53188-57-1; **13b,** 53188-58-2; **14,** 22700-58-9; **15,** 53188-59-3; **16,** 2815-45-4; **17b,** 2043-61-0; **18b,** 53188-60-6; **19b,** 53188-61-7; **20a,** 53188-62-8; **20a** 2,4-DNP, 53188-63-9; **20b,** 29517-58-6; **21,** 53188-64-0; **22,** 53188-65-1; **23,** 15763-62-9; **24,** 15763-61-8; **25,** 53188-66-2; **26,** 53188-67-3; **27,** 53188-68-4; **28,** 31865-37-9; **30,** 53188-69-5; **31,** 53188-70-8; 4-*tert*-butylcyclohexanone, 98-53-3; ethyl cyanoacetate, 105-56-6; allyl alcohol, 107-18-6; 4-*tert*-butyl-1-cyclohexenylnitrile, 7370-14-1.

References and Notes

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Electron Impact Induced Fragmentation of Macrocyclic Polyethers (Crown Ethers)[1]

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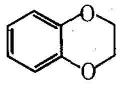
The mass spectra of catechol ethylene diether (1) and a series of macrocyclic polyethers (crown ethers) of the general class benzo-3*n*-crown-*n* (*n* = 3, 4, 5, 6) were correlated. The molecular ion (M) of benzo-18-crown-6 (5) loses C$_2$H$_4$O to give a peak at *m/e* 268. Other important peaks were found at *m/e* 224, 180, and 136, which formally correspond to the loss of two, three, and four C$_2$H$_4$O units, respectively, from M. Mass spectra of 2, 3, and 4 also displayed a series of peaks corresponding to the formal loss of C$_2$H$_4$O units from M; a peak at *m/e* 136 was the terminus in this series for each crown ether. Mass spectra of open-chain analogs 6 and 7 were compared with those of 3 and 4, respectively. Mass spectra of deuterated analogs 4a and 4b allowed formulation of plausible fragmentation pathways for 4.

Macrocyclic polyethers (crown ethers)[2] have unique chemical properties associated with their ability to form complexes with cations[2,3] and with other species.[4] Crown ethers have been employed in mechanistic,[5] physical,[6] and synthetic[7] studies and in chromatographic processes.[8] The chemical importance of crown ethers warranted study of their electron impact induced fragmentation pathways for qualitative identification purposes. Also, it was hoped that the novel chemical properties of crown ethers might be paralleled by unusual mass spectral fragmentation characteristics.

Aliphatic, aryl alkyl, and aromatic ethers have been subjects of numerous mass spectrometry investigations.[9] Several studies have included cyclic ethers,[10] notably catechol polymethylene diether derivatives[10a] and methylene dioxybenzenes.[10c,d] In the present investigation mass spectra of a homologous series of crown ethers were correlated and compared with those of open-chain analogs.

The mass spectra of catechol ethylene diether (1),[11,12] benzo-9-crown-3 (2),[2a,13] benzo-12-crown-4 (3),[2a] and benzo-18-crown-6 (5)[2a] are compiled in Table I, and that of benzo-15-crown-5 (4)[2a] is given in Figure 1. The mass spectrum of 5 displayed a base peak at *m/e* 136 and other important peaks at *m/e* 268, 224, 180, 121, 110, 109, 108, 80, and 52. The elemental compositions of most of the important fragment ions for 5 were determined by high-resolution mass spectrometry and are listed in Table II. The results indicate that the molecular ion (M) of 5 loses C$_2$H$_4$O to give the mass 268 ion and that ions of *m/e* 224, 180, and 136 formally correspond, respectively, to the loss of two, three, and four C$_2$H$_4$O units from M. The mass spectra of


1

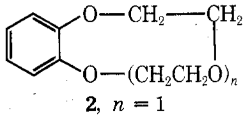

2, *n* = 1
3, *n* = 2
4, *n* = 3
5, *n* = 4

Table I
Mass Spectra of Compounds 1, 2, 3, and 5[a]

Ion m/e	Relative Abundance 1	2	3	5
41		6	7	7
43	2	17	20	21
44		2	3	3
45		16	38	37
50	37	11	4	1
51	33	18	8	1
52	100	48	27	7
53	9	8	5	1
63	12	21	7	2
64	6	18	10	3
65	5	17	11	6
71		1	6	9
73	1	1	7	9
77	6	11	8	3
79	4	6	4	2
80	83	100	71	28
81	11	18	12	4
91		6	8	2
92		6	4	2
108	12	31	23	16
109	5	6	7	5
110	3	18	11	7
121	11	92	75	35
135	1	5	5	3
136	48[b]	94	100	100
149			1	1
154			1	1
180		80[b]	2	6
224			54[b]	3
268				3
312				18[b]

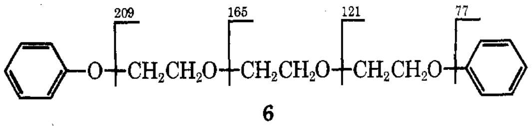
[a] Peaks with relative abundance ≥5 in the spectrum of at least one compound are included for m/e 41–140, and all peaks with m/e >140 are listed. Peaks due solely to isotope contributions in the spectra of all compounds are not listed, however. [b] Molecular ion.

