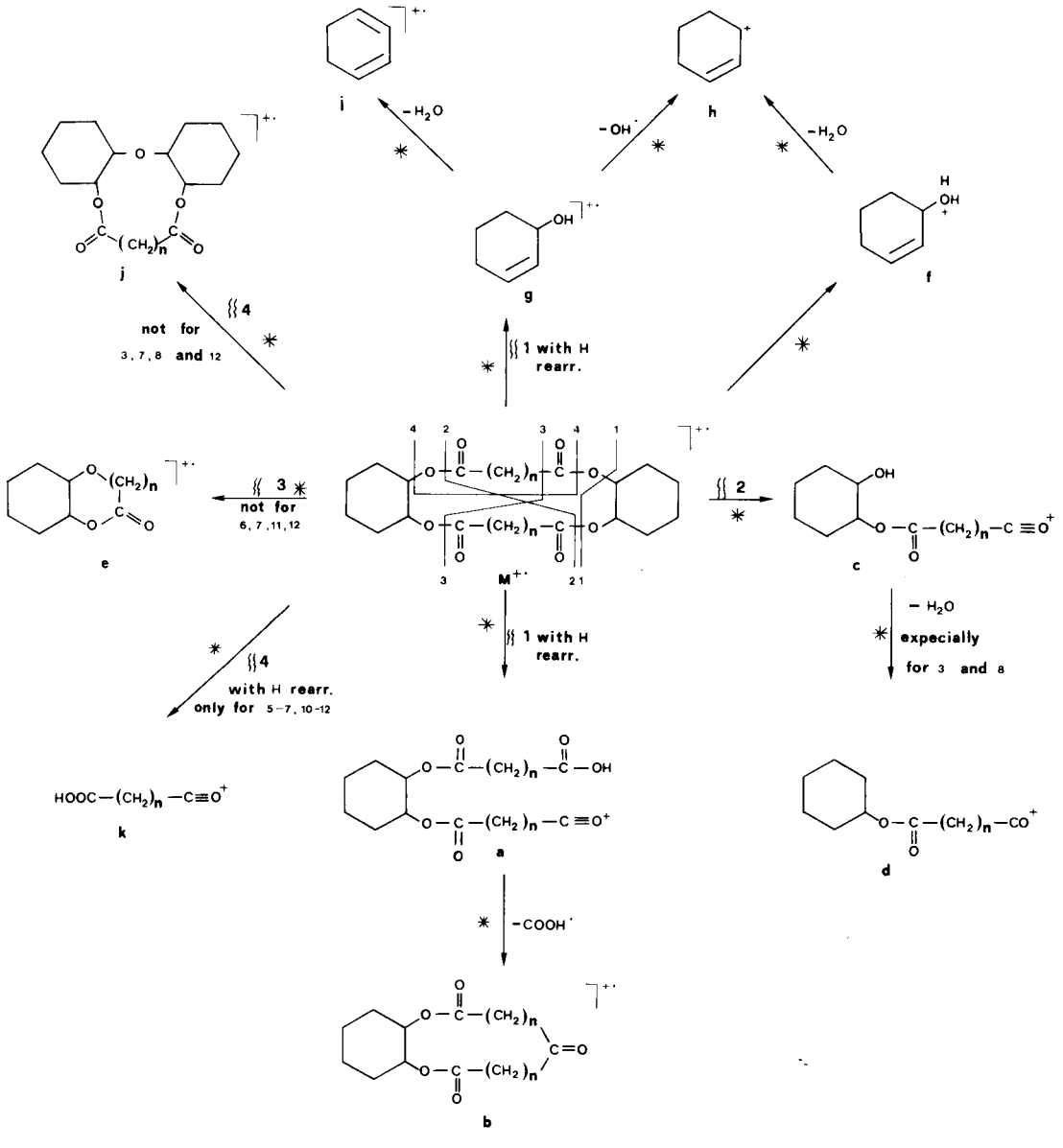
Results and Discussion.

