The Nominal Butyl Ester Ion in the Mass Spectra of Long-Chain *n*-Alkyl Esters: A Postscript

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n-Octadecyl benzoate, taken as a model for long-chain *n*-alkyl carboxylates generally, loses $C_{14}H_{28}$ under electron impact to yield a product with the same elemental composition as the butyl benzoate molecular ion. This product retains quantitatively one hydrogen from C-6, and seems to be formed as an oxygen-protonated 4-benzoyloxybutyl radical. It reacts further to lose H_2O , in which deuterium labeling demonstrates that the second hydrogen atom comes predominantly from C-4. The intermediate reorganization, for which the driving force is presumably furnished by the instability associated with a primary radical, is pictured in terms of cyclization via bonding between the C-4 radical site and the benzoyl carbon concerted with hydrogen migration via a 4-membered quasicyclic transition state.

INTRODUCTION

The mass spectra of *n*-heptyl and homologous higher carboxylates characteristically contain a small peak due to an ion with the composition of the corresponding butyl ester.^{1,2} Its intensity is low, of the order of 0.1% of total ion intensity, but it is generally the most intense peak in its immediate mass region, and greater by factors of 2 to $10 \times$ than peaks attributable to higher and lower homologs of this ion. A labeling study employing *n*-octadecyl-2,2- d_2 , -6,7- d_2 , -9,10- d_2 and $9,10,12,13-d_4$ benzoates identified two contributing reaction paths.² The dominant path, shown in Scheme 1, the source of some 66-69% of the observed abundance of this ion, $[C_{11}H_{14}O_2]^{+}$, apparently is initiated by γ -hydrogen migration—that is, from C-2-to the carbonyl oxygen, followed by a 1,5hydrogen-migration step from C-6 to C-2, and β cleavage with respect to the radical center on C-6. An estimated 19% of the observed [C11H14O2]+ abundance arises apparently by hydrogen migration directly from C-6 to the carbonyl oxygen, as part of a homologous series of ions arising via nonselective hydrogen abstraction from the octadecyl methylene groups by the radical site on the ionized oxygen atom; the abstraction step is followed by β -cleavage as in Scheme 1. The 12-15% that remains unaccounted for may reflect isotope effects; the intervention of other,



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Scheme 1

unspecified, molecular events; or simply uncertainties in the experimental data.

The resulting primary radical **1** would be expected to undergo some further reorganization to a more stable configuration. The $[C_{11}H_{14}O_2]^+$ ion breaks down further to some extent by eliminating H₂O to yield $[C_{11}H_{12}O]^+$, and the data on this product were examined in a search for clues to the structure of the intermediate. These data appeared to rule out an



earlier proposed¹ structure, the cyclic hemiacetal 2;



they led to the suggestion of Scheme 2 as an alternative, involving migration of an activated hydrogen atom from C-3 to the carbonyl oxygen to yield the terminal-olefinic structure $3.^2$ A H₂O molecule lost from 3 would carry with it a hydrogen atom originally on C-3. To test the suggestion, we have now prepared three additional *n*-octadecyl benzoates, $1,1-d_2, 3,3-d_2$ and $4,4-d_2$, and studied their mass spectra.

RESULTS AND DISCUSSION

Table 1 lists the isotopic compositions of the three specifically labeled *n*-octadecyl benzoates and of the $[C_{11}H_{14}O_2]^+$ and $[C_{11}H_{12}O]^+$ ions in the three spectra. Table 2 lists the derived losses of a deuterium atom from each of the labeled species in the elimination of $C_{14}H_{28}$ from the molecular ion and in that of H_2O from $[C_{11}H_{14}O_2]^+$, as estimated from the values in Table 1 for the various d_2 species.

