Chemistry of Crown Ethers: the Mass Spectra of Macrocyclic Polyethers

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A detailed evaluation of the mass spectral fragmentation patterns of several series of crown ethers has been made. Included are compounds containing one or two aromatic or heteroaromatic rings linked through carbon atoms to polyether chains of various lengths. Although such molecules are highly functionalized and have high molecular weights, molecular ion peaks were always observed, and a large percentage of the total ion current was carried by a small number of fragment ions. Only small differences were observed in the mass spectra of compounds having different aromatic ring substitution patterns. The fragmentation patterns for each set of compounds pointed to the formation of fragment ions in which the positive charge was localized on: (i) ions containing only polyether ring carbon and oxygen atoms; in the majority of cases such an ion (protonated ethylene oxide at *m/e* 45) provided the base peak: (ii) ions containing the aromatic (heteroaromatic) nucleus and no polyether ring carbon atoms; (iii) ions containing the aromatic (heteroaromatic) nucleus together with part of the polyether chain. High resolution measurements and metastable analysis provided confirmation for the postulated fragmentation mechanisms and product ion structures. Hydrogen and carbon rearrangements are involved in some cases. Components of higher molecular weight crown ether mixtures have been identified by mass spectrometry on the basis of their molecular ion peaks.

WE have recently reported the results of an investigation into the synthesis and chemistry of novel macrocyclic polyethers (crown ethers).[1,2] Several series of new compounds were described, each containing an aromatic

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[1] D. N. Reinhoudt, R. T. Gray, C. J. Smit, and I. Veenstra, *Tetrahedron*, 1976, **32**, 1161.

[2] R. T. Gray, D. N. Reinhoudt, C. J. Smit, and I. Veenstra, *Rec. Trav. chim.*, in the press.

or heteroaromatic ring linked through benzylic carbon atoms to polyether chains of various lengths. The two general methods used for their synthesis, *viz.* the reaction between a bis(halogenomethyl)-substituted aromatic (heteroaromatic) compound and a polyethylene diglycolate and the reaction between a polyethylene glycol ditosylate and the disalt of a bis(hydroxymethyl)-substituted aromatic (heteroaromatic) compound, both gave complex mixtures of products. Each mixture was separated (by chromatography and distillation) into three fractions, a 1 : 1 cyclic reaction product, a 2 : 2 cyclic reaction product, and a residue containing cyclic compounds of higher molecular weight. Structural assignments were made on the basis of ^{1}H and ^{13}C n.m.r. and mass spectrometry. The last mentioned technique proved particularly useful in this regard, not only for assignment of molecular weights, but also because confirmatory information regarding the structure of these high molecular weight compounds was obtained from their fragmentation patterns. We here present a detailed evaluation of the fragmentation patterns of these novel crown ethers. Although isotopic labelling studies have not been performed, structures for daughter ions and fragmentation pathways for their formation have been postulated on the basis of high resolution studies and metastable analysis and by comparison with fragmentation pathways for compounds with similar functional groups. The mass spectral characteristics of each series will be presented in turn, together with possible structures for the important fragment ions and postulated pathways for their formation.*

TABLE 1

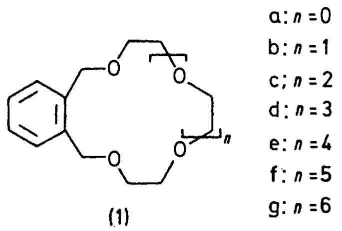
Principal fragment ions (relative abundances) in the mass spectra of crown ethers containing one 1,2-xylenyl unit

Fragment ion (*m/e* value)	(1a)	(1b)	(1c)	(1d)	(1e)	(1f)	(1g)	Elemental composition
$M^{+\cdot}$ *	208 (24)	252 (6)	296 (3)	340 (3)	384 (4)	428 (1)	472 (1)	
45	100	100	100	100	100	100	100	C_2H_5O
65	6	3	3	2	4	2	1	C_5H_5
77	8	3	4	3	3	3	2	C_6H_5
78	12	4	4	3	4	4	2	C_6H_6
89	18	17	20	21	36	18	21	$C_4H_9O_2$
91	18	8	9	9	8	10	8	C_7H_7
103	11	3	4	4	3	4	2	C_8H_7
104	63	21	24	28	37	26	27	C_8H_8
105	15	8	10	15	22	14	16	C_8H_9
117	7	2	5	6	7	5	5	C_9H_9
118	3	2	2	6	8	2	2	C_9H_{10}
119	21	5	4	7	6	5	5	C_8H_7O
120	24	3	3	3	4	2	2	C_8H_8O
121	4	1	1	1	1		1	C_8H_9O
133	2	5	4	7	13	5	7	$\left\{\begin{matrix}C_6H_{13}O_3\\C_9H_9O\end{matrix}\right.$
177			2	1	3	1	1	$C_8H_{17}O_4$
209					2	1	1	
253				1		1	1	
297					2			

* Molecular ion, given as *m/e* value (relative abundance).

RESULTS AND DISCUSSION

(A) *Crown Ethers containing One* 1,2-*Xylenyl Unit.*—The most important fragment ions from the spectra of



(1)

the 1 : 1 cyclic reaction products derived from 1,2-disubstituted benzene (1a—g) are given in Table 1.† The spectra of all these compounds feature the same peaks at low mass values (< *m/e* 150), indicating that they all undergo similar fragmentations and suggesting that the constitution and elemental composition of the fragment ions will be the same.

A striking characteristic of each spectrum is the appearance of a molecular ion peak of unusually high intensity for such highly functionalized compounds. In contrast, high molecular weight linear polyethylene glycol benzyl ethers [such as pentaethylene glycol dibenzyl ether (2) ‡] do not exhibit molecular ions. Even αω-bis(benzyloxy)alkanes, which recently have been thoroughly studied,[3] show very weak molecular ions, but very intense ions due to the loss of a benzyl radical, which we also observed in the spectrum of (2). The aromatic nucleus, though providing a centre of low ionization potential, is presumably insufficient to provide

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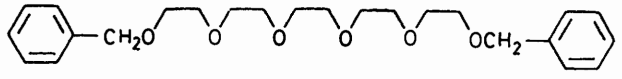
* In several fragmentation schemes mechanisms are proposed involving discrete hydrogen transfers following cleavage of a certain bond. Although they are schematically formulated involving stepwise mechanisms it is recognized that in reality such decompositions may involve concomitant fission and hydrogen transfer steps.

