MASS-SPECTROMETRIC INVESTIGATION OF IONOPHORIC DERIVATIVES OF BENZO- AND DIBENZOCROWN ETHERS.

4.* 4'-ACYL DERIVATIVES OF BENZO-15-CROWN-5 AND BENZO-18-CROWN-6

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The mass spectra of 4'-acyl derivatives of benzo-15-crown-5 and benzo-18-crown-6 were studied by the method of direct analysis of the daughter ions (DADI). It was established that the fragmentation of the M^+ ions of the investigated compounds under electron impact proceeds via the scheme of the McLafferty rearrangement with the simultaneous elimination of ethylene oxide. The degree of occurrence of the McLafferty rearrangement increases with an increase in the length of the side chain.

In a continuation of our research on the mass spectrometry of derivatives of crown ethers [1-3] we investigated the 4'-acetyl, 4'-propionyl, 4'-butyryl, 4'-valeryl, and 4'-hexanoyl derivatives (I-V) of benzo-15-crown-5 and 4'-acetyl, 4'-propionyl, 4'-butyryl, and 4'-valeryl derivatives (VI-IX) of benzo-18-crown-6.

Intense molecular-ion peaks (M^+) and a number of low-intensity peaks of ions corresponding to the elimination of one or several molecules of ethylene oxide appear in the mass spectra of these compounds. The fragmentation of the polyether ring terminates with the formation of an acetyl-substituted benzodioxane with m/z 178. The latter is the precursor of the ion with m/z 163, the peak of which in the mass spectra of I-IX has the highest intensity (Table 1).

Another pathway of the fragmentation of the M^+ ions of these compounds involves cleavage of the side chain. The length of the acyl residue has an appreciable effect on this cleavage. Thus, for example, the fragmentation of the acetyl (I, VI) and propionyl (II, VII) derivatives proceeds only through simple cleavage of the C—C bonds with splitting out of, respectively, methyl and ethyl radicals from the M^+ ions and other fragment ions. This fragmentation pathway is not displayed in the DADI spectra of the M^+ ions of I, II, VI, and VII. As an illustration, in Fig. 1a we present the DADE spectrum [4, 5] of the M^+ ion of I, which consists only of peaks of ions with m/z 266 (F_3), 222 (F_2), and 178 (F_1), which correspond to contraction of the polyether ring via the elimination of one, two, or three molecules of ethylene oxide.

Commencing with the butyryl derivatives of the crown ethers, peaks of ions that develop both through the McLafferty rearrangement [6-8] or simple detachment of the alkyl radical of the side chain and through the formation of F_1-F_n fragments (n = 2, 3, 4) appear in the mass spectra as the side chain is increased by a CH_2 group; this is apparent from the DADI spectrum of the M^+ ions of V (Fig. 1b).

Its fragmentation proceeds via the competitive pathways indicated above. These pathways are the elimination of ethylene oxide molecules from the M^+ ion, which leads to ions with m/z 322, 278, and 234, the elimination of a neutral butylene molecule with migration of hydrogen to the α-carbon atom, i.e., the McLafferty rearrangement (the intense ion peak with m/z 310), and splitting out of an alkyl fragment (the ion with m/z 295). The simultaneous occurrence of a rearrangement process and contraction of the macrocyclic ring lead to ions with m/z 266, 222, and 178. It should be noted that the longer the side chain, the more intense the peaks of the rearrangement process.

Similar patterns are observed in the DADI spectra of the M^+ ions of III-V, VIII, and IX. Both the mass spectra and the DADI spectra of the M^+ ions of I and IV, as well as III-V, VIII,

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*See [3] for communication 3.

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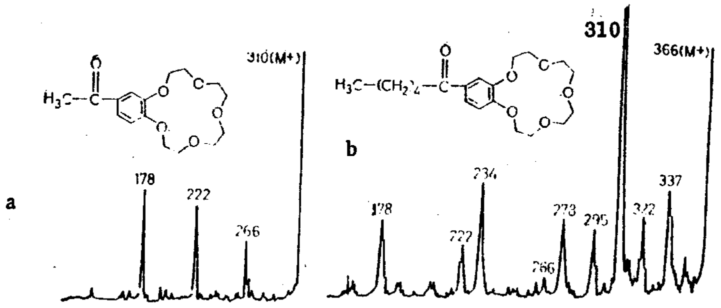


Fig. 1. DADI spectra of the M^+ ions of I (a) and V (b).

