Complex Dibenzofurans

XII.* The Use of Oxygen-18 Labelling in the Interpretation of Mass Spectra of Some Biphenyl and Dibenzofuran Derivatives

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The mass spectra of dibenzofuran (I), 2-methoxydibenzofuran (II), 3-methoxydibenzofuran (III), 2-hydroxydibenzofuran (IV), 3-hydroxydibenzofuran (V), 2,5,2′-trimethoxybiphenyl (VI), and 2,4,2′-trimethoxybiphenyl (VII) are reported and discussed. Compounds II—V have been labelled in the 5-position and compounds VI and VII in the 2′-methoxyl group with oxygen-18. It has been found that the dibenzofuran ring system is considerably stable to electron impact and there is strong evidence that it arises during fragmentation of the 2,2′-dimethoxybiphenyls discussed here.

In connection with an investigation on the mechanism of acid-catalysed dehydration of 2,2′-dihydroxybiphenyls, the mass spectra of some oxygen-18-labelled trimethoxybiphenyls, hydroxydibenzofurans, and methoxydibenzofurans were obtained.[1] These spectra have now been shown to be of considerable value in the interpretation of the spectra of the unlabelled compounds (II to VII).

Although oxygen-18-labelled compounds have been analysed directly by mass spectroscopy (e.g. Refs. 2—5), comparatively little work has been done on the interpretation of mass spectra of oxygen-18-labelled compounds. However, oxygen-18 labelling has been used in a few cases to determine the mechanism of a particular transition.[6]

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The mass spectrum of dibenzofuran (I) has been reported previously [7] though no detailed interpretation of the spectrum has been attempted. The molecular ion (m/e 168, 100.0 %) is very stable (see Fig. 1) and the only other peak in the spectrum greater than 10 % of the base peak is at m/e 139 (38.4 %) due to loss of carbon monoxide from the molecular ion followed by loss of a hydrogen atom. Metastable ions at 116.5 and 138.0 correspond to the transitions $(168)^+ \rightarrow (140)^+ + 28$ and $(140)^+ \rightarrow (139)^+ + 1$, respectively. Barnes and Occolowitz [7] have reported these metastable ions as being at 111.5 and 138.0. The former figure is a printer's error.[8] Regarding the structure of the ion at m/e 139, it may be noted that Beynon and Williams [9] have observed an ion of exceptional stability at m/e 139 in the spectra of 1-hydroxyanthraquinone, 2-hydroxyanthraquinone, 1-methoxyanthraquinone, 2-methoxyanthraquinone, 1-aminoanthraquinone, and 2-aminoanthraquinone and have suggested the structure a (Scheme 1). As evidence for the considerable stability of this ion, they cite the presence of a peak, large for a doubly-charged ion at 69.5 ($ca.$ 4 %) in the spectra of these compounds. (The fragmentation pattern of 2-hydroxyanthraquinone leading to the ion at m/e 139 is given elsewhere.[10])
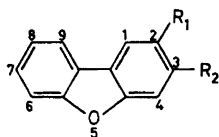
I	$R_1 = R_2 = H$
II	$R_1 = OCH_3$, $R_2 = H$
III	$R_1 = H$, $R_2 = OCH_3$
IV	$R_1 = OH$, $R_2 = H$
V	$R_1 = H$, $R_2 = OH$
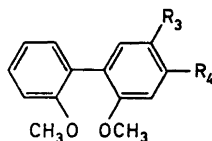
| VI | $R_3 = OCH_3$, $R_4 = H$ |
| VII | $R_3 = H$, $R_4 = OCH_3$ |

Note: The corresponding 5-^{18}O-dibenzofurans and 2'-methoxy-^{18}O-labelled trimethoxybiphenyls are denoted by the suffix "a" after the Roman numeral.