† The full spectra will be submitted to the mass spectrometry data centre at AWRE, Aldermaston.

‡ Prepared in 73% yield from triethylene glycol ditosylate and potassium benzyloxyethoxide.

[3] A. P. Bruins and N. M. M. Nibbering, *Tetrahedron*, 1974, **30**, 493.

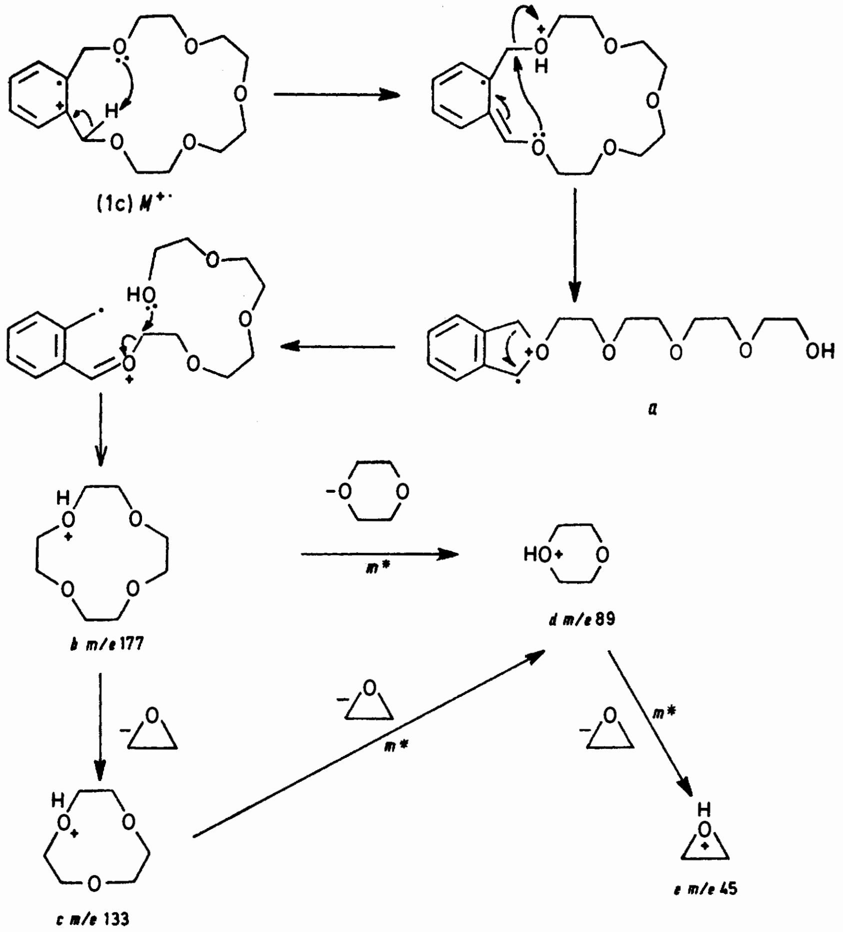
molecular ion stability in the crown ethers. However, any simple cleavage of the macrocyclic ring still proceeds with conservation of molecular weight. Thus, even for



(2)

compounds (1f and g) derived from hepta- and octa-ethylene glycols with 26 and 29 ring atoms and molecular weights of 428 and 472, respectively, molecular ions of 1% of the base peak were observed. We were thus able to identify the molecular species of individual components of the complex mixtures in which they were formed.

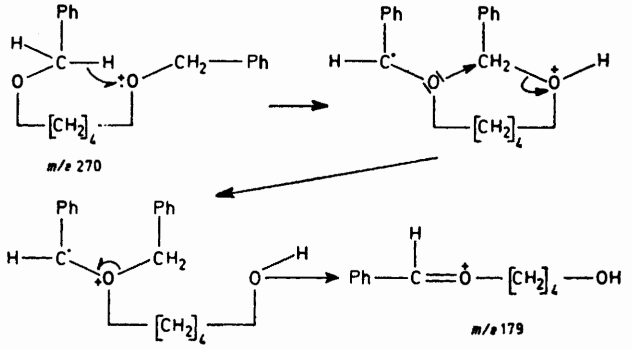
Since the spectra of all the members of this series are so similar, it may suffice to discuss the fragmentation pattern of only one of them, *e.g.* compound (1c) derived from tetraethylene glycol.



Scheme 1

The daughter ions derived from fragmentation of (1) fall into three groups, (i) one which contains atoms derived from the polyether chain, (ii) one which contains the aromatic ring together with part of the polyether chain, and (iii) one which contains the aromatic ring but no carbon atoms from the polyether chain.

The fragmentation mechanism for αω-bis(benzyloxy)-alkanes has been thoroughly studied recently [3] using D



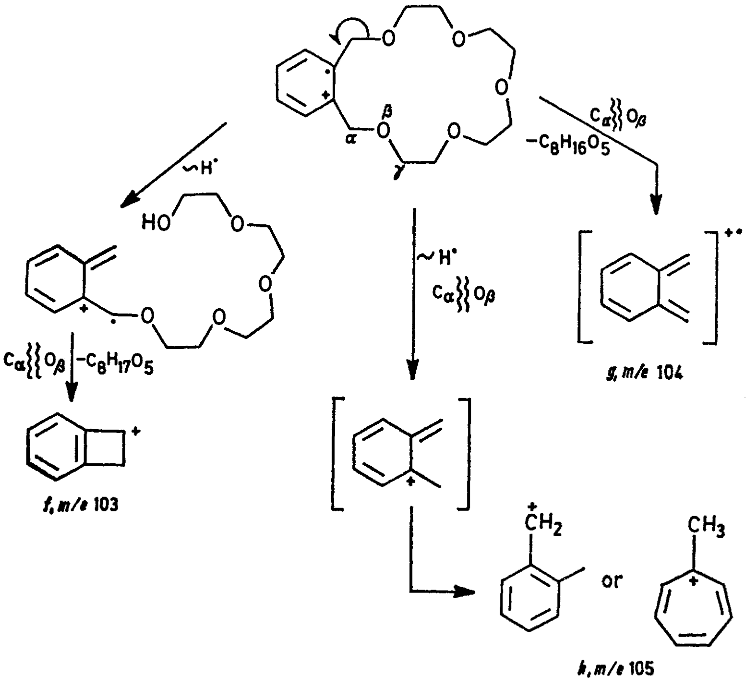
Loss of a benzyl radical from the molecular ion of 1,4-bis(benzyloxy)butane

and ^{18}O labelling. A mechanism consistent with all labelling experiments was formulated with charge localization on one benzylic oxygen and hydrogen transfer from the other benzylic carbon atom. The first benzylic group then rearranges and is cleaved *via* a cyclic structure. Preferably,[4] however, the first step in the mechanism is formulated as benzylic proton ab-

