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THE MASS SPECTRAL BEHAVIOR OF ß-BROMOETHYL BENZOATE AND SOME OF ITS RING SUBSTITUTED DERIVATIVES: EVIDENCE FOR OXYGEN PARTICIPATION IN THE FORMATION OF [M − Br]$^+$

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Abstract—The expulsion of a bromine atom from the molecular ion of β-bromoethyl benzoate displays a kinetic behavior which resembles that of a rearrangement reaction. The two oxygen atoms in the resulting [M − Br]$^+$ ion become equivalent before or during the secondary decomposition of this ion, as shown by oxygen labeling. In addition, the primary ions generated from benzophenone ethylene ketal and acetophenone ethylene ketal by phenyl and methyl expulsion, respectively, undergo subsequent fragmentation in the same way as the [M − Br]$^+$ from β-bromoethyl benzoate. These results strongly indicate that the carbonyl-oxygen atom participates in the expulsion of bromine. The effect of ring substituents on the competing loss of bromine and McLafferty rearrangement is also discussed.

INTRODUCTION

DURING recent years there have been several reports of anchimeric assistance in reactions occurring in the ion source of a mass spectrometer.[1 to 6] For example, DeJongh and co-workers, using the kinetic approach of Bursey and McLafferty,[7] provided evidence that the expulsion of bromine from the molecular ions of *exo*-norbornyl bromide and *exo*-8-bromobicyclo[3.2.1]octane, which are generated either by electron-impact or photon-impact, is facilitated by sigma-participation.[2] In addition, we have recently reported that the kinetic behavior and substituent effects observed in the formation of [M − Br]$^+$ ion from ring-substituted β-phenylethyl bromides were consistent with phenyl participation in the expulsion of bromine.[6] The other reports[3,4,5] contained fragmentation data which were totally compatible with anchimeric assistance.

This paper reports an investigation of the electron-impact reactions of β-bromoethyl benzoate and several of its ring substituted derivatives. Of prime interest to us was whether the carbonyl oxygen participated in the expulsion of bromine from the molecular ions. Our approach to this problem involved the use of the kinetic method developed by Williams and Cooks,[8] as employed by us in our study of β-phenylethyl bromides,[6] oxygen-18 labeling and comparison of the subsequent behavior of the [M − Br]$^+$ ion from β-bromoethyl benzoate with that of the [M − C_6H_5]$^+$ ion from benzophenone ethylene ketal and the [M − CH_3]$^+$ ion from acetophenone ethylene ketal. All of our data are consistent with oxygen participation and lead us to conclude that the [M − Br]$^+$ ion from β-bromoethyl benzoate has symmetrically disposed oxygen atoms and, in fact, has the same structure as the primary fragment ions generated from the ethylene ketals.

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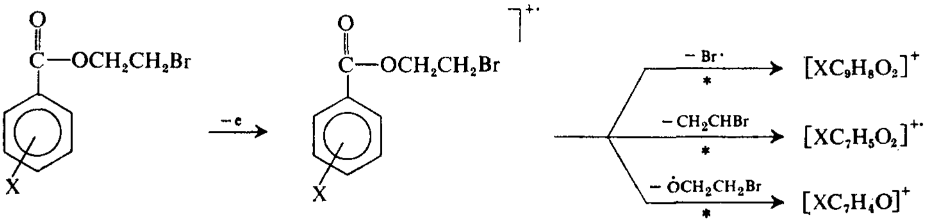
The effect of ring substituents was also investigated and it appears that electron-withdrawing groups enhance the expulsion of bromine relative to the competing expulsion of vinyl bromide.

RESULTS AND DISCUSSION

Upon electron-impact, β-bromoethyl benzoate (1, X = H) and its ring substituted derivatives undergo three competing reactions: (1) the expulsion of bromine, (2) the expulsion of the elements of vinyl bromide (McLafferty rearrangement) and (3) the expulsion of $C_2H_4BrO\cdot$ (simple cleavage). The primary ions resulting from the



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expulsion of Br· and C_2H_3Br undergo secondary fragmentation, at high ionizing energies (>~20 eV), losing C_2H_4O and OH·, respectively to give benzoyl cations.

$$[XC_9H_8O_2]^+ \xrightarrow[*]{-C_2H_4O} [XC_7H_4O]^+ \xleftarrow[*]{-OH\cdot} [XC_7H_5O_2]^{+\cdot}$$