A doubly-charged ion at m/e 69.5 is present in the spectrum of dibenzofuran (I) and is 4.3 % of the base peak. (Non-integral doubly-charged ions are not shown in the figures). Thus, it seems possible that the ion at m/e 139 in the spectrum of dibenzofuran (I) has the same structure as ion a. The formation of this ion can be envisaged as occurring by homolytic fission of a C—O bond in the dibenzofuran ion followed by loss of carbon monoxide. Reunification of the carbon skeleton gives a cyclopentadiene ring with a loose one-electron bond to the phenyl radical part of the ion. Such one-electron bonds were originally postulated by Beynon, Lester and Williams [11] in connection with the mass spectra of anthraquinone, fluorenone, and diphenyl ether. Loss of a hydrogen ion from the ion at m/e 140 (6.2 %, of which $ca.$ 4 % is due to the natural abundance of carbon-13 and deuterium from m/e 139) provides an
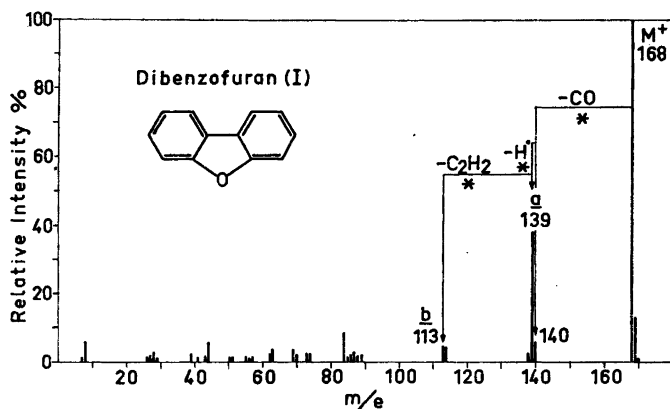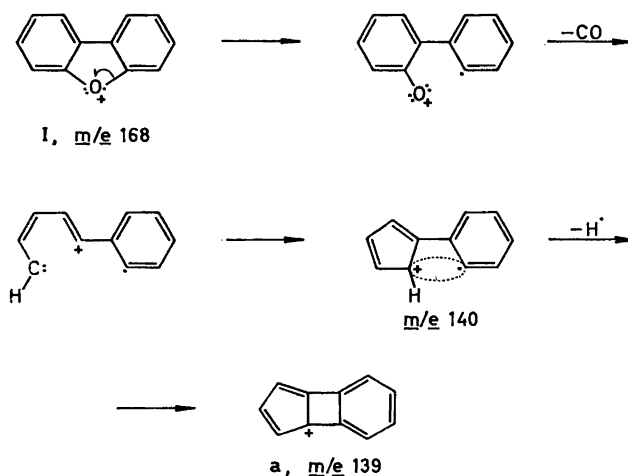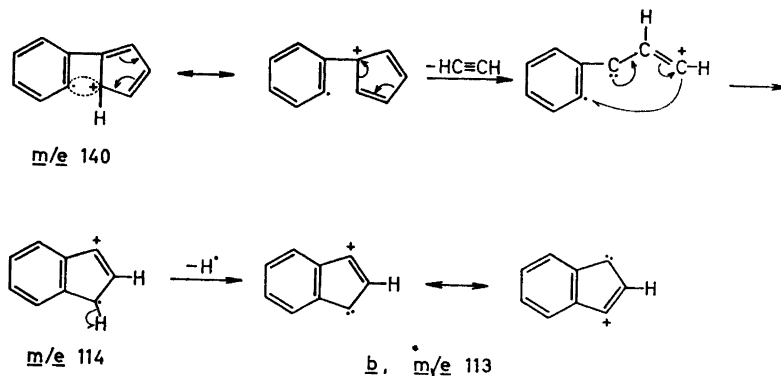
Fig. 1. Mass spectrum of dibenzofuran (I).

Scheme 1. Proposed mechanism of formation of the ion *a* at *m/e* 139 from the dibenzofuran ion.

electron for formation of a normal bond. The proposed mechanism is shown in Scheme 1.

The ion at *m/e* 114 (4.7 %) is probably due to loss of acetylene from the ion at *m/e* 140 whereas the ion at *m/e* 113 (4.9 %) arises both by loss of acetylene from *m/e* 139 (*m** 91.9) and by loss of a hydrogen atom from *m/e* 114 (*m** 112.0). These ions occur in the spectra of the anthraquinone derivatives mentioned previously.[9] Their structures are uncertain, but a resonance structure for *m/e* 113 such as *b* (Scheme 2) possesses aromatic stability (10 π-electrons)[12] and is feasible. A proposed mechanism for the formation of these ions is given in Scheme 2.

m/e 140

m/e 114   b, m/e 113

Scheme 2. A proposed mechanism of formation of the ion *b* at *m/e* 113 in the mass spectrum of dibenzofuran (I).
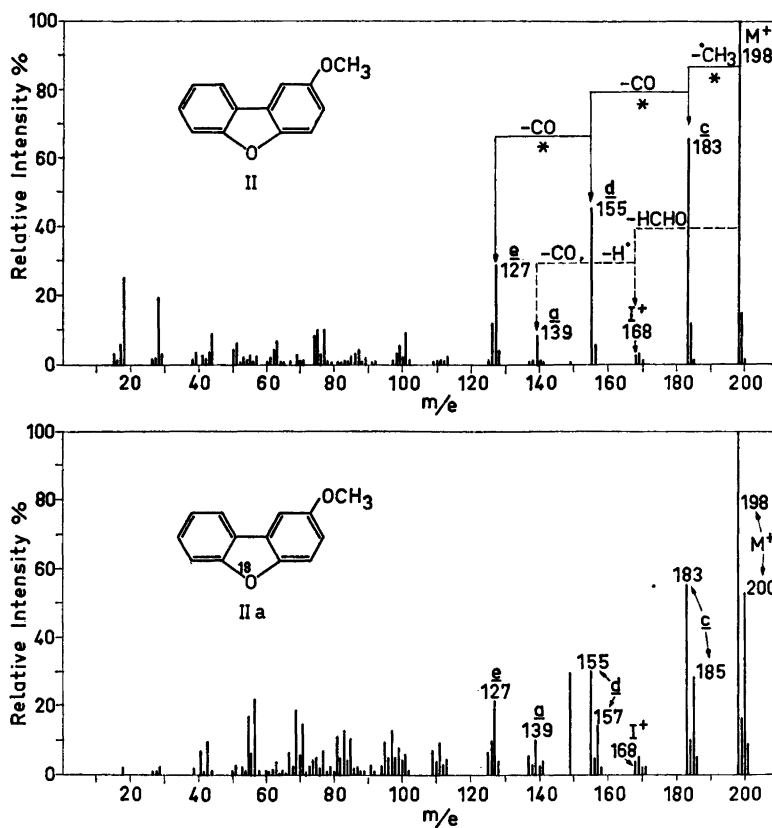