The EI mass spectra of compounds **3-12** are reported in the Table. Quite abundant molecular ions are always present, while the $[M + H]^+$ species, common in the EI mass spectrometry of macrocyclic polyether-ester compounds [2a], are completely absent.

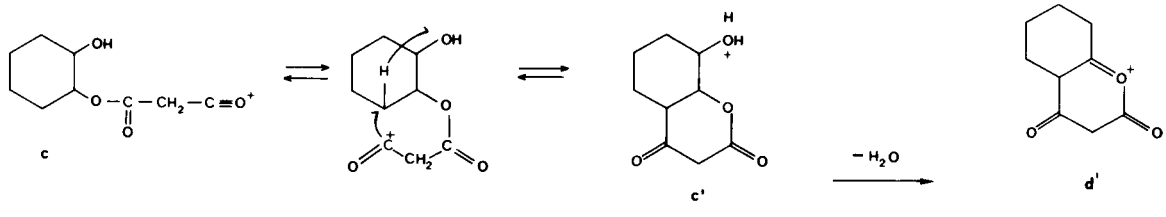
By means of linked scans and exact mass measurements, the common fragmentation pattern reported in Scheme 2 has been obtained. Quite intense ions **a** are present for all the examined compounds, originating from the rupture of ethereal and esteric bonds with H rearrangement.

With respect to the process observed for the analogous macrocycles containing catecholic species [2c], this process is very interesting. In the former case hydrogen transfer was observed from the acylic chain to the catecholic moieties, while in the latter case the H transfer is the con-

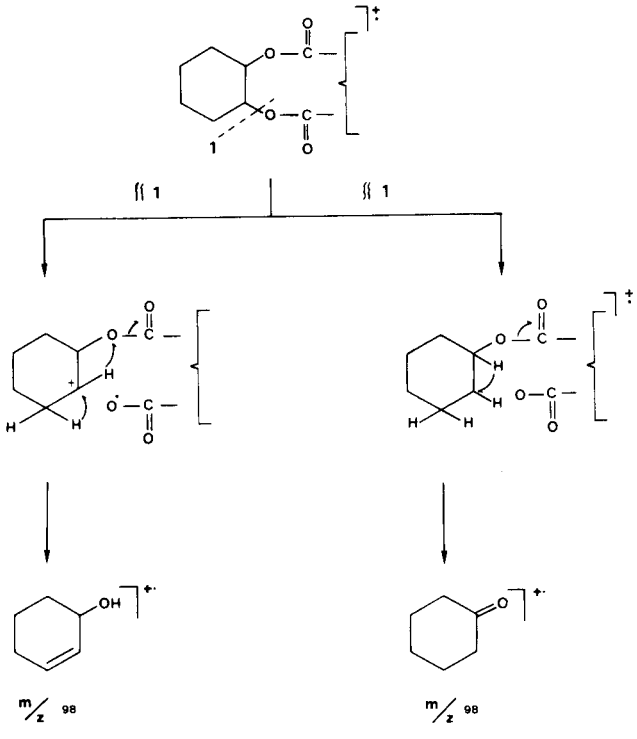
Scheme 2



Scheme 3



Scheme 4



trary, *i.e.* from the cyclohexane ring to the acylic species, giving rise to acidic moieties **a**. The acid character of the latter is proved by the further loss of a carboxylic group, which leads to ions **b**.

Another primary decomposition gives rise to the usual $[M/2 + H]^+$ species (ions **c**) for which we give one of the possible structures in Scheme 2. In fact these ions could originate different symmetrical bond ruptures, proving ions of the same mass and composition. The proposed structure, however, is well supported by the observed further loss of H_2O, leading to ion **d**, which could be explained by the presence of a hydroxyl group on the cyclohexane ring. However, the strong differences in ion abundances of ions **d** for compounds **3** and **8** with respect to all others, seems to indicate that this process is more complex and/or is strictly related to different structures of ions **c**. Therefore, for compounds **3** and **8**, the alternative mechanism reported in Scheme 3 is proposed. The difference in ionic abundances for ions **d'** between compounds **3** and **8** could be well explained with respect to their steric configuration which strongly affects the H transfer on the hydroxylic group.