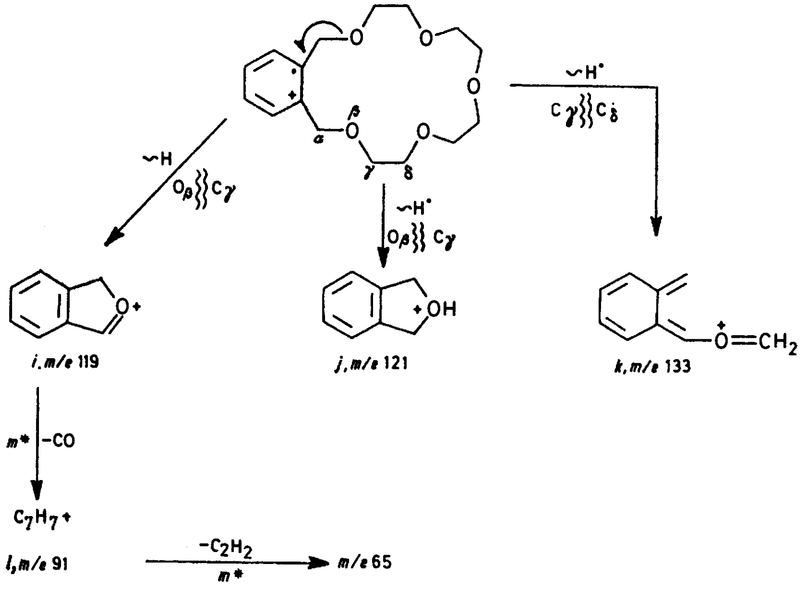
[4] N. M. M. Nibbering, personal communication.

straction by the second benzylic ether oxygen, with charge localization on the first aromatic nucleus.

If such a mechanism is operative in the crown ethers studied, this can be formulated as in Scheme 1.[5] Hydrogen abstraction followed by ring closure results in ion *a*, which can further fragment to give *b* (*m*/*e* 177, $C_8H_{17}O_4$). This ion decomposes further with loss of ethylene oxide or 1,4-dioxan.* Diffuse peaks (denoted m*) are seen for some of these fragmentations. For each compound in the series (1a—g), the final ion in this sequence, at *m*/*e* 45, is the base peak of the spectrum and in some cases [*e.g.* (1c)] carries as much as 37% of the total ion current.



SCHEME 2



SCHEME 3

Alternative modes of fragmentation of $M^{+\bullet}$, with initial benzylic cleavage and charge localization on the

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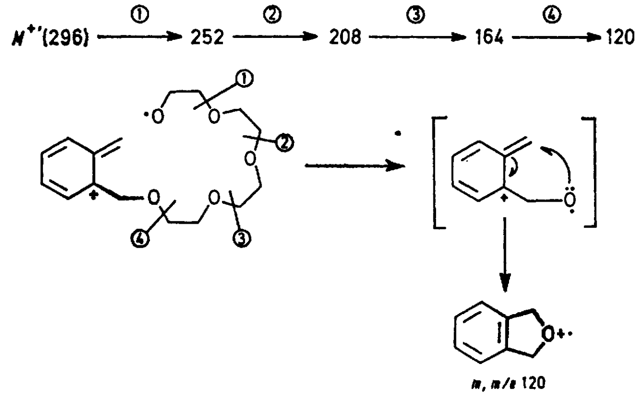
* While our work was in progress Liotta *et. al.*[6] reported the presence of intense fragment ions at *m*/*e* 133, 89, and 45 in the spectra of 12-crown-4[$(CH_2CH_2O)_4$] and 15-crown-5[$(CH_2CH_2O)_5$], thereby giving support to our structural assignments for these particular ions.

[5] The conventions of symbols used in the Schemes are standard in describing the mass spectral fragmentation of organic compounds. They originate from J. S. Shannon, *Proc. Royal Austral. Chem. Inst.*, 1964, 328.

[6] F. L. Cook, T. C. Caruso, M. P. Byrne, C. W. Bowers, D. H. Speck, and C. L. Liotta, *Tetrahedron Letters*, 1974, 4029.

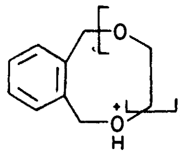
benzene ring, result in the formation of several important hydrocarbon and oxygen-containing fragments (Schemes 2 and 3, respectively). The important ions *g* (C_8H_8) [7,8] and *h* (the methyltropylium ion, C_8H_9),[9] commonly found in the spectra of disubstituted aromatics, may both be formed by fission of the C_α–O_β bond. Hydrogen transfers, followed by cleavage of the appropriate C–O bond, probably account for the appearance of *i*—*k* in the spectrum. Alternatively the formation of *i* may be rationalized by assuming an α-cleavage of the O_β–C_γ bond in ion *a* (Scheme 1). High resolution measurements indicated that the ion at *m*/*e* 133 was composed of two different fragment ions, *k* (C_9H_9O) and *c* ($C_6H_{13}O_3$). A diffuse peak was observed for the decomposition of *i* with loss of 28 mass units (CO) to the tropylium ion *l*, which fragments further by loss of acetylene to the fragment ion at *m*/*e* 65.

Accurate mass measurements have shown that the spectrum of (1c) comprises several ions containing the benzene ring together with part of the polyether chain. The appearance of small peaks at *m*/*e* 252, 208, 164, and 120 (*m*) indicates that, to some degree, decomposition of the molecular ion occurs through the sequential losses of ethylene oxide units (Scheme 4).*



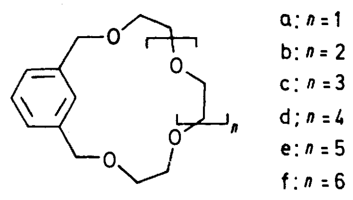
SCHEME 4

In addition, there is a series of peaks depending on the size of the polyether ring (Table 1, ions *n*), at *m*/*e* 121 (=*j*), 209 ($n = 2$), 253 ($n = 3$), and 297 ($n = 4$). These fragments are formed through partial loss of the polyether ring, accompanied by hydrogen transfer to the charged species.



n

Additional ions of medium intensity, whose genesis is not apparent from the data in hand, occur at *m*/*e* 77 (phenyl), 78 (ionized benzene), 117 (C_9H_9), and 118 (C_9H_{10}). Since the structures of the parent molecules do not contain nine adjacent carbon atoms, the latter two fragment ions must be generated through an unidentified carbon rearrangement process.