The loss so revealed of atoms from C-1, C-3 and C-4 in the first decomposition step was unexpected. Mechanistic implications are obscure. Presumably some 2-way traffic of hydrogen atoms occurs between these methylene groups and the terminal C_{14} chain segment before the latter is eliminated as $C_{14}H_{28}$. Such exchange may occur by way of intermediates in which the initial hydrogen migration to the carbonyl oxygen is followed by one or more hydrogen abstrac-

Table 1. Isotopic compositions of labeled *n*-octadecyl benzoates and of the $[C_{11}H_{14}O_2]^+$ and $[C_{11}H_{12}O]^+$ ions in their mass spectra

Isotopic ester	lon	ďo	d1	d2
1,1-d ₂	[M] ^{+• a,b}	0.1%	1.4%	98.5%
	[C ₁₁ H ₁₄ O ₂] ^{+·}	1	8	91
	[C ₁₁ H ₁₂ O] ⁺⁻	2	13	85
3,3-d ₂	[M] ^{+• a,b}	0.1	1	98.9
	[C ₁₁ H ₁₄ O ₂] ⁺⁺	0	7	93
	[C ₁₁ H ₁₂ O] ⁺⁻	8	8	84
4,4-d ₂	[M] ^{+• a,b}	0.2	3	96.8
	[C ₁₁ H ₁₄ O ₂] ^{+∙}	4	13	83
	[C ₁₁ H ₁₂ O] ⁺	15	64	21

^a [M]⁺ = molecular ion.

^b The isotopic compositions shown for the molecular ions were actually measured on the $[M-CH_3]^+$ peaks in the spectra of trimethylsilyl ethers of the labeled octadecanols used to prepare the respective octadecyl benzoates.

Table 2. Derived deuterium losses in the sequential elimina- tions of $C_{14}H_{28}$ and H_2O							
Loss in elimination of:							
Isotopic ester	C14H28	H₂O					
1,1-d₂	8%	7%					
3,3-d ₂	6	10					
4,4-d ₂	14	75					

tions from a methylene group by an alkyl radical site before the reaction products separate.

The second hydrogen atom eliminated as part of the H_2O molecule in the second step stems predominantly from C-4—an even more surprising finding.

At this point, we made a slight detour to consider the possibility that the identifications of the $3,3-d_2$ and $4,4-d_2$ isotopomers might have been inadvertently switched. To settle this question, we examined the data for the nominally benzoyloxyalkyl ions $[C_6H_5CO_2(CH_2)_i]^+$, where $1 \le j \le 5$, in the two spectra, and also, as a further check on internal consistency, in that of the $1,1-d_2$ species. Table 3 lists the lowest-mass dioxygen-containing ions observed in the mass region corresponding to each of these compositions. For each value of *j*, the fragment ion appears to retain exclusively the alkyl hydrogen atoms incorporated in the first j methylene groups of the ester molecule. This is what one would expect from simply nonspecific homolysis of alkyl carbon-carbon bonds or, for $j \ge 2$, from a suggested^{2,4} lower-energy path consisting of nonspecific hydrogen abstraction by the carbonyl oxygen followed by β carbon-carbon bond cleavage on the far side of the radical site so created. In any case, the data leave no doubt that the isotopomer samples were correctly identified.

To rationalize the highly selective incorporation of a C-4 hydrogen atom in the H₂O molecule eliminated, we picture the process in terms of Scheme 3. Electron delocalization over the C=O group in 1 may leave substantial radical character on the benzoyl carbon atom. Pairing of this site with the terminal (C-4) free radical, coupled with hydrogen migration from C-4 to the oxygen via a 4-membered quasicyclic transition state, accomplishes the required end. The resulting structure 4 may then eliminate H₂O and yield a $[C_{11}H_{12}O]^{+}$ product 5 that should have high stability by virtue of the newly formed double bond (pictured here as the site of the charge) and, in the specific case of a benzoate ester, of the extended conjugation.