Table II
Elemental Compositions of Fragment Ions in the Mass Spectrum of 5

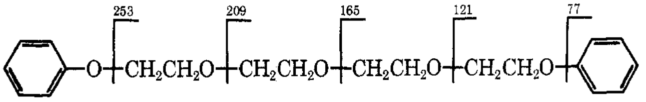
Mass	Composition	Mass	Composition
268	$C_{14}H_{22}O_5$	110	$C_6H_6O_2$
224	$C_{12}H_{18}O_4$	109	$C_6H_5O_2$
180	$C_{10}H_{14}O_3$	108	$C_6H_4O_2$
136	$C_8H_{10}O_2$	80	C_5H_4O
121	$C_7H_5O_2$		

2, **3**, and **4** also displayed series of peaks corresponding to the formal loss of C_2H_4O units from M to yield a peak at m/e 136 as the terminus in the sequence in each case. This sequence of peaks starting with M and ending with m/e 136 with members separated by 44 mass units is unusual and diagnostic for benzo-3*n*-crown-*n* ethers.

Open-chain analogs of **3** and **4** are represented by 1,8-diphenoxy-3,6-dioxaoctane (**6**) and 1,11-diphenoxy-3,6,9-trioxaundecane (**7**), respectively, and their mass spectra are compiled in Table III (Experimental Section). Peaks were not observed at M − 44 (m/e 258) and M − 88 (m/e 214) with **6** nor at M − 44 (m/e 302), M − 88 (m/e 258), and M − 132 (m/e 214) with **7** as they were with **3** and **4**, respectively. However, starting with the peak at m/e 253 in the spectrum of **7**, a series was observed at m/e 209, 165, 121, and 77, which corresponds to the loss of one, two, three, and four C_2H_4O units, respectively. Likewise, starting with m/e 209 in the spectrum of **6**, an analogous series was observed at m/e 165, 121, and 77. Possible fragmentations leading to the above series with **6** and **7** are indicated.



6



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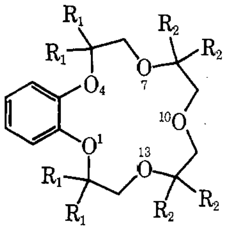
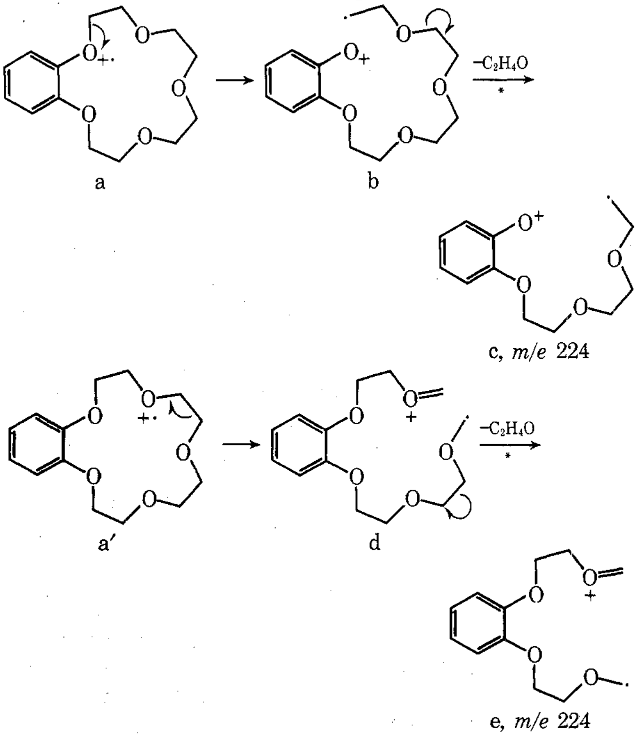
The mass spectra of deuterated crown ethers **4a** and **4b** are given in Figures 2 and 3, respectively. With the use of these spectra and high-resolution data of Table II[14] it is possible to formulate plausible fragmentation pathways for **4**. The formal loss of C_2H_4O units from M of **4** to give peaks at m/e 224, 180, and 136 can occur by several routes.