(3)

(B) *Crown Ethers containing One* 1,3-*Xylenyl Unit.*—A comparison of the highlights from the mass spectra of the six compounds synthesized [2] in this series (Table 2) with those of the 1,2-xylenyl crown ethers (Table 1) showed that the two series contain the same major fragment ions, suggesting that they cleave by similar mechanisms. The daughter ions from (3a—f) at *m*/*e* <150 are generally more intense than their counterparts from (1), even though the 1,3-substitution pattern does not permit formulation of such energetically favourable structures for the phenyl-containing fragments.

TABLE 2

Principal fragment ions (relative abundances) in the mass spectra of crown ethers containing one 1,3-xylenyl unit

Fragment ion (*m*/*e* value)	(3a)	(3b)	(3c)	(3d)	(3e)	(3f)	Elemental composition
$M^{+\cdot}$	252 (9)	296 (2)	340 (3)	384 (3)	428 (1)	472 (5)	
45	67	100	100	100	100	100	C_2H_5O
59	1	3	6	4	6	5	C_3H_7O
65	4	5	4	1	2		C_5H_5
77	5	7	5	2	3	2	C_6H_5
78	9	15	8	4	7	1	C_6H_6
79	2	4	4	2	3		C_6H_7
89	23	18	34	28	15	47	$C_4H_9O_2$
91	6	11	9	4	6	3	C_7H_7
103	9	14	8	5	6	3	C_8H_7
104	100	50	35	47	31	38	C_8H_8
105	16	19	19	17	19	18	C_8H_9
117	5	6	6	5	5	5	C_9H_9
118	5	3	5	4	2	3	C_9H_{10}
119	5	6	13	7	9	6	C_8H_7O
120	2	2	3	1	1	1	C_8H_8O
133	18	3	14	8	5	12	$C_6H_{13}O_3$ C_9H_9O
177		2	2	2	1	2	$C_8H_{17}O_4$

Thus the ions at *m*/*e* 177, 133, 89, and 45 [base peak except for (3a)] are derived from the polyether chain, and are postulated to have structures similar to those of the corresponding ions from (1) (Scheme 1). The aromatic ions at *m*/*e* 103, 104, and 105 are particularly strong for this series [indeed for (3a), *m*/*e* 104 is the base peak of the spectrum] and they may be formed as shown in Scheme 5. A diffuse peak is observed for the further decomposition of ion *p*, with loss of acetylene, to ionized benzene (*m*/*e* 78, C_6H_6). Although the ions at

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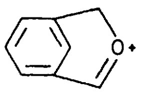
* Recently Jaeger and Whitney, *J. Org. Chem.*, 1975, **40**, 92, observed an important series of peaks due to the formal loss of C_2H_4O units from *M* in crown ethers of the class benzo-3*n*-crown-*n*, derived from catechol.

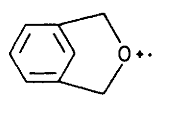
[7] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden Day, San Francisco, 1967, pp. 88 and 120.

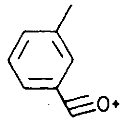
[8] T. Aczel and H. E. Lumpkin, *Analyt. Chem.*, 1960, **32**, 1819.

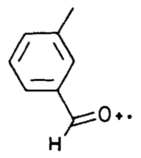
[9] F. Meyer and A. G. Harrison, *J. Amer. Chem. Soc.*, 1964, **86**, 4757.

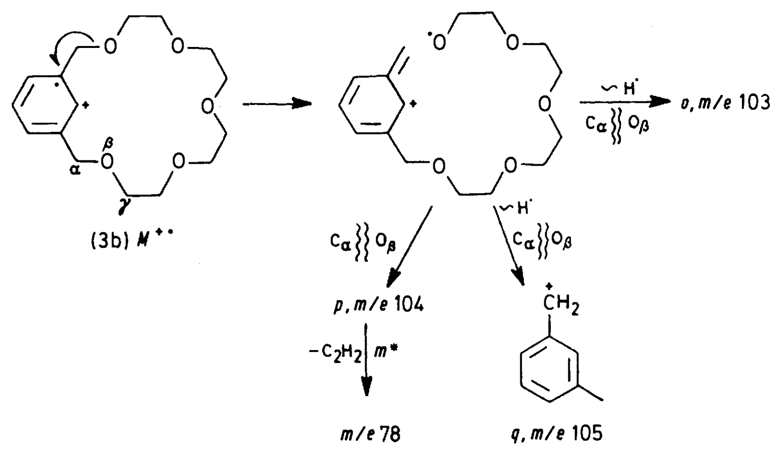
m/*e* 119 and 120 derived from (3) may have structures such as *r* and *s*, further hydrogen rearrangements would perhaps result in the more stable open-chain structures *r*′ and *s*′. Similar to the corresponding ion from the 1,2-xylenyl crown ethers (1), the *m*/*e* 120 ion from (3) is also derived by the sequential loss of ethylene oxide units from $M^{+\cdot}$. However, the intensities of the intermediate ions of higher mass values are generally lower for the 1,3- than for the 1,2-xylenyl series.


r, *m*/*e* 119


s, *m*/*e* 120

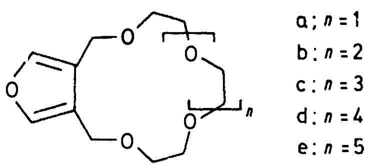

r′, *m*/*e* 119


s′, *m*/*e* 120



SCHEME 5

(C) *Crown Ethers containing One* 3,4-*Furanyl Unit*.—



(4)

The mass spectra of the five crown ethers containing polyether chains linked to the 3,4-positions of a furan ring (4a—e) are dominated by four major fragment ions at *m*/*e* 45, 89, 94, and 95 (Table 3). According to high resolution measurements the former two fragments are derived entirely from the polyether ring, while the latter two contain the intact furan ring. Thus retention of the positive charge may occur on both portions of the molecule for these compounds also, as we found for the xylenyl crown ethers (1) and (3).