A peculiar mass spectrometric behaviour of compounds **3-5, 8-10** (for which n = 1, 3 and 5) is given by the forma-

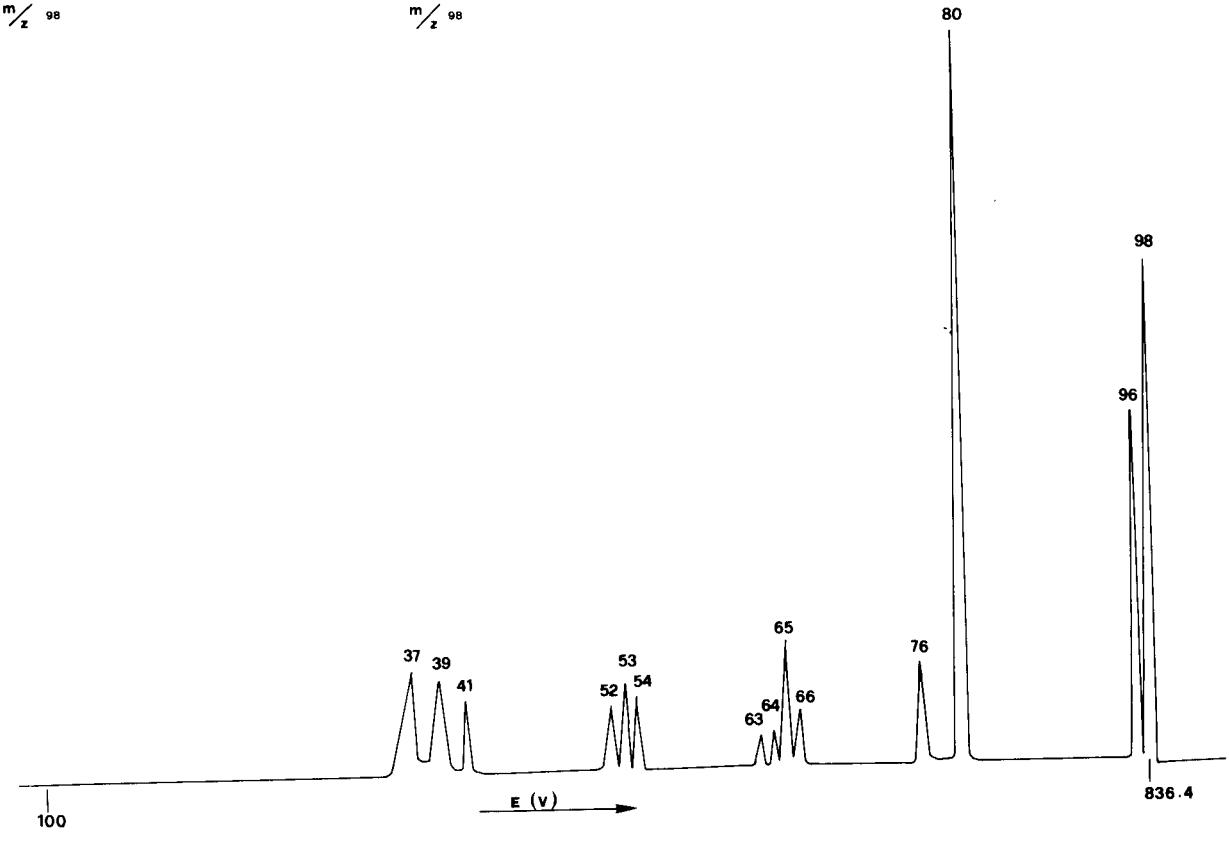


Figure 1. CAD MIKES of ionic species at m/z 98 in the mass spectra oc compounds 3-12.