4, $R_1 = R_2 = H$
4a, $R_1 = D$; $R_2 = H$
4b, $R_1 = H$; $R_2 = D$

The mass spectrum of **4a** displayed peaks at m/e 226 and 228 and that of **4b** a peak at m/e 228. These results indicate that with **4**, C-8 and C-12 are not involved in the process M − C_2H_4O to give a peak at m/e 224 and C-5, C-9, C-11, and C-15 are. A metastable transition was observed for this process, and a combination of the two mechanisms outlined in Scheme I is consistent with the deuterium la-

Scheme I



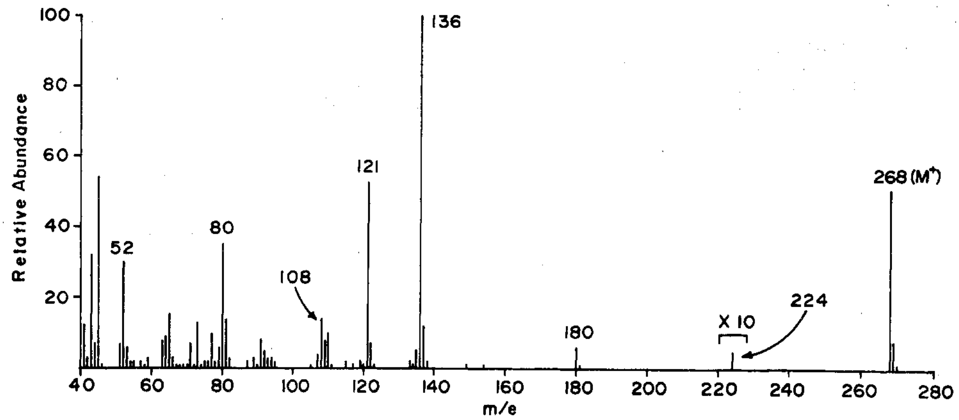


Figure 1. Mass spectrum of 4.

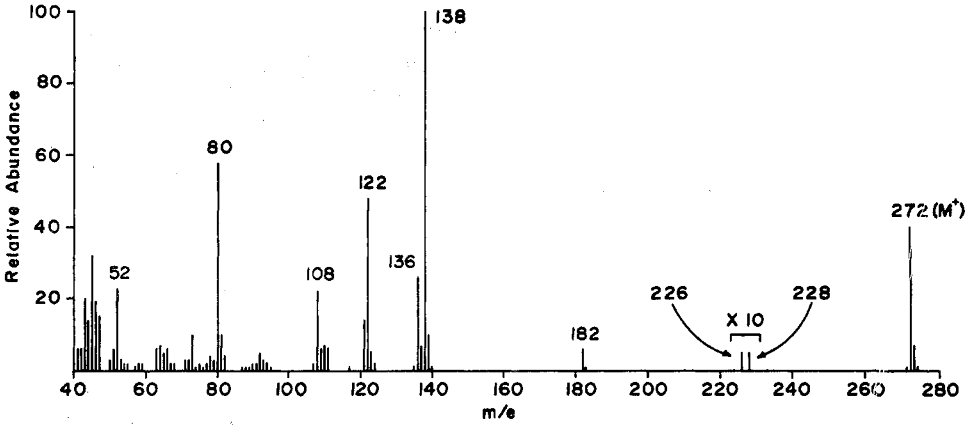


Figure 2. Mass spectrum of 4a.