In order to determine if the formation of the $[M - Br]^+$ ion is aided by carbonyl-oxygen participation, we employed the kinetic approach of Williams and Cooks[8] which depends on the principle that those rearrangement processes which have low frequency factors and low activation energies will become more dominant, relative to simple cleavages, as the ionizing energy is decreased. Employment of benzoyl ion formation as an internal average rate standard is prohibited in our system because of the three different routes of benzoyl ion formation, only one of which is a simple cleavage. Therefore, the competing McLafferty rearrangement was used as the comparative reaction. It would then be expected if the formation of $[M - Br]^+$ proceeded by way of a 'rearrangement-like' transition state, the abundance of $[M - Br]^+$ and $[M - C_2H_3Br]^{+\cdot}$ will follow a similar dependence on ionizing energy. The relative intensities of these ions as a function of ionizing energy are presented in Table 1. In all cases, as the data in Table 1 shows, the relative abundance of $[M - Br]^+$ either increases or remains constant with respect to the relative abundance of $[M - C_2H_3Br]^{+\cdot}$ as the ionizing energy is decreased. From these results, it can be concluded that the expulsion of bromine from the molecular ions involves a highly ordered transition state (i.e. low frequency factor) and that the activation energy for this reaction is lowered by outside assistance.

Several studies have shown that the carbonyl-oxygen of esters can participate in solvolysis reactions.[9,10,11] In light of these studies, a reasonable mechanism, which is compatible with our data, involves participation of the carbonyl-oxygen as shown.

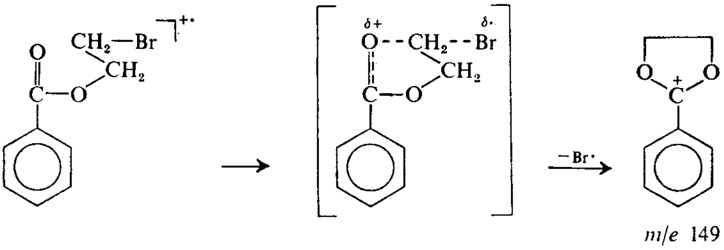
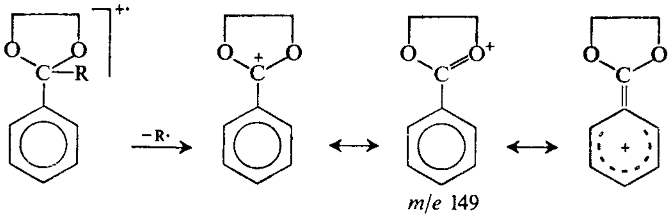


TABLE 1. EFFECT OF IONIZING ENERGY ON THE RELATIVE ABUNDANCES OF $[M - Br]^+$ AND $[M - C_2H_3Br]^{+\cdot}$ FROM RING SUBSTITUTED β-BROMOETHYL BENZOATES
$[M - Br^+]/([M - Br^+] + [M - C_2H_3Br^{+\cdot}])$ AT

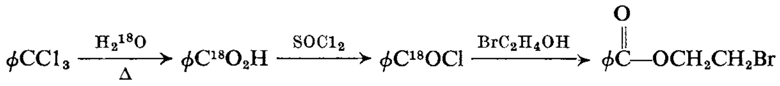
Substituent	20 eV	19 eV	18 eV	17 eV	16 eV	15 eV	14 eV	13 eV
m-NO_2	0·743	0·769	0·769	0·770	0·809	0·835	0·910	1·00
p-NO_2	0·691	0·715	0·724	0·740	0·759	0·764	0·813	0·965
m-CF_3	0·556	0·567	0·584	0·597	0·619	0·652	0·695	0·810
p-CF_3	0·535	0·556	0·568	0·578	0·602	0·639	0·695	0·800
H	0·206	0·218	0·224	0·230	0·244	0·270	0·286	0·338
m-F	0·033	0·034	0·038	0·038	0·039	0·039	0·046	0·054
p-F	0·070	0·076	0·076	0·076	0·080	0·084	0·099	0·119
m-Cl	0·022	0·022	0·023	0·024	0·026	0·029	0·039	0·051
p-Cl	0·022	0·023	0·025	0·026	0·027	0·029	0·032	0·039
m-CH_3	0·034	0·036	0·038	0·038	0·038	0·042	0·048	0·061
p-CH_3	0·034	0·034	0·034	0·034	0·034	0·036	0·041	0·054
m-OCH_3	0·014	0·014	0·015	0·010	0·014	—	—	—
p-OCH_3	0·004	0·004	0·005	0·006	0·006	—	—	—

If the $[M - Br]^+$ ion is produced by such a mechanism, then it is expected that this resonance stabilized ion would be structurally identical with those generated by simple cleavage of the molecular ions of ethylene ketals derived from phenones.