Table

EI Mass Spectra of Compounds **3-12** [m/z (relative abundance)]

Compounds ionic species	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
$M^{+\cdot}$	368	424	480	536	564	368	424	480	536	564
	(1)	(10)	(12)	(5)	(5)	(1)	(1)	(1)	(3)	(1)
a	271	327	383	439	467	271	327	383	439	467
	(10)	(3)	(42)	(27)	(72)	(22)	(3)	(6)	(27)	(10)
b	226	282	338	394	422	226	282	338	394	422
	(4)	(12)	(16)	(7)	(17)	(5)	(8)	(6)	(14)	(8)
c	185	213	241	269	283	185	213	241	269	283
	(46)	(100)	(58)	(3)	(38)	(10)	(2)	(11)	(1)	(5)
d	167	195	223	251	265	167	195	223	251	265
	(100)	(2)	(2)	(5)	(8)	(12)	(3)	(1)	(2)	(3)
e	140	168	196	—	—	140	168	196	—	—
	(33)	(10)	(6)	—	—	(9)	(4)	(3)	—	—
f	99	99	99	99	99	99	99	99	99	99
	(46)	(26)	(30)	(15)	(37)	(95)	(55)	(29)	(10)	(15)
g	98	98	98	98	98	98	98	98	98	98
	(65)	(98)	(96)	(100)	(100)	(100)	(100)	(82)	(44)	(75)
h	81	81	81	81	81	81	81	81	81	81
	(60)	(48)	(50)	(45)	(95)	(43)	(30)	(30)	(30)	(14)
i	80	80	80	80	80	80	80	80	80	80
	(18)	(10)	(26)	(5)	(23)	(23)	(9)	(21)	(8)	(14)
j	—	310	338	336	—	—	310	338	366	—
	—	(9)	(16)	(3)	—	—	(2)	(6)	(1)	—
k	—	—	143	171	185	—	—	143	171	185
	—	—	(100)	(81)	(41)	—	—	(100)	(100)	(100)