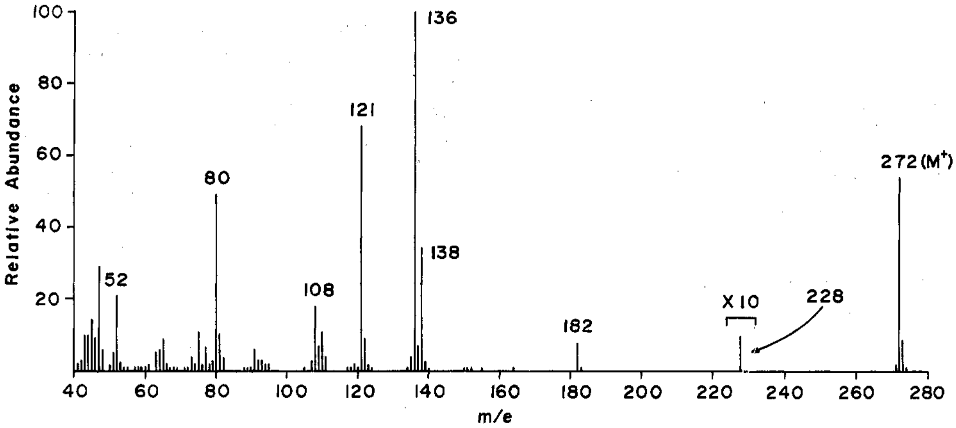


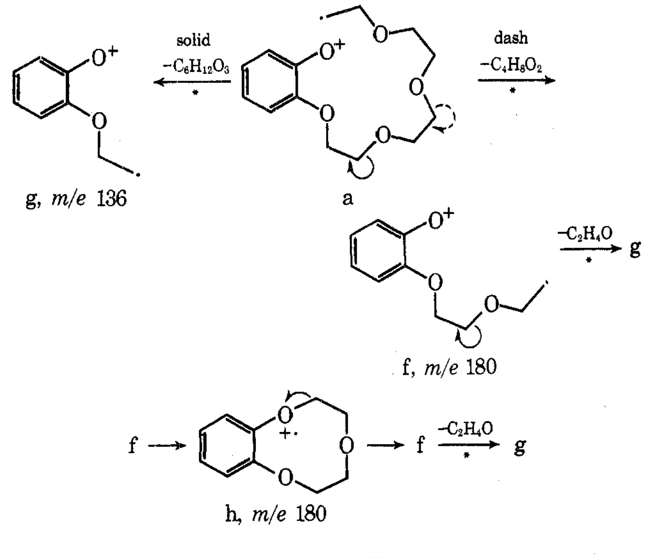
Figure 3. Mass spectrum of 4b.

beling results.[15] The pathway to ion c involves initial cleavage of the bond between O-4(1) and C-5(15) in a[16] and that to ion e involves initial α cleavage of the bond between C-8(12) and C-9(11) in a′.

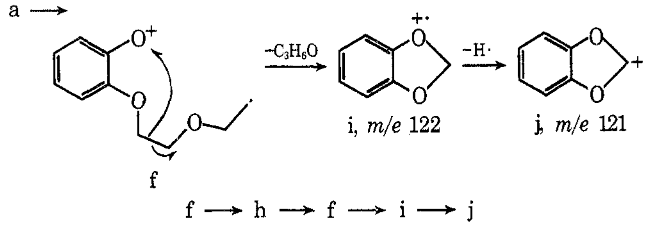
A metastable transition was observed for the process M − $C_4H_8O_2$ to give the *m/e* 180 peak with **4**. In the spectra of **4a** and **4b** a peak was observed at *m/e* 182. Additionally, with **4** metastable transitions were observed for the processes *m/e* 268 and *m/e* 180 → *m/e* 136. In the spectra of both **4a** and **4b** peaks were displayed at *m/e* 136 and 138. Mechanisms for generation of mass 136 and 180 ions are given in Scheme II. Formation of the mass 180 ion f can be rationalized in a straightforward manner as indicated. The pathway for formation of the mass 136 ion is more complicated since spectra of both **4a** and **4b** contained peaks at *m/e* 136 and 138. Therefore, ion a and ion f formed *directly* from a cannot be the only precursors of the mass 136 ion since **4a** would yield *only* an ion of *m/e* 138 and **4b** *only* an ion of *m/e* 136. It is proposed that ion f closes to give h, the molecular ion of **2**. Then h opens to regenerate ion f and subsequently g. However, this pathway through h cannot be the *sole* route to the mass 136 ion because the *m/e* 136 and 138 peaks in spectra of **4a** and **4b** would be expected to be approximately equal in intensity, which they clearly are not. In the spectrum of **4a** the ratio of intensity of the *m/e* 138 peak to that of the *m/e* 136 peak was 1:0.26 whereas in the spectrum of **4b** the ratio was 0.34:1. A combination of the above three pathways to g is consistent with the deuterium labeling results. It is proposed that all or a portion of ion f produced directly from a closes to give h and subsequently g; any remainder can lead *directly* to g.

The peaks at *m/e* 121, 110, 109, 108, 80, and 52 in the spectrum of **4** are also characteristic of benzo-3*n*-crown-*n* ethers. In the spectrum of **4a** peaks were observed at *m/e* 121 and 122 and in that of **4b** a peak was observed at *m/e* 121. Pathways for formation of the mass 121 ion are given

Scheme II



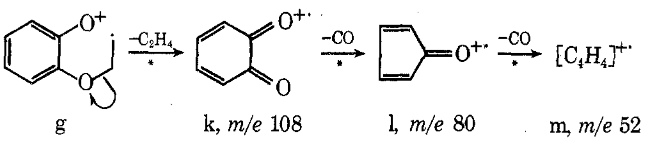
Scheme III



in Scheme III. Although neither a discrete peak at *m/e* 122 nor a metastable peak at *m/e* 120.0 for the process *m/e* 122 → 121 was observed, ion i is a reasonable intermediate in the formation of ion j.[17] Formation of j *directly* from a through f and i cannot be the *only* route because the spectrum of **4a** displayed peaks at *m/e* 121 *and* 122. However, a combination of this route and the second of Scheme III which involves closure of f to h and regeneration of f is consistent with the deuterium labeling results. Such a combination is also compatible with the blend of mechanistic pathways proposed for formation of the mass 136 ion in Scheme II.

