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STUDIES IN ORGANIC MASS SPECTROMETRY—XXIV[a]

EVIDENCE FOR THE GAS PHASE OCCURRENCE OF THE O-METHYL TETRAHYDROFURANIUM ION

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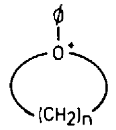
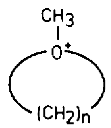
Abstract—The electron impact induced loss of a phenoxy radical from the molecular ions of ω-phenoxyalkyl methylethers $\phi O(CH_2)_nOCH_3$ (I_n; n = 2–6) is the result of a functional group interaction. Labeling data provide evidence for the O-methyl tetrahydrofuranium structure of the resulting decomposing species (lifetime between 10^{-6} and 10^{-5} sec) in the case of $n = 4$.

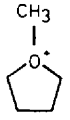
In a recent communication[1] we have reported evidence for the gas phase existence of cyclic O-phenyl oxonium ions **1**$_n$ (n = 4, 5) in the lifetime window 10^{-6}–10^{-5} sec (unimolecular metastables). To our knowledge these species have not yet been demonstrated in the solute phase, although related ions such as (i) the dimethylphenyloxonium ion[2] and (ii) the O-methyldihydrobenzofuranium[3] and chromanium[3] ions can exist in solution. As a result of this discrepancy between gas and solute phases, we decided to investigate the well known cyclic O-methyl oxonium ions **2**$_n$,[3,4] which in some instances have been isolated as stable salts.



1n



2n



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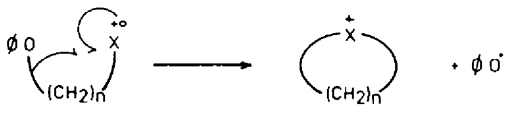
Functional group interactions in gaseous organic ions have been the subject of extensive studies in the past few years.[5] Particular efforts have been made in the investigation of unusual reactions which do not otherwise occur in monofunctional compounds. Among these are fragmentations which are the result of an S_Ni type reaction[6] and which should therefore yield cyclic ions. Our own studies of the mass spectral behavior of ω-phenoxyalkylbromides,[7] α,ω-diaryloxyalkanes[1] and ω-thiophenylalkyl phenylethers[8] have shown that the molecular ions of compounds $\phi O(CH_2)_nX$ (X = Br, OAr, Sϕ) undergo such reactions: loss of phenoxy radical (Scheme 1) is indeed an important fragmentation.

Hence we expected cyclic O-methyl oxonium ions **2**$_n$ to be generated from the molecular ions of ω-phenoxyalkyl methyl-ethers I_n by the mechanism of

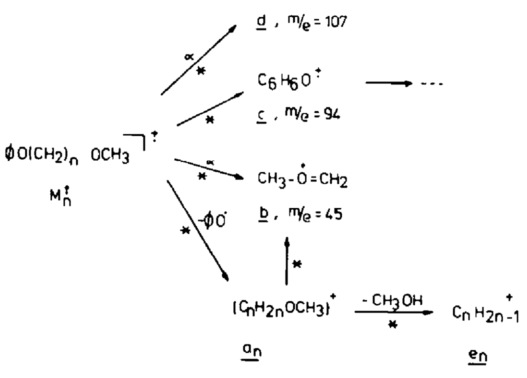
$$I_n:\quad \phi O(CH_2)_nOCH_3 \quad (n = 2\text{–}6).$$

Scheme 1 ($X = OCH_3$), even though no such reaction occurs in α,ω-dialkoxyalkanes[9] nor in related substances.[10]



Scheme 1

The mass spectral behavior of compounds I_n is outlined in Scheme 2; the abundances of peaks relevant for this study are collected in Table 1. As can be seen from Scheme 2 and Table 1, there are only two important primary breakdown modes ($M_n^+ - $ **b** and $M_n^+ - $ **c**) competing with loss of a phenoxy radical ($M_n^+ - $ **a**$_n$). For reasons similar to those enumerated earlier,[1,8] these competitions will be fairly constant with increasing n: see for instance [**c**] in Table 1. The abundance [**b**] however shows a sharp increase for n > 2: this is due to the interference of reaction **a**$_n$ − **b** which for n = 2 amounts to carbene loss and consequently does not occur. The abundance of ions **a**$_n$ (Table 1) clearly is dependent on the length of the chain separating the two functionalities in compounds I_n. The variation of [**a**$_n$] with n reflects (i) the probability of the correct configuration in which the ends of the chain can meet (maximal for n = 2), and (ii) the activation energy necessary to make the ends actually meet (minimal for n = 4). It is therefore to be interpreted in terms of an interaction between the phenoxy and methoxy moieties,



Scheme 2

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[a] Part XXIII: see Ref. 8.