In the spectrum of (4b) we find a series of peaks at *m*/*e* 177, 133, 89, and 45 (*cf*. *b*—*e* in Scheme 1), derived by fragmentation of the polyether chain. This mechanism for their formation is supported by the appearance of the appropriate metastable ions. Protonated ethylene oxide (*m*/*e* 45) provides the base peak of the spectrum and for (4b) carries *ca*. 40% of the total ion current.

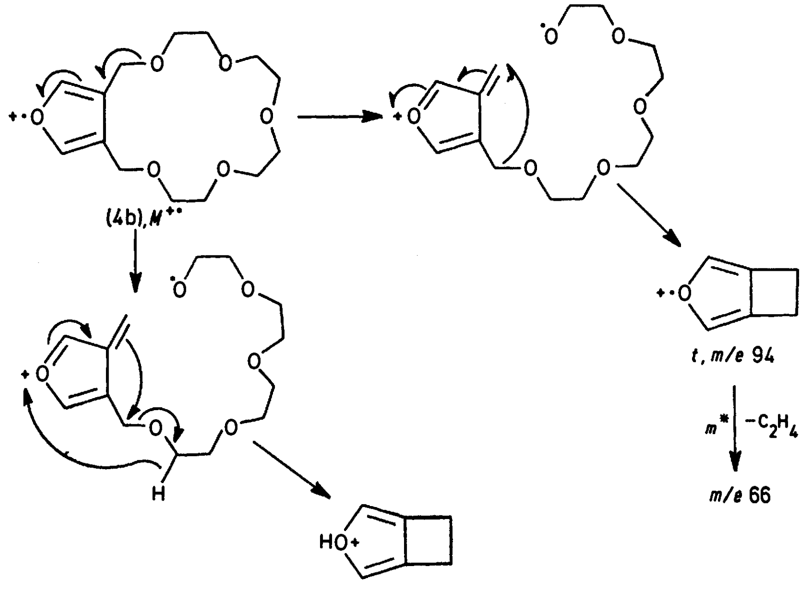
The other major fragment ions are associated with the furan ring system and do not contain carbon atoms from the polyether chain. The most important of these, at *m*/*e* 94 (C_6H_6O) and 95 (C_6H_7O) correspond to *m*/*e* 104 and 105 from (1) and (3) and are best represented by structures *t* and *u* (Scheme 6). An intense diffuse peak corresponding to the subsequent decomposition of *t* with loss of the elements of ethylene, is observed in the spectrum of (4b). Of the other ions in the spectrum, those at *m*/*e* 53, 65, 67, and 79 are derived from decomposition of the furan nucleus, and those at *m*/*e* 107 and

TABLE 3

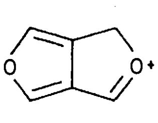
Principal fragment ions (relative abundances) in the mass spectra of crown ethers containing one 3,4-furanyl unit

Fragment ion (*m*/*e* value)	(4a)	(4b)	(4c)	(4d)	(4e)	Elemental composition
$M^{+\cdot}$	242 (5)	286 (10)	330 (2)	374 (1)	418 (6)	
45	100	100	100	100	100	C_2H_5O
53	9	4	6	8	2	
65	8	3	5	7	2	
66	11	5	8	14	4	
67	3	2	3	6	2	
79	3	3	1	6	2	
89	11	27	12	17	21	$C_4H_9O_2$
94	34	30	28	38	22	C_6H_6O
95	13	15	17	26	17	C_6H_7O
107	1	2	8	2	1	C_7H_7O
108	1	3		2	3	C_7H_8O
109	7	6	3	10	5	$C_5H_5O_2$
110	3	3	1	2	2	$C_6H_6O_2$
133	5	4	3	4	5	$C_6H_{13}O_3$
177		5		2	1	$C_8H_{17}O_4$

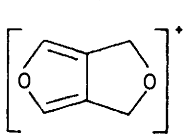
108 from an unknown carbon migration mechanism [compare m/e 117 and 118 from (1) and (3)]. The two ions at m/e 109 and 110, both containing an ether ring oxygen atom, have possible structures *v* and *w* and are presumably formed by mechanisms analogous to those shown in Schemes 3 and 4 for ions *i* and *m* from (1).



SCHEME 6

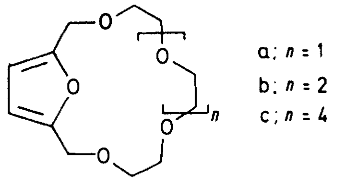


v, m/e 109



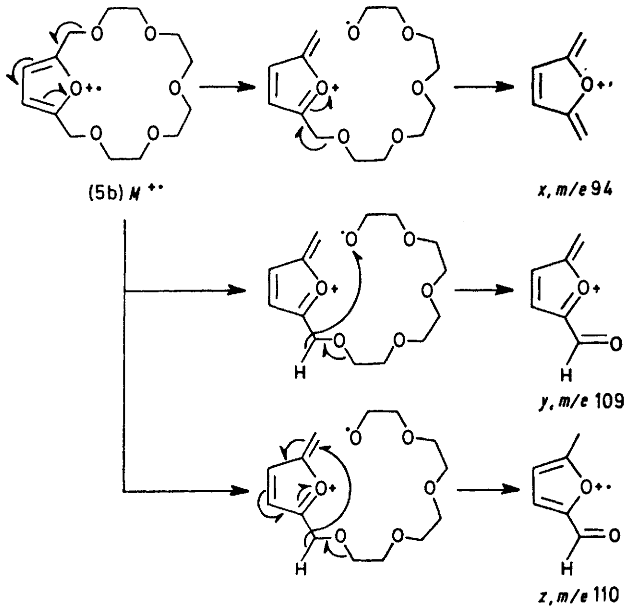
w, m/e 110

(D) *Crown Ethers containing One* 2,5-*Furanyl Unit*.—The three crown ethers we have synthesized with a polyether chain linked to the 2,5-positions of a furan ring (5a—c) display very simple mass spectra (Table 4). The mass values and relative intensities of the fragment ions are very similar to those derived from the isomeric furans (4), the most noticeable difference being the decreased intensity of the m/e 95 ion relative to that at 94. This might be due to the fact that the 2,5-configuration permits the formulation of a conjugated structure for the latter fragment (*x*, Scheme 7).[*] Two other furan-containing fragments, at m/e 109 and 110, are best represented in this series by structures containing formyl groups (*y* and *z* in Scheme 7).