Metastable transitions were observed for the *m/e* 136 → 108, *m/e* 108 → 80, and *m/e* 80 → 52 processes in the spectrum of **4**. In Scheme IV plausible mechanistic pathways

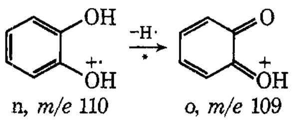
Scheme IV



are given for the formation of ions of mass 108, 80, and 52. It is certainly possible that ion g closes to form the molecular ion of **1** before ethylene is lost to give k. Ions k, l, and m were also implicated in the mass spectral fragmentation of *o*-phenylene sulfite.[18]

A metastable transition was observed for the *m/e* 110 → 109 process in the spectrum of **4**. In Scheme V plausible

Scheme V



structures are given for the mass 110 and 109 ions. In the spectra of both **4a** and **4b** a peak was observed at *m/e* 111 which is not found in that of **4**. The mechanistic pathway(s) leading to ion n cannot be formulated with certainty although in at least one precursor hydrogen transfer from what was initially C-5(15) or C-8(12) must take place. Ions i, j, k, l, m, n, and o were also indicated as fragment ions in the electron impact induced fragmentation of a series of homologous catechol polymethylene diethers.[10a] Ring opening and subsequent closure to yield i and j were proposed.

In formation of all of the preceding ions no deuterium scrambling was detected either between methylene positions or between aromatic and methylene positions. The mechanistic pathways given are in part supported by metastable data. Other routes consistent with the deuterium labeling data for which metastable transitions were not observed certainly could be operative also. In the mass spectra of **1–3** and **5** many metastable transitions were detected identical with those of **4**, and all important metastable transitions for **1–5** are given in the Experimental Section. It can be reasonably assumed that electron impact induced fragmentation pathways for **1–3** and **5** are analogous and in some cases identical with those of **4**.

Experimental Section

General. Low-resolution mass spectra were recorded with a Varian MAT CH-5 spectrometer. The ionizing voltage was 70 eV, the filament current, 300 μA, and the ion-source temperature, 150°. Compound **1** was introduced by heated inlet with inlet temperature 200°, and all other compounds by direct insertion with probe temperature 12–85°. High-resolution mass spectra were recorded with a Du Pont 21-110B spectrometer and processed with a Grant microdensitometer. The pmr spectra were obtained with a Varian HA-100 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Three columns were employed for analyses and preparative separations by vpc: column A, 5 ft × 0.25 in. stainless steel column packed with 3% SE-30 on 100–120 mesh Varaport 30; column B, 5 ft × 0.25 in. stainless steel column packed with 1% OV-101 on 100–120 mesh Chromosorb G; column C, 6 ft × 0.25 in. aluminum column packed with 1% SE-30 on 60–80 mesh AW-DMCS Chromosorb W. All melting and boiling points are uncorrected. Microanalyses were performed by Huffman Laboratories, Wheat Ridge, Colo.

Catechol Ethylene Diether, 2,3-Benzo-1,4-dioxacyclohexa-2-ene (1). Compound **1**, bp 94–95° (12 mm), lit.[11] 125° (25 mm), was prepared as previously described,[11] and preparative vpc (column A, 100°) yielded a sample for mass spectrometry.

2,3-Benzo-1,4,7-trioxacyclonona-2-ene, Benzo-9-crown-3 (2). Crown ether **2**, mp 66–67° (hexane), lit.[2a] 67–69°, was prepared as previously described,[2a] and preparative vpc (column A, 125°) yielded a sample for mass spectrometry.

2,3-Benzo-1,4,7,10-tetraoxacyclododeca-2-ene, Benzo-12-crown-4 (3). Crown ether **3**, mp 46–46.5°, lit.[2a] 44–45.5°, was prepared as previously described[2a] and employed for mass spectrometry. By vpc (column B, 240°) **3** was homogeneous.

2,3-Benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene, Benzo-15-crown-5 (4). Crown ether **4**, mp 79.5–80° (hexane), lit.[2a] 79–79.5°, was prepared as previously described[2a] and employed for mass spectrometry. By vpc (column B, 240°) **4** was homogeneous.

2,3-Benzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2-ene, Benzo-18-crown-6 (5). Crown ether **5**, mp 43.5–44° (hexane), lit.[2a] 43–44°, was prepared as previously described[2a] and employed for mass spectrometry. By vpc (column B, 240°) **5** was homogeneous.

2,3-Benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene- *5,5,15,15-*d_4 **(4a).** To a stirred slurry of 0.60 g (25 mmol) of NaH in 100 ml of dimethoxyethane under nitrogen was added 2.66 g (25.0 mmol) of diethylene glycol followed by 4.18 g (25.0 mmol) of ethyl bromoacetate after gas evolution ceased. The mixture was refluxed for 4 hr, 0.60 g of NaH and then 4.18 g of ethyl bromoacetate were added, and reflux was continued for 12 hr. The mixture was filtered and concentrated by rotary evaporation, and the residue was fractionally distilled to yield 1.5 g (21%) of diethyl 3,6,9-trioxaundecanedicarboxylate, bp 126–128° (0.05 mm). The pmr spectrum of the diester displayed a triplet at δ 1.22 (J = 7 Hz, 6 H, CH_3); a singlet at δ 3.63 (8 H, CH_2CH_2); and a singlet at δ 4.05 (OCH_2CO_2)

overlapping with a quartet at δ 4.13 (J = 7 Hz, CH_2OCO, 8 H total). For elemental analysis a sample was purified by preparative vpc (col C, 175°).