[b] Aangesteld Navorser of the "Belgisch Nationaal Fonds voor Wetenschappelijk Onderzoek" (NFWO).

Table 1. Partial mass spectra of compounds I_n (% Σ_{30})

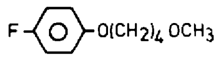
n	[$M^{+\cdot}$]	[$\underline{a}_n$]	[$\underline{b}$]	[$\underline{c}$]	[$\underline{d}$]	[$\underline{e}$]
2	5.28 (152)	13.53 (59)	6.09 (45)	7.58 (94)	1.96 (107)	3.79 (27)
3	5.69 (166)	8.31 (73)	18.67 (45)	8.40 (94)	0.62 (107)	6.21 (41)
4	0.97 (180)	10.77 (87)	11.40 (45)	7.63 (94)	2.17 (107)	7.29 (55)
5	0.96 (194)	5.62 (101)	16.05 (45)	10.60 (94)	1.00 (107)	8.99 (69)
6	3.04 (208)	2.72 (115)	15.05 (45)	16.01 (94)	1.36 (107)	7.84 (83)

≠ the m/e values are indicated between brackets.

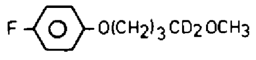
especially as the corresponding reaction does not occur in n-alkyl methylethers.[11] This is by no means proof that ions $\mathbf{a}_n$ have structure $\mathbf{2}_n$; however, it is hard to visualize such a functional group interaction without the operation of the mechanism of Scheme 1. Consequently the cyclic structure $\mathbf{2}_n$ is highly probable for ions $\mathbf{a}_n$.

Compound II_4 was selected for further investigation,

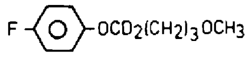
II_4:



III_4:



IV_4:



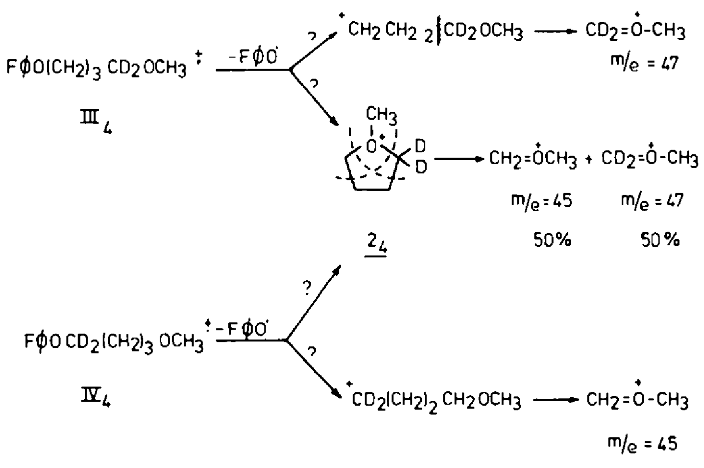
the only reason for the para fluorine atom being the availability of a labeled precursor[1] for III_4. We have focused on the decomposition reaction $\mathbf{a}_4 - \mathbf{b}$ (see Scheme 2; n = 4): if ions $\mathbf{a}_4$ have structure $\mathbf{2}_4$, the product $\mathbf{b}$ must contain one of the two methylene groups vicinal to the oxygen in the cyclic ion (Scheme 3), with equal probability for both because of the symmetry of $\mathbf{2}_4$. In the labeled compounds III_4 and IV_4 structure $\mathbf{2}_4$ must then lead to equal amounts of $CH_3\overset{+}{O}{=}CH_2$ (m/e = 45) and $CH_3\overset{+}{O}{=}CD_2$ (m/e = 47), whereas an open structure can only yield $CH_3\overset{+}{O}{=}CD_2$($III_4$) or $CH_3\overset{+}{O}{=}CH_2$($IV_4$). Hydrogen-deuterium scrambling can of course occur prior to decomposition of ions $\mathbf{a}_4$ and may render differentiation more difficult. Total scrambling in ions $\mathbf{a}_4$ or complete scrambling in the central chain will of course produce identical results for III_4 and IV_4 no matter what structure ions $\mathbf{a}_4$ have. Once these two possibilities are eliminated, identical relative abundances of $C_2H_xD_yO^+$ products ($\mathbf{b}$, x: 3–5, y = 5 − x) from ions $\mathbf{a}_4$ in III_4 and IV_4 must be due to the occurrence of a species symmetrical with respect to the terminal carbons of the aliphatic chain in II_4, i.e. ions $\mathbf{2}_4$.