Fig. 2. Mass spectra of 2-methoxydibenzofuran (II) and the 5-^{18}O-labelled compound (IIa).

The peak at m/e 84 (8.8 %) is a doubly-charged molecular ion as indicated by the accompanying peak at m/e 84.5 (1.1 %). The relatively high intensity of these peaks for doubly-charged ions illustrates the stability of the dibenzofuran ion.

As the mass spectra of 2-methoxydibenzofuran (II) and 3-methoxydibenzofuran (III) are quite similar, only that of II is given together with that of the 5-^{18}O-labelled compound (IIa) (Fig. 2). The molecular ion (m/e 198) is the base peak for both isomers and loss of a methyl radical gives a strong ion c (Scheme 3) at m/e 183 (66.0 % for II and 70.8 % for III; m^* 169.2). This ion then loses carbon monoxide giving d (Scheme 3) at m/e 155 (45.6 % for II and 30.3 % for III; m^* 131.2). There is retention of 5-O in these transitions as shown by the spectra of the 5-^{18}O-labelled compounds (IIa and IIIa, see Table 1).

Table 1. Ratio of the relative intensities of the ^{18}O-containing ions to the corresponding ^{16}O-containing ions in the mass spectra of the ^{18}O-labelled compounds.

Ratio $(m + 2)^+/m^+$	^{18}O-labelled compound					
	IIa	IIIa	IVa	Va	VIa	VIIa
$(246)^+/(244)^+$					0.502	0.503
$(231)^+/(229)^+$					0.509	0.509
$(216)^+/(214)^+$					0.495	0.500
$(200)^+/(198)^+$	0.516	0.499			*	*
$(186)^+/(184)^+$			0.497	0.503		
$(185)^+/(183)^+$	0.498	0.499			0.183	0.194
$(173)^+/(171)^+$					*	*
$(170)^+/(168)^+$	*	*				
$(157)^+/(155)^+$	0.483	0.486	0.346	0.369	0.187	0.199

The ratios are corrected empirically by subtracting the ratio $(m + 2)^+/m^+$ obtained from the spectra of the unlabelled compounds from that for the labelled compounds.
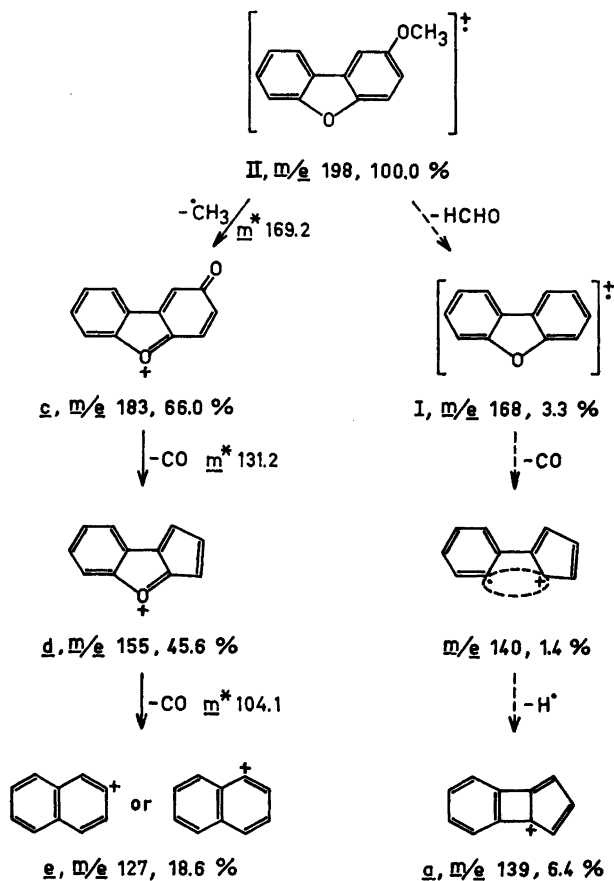
* Although the presence of an ^{18}O-containing ion is apparent, these ratios have not been evaluated since the error involved due to superimposed peaks will be large.