Anal. Calcd for $C_{12}H_{22}O_7$: C, 51.79; H, 7.97. Found: C, 51.85; H, 8.08.

Reduction of 2.50 g (9.00 mmol) of the above diester with 0.53 g (13 mmol) of $LiAlD_4$ (99% D) in ether gave 1.30 g (73%) of 3,6,9-trioxaundecane-1,11-diol-*1,1,11,11-d*$_4$ which was converted (62%) to 3,6,9-trioxaundecane-1,11-diol-*1,1,11,11-d*$_4$ di-*p*-toluenesulfonate using the procedure[19] for perprotio material.

Under nitrogen with stirring, a mixture of 148 mg (3.70 mmol) of NaOH, 193 mg (1.75 mmol) of catechol, and 0.77 g (1.5 mmol) of the above di-*p*-toluenesulfonate in 0.18 ml of water and 2.8 ml of 1-butanol was refluxed for 26 hr. After addition of 0.04 ml of concentrated hydrochloric acid, the reaction mixture was filtered and rotary evaporated. The residue was extracted with hexane to yield 300 mg of crude **4a** as an oil which was purified by column chromatography on silica gel packed in hexane. Elution with 75% ether–hexane yielded **4a** which was recrystallized from hexane to give **4a**, mp 79–80°, lit.[2a] for **4**, 79–79.5°. The pmr spectrum of **4a** displayed a singlet at δ 3.68 (8 H, CH_2CH_2); a singlet at δ 3.82 (4 H, CD_2CH_2); and a singlet at δ 6.81 (4 H, aromatic). The pmr spectrum of **4** was identical except that the singlet at δ 3.82 was replaced by an A_2B_2 pattern with multiplets at δ 3.78–3.93 (4 H) and δ 4.01–4.18 (4 H).

2,3-Benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene-*8,8,12,12-d*$_4$ (4b). Esterification of 2,2′-oxydiacetic acid (MCB) in absolute methanol with concentrated sulfuric acid as catalyst yielded (58%) dimethyl 2,2′-oxydiacetate, mp 36–38°, lit.[20] 36°.

Reduction of 9.00 g (55.6 mmol) of dimethyl 2,2′-oxydiacetate with 2.5 g (60 mmol) of $LiAlD_4$ (99% D) in ether gave 2.94 g (48%) of 3-oxapentane-1,5-diol-*1,1,5,5-d*$_4$. The pmr spectrum of this material displayed a singlet at δ 3.49 (4 H) and a broad peak at δ 4.25 (2.5 H) whereas that of perprotio material displayed an A_2B_2 pattern centered at δ 3.58 (8 H) and a sharp singlet at δ 4.60 (2 H).

The crude 3-oxapentane-1,5-diol-*1,1,5,5-d*$_4$ was converted (71%) to bis-2-chloroethyl-*2,2-d*$_2$ ether with the general procedure of Perry and Hibbert.[21] The pmr spectrum of this material displayed a singlet at δ 3.69 whereas that of perprotio material displayed an A_2B_2 pattern centered at δ 3.61.

The bis-2-chloroethyl-*2,2-d*$_2$ ether was converted (~74%) to 3,6,9-trioxaundecane-1,11-diol-*4,4,8,8-d*$_4$ using a modified procedure of Perry and Hibbert.[21] In dry glassware under nitrogen 1.06 g (46.2 mmol) of clean Na was dissolved in 18.0 ml (0.32 mol) of ethylene glycol. To the stirred solution at 75° was added dropwise during 10 min 2.76 g (19.4 mmol) of bis-2-chloroethyl-*2,2-d*$_2$ ether. The mixture was then stirred at 75° for 23 hr, diluted with absolute ethanol and ether, and filtered to remove precipitated NaCl. The filtrate was concentrated by rotary evaporation, and the residue, pH 10, was neutralized to pH 7 with 10% hydrochloric acid. From the resulting mixture water and excess ethylene glycol were removed by fractional distillation to leave a residue containing NaCl. This material was diluted with absolute ethanol, filtered, and concentrated by rotary evaporation to leave 2.77 g of crude 3,6,9-trioxaundecane-1,11-diol-*4,4,8,8-d*$_4$ containing a small amount of NaCl.