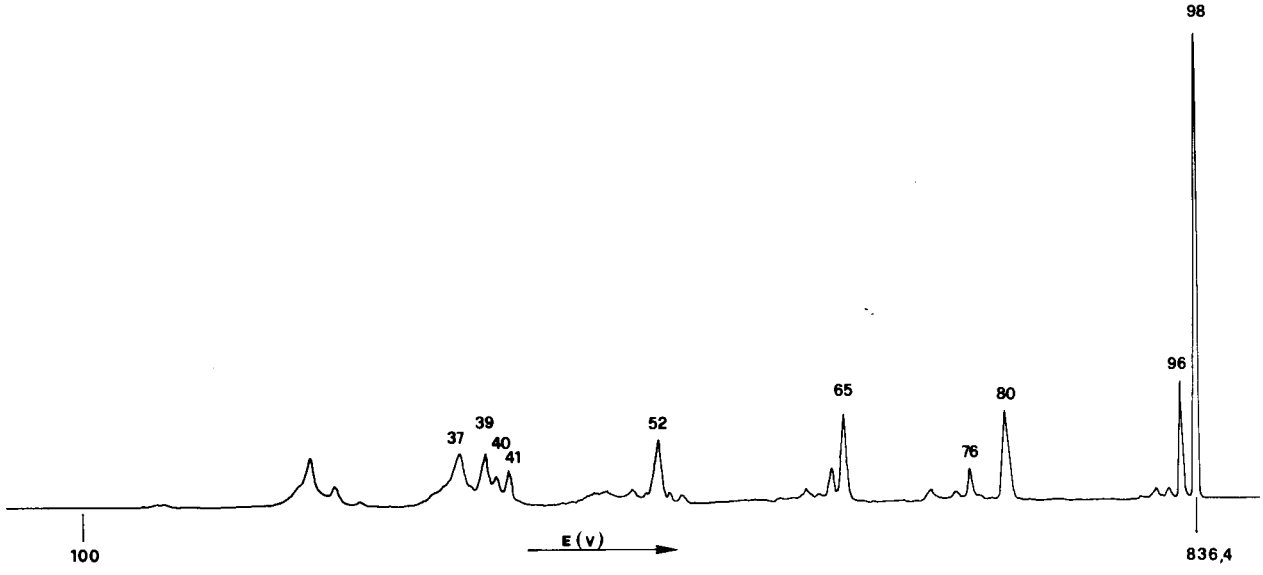


Figure 2. CAD MIKES of $[M-H_2O]^{+\cdot}$ species (m/z 98) originating from primary H_2O loss in EI mass spectrometry of 1,2-cyclohexanediol.

tion of ions **e**, due to the cleavage of the ester bond followed by the usual cleavage in α position of the CO group (see ∫∫ 3 in Scheme 2). For ions **e**, we propose a cyclic structure. This annulation reaction is strongly dependent on the length of the acylic chain, *i.e.* the abundance of these ions decreases on increasing the length of the acylic chain (see Table), and for $n>5$ the ions are completely absent. An analogous decrease of relative abundances is observed on passing from the *trans* to the *cis* species even though their acylic chain is of the same length.