I	sotopic ester	1,1-d ₂	3,3-d₂	4,4-d ₂	Number of	Theoretical mass for assigned
,	lon		Measured mass		deuterium atoms	isotopic composition
1	[C_H_O_]+		135.0449	135.0447	0	135.04460
•	108.17021	137.0589			2	137.05715
2	[C_H_O_]+		149.0608	149.0603	0	149.06025
		151.0704			2	151.07280
3	[C ₁₀ H ₁₁ O ₂] ⁺			163.0759	0	163.07590
		165.0888	165.0879		2	165.0 884 5
4	[C11H13O2]+	179.1024	179.1032	179.1043	2	179.10410
5	[C ₁₂ H ₁₅ O ₂] ⁺	а	193.1213	193.1209	2	193.11974
^a Not d	detected.					

Table 3. Lowest-mass dioxygen-containing species in the mass regions of $[C_6H_5CO_2(CH_2)_j]^+$ ions in the mass spectra of labeled *n*-octadecyl benzoates

Thus, the data have brought us back to a cyclic structure similar to that originally proposed by Ryhage and Stenhagen¹ but differing from theirs by the requirement that ring closure and the final hydrogen-migration step are most likely concerted.

We recognize, of course, that our data apply strictly only to those $[C_{11}H_{14}O_2]^+$ ions that decompose further to $[C_{11}H_{12}O]^+ + H_2O$.

EXPERIMENTAL

Preparation of octadecyl-1,1-d₂ benzoate

Methyl stearate (32.15 g, 0.108 mol), lithium aluminum deuteride (5 g, 0.119 mol), and 250 cm³ of Et₂O were heated at reflux for 16 h. After destruction of excess $LiAlD_4$ with a saturated solution of Na_2SO_4 , the slurry was filtered and the filtrate dried over MgSO₄. Removal of solvent in vacuo yielded 28.4 g (94.7%) of 1-octadecanol-1,1-d₂, m.p. 58-59 °C (lit. (unlabeled) m.p. 57.9 °C). This was dissolved in 150 cm³ of 1:1 benzene:toluene. Benzoyl chloride (13 cm³, 0.112 mol) and pyridine (9 cm³, 0.112 mol) were added and the mixture was heated at reflux for 0.5 h, then stirred at room temperature for 2 days. Ether was added and the solution was washed twice with water, once with 5% NaHCO₃, and once again with water. After drying (MgSO₄), the organic layer was stripped of solvent in vacuo to obtain 19.55 g (49.8%) of octadecyl-1,1- d_2 benzoate, m.p. 42.5-44 °C (lit.⁴ (unlabeled) m.p. 42.5-44.0 °C). Mass spectra revealed no chemical impurities.

Preparation of octadecyl-3,3-d₂ benzoate

The synthetic route employed is similar to that reported in a previous paper to prepare labeled hexanols⁵ via lengthening of the carbon chain of the appropriate labeled intermediate by means of trimethylene oxide.⁶ To prepare the intermediate required for the present synthesis, methyl hexadecanoate was reduced as described above for methyl stearate to give 1-hexadecanol-1,1- d_2 , m.p. 48 °C [lit.⁷ (unlabeled) m.p. 49.5 °C]. The yield was 24.0 g, nearly theoretical. IR: $\nu_{max} = 3340$ (OH); 2080, 2190 cm⁻¹ (CD stretch).

Phosphorus tribromide (28 g; 0.1 mol) was added dropwise with stirring to the hexadecanol-1,1- d_2 in a 250-cm³ round-bottomed flask with a separatory funnel and a reflux condenser. At the end, the reaction mixture was heated to 75 °C, cooled, and poured into ice-cold water. The semi-solid oil was taken up in ether, and the ether solution was washed with several portions of water until the washings were no longer acidic. The ether was dried over magnesium sulfate and distilled. Bulb-to-bulb distillation in an air bath at 130 °C under vacuum (0.2 Torr) gave 18.0 g (60% of theoretical) of 1-bromohexadecane-1,1- d_2 . IR: $\nu_{max} =$ 2150, 2260 cm⁻¹ (CD stretch).