Thus it is the oxygen of the methoxyl group originally present that is lost as carbon monoxide in the transition $(183)^+ \rightarrow (155)^+ + 28$. Further loss of carbon monoxide, this time from the ring, gives e (Scheme 3) at m/e 127 (29.0% for II and 18.6% for III; m^* 104.1). This ion is probably a naphthyl ion. It is present in the mass spectra of benztropone and naphthalene.[11] The spectra of 2-methoxydibenzofuran (II), 3-methoxydibenzofuran (III), benztropone, and naphthalene are very similar below m/e 128.

Loss of formaldehyde from the molecular ions of the methoxydibenzofurans II and III occurs to only a small extent since the ion at m/e 168 is 3.3 % for II and 2.0 % for III. There appears to be retention of 5-O (see Fig. 2), but due to the low intensity of these peaks and to the presence of a contiguous peak at m/e 169, no accurate evaluation of isotope ratios can be made. However, it can be ascertained that the ion at m/e 168 is a dibenzofuran ion since

the fragmentation pattern of this ion is present, *i.e.* ions at m/e 140 (1.4 % for II and 1.2 % for III) and at m/e 139 (ion *a*) (8.7 % for II and 6.4 % for III). The characteristic doubly-charged ion at m/e 69.5 is also present (3.3 % for II and 2.0 % for III).

The stability associated with the dibenzofuran structure is illustrated by a doubly-charged molecular ion at m/e 99 (5.9 % for II and 3.1 % for III) together with the accompanying peak at m/e 99.5. The proposed fragmentation pattern of 2-methoxydibenzofuran (II) is given in Scheme 3.

II, m/e 198, 100.0 %

$-\overset{\cdot}{C}H_3 \quad \underline{m}^*$ 169.2 $-HCHO$

c, m/e 183, 66.0 %   **I, m/e 168, 3.3 %**

$-CO \quad \underline{m}^*$ 131.2 $-CO$

d, m/e 155, 45.6 %   **m/e 140, 1.4 %**

$-CO \quad \underline{m}^*$ 104.1 $-H^{\cdot}$

or

e, m/e 127, 18.6 %   **a, m/e 139, 6.4 %**

Scheme 3. Proposed fragmentation pattern for 2-methoxydibenzofuran (II).

Note: Transitions supported by the presence of metastable ions are shown with full arrows.

2-Hydroxydibenzofuran (IV) and 3-hydroxydibenzofuran (V) give very similar mass spectra. That of the former is given in Fig. 3 together with the mass spectrum of the corresponding 5-^{18}O-labelled compound (IVa). The

molecular ions form a greater percentage of the total ionization with these compounds than with the corresponding methoxydibenzofurans. Loss of a hydrogen atom from the molecular ion (m/e 184, 100.0 %) gives a small peak at m/e 183 (2.4 % for IV and 3.0 % for V; m^* 182.0), the structure of this ion corresponding to c in Scheme 3. Loss of carbon monoxide from the molecular ion occurs giving ions f, f', f'', and f''' (Scheme 4) at m/e 156 (3.2 % for IV and 2.3 % for V; m^* 132.2) and these ions lose a hydrogen atom giving d, d', and d'' (Scheme 4) at m/e 155 (11.9 % for IV and 10.5 % for V; m^* 154.0). Examination of the spectra of the 5-^{18}O-labelled compounds indicates that part of the lost carbon monoxide contains 5-O (see Fig. 3). After an empirical correction for the accompanying peak to m/e 156 at m/e 157 due to the natural abundance of deuterium, carbon-13 and oxygen-17, the ratio $(157)^+/(155)^+$ is 0.346 for 2-hydroxydibenzofuran-5-^{18}O (IVa) and 0.369 for 3-hydroxydibenzofuran-5-^{18}O (Va) whereas the ratio of the molecular ions $(186)^+/(184)^+$ is 0.497 and 0.503, respectively. Thus the carbon monoxide lost in the formation
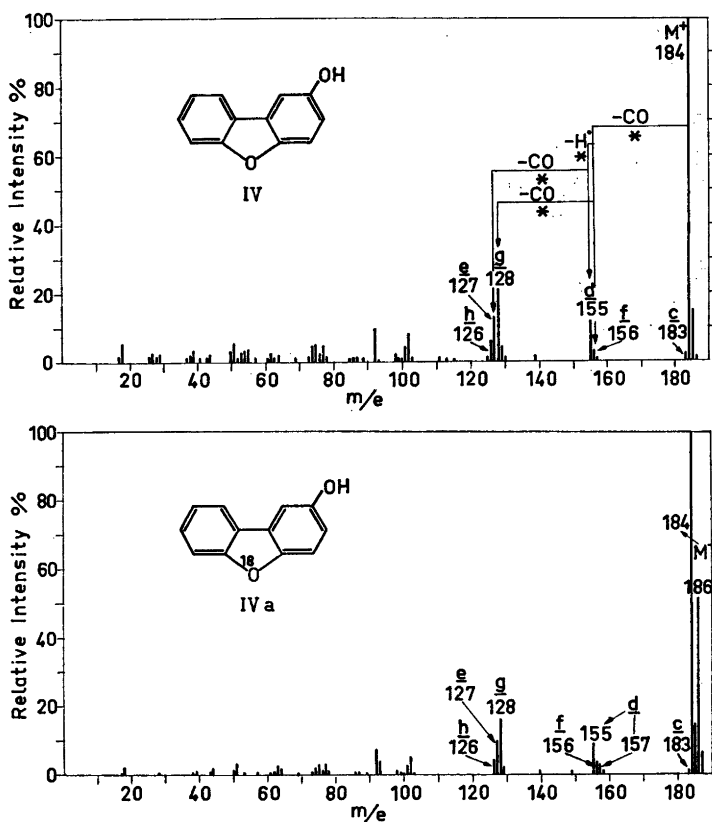