TABLE 1. m/z Values (relative intensities, %) of the M^+ Peaks and the Characteristic Ions in the Mass Spectra of I-IX

Compound	M^+	F_4	F_3	F_2	F_1	Other characteristic ion peaks
I	310 (70)	—	266 (2)	222 (10)	178 (36)	163 (100), 135 (12)
II	324 (32)	—	280 (2)	236 (8)	192 (9)	295 (6), 251 (3), 207 (18), 163 (100), 135 (24)
III	338 (36)	—	294 (2)	250 (6)	206 (10)	310 (3), 295 (4), 251 (5), 207 (20), 163 (100), 135 (20)
IV	352 (43)	—	308 (4)	264 (1)	220 (2)	336 (2), 310 (16), 295 (12), 266 (4), 251 (4), 222 (18), 207 (12), 178 (65), 163 (100), 135 (9)
V	366 (36)	—	322 (2)	278 (2)	234 (4)	310 (18), 295 (14), 266 (7), 251 (4), 222 (18), 207 (10), 178 (74), 163 (100), 135 (16)
VI	354 (12)	310 (8)	266 (4)	222 (9)	178 (36)	163 (100), 135 (12)
VII	368 (15)	324 (1)	280 (2)	236 (3)	192 (7)	339 (1), 295 (1), 251 (3), 207 (7), 163 (100), 135 (3)
VIII	382 (17)	338 (2)	294 (2)	250 (1)	206 (2)	295 (2), 251 (6), 207 (12), 178 (12), 163 (100), 135 (3)
IX	396 (17)	352 (5)	308 (3)	264 (2)	220 (4)	354 (5), 310 (9), 266 (2), 222 (18), 178 (82), 163 (100), 135 (15)

and IX, in which the occurrence of the McLafferty rearrangement under the influence of electron impact is possible, contain an ion peak with m/z 178, which corresponds to the molecular ion of 4'-acetylbenzodioxane; the peak of this ion has a tendency to increase as the acyl chain becomes longer. In acetyl derivatives of the crown ethers it is formed only through contraction of the macrocycle from M^+ and fragments of F_2 and its higher analogs. In other cases the indicated pathway alone is not sufficient for its manifestation, and the simultaneous occurrence of the McLafferty rearrangement in the molecular ion and fragments of the F type is still necessary.

One should have expected that this different way of development of the ion from the M^+ ions of the indicated compounds should be reflected in redistribution of their initial kinetic energies. This, in turn, should be displayed in the DADI spectra of the ion with m/z 178, which has different pathways of formation and different precursors. In fact, a comparison of the DADI spectra of the ion with m/z 178 that is formed from I and VI showed that they are identical. The spectra contain one lone peak of extremely high intensity that corresponds to splitting out of a methyl radical (the ion with m/z 163). The high intensity of this ion indicates the primarily rearrangement character of its formation, i.e., through contraction of the benzodioxane ring, as we previously observed in a number of different derivatives of crown ethers [1-3].

Although the ion peak with m/z 163 has the maximum intensity in the DADI spectra of this ion, which is formed from V (Fig. 2a) and IX (Fig. 2b), other ion peaks with m/z 153, 136, and 119 (Fig. 2b) and 156, 154, 143, 142, and 136 (Fig. 2a) appear in the spectra along with it. It is difficult to explain the m/z values and the unusually narrow forms of the ion peaks with m/z 119, 142, 143, and 156. The reproducibility of these spectra was proved by repeated recording of them (see scheme on following page).

As noted above, the ion peak with m/z 163 in both the mass spectra and the DADI spectra of the ion with m/z 178 has an extremely high intensity, which indicates its high stability.

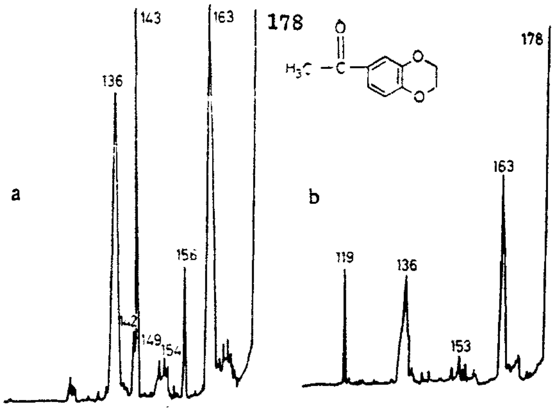
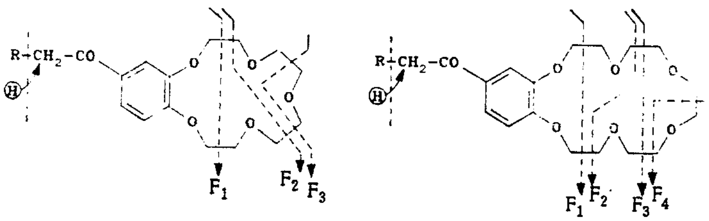


Fig. 2. DADI spectra of the ion with m/z 178 for V (a) and IX (b).