A Grignard reagent was prepared from the bromide (15.0 g; 0.045 mol), magnesium (3.0 g; 0.125 mol), and absolute ether (60 cm³) in a 250-cm³ flask with a separatory funnel and a reflux condenser. The reaction had to be initiated by adding a crystal of iodine and a few drops of ethyl bromide. A solution of ethene oxide (10 g; 0.227 mol) in benzene (50 cm³) was added in portions. A vigorous reaction occurred. More benzene was added to raise the boiling point to 50-55 °C. After 1-2 h heating under reflux a thick gel formed. The reaction mixture was then cooled and decomposed by adding to it ice-cold water containing a little sulfuric acid. The benzene-ether solution was dried over MgSO₄ and then freed of solvent. Bulb-to-bulb distillation of the residue under vacuum (0.2 Torr) gave 7.2 g (58%) of octadecanol-3,3-d₂, b.p. 130-135 °C. IR: $\nu_{\text{max}} = 3360$ (OH); 2090, 2180 cm⁻¹ (CD stretch).

Octadecyl-3,3- d_2 benzoate was prepared from the labeled alcohol as described for octadecyl-1,1- d_2 benzoate. Yield: 0.6 g, m.p. 43 °C. IR: $\nu_{max} = 1720$ (C=O); 2100, 2160 cm⁻¹ (CD stretch). Trace impurities detected by mass spectrometry were removed by preparative-scale liquid chromatography. We employed a Waters Associates Prep 500 Liquid

Chromatograph equipped with a Prep PAK-500 C_{18} column and a refractive index detector. The mobile phase was acetonitrile at a flow rate of 200 cm³ min⁻¹.

Preparation of octadecyl-4,4- d_2 benzoate

Methyl *n*-pentadecanoate (23 g; 0.1 mol) was reduced to 1-pentadecanol-1,1- d_2 and the alcohol converted to 1-bromopentadecane-1,1- d_2 as described above in the preparation of octadecyl-3,3- d_2 benzoate. The chain was lengthened, also as described above but with trimethylene oxide in place of ethene oxide, and esterification with benzoyl chloride yielded octadecyl-4,4- d_2 benzoate, which was again subjected to final clean-up by liquid chromatography.

Mass spectrometry

Molecular-ion peaks of the esters were judged unsuitable for isotopic analysis, as in our earlier work,^{2,4} because of interference from low levels of protonated molecules. As our method of choice, we converted the respective labeled octadecanol intermediates to trimethylsilyl ethers by reaction with N,0bis(trimethylsilyl)benzamide (BSA),⁸ measured the mass spectra of these ethers on a duPont Model 21-104 instrument, and calculated the isotopic composition from the $[M-CH_3]^+$ peak-intensity⁹ distributions. The silylation was carried out on a 10-20 mg sample of the labeled alcohol, dissolved in 1 cm^3 of the BSA reagent (Pierce Chemical Co.). Excess reagent was blown off with a nitrogen purge on a steam bath and the resulting crude product was analyzed without further purification.

Measurements on the $[C_{11}H_{14}O_2]^+$ and $[C_{11}H_{12}O]^+$ peaks require high mass resolution to separate them from ion species of the same nominal masses but of differing elemental compositions.² In addition, these ions comprise only 0.08% and 0.01%, respectively, of total ion current in the mass spectrum of octadecyl benzoate. Hence the information we were seeking required that the measurements be made at greater than usual sensitivity. To meet these demands, we measured the spectra on a CEC Model 21-110B instrument, with sample introduction via direct-injection probe, probe and source temperatures respectively at ~160 °C and 250 °C, electron energy of 70 eV, resolution of $\sim 10\,000$, scan rate of $\sim 10\,\text{sec}\,\text{u}^{-1}$ through the mass regions of interest, (vs our normal scan rate of $\sim 0.1 \text{ sec u}^{-1}$) and analog recording. The low scan rate allowed a sensitivity increase of $\sim 40 \times$ over normal operation.

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