Fig. 3. Mass spectra of 2-hydroxydibenzofuran (IV) and the 5-^{18}O-labelled compound (IVa).

of the ions at m/e 155 (d, d', and d'') contains *ca.* 20 % 5-O and *ca.* 80 % phenolic-O in each case. No allowance has been made for an isotope effect, but it is not possible to detect one by studying the mass spectra of 2-methoxy-dibenzofuran-5-^{18}O (IIa) and 3-methoxydibenzofuran-5-^{18}O (IIIa). These compounds are well suited for the study of an isotope effect since the ratio $(185)^+/(183)^+$ should not be influenced by this factor whereas the ratio $(157)^+/(155)^+$ should be. Breakdown of ion c does not involve fission of a bond to 5-O whereas breakdown of ion d does (see Scheme 3). However, the difference in these ratios is so small that it is not possible to detect an isotope effect (see Table 1).

The ion at m/e 155 formed by loss of phenolic-O as carbon monoxide followed by loss of a hydrogen atom must have the same structure as ion d in the spectra of the methoxydibenzofurans (see Scheme 3). However, the ion at m/e 155 due to loss of 5-O as carbon monoxide followed by loss of a hydrogen atom corresponds to the ion a in the spectrum of dibenzofuran (I) substituted with a hydroxyl group, *i.e.* d' or d'' in Scheme 4. This structure has been suggested for the ion at m/e 155 in the spectra of a number of dihydroxyanthraquinones.[9]

Loss of carbon monoxide from ions at m/e 156 gives g (Scheme 4) at m/e 128 (21.2 % for IV and 17.0 % for V; m^* 105.0). The ions at m/e 155 also lose carbon monoxide giving e and e' (Scheme 4) at m/e 127 (13.1 % for IV and 9.3 % for V; m^* 104.1). The ion g is probably a naphthalene ion and e a naphthyl ion since the spectra of compounds IV and V are very similar to that of naphthalene [11] below m/e 129. The ion at m/e 126 (6.2 % for IV and 4.6 % for V) is probably formed by loss of a hydrogen atom from e or e'. Beynon and Williams [9] have suggested the structure h (Scheme 4) for the ion at m/e 126 in the spectra of dihydroxyanthraquinones. This structure seems possible for those ions at m/e 126 in the spectra of IV and V which arise from the ion at m/e 155 formed by loss of 5-O if the structure of this ion is d'', *i.e.* if the monohydroxy-substituted benzene ring remains intact during elimination of 5-O as carbon monoxide from the molecular ion. However, a more plausible structure for those ions at m/e 126 formed *via* initial loss of phenolic-O as carbon monoxide from the molecular ion is that of the 1-naphthalyne ion, h' (Scheme 4). Ions at m/e 126 formed *via* initial loss of 5-O as carbon monoxide if the non-hydroxy-substituted benzene ring remains intact may also have the structure h'. It is not known, however, what skeletal rearrangements may take place in these circumstances.

Once again, the stability of dibenzofuran structure is indicated by the presence of a fairly strong doubly-charged molecular ion at m/e 92 (9.9 % for IV and 6.6 % for V) together with the accompanying peak at m/e 92.5. The proposed fragmentation pattern of 2-hydroxydibenzofuran (IV) is given in Scheme 4.