(5)

Also significant in the spectra of (5) is the series of fragments derived from the polyether chain (*b*—*e*). The fragment terminating the sequence (*e*, m/e 45) is again the base peak in two of the spectra, and each fragmentation step is accompanied by the appropriate diffuse peak. Of much less importance are the ions at m/e 52, 53, 66, and 81, derived from the furan ring, and those at m/e 107 and 108, which are formed by an unknown rearrangement mechanism.



SCHEME 7

(E) *Crown Ethers containing One* 3,4-*Thiophenyl Unit.*

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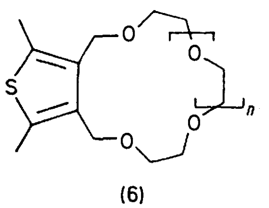
[*] The participation of the furan oxygen in the fragmentation mechanisms of substituted furans is briefly discussed in ref. 6, p. 618.

We have synthesized six crown ethers containing a polyether chain linked through carbon atoms to the

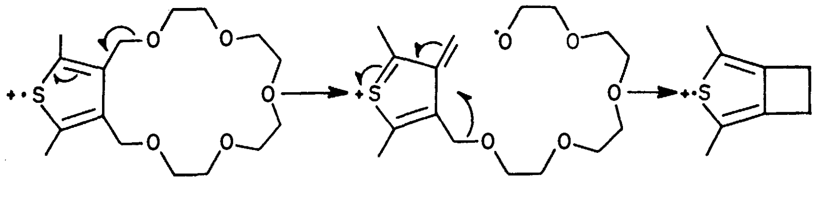


a: n = 1
b; n = 2
c : n = 3
d: n = 4
e: n = 5
f; n = 6

(6)

3,4-positions of 2,5-dimethylthiophen (6a—f). The details of their mass spectra are summarized in Table 5.

Each thiophen crown ether displays a stronger molecular ion peak than the corresponding benzene derivatives, as might be expected from the ionization potentials of benzene and thiophen. Otherwise, similar fragmentation patterns are observed. High resolution measurements have not been performed for a member of this series. However, on the basis of the fragmentations of crown ethers (1) and (3)—(5), plausible fragmentation mechanisms and ion structures may be formulated.



(6b), $M^{+\cdot}$

cc, *m/e* 138

SCHEME 8

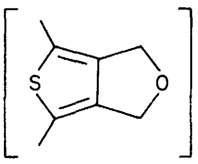
Peaks corresponding to the sequential loss of the elements of ethylene oxide are stronger in the spectrum of the thiophens than in those of the other crown ethers studied. Thus, ions at *m/e* 286, 242, 198, and 154 are observed in the spectrum of (6b). A plausible structure for the terminal ion in this sequence (*aa*) corresponds to ion *w* from the corresponding furanyl compound.

TABLE 4

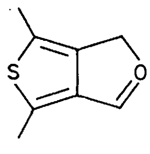
Principal fragment ions (relative abundances) in the mass spectra of crown ethers containing one 2,5-furanyl unit

Fragment ion (*m/e* value)	(5a)	(5b)	(5c)	Elemental composition
$M^{+\cdot}$	242 (8)	286 (4)	374 (2)	
45	92	100	100	C_2H_5O
52	6	2	1	
53	6	2	2	
66	7	2	1	
81	6	3	2	
89	21	27	22	$C_4H_9O_2$
94	100	47	24	C_6H_6O
95	8	6	5	C_6H_7O
107	3	2	2	C_7H_7O
108	3	4	2	C_7H_8O
109	5	5	3	$C_6H_5O_2$
110	8	6	2	$C_6H_6O_2$
133	14	4	5	$C_6H_{13}O_3$
177		3	1	$C_8H_{17}O_4$

The ubiquitous set of fragments at *m/e* 177, 133, 89, and 45, stemming from the polyether portion of the crown ether, is also very strong for this series. The appropriate diffuse peaks (*cf.* Scheme 1) are also observed. Loss of 177 mass units from the molecular ion, with the positive charge being retained by the thiophen gives rise to the ion (*bb*) at *m/e* 153.



aa, *m/e* 154



bb, *m/e* 153

$CH_3-C\equiv S^+$

dd, *m/e* 59

A strong diffuse peak (*m/e* 66.6) is observed for the formation of the second strongest peak in the spectrum at *m/e* 138, which is generated directly from the molecular ion (*cc*, Scheme 8). Presumably the neighbouring peaks are formed by similar mechanisms, but with concomitant hydrogen transfers. The ion at *m/e* 59 (*dd*) has been found to be characteristic of several other 2,5-dimethylthiophens,[10] and has been investigated in detail as to the mechanism of its formation.[11]

TABLE 5

Principal fragment ions (relative abundances) in the mass spectra of crown ethers containing one 3,4-thiophenyl unit

Fragment ion (*m/e* value)	(6a)	(6b)	(6c)	(6d)	(6e)	(6f)
$M^{+\cdot}$	286 (26)	330 (60)	374 (22)	418 (21)	462 (14)	506 (13)
45	100	100	100	100	100	100
59	12	8	8	7	5	4
89	16	57	21	21	18	19
123	3	4	2	2	1	1
124	2	3	3	3	2	2
125	4	5	4	4	3	3
133	4	6	4	3	3	3
137	7	10	8	9	7	8
138	25	72	67	80	74	75
139	13	23	22	36	24	26
153	10	14	8	8	6	6
154	8	17	6	6	5	4
177		2		1		1
198	1	4	2	2	1	2
242		1				
286	26	3				

(F) *Crown Ethers containing Two Xylenyl Units.*—

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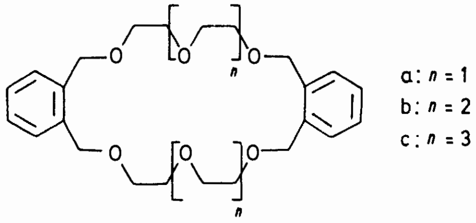
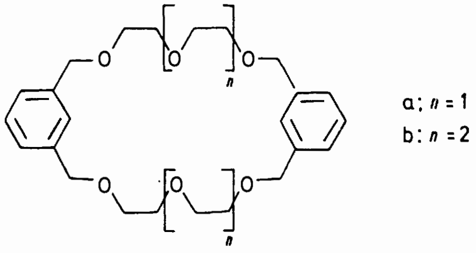
[10] I. W. Kinney and G. L. Cook, *Analyt. Chem.*, 1952, **24**, 1391.