As expected, the peak corresponding to ions $\mathbf{a}_4$ is quantitatively shifted over 2 amu ($m/e = 87 \rightarrow m/e = 89$) in the mass spectra of III_4 and IV_4. An investigation of ion source decomposing ions $\mathbf{a}_4$ (lifetimes $<10^{-6}$ sec) is impossible because of interference of reaction $M_n^+ - \mathbf{b}$ with $\mathbf{a}_4 - \mathbf{b}$ (Scheme 2). This interference is avoided in the metastable decompositions: hence ions $\mathbf{a}_4$, generated from III_4 and IV_4 and fragmenting in the first field free region of a double focusing mass spectrometer have been studied through the metastables associated with the transitions $\mathbf{a}_4 - \mathbf{b}$ ($\mathbf{b}$: $m/e = 45$, 46 and 47). Quantitative data are gathered in Table 2. Moreover, a number of hypothetical cases have been calculated and are also included:

α—ions $\mathbf{a}_4$ have open, unscrambled structure (Scheme 3);

β—ions $\mathbf{a}_4$ have unscrambled cyclic structure $\mathbf{2}_4$ (Scheme 3);

γ—ions $\mathbf{a}_4$ have cyclic structure but hydrogen scrambling occurs between the two C atoms adjacent to the



Scheme 3.

Table 2. Metastable decompositions* of ions **a**$_4$ to **b** in compounds III$_4$ and IV$_4$

Transition	Abundance							
	experimental		predicted					
	III_4	IV_4	$\alpha(III_4)$	$\alpha(IV_4)$	β	γ	δ	ϵ
89 - 45	54.4	55.4	-	100	50.0	16.66	53.57	27.27
89 - 46	19.0	17.7	-	-	-	66.67	42.86	54.55
89 - 47	26.6	26.9	100	-	50.00	16.66	3.57	18.18

* The abundances within each triplet have been normalized to a sum = 100 and are averaged over three separate runs.

oxygen (compare with the tetramethylenechloronium ion[12]);

δ—hydrogen scrambling in the aliphatic chain prior to decomposition: differentiation is no longer possible;

ε—total hydrogen scrambling: again differentiation is impossible.

The data in Table 2 indicate that case δ or ε does not occur. As explained (*vide supra*) the virtual identity of the data for III$_4$ and IV$_4$ can only be rationalized in terms of O-methyl tetrahydrofuranium ions 2_4. The experimental abundances in Table 2 can be fitted by 55% β + 45% δ which indicates that partial scrambling prior to decomposition has occurred in the ring.

It should finally be pointed out that this evidence for structure 2_4 of ions **a**$_4$ refers to decomposing species in the lifetime window 10^{-6} sec–10^{-5} sec. Ions **a**$_4$ contributing to the abundance of the corresponding peak in the mass spectrum ($m/e = 87$ for II$_4$) have lifetimes $>10^{-6}$ sec and do not necessarily have the same structure as they contain less internal energy. Consequently the above evidence cannot be inferred in a structure assignment for these long living ions **a**$_4$, although it strengthens our suspicion (*vide supra*) that 2_4 is also their structure.

EXPERIMENTAL

Instruments. Mass spectra were recorded on a Dupont-CEC 21-104 instrument: electron energy 70 eV, source temp. 150°, direct insertion probe. First field free region metastables were determined by combined E, V-scan[13] on an AEI MS-50 mass spectrometer adapted[1] for slow recording of metastables.

Compounds. The unlabeled compounds I$_n$ were synthesized as follows:

$$HO\text{-}(CH_2)_n/OH \xrightarrow[\text{pyridine}\ 0°C]{TsCl} TsO\text{-}(CH_2)_n/OH$$

$$\frac{\phi ONa}{DMSO}\ \phi O\text{-}(CH_2)_n\text{-}OH\ \frac{NaH}{CH_3I}\ I_n$$

phenol was substituted by 4-fluorophenol in the preparation of II$_4$. Williamson ether synthesis yielded III$_4$ from $F\phi O(CH_2)_3CD_2OH$, available from an earlier study.[1] Compound IV$_4$ was obtained from 4-methoxybutyric acid methyl ester:

$$CH_3O(CH_2)_3COOMe \xrightarrow{LiAlD_4} CH_3O(CH_2)_3CD_2OH$$

$$\xrightarrow[\text{pyridine}\ 0°C]{TsCl} CH_3O(CH_2)_3CD_2OTs \xrightarrow[DMSO,\,RT]{F\phi ONa} IV_4.$$

Purity and identity of all compounds was checked with spectroscopic methods. In the case of the labeled compounds the d_2-content was determined by MS (>98.8% d_2). Positional retention of the label was checked by 100 MHz ^{1}H NMR and could be verified by MS (ion **d**).

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