Without further purification 1.5 g (7.6 mmol) of the above diol was converted[20] to 2.8 g (73%) of 3,6,9-trioxaundecane-1,11-diol-*4,4,8,8-d*$_4$ di-*p*-toluenesulfonate. With the procedure for **4a**, 2.80 g (5.54 mmol) of di-*p*-toluenesulfonate yielded 0.45 g (30%) of crystalline **4b** which was recrystallized three times from hexane to give **4b**, mp 78.5–79.5°, lit.[2a] for **4**, 79–79.5°. The pmr spectrum of **4b** displayed a singlet at δ 3.67 (4 H, CD_2CH_2); an A_2B_2 (CH_2CH_2) pattern with multiplets at δ 3.78–3.90 (4 H) and δ 3.99–4.15 (4 H); and a singlet at δ 6.80 (4 H, aromatic).

1,8-Diphenoxy-3,6-dioxaoctane (6). A solution of 8.00 g (0.200 mol) of NaOH, 18.8 g (0.200 mol) of phenol, and 9.35 g (0.050 mol) of 1,8-dichloro-3,6-dioxaoctane (Baker) in 40 ml of 50% aqueous ethanol was refluxed for 16 hr. The solution was filtered, and an ether solution of the filtrate was washed twice with 5% aqueous NaOH, twice with water, and once with saturated aqueous NaCl, and dried ($MgSO_4$). Rotary evaporation of ether left 9.72 g (64%) of crystalline material which was recrystallized twice from aqueous ethanol to give **6**, mp 43.5–45°. The pmr spectrum of **6** displayed a singlet at δ 3.64 (4 H, $CH_2OC\mathit{H}_2C\mathit{H}_2OCH_2$); an A_2B_2 pattern with multiplets at δ 3.68–3.84 and 3.94–4.12 (8 H total, $C_6H_5OC\mathit{H}_2C\mathit{H}_2O$); a multiplet at δ 6.73–6.98 (6 H, ortho and para); and a multiplet at δ 7.07–7.30 (4 H, meta). For mass spectrometry and elemental analysis samples were purified by preparative vpc (column C, 200°).

Table III
Mass Spectra of Open Chain Analogs 6 and 7[a]

Ion	Relative Abundance		Ion	Relative Abundance	
m/e	6	7	m/e	6	7
41	8	12	103	8	9
43	22	25	105	6	5
44	11	11	106	6	1
45	31	58	107	6	9
47	13		118	5	
49	6		119	6	8
50	37	8	120	19	42
51	53	20	121	61	73
52	22	3	127	1	
54		5	128	1	
55	9		133	2	8
59	5	7	135	2	3
62	5	2	136	1	1
63	15	5	137	1	1
65	37	40	138	2	3
66	22	24	147	2	3
71	2	6	149	1	2
73	10	17	151	1	2
74	5	2	159		2
76	5	2	164	3	5
77	100	100	165	4	11
78	53	10	166	1	2
79	10	8	182	8	2
87	1	7	208	2	1
89	5	8	209	6	1
91	33	31	253		2
92	7	3	302	10[b]	
93	48	59	346		8[b]
94	30	36			

[a] Peaks with relative abundance ≥5 in the spectrum of either ether are included for m/e 41–121, and all peaks with m/e >121 are listed. Peaks due solely to isotope contributions in the spectra of both ethers are not listed, however. [b] Molecular ion.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.34. Found: C, 71.26; H, 7.40.

1,11-Diphenoxy-3,6,9-trioxaundecane (7). With the procedure for **6**, 1,11-dichloro-3,6,9-trioxaundecane[2a] was converted (39%) to **7**, isolated as an oil. The pmr spectrum of **7** displayed a singlet at δ 3.58 (8 H, $CH_2O(C\mathit{H}_2C\mathit{H}_2O)_2CH_2$); an A_2B_2 pattern with multiplets at δ 3.66–3.86 and 3.94–4.12 (8 H total, $C_6H_5OC\mathit{H}_2C\mathit{H}_2O$); a multiplet at δ 6.75–6.96 (6 H, ortho and para); and a multiplet at δ 7.08–7.32 (4 H, *meta*). For mass spectrometry and elemental analysis samples were purified by preparative vpc (column C, 250°).

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.16; H, 7.58.

Important Metastable Transitions in the Mass Spectra of 1–5. For **1**, **2**, **3**, and **4** a metastable transition was observed for the process m/e 80 → 52. For all compounds metastables were observed for m/e 110 → 109, m/e 108 → 80, and m/e 136 → 108. For **2**, **3**, **4**, and **5** a metastable was observed for m/e 180 → 136. For **3** metastables were observed for m/e 224 → 136 and 180; for **4** metastables for m/e 268 → 180 and 224; and for **5** a metastable for m/e 312 → 268.