[11] Ref. 7, ch. 24.

Five crown ethers containing two xylenyl units have been synthesized [(7a—c) and (8a and b)].[1,2] As may be expected their mass spectra are more complicated



(7)



(8)

than those of the corresponding 1 : 1 cyclic reaction products (1) and (3) with many ions of low intensity. Even so, a molecular ion peak is observed for each compound (Table 6) and a large percentage of the ion current is carried by a small number of ions.

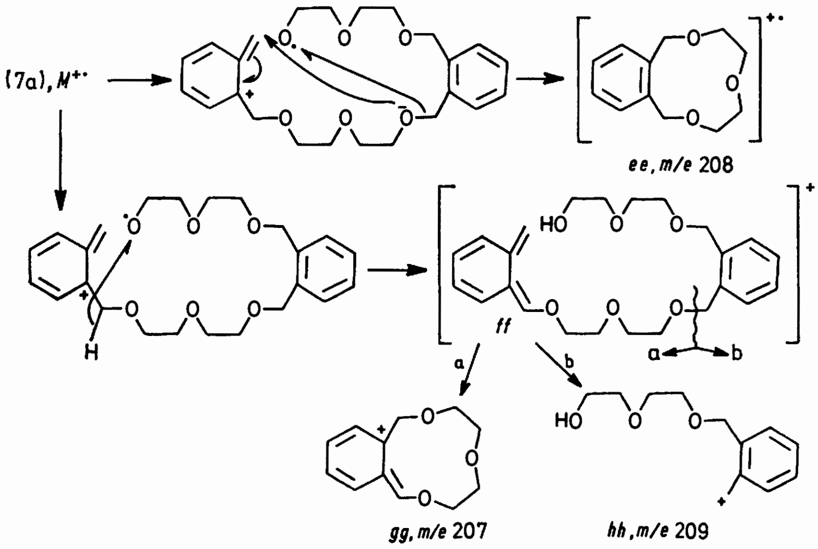
Compounds in both groups give fragments with similar *m/e* values (Table 6), and no fragment ions are observed with mass values greater than about half the molecular weight. Since these values are identical to those of the ions obtained from (1) and (2), it is reasonable to assign them similar structures.

TABLE 6

Principal fragment ions (relative abundances) in the mass spectra of crown ethers containing two xylenyl units

Fragment ion (*m/e* value)	(7a)	(7b)	(7c)	(8a)	(8b)
$M^{+\cdot}$	416 (4)	504 (2)	592 (2)	416 (5)	504 (1)
45	100	100	100	100	85
59	2	4	5	2	5
65	4	2	2	4	6
77	6	3	3	8	11
78	9	4	3	13	22
79	4	2	2	7	12
87	5	11	15	2	4
89	15	22	43	23	22
91	25	13	14	13	20
103	9	4	4	13	21
104	50	40	51	64	91
105	67	56	80	89	100
117	5	6	7	5	11
119	19	15	34	18	23
120	6	4	5	3	4
133	2	12	11	2	8
177		1	6	1	1
$(M - 2)/2$ *	207 (3)	251 (17)	295 (9)	207 (3)	251 (1)
$M/2$ *	208 (11)	252 (6)	296 (4)	208 (2)	252 (1)
$(M + 2)2$*	209 (6)	253 (6)	297 (8)	209 (1)	253 (—)

* Ion expressed as *m/e* value (relative abundance).

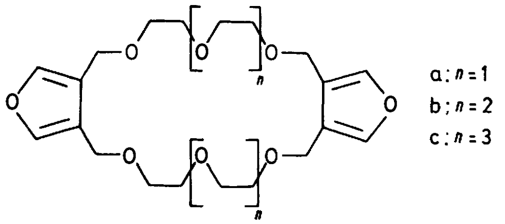


SCHEME 9

Thus for (7b) and (8b) we find a group of ions at *m/e* 177, 133, 89, and 45, derived from the polyether ring. We also find strong ions for phenyl (*m/e* 77), ionized benzene [*m/e* 78, especially strong for (8b)], protonated benzene (*m/e* 79), and the tropylium ion (*m/e* 91). The formation of each of these must involve at least one at *m/e* 104 (*g* or *p*) and *m/e* 105 [*q*, base peak for (8b)] are also much more intense than those from (1) and (3), and since the formation of the latter must also involve hydrogen migration it appears that such rearrangements are more facile in such a system.

An interesting group of peaks at mass values $(M + 2)/2$, $M/2$, and $(M - 2)/2$ appears in the spectra of (7a—c) [also to a lesser extent in (8a)]. A possible rationale for their formation is given in Scheme 9 for (7a). Initial fragmentation of a benzylic carbon–oxygen bond may be followed either by cleavage of a similar bond associated with the other ring to give ion *ee* (*m/e* 208) or by hydrogen migration to give an intermediate ion *ff*. Cleavage of the second benzylic bond then produces two fragments (*gg* and *hh*), each of which is capable of stabilizing the positive charge.

(G) *Crown Ethers containing Two* 3,4-*Furanyl Units.*—



(9)

As might be expected for such highly functionalised compounds, the mass spectra of (9a—c) are very complex and display peaks along the whole mass range (Table 7). However the majority of fragment ions are of low intensity, and those of importance can be rationalized in terms of structure and mechanism of formation.