The mass spectra of 2,5,2'-trimethoxybiphenyl (VI) and 2,4,2'-trimethoxy-biphenyl (VII) are complex but similar, so those of the former and the corresponding oxygen-18 labelled compound (VIa) only are given in Fig. 4. One notable difference between the spectra of VI and VII is that the molecular ion forms a greater percentage of the total ionization for VII than for VI.
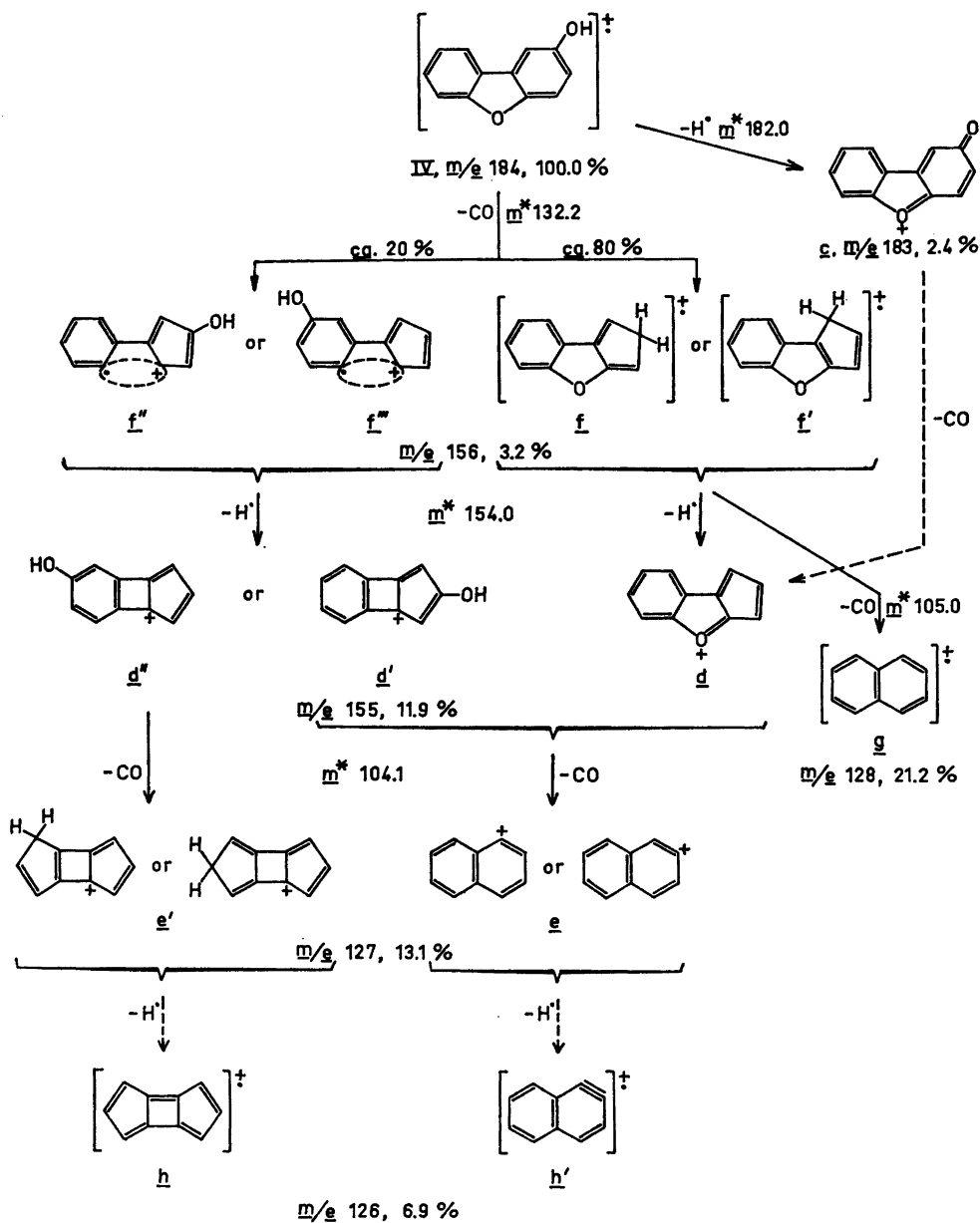
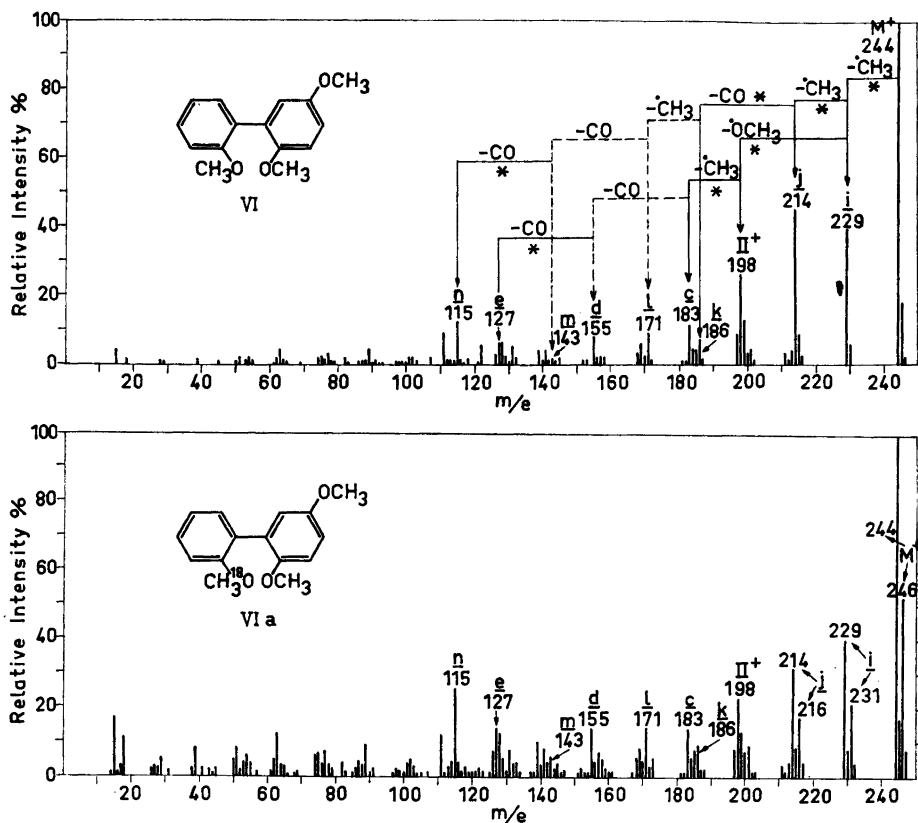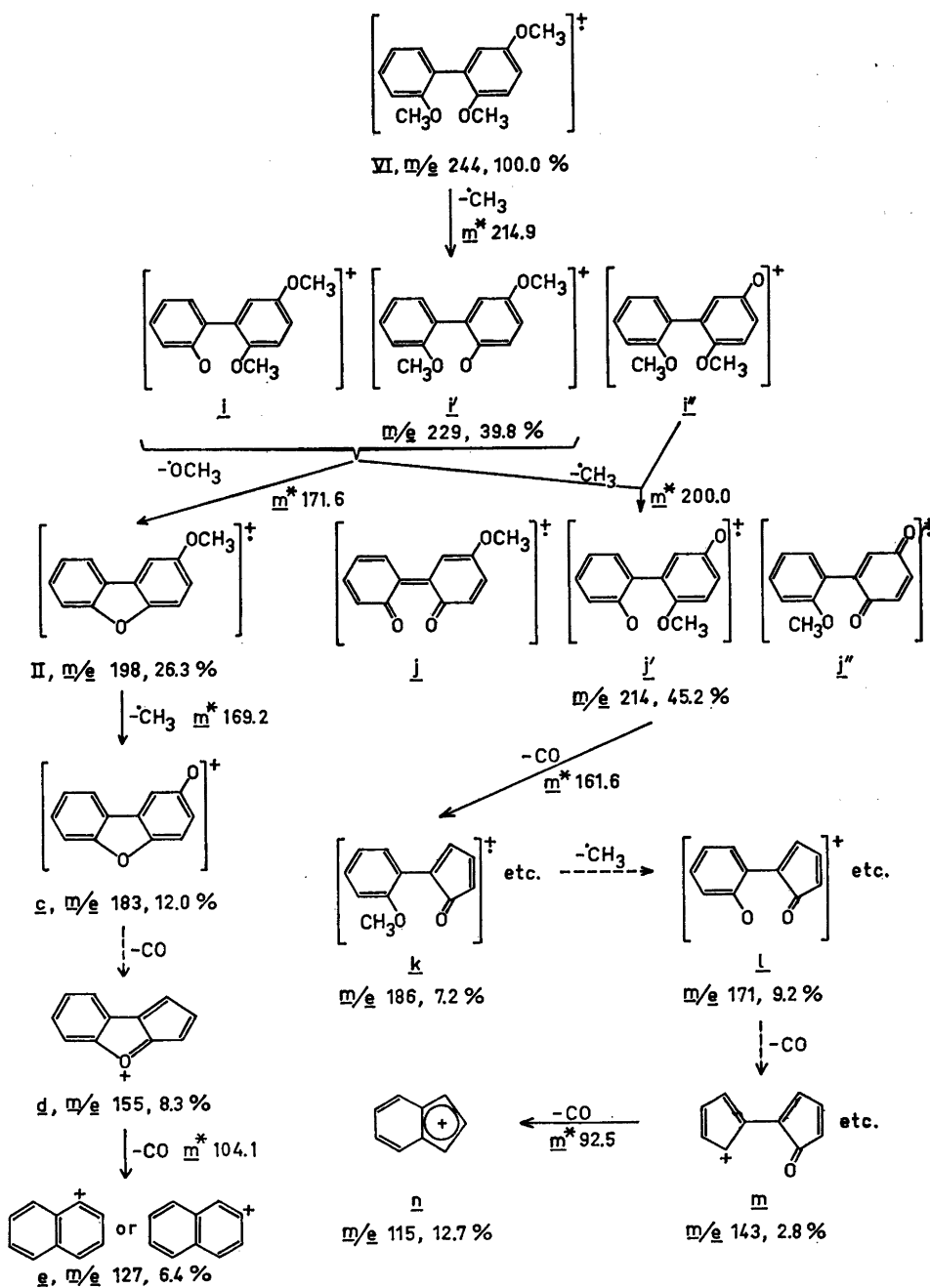Scheme 4. Proposed fragmentation pattern for 2-hydroxydibenzofuran (IV).