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Registry No.—**1**, 493-09-4; **2**, 17454-39-6; **3**, 14174-08-4; **4**, 14098-44-3; **4a**, 53129-26-3; **4b**, 53129-27-4; **5**, 14098-24-9; **6**, 53129-28-5; **7**, 20768-77-8; diethylene glycol, 111-46-6; ethyl bromoacetate, 105-36-2; diethyl 3,6,9-trioxaundecanedicarboxylate, 53129-29-6; 3,6,9-trioxaundecane-1,11-diol-*1,1,11,11-d*$_4$, 53129-30-9; 3,6,9-trioxaundecane-1,11-diol-*1,1,11,11-d*$_4$ di-*p*-toluenesulfonate, 53129-31-0; 2,2′-oxydiacetic acid, 110-99-6; 3-oxapentane-

1,5-diol-*1,1,5,5-*d_4, 53129-32-1; dimethyl 2,2′-oxydiacetate, 7040-23-5; 3,6,9-trioxaundecane-1,11-diol-*4,4,8,8-*d_4 di-*p*-toluenesulfonate, 53129-33-2; bis-2-chloroethyl-*2,2-*d_2 ether, 53129-34-3; 3,6,9-trioxaundecane-1,11-diol-*4,4,8,8-*d_4, 53129-35-4; phenol, 108-95-2; 1,8-dichloro-3,6-dioxaoctane, 112-26-5; 1,11-dichloro-3,6,9-trioxaundecane, 638-56-2.

References and Notes

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(12) The mass spectrum of **1** has been reported previously.[10a]
(13) Trivial names as suggested by Pedersen[2a] are employed for this and other cyclic polyethers. Systematic names are given in Experimental Section.
(14) The reasonable assumption is made that elemental compositions of fragment ions of **4** are identical with those of isobaric fragment ions of **5**.
(15) Structural identities of the C_2H_4O species lost are uncertain. They could be open chain species as indicated, or ring closure concomitant with bond cleavage would yield ethylene oxide.
(16) A mechanism initiated by cleavage of the bond between O-4(1) and C-5(15) of **a** with charge retention by carbon cannot be distinguished from that given. It is also possible but unlikely that initial cleavage in **a** involves the bond between O-4(1) and C-3(2).
(17) However, the mass spectrum (70 eV) of catechol methylene diether displays a molecular ion (*m/e* 122) with relative intensity ~75; the base peak is at *m/e* 121.[10a]
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Electrochemical and Electron Spin Resonance Studies of the Dibenzonorcaradiene Anion Radical

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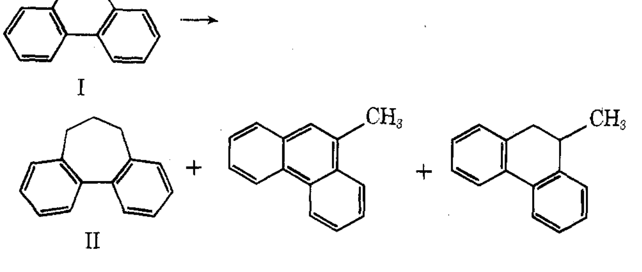
Electrochemical and esr studies of dibenzonorcaradiene have been carried out. Cyclic voltammetry data and esr hyperfine coupling constants are consistent with the reversible formation of a stable radical anion which does not undergo rapid isomerization to the anion radical of dibenzo[*a,c*]cycloheptatriene. Possible mechanisms for the cyclopropane ring opening in the parent radical anion are discussed in terms of correlation diagrams.

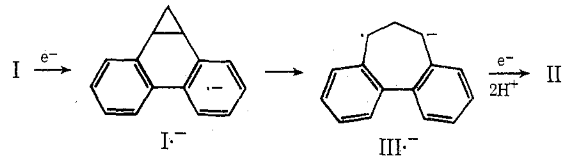
Isomerization reactions of ion radicals have received limited attention but are of some theoretical interest. In particular, a model to handle the influence of orbital symmetry on reactions of these open-shell species has not been well defined. With this in mind, the electron-transfer reduction of dibenzonorcaradiene (DBNC) had been investigated previously.[1] The reduction products from I and sodium in glyme include dibenzo[*a,c*]cycloheptadiene, II.



I

II

This product might arise from the concerted reaction



$\mathrm{I}\cdot^{-}$ $\mathrm{III}\cdot^{-}$

As described earlier[1] the bond cleavage is sterically constrained to occur in a disrotatory fashion and thus the presence or absence of this mechanism provides a test of the influence orbital symmetry considerations on the paths of ion radical isomerizations.

A correlation diagram for the $\mathrm{I}\cdot^{-} \rightarrow \mathrm{III}\cdot^{-}$ reaction (*vide infra*) predicts the product of the allowed thermally initiated reaction will be electronically excited $\mathrm{III}\cdot^{-}$ while the forbidden photochemical product will be ground-state $\mathrm{III}\cdot^{-}$. Using a combination of cyclic voltammetry and electron spin resonance spectroscopy, we will show below that neither of these processes actually occurs.