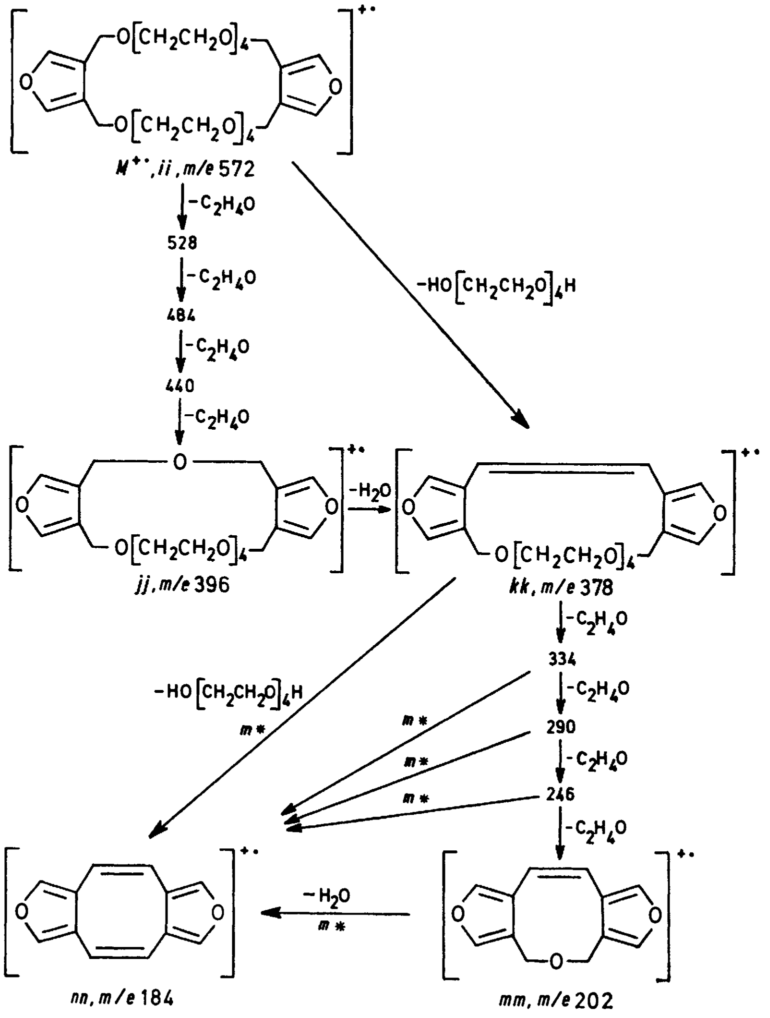
TABLE 7

Principal fragment ions (relative abundances) in the mass spectra of crown ethers containing two 3,4-furanyl units

Fragment ion (*m/e* value)	(9a)	(9b)	(9c)	Elemental composition
$M^{+\cdot}$	396 (4)	484 (11)	572 (8)	
45	54	92	100	C_2H_5O
66	12	32	6	
89	10	72	63	$C_4H_9O_2$
94	52	79	60	C_6H_6O
95	100	100	100	C_6H_7O
109	19	5	22	$C_6H_5O_2$
110	4	11	4	$C_6H_6O_2$
133	1	33	12	$C_6H_{13}O_3$
177			4	$C_8H_{17}O_4$
184	27	91	100	$C_{12}H_8O_2$
185	7	42	23	$C_{12}H_9O_2$
186	4	34	21	$C_{12}H_{10}O_2$
187	4	11	8	$C_{12}H_{11}O_2$
202	4	11	6	$C_{12}H_{10}O_3$
M − glycol *	290 (9)	334 (30)	378 (13)	

* Expulsion from the molecular ion of the elements of polyethylene glycol $HO[CH_2CH_2O]_nCH_2CH_2OH$.

We find several ions with the same *m/e* values as the significant fragments from the 1 : 1 compounds (4). Thus ions at *m/e* 109 (*v*), 110 (*w*), 94 (*t*), 95 [*u*, base peak from (9a—c)], and 66, all containing one furan ring, are



SCHEME 10

present and are presumably formed by similar mechanisms to those described for (4). Also observed is the series of ions (at *m/e* 177, 133, 89, and 45) derived exclusively from the polyether ring.

In addition, we find several groups of ions which, according to accurate mass measurements, are composed of fragments differing by one hydrogen atom each time. Although with the data in hand it is impossible to formulate fragmentation pathways for each of these peak groups, we are able to rationalize the formation of the significant ions [Scheme 10 for (9c)].

The molecular ion *ii* may fragment either by loss of tetraethylene glycol, with simultaneous carbon–carbon bond formation, to give *m/e* 378 (*kk*), or by sequential loss of four molecules of ethylene oxide to give *m/e* 396 (*jj*). All intermediate ions are observed in the spectrum. The (M − glycol) ion can then decompose further by loss of a second molecule of glycol, to give the highly conjugated rearrangement ion (*nn*), or by a similar sequence of ethylene oxide eliminations to yield the oxygenated ion (*mm*) at *m/e* 202. Further losses of ethylene oxide units from ion *jj* are not apparent. That the ion at *m/e* 184 has the stable structure *nn* is supported by its high intensity, 100% from (9c), a characteristic of stable, highly conjugated systems. This ion is also formed from the intermediate ions at *m/e* 334, 290, 246, and 202 by loss of the appropriate polyglycol or water (Scheme 10), as was shown in a high voltage scan experiment on *m/e* 184. This experiment also showed that *nn* is formed from ions at *m/e* 528 and 484 and *m/e* 572, the molecular ion, in two-step processes *via kk* at *m/e* 378.

The additional ions in this peak group (at *m/e* 185, 186, and 187) may be formed by similar mechanisms involving an appropriately smaller number of hydrogen atoms.

(H) *Crown Ethers containing more than Two Aromatic Units*.—In the preparation of crown ethers from a bis(halogenomethyl)-substituted aromatic compound and a polyethylene diglycolate, we obtained, besides the 1 : 1 and 2 : 2 cyclic reaction products, residues which could not be distilled at 1 Pa.

Mass spectrometry has enabled us to identify 3 : 3 and 4 : 4 cyclic reaction products in several of these product mixtures. Although these are compounds of molecular weight *ca.* 1 000, which fragment extensively upon electron impact, the presence of small molecular ion peaks still allowed a positive identification to be made.

EXPERIMENTAL

The synthesis of the crown ethers studied has been reported elsewhere.[1,2]

Mass spectra were recorded on an A.E.I. MS902 or Varian MAT 731 mass spectrometer operated at 70 eV electron energy and 800—1 000 resolution; the ion source temperatures were 160—200 °C. Samples were introduced using a direct insertion technique and studied under optimal evaporation conditions (sample temperature programmed).

High resolution mass spectra were recorded on a Varian MAT 731 double-focusing mass spectrometer operated at 70 eV electron energy and 10 000 resolution; the ion source temperature was 200 °C. Data acquisition was carried out on a Varian SpectroSystem 100 MS, with subsequent data processing on an RXDS Sigma 7 computer, using a multiscan averaging technique for enhanced precision.

Metastable transitions in the first field-free region were measured by using the high voltage scan technique[12] on the A.E.I. MS902 double focusing masss pectrometer under the following conditions: electron energy 70 eV, emission current 100 μA.

[6/442 *Received, 4th February*, 1976]

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[12] K. R. Jennings, *J. Chem. Phys.*, 1965, **43**, 4176.