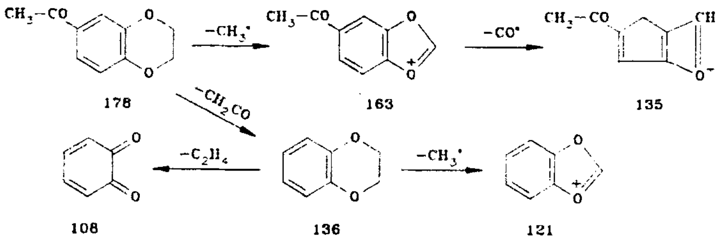
General Fragmentation Scheme



Acylbenzo-15-crown-5 Acylbenzo-18-crown-6

In the DADI spectrum the ion peak with m/z 163 has the same form, regardless of the substance from which it is formed, and consists of ion peaks with m/z 135 (maximally intense), 149, and 154.

The pathways of the fragmentation of the ions with m/z 178 and 163, which were established from their DADI spectra, are presented in the scheme.



Thus it was established by the DADI method that the fragmentation of the M^+ ions of 4'-acyl derivatives of benzo-15-crown-5 and benzo-18-crown-6 under electron impact proceeds via the scheme of the McLafferty rearrangement with the simultaneous elimination of ethylene oxide molecules from the macrocycle.

Judging from the DADI spectra of the investigated compounds, the degree to which the McLafferty rearrangement occurs increases with an increase in the length of the side chain.

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT-311 mass spectrometer with an SS-100 MS system for data processing; the ionizing-electron energy was 70 eV, the accelerating voltage was 3 kV, the sample-vaporization temperature was 50-80°C, and the ionizing-chamber temperature was 150°C. In the DADI spectra the mass of each daughter ion (m_2) was calculated from the formula

$$m_2 = m_1 \cdot (E_1/E_0),$$

where m_1 is the mass of the ion of the precursor, E_1 is the voltage of the electrostatic field at which m_2 was recorded, and E_0 is the starting voltage of the electrostatic analyzer at which m_1 was recorded.

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SYNTHESIS, STRUCTURES, AND REDOX PROPERTIES OF SOME NEW DITHIOCARBAMATES THAT INCLUDE A HETEROAROMATIC RING

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New Cu, Ni, Pb, Zn, Co. Fe, Mn, Sb, and Bi dithiocarbamates that include 2-thenyl and 2-furfuryl radicals were synthesized. The potentials of polarographic oxidation on a rotating platinum electrode were determined for them and for the previously synthesized N-substituted unsymmetrical dithiocarbamates of the same metals. The results of x-ray diffraction analysis of bis-(di-2-thenyldithiocarbamato)nickel(2^+) are presented and discussed.

It is known [1, 2] that chelate compounds of metals having a variable valence with sulfur-containing M(N, S) and M(S, S) chelate nodes inhibit the oxidation of hydrocarbons by oxygen and stabilize a number of polymers under conditions of thermal-oxidative destruction and photodestruction. A correlation between the inhibiting activity and the potentials of polarographic oxidation of chelates has been established for some classes of such chelate compounds [3]. In this connection the synthesis of compounds of this type and the investigation of their properties and inhibiting activities are of considerable interest.

In the present research we accomplished the synthesis of 12 new dithiocarbamates (XIII-XXIV) by the successive conversion of furfural (I) or 2-formylthiophene (II) to azomethines (III, IV) [4, 5] and amines (VIII, IX) (see Table 1).

By reducing azomethines III and IV in the presence of $NaBH_4$ we attempted to obtain amine V (X = O) and its thiophene analog VI (X = S). However, according to the results of gas-liquid chromatography (GLC), V and VI were not detected in the reduction products, and only amines VIII and IX were isolated.

Amine V, which is the product of hydrogenation of azomethine III over platinum [6], is not converted to ligand VII ($M_1 = NH_4$, Na, or K), evidently because of steric hindrance. Amines VIII and IX, the structures of which are similar to the structure of amine V, are readily converted to alkali-metal salts of N,N-disubstituted dithiocarbamic acids.

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