Fig. 4. Mass spectra of 2,5,2'-trimethoxybiphenyl (VI) and the 2'-methoxy-^{18}O-labelled compound (VIa).

The molecular ion (m/e 244), which forms the base peak, loses a methyl radical giving ions i, i' or i'' (Scheme 5) at m/e 229 (39.8 % for VI and 13.4 % for VII; $m*$ 214.9). The spectra of the ^{18}O-labelled compounds (VIa and VIIa) show the expected retention of heavy isotope (see Table 1). The ions j, j' or j'' (Scheme 5) at m/e 214 (45.2 % for VI and 16.0 % for VII) are due to loss of a second methyl radical from the molecular ion ($m*$ 200.0 corresponding to the transition $(229)^+ \rightarrow (214)^+ + 15$) and there is retention of 2'-O (see Table 1). An alternative way of formation of ions at m/e 214 is loss of formalde-hyde from the molecular ion. However, no metastable ion corresponding to this transition is present.

Loss of carbon monoxide occurs from the ions at m/e 214 giving ions k (Scheme 5) at m/e 186 (7.2 % for VI and 2.4 % for VII; $m*$ 161.6). It can be seen from the mass spectrum of VIa (Fig. 4) that part of the heavy isotope is retained. The ions l (Scheme 5) at m/e 171 (9.2 % for VI and 7.2 % for VII)

Scheme 5. Proposed fragmentation pattern for 2,5,2'-trimethoxybiphenyl (VI).

may be formed by loss of a methyl radical from ions k, but no metastable ion corresponding to this transition could be observed. There is at least partial retention of 2'-O (see Fig. 4). The ions m (Scheme 5) at m/e 143 (2.8 % for VI and 1.2 % for VII) probably arise by loss of carbon monoxide from ions l. A predominant ion is present at m/e 115 (12.7 % for VI and 7.3 % for VII) and arises from the ions m by loss of carbon monoxide (m^* 92.5). A relatively stable ion at m/e 115 has been observed in the spectra of alkylated naphthalenes [13] and diphenyl ether [11] where it is formed by loss of acetylene from a benztropylium ion. The structure of this ion is n (Scheme 5).[14]

A predominant ion in the spectra of VI and VII occurs at m/e 198 (26.3 % for VI and 13.5 % for VII). There is substantial evidence in the spectra of both compounds that this is a methoxydibenzofuran ion since the fragmentation patterns of 2-methoxydibenzofuran (II) and 3-methoxydibenzofuran (III) can be recognized in the spectra of compounds VI and VII, respectively. For example, loss of a methyl radical gives ion c (Scheme 5) at m/e 183 (12.0 % for VI and 7.3 % for VII; m^* 169.2) and loss of carbon monoxide from c gives ion d (m/e 155; 8.3 % for VI and 4.1 % for VII). Further loss of carbon monoxide gives the naphthyl ion e at m/e 127 (6.4 % for VI and 4.0 % for VII; m^* 104.1). Examination of the spectra of the 2'-methoxy-^{18}O-labelled compounds (VIa and VIIa) indicates that $ca.$ 50 % of the 2'-oxygen has been lost in the formation of c and d (Table 1). Such measurements cannot be made for the ion at m/e 198 due to a considerable peak at m/e 199. Presumably $ca.$ 50% of the 2'-oxygen has been lost in the formation of this ion as we have found that there is retention of 5-O in the spectra of compounds II and III in the transitions $(198)^+ \rightarrow (183)^+ + 15$ and $(183)^+ \rightarrow (155)^+ + 28$. A metastable ion at 171.6 indicates that the ion at m/e 198 arises by loss of a methoxyl radical from ions at m/e 229. A similar transition in the spectrum of 2,2'-dimethoxybiphenyl has been reported recently by Barnes et $al.$[15] Here, loss of a methoxyl radical from the P — 15 ion gives m/e 168, which is probably a dibenzofuran ion. The proposed fragmentation pattern of 2,5,2'-trimethoxybiphenyl (VI) is given in Scheme 5.

EXPERIMENTAL

The syntheses of the ^{18}O-labelled compounds, which all contain $ca.$ 30 atom % ^{18}O at the labelled positions, are described elsewhere.[1] All the substances were purified by sublimation in $vacuo$. 2-Methoxydibenzofuran-5-^{18}O (IIa) was isolated by means of thin layer chromatography and gave one peak with the same retention time as an authentic sample of 2-methoxydibenzofuran (II) on gas liquid chromatography.[1] However, the mass spectrum indicates that small amounts of impurity are present. There are unexpectedly high peaks at m/e 43, 55 to 57, 67 to 71, 94 to 97, 109 to 113, and 149 (see Fig. 2).

The mass spectra were obtained on a modified 180° mass spectrometer,[16] the electron energy being 70 eV. The temperature of the inlet system was kept between 80° and 150°. Spectra were also recorded on Atlas CH4 and LKB 9000 instruments for the study of metastable ions.

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