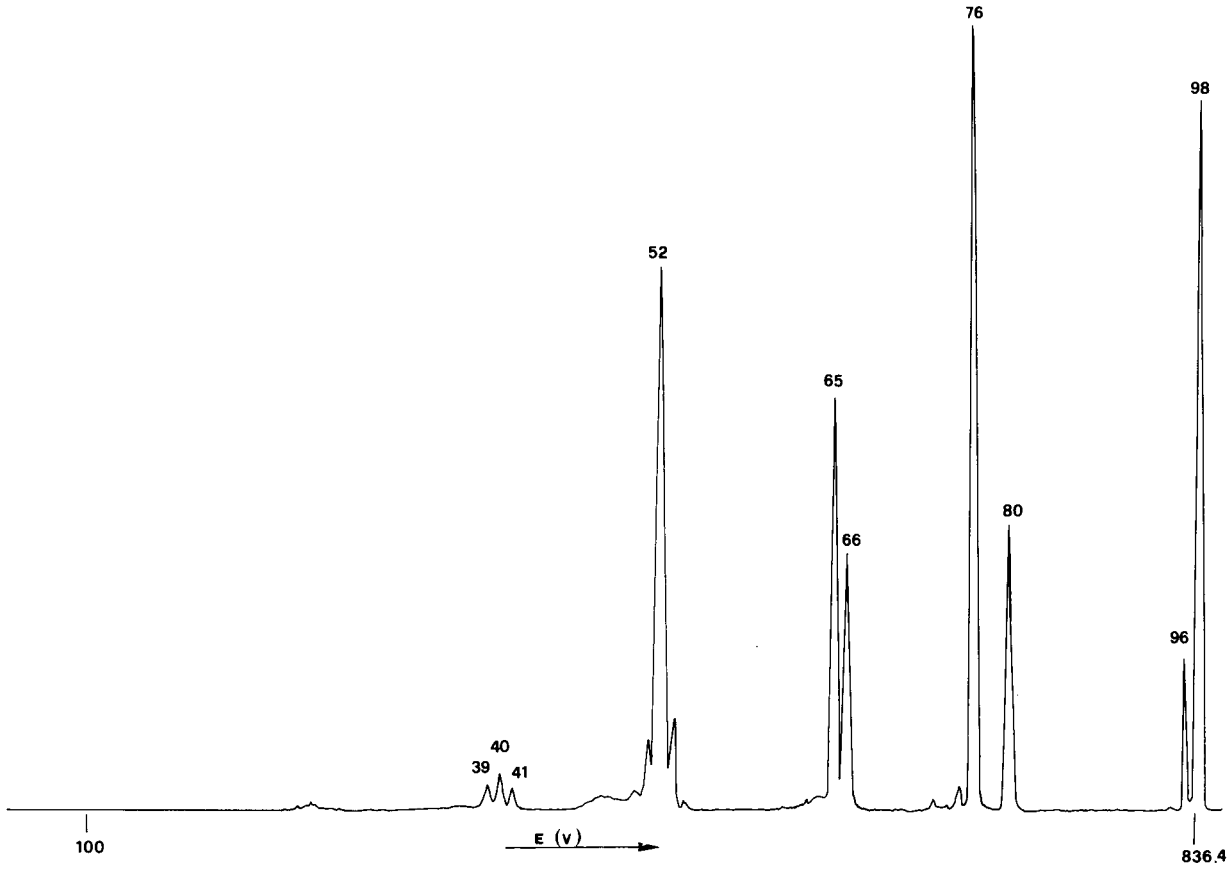


Figure 3. CAD MIKES of $[M]^{+\cdot}$ of cyclohexanone (m/z 98).

Ions **f** and **g** are primary fragments, originating from cleavage **1** with H rearrangements. The latter, at a glance, is very similar to the $[M-H_2O]^{+\cdot}$ species originating from 1,2-cyclohexandiol. To deepen the formation mechanism (or mechanisms) of ions **g**, we have then thought it interesting to undertake a CAD MIKE analysis of their structure.

In Figure 1 the CAD MIKES of ionic species **g**, originating from compounds **3** (which are identical for all the examined compounds) are reported.

In Figure 2 we report the CAD MIKES of ionic species at m/z 98 originating from a loss of water from $[M]^{+\cdot}$ of 1,2-cyclohexane diol. It is easy to observe that strong differences are present in the relative abundances of the collisionally activated decomposition products, thus indicating a different structure for the above-mentioned ions **g**.

In Figure 3 we report the CAD MIKES of $[M]^{+\cdot}$ of cyclohexanone, chosen as an alternative model for the structure of ions **g**. Also, this proves to be partiallty different from the CAD MIKE spectra on ions **g** (Figure 1). By comparison of the CAD spectra reported in Figures 1-3, it is reasonable to consider the CAD MIKE spectra of ions **g** due to the overlapping of two different structures: the first identical to that of $[M-H_2O]^{+\cdot}$ species originating from 1,2-cyclohexandiol (Figure 2), and the second identical to that of $[M]^{+\cdot}$ of cyclohexanone. Therefore for the **g** ion formation, we propose the different mechanism reported in Scheme 4. The ionic species **i** and **h** arise from H_2O and $OH\cdot$ losses from ions **g** and **f**.

A peculiar behaviour of the compounds for which n = 3, 5 and 7 (**4-6** and **9-11**), is the formation of ions **j** (see Scheme 2), for which we propose a cyclic structure, suggested by the fact that this fragmentation process depends on the length of the acylic chain. For compounds **2-8** and **10-11** the same cleavages leading to the ions **j** (∫∫ 4, Scheme 2), with H rearrangement give rise to species **k**. Finally some considerations must be made on the different mass spectrometric behaviours of the two classes of stereoisomers. Even though the complete separation of (see Introduction) the four stereoisomers that arise from the reaction has not been carried out, the compounds arising from the reaction of *trans*- cyclohexanestibolane (**3-7**) and *cis*-cyclohexanestibolane (**8-12**) show very different ionic abundances (see Table).

EXPERIMENTAL

Compounds **3** to **12** were analytically pure samples synthesized as previously reported in literature [1]. The electron impact (EI) mass spectra were run on a VG ZAB-2F instrument operating at 70 eV (200 μA) and with a source temperature of 200°. Samples were introduced under direct electron impact (DEI) [3] conditions. Metastable transitions were detected by B/E and B^2/E linked scans [4]. Exact mass measurements were performed with the peak matching technique at a 30.000 resolving power (10% valley definition). Collisionally activated decomposition spectra (CAD MIKES) were obtained with 8 KeV ions colliding with nitrogen in the second field free region.

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REFERENCES AND NOTES

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