A comparison was made of the metastable behavior of the mass 149 ion generated from β-bromoethyl benzoate, benzophenone ethylene ketal and acetophenone ethylene ketal. In all cases the mass 149 ion decomposes to a mass 105 (benzoyl) ion and these transitions are marked by metastables at *m/e* 74·0, which have the same shape (slight tailing on the high mass side). Although this presumptive test is not considered to be proof of the identity of the three ions in question, it is consistent with identity.

If, however, the $[M - Br]^+$ ion from β-bromoethyl benzoate has the same structure as that expected for the mass 149 ion from the ethylene ketals, then it is apparent that the two oxygen atoms in this ion must be equivalent. An ^{18}O-experiment was performed in order to determine whether the oxygen atoms in the $[M - Br]^+$ ion did, in fact, become equivalent before its secondary decomposition to benzoyl ions. β-Bromoethyl benzoate with a labeled carbonyl-oxygen was prepared by the following route.



$$\phi CCl_3 \xrightarrow[\Delta]{H_2{}^{18}O} \phi C^{18}O_2H \xrightarrow{SOCl_2} \phi C^{18}OCl \xrightarrow{BrC_2H_4OH} \phi\overset{O}{\overset{\|}{C}}\text{—}OCH_2CH_2Br$$

If the oxygen atoms in the $[M - Br]^+$ ion generated from the labeled precursor are equivalent, then this ion will decompose equally to benzoyl ions (*m/e* 105) and labeled benzoyl ions (*m/e* 107), disregarding the predictably small isotope effect. Since the simple cleavage route to benzoyl ions yields a mass 107 ion and the McLafferty rearrangement route yields both mass 105 and 107 ions,[12] relative metastable ion intensities for the 151 → 107 ($m_1{}^* = m/e$ 75·8) and 151 → 105 ($m_2{}^* = m/e$ 73·0) were compared.* The $[m_2{}^*]/[m_1{}^*]$ area ratio was measured and was determined to be 1·04 ± 0·12 at all ionizing energies between 15 to 20 eV. This result strongly suggests that the oxygen atoms in the $[M - Br]^+$ ion are equivalent. Since the average ratio is slightly above one, it is possible that a small ^{18}O-isotope effect was observed.

It is recognized that the kinetic method employed in this investigation was designed to determine something about the nature of the transition state in the *formation* of the $[M - Br]^+$ ion; whereas, the comparative studies and ^{18}O-experiment were concerned with the *decomposition* of this ion. Nevertheless, all of our results strongly indicate that the $[M - Br]^+$ ion generated from β-bromoethyl benzoate decomposes as it was formed and that this ion is structurally identical with the $[M - R]^+$ ions generated from phenone ethylene ketals.

Referring again to Table 1, one can see the effect of substituents on the two competing rearrangement reactions. The powerful electron-withdrawing substituents (i.e. NO_2, CF_3) either enhance the expulsion of bromine relative to the McLafferty rearrangement, inhibit the McLafferty rearrangement relative to the expulsion of bromine, or a combination of both. All of the other substituents appear to have the opposite effect. Boer, Shannon and McLafferty have presented evidence that the migrating hydrogen in the McLafferty rearrangement is electron deficient and therefore this reaction should be aided by substituents which tend to make the hydrogen-accepting carbonyl-oxygen more electron rich.[13] Groups which are capable of electron-donation by a mesomeric effect will satisfy this criterion since the aromatic ring can then bear more of the positive charge in the molecular ion, as shown in the following

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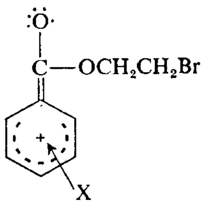
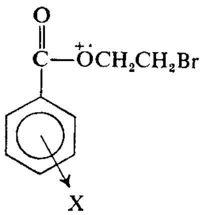
* The metastable ion for the 149 → 105 transition appears at *m/e* 74·0 and did not interfere with the measurements. The mass 149 ion was generated from an unlabeled contaminant.

contributing structure.*



Since the formation of $[M - Br]^+$ is favored over the McLafferty rearrangement when electron-withdrawing substituents are present, we are led to speculate that withdrawing groups force a large portion of the positive charge to reside on the ether-oxygen in the molecular ion as shown in the following contributing structure. In this contributing structure the electron deficient center is insulated from the electron-withdrawing group. It follows, from such an argument, that when electron-withdrawing groups force much of the charge to reside on the ether-oxygen, the favored



reaction is the expulsion of bromine which is aided by the electron rich (in a relative sense) carbonyl-oxygen. Although this argument is highly speculative, it not only explains our observed data, but it is also consistent with the behavior of β-bromoethyl acetate.[16] This aliphatic analog undergoes bromine expulsion to a far greater extent than the competing McLafferty rearrangement. Since the molecular ion of this compound has no aromatic ring to delocalize the positive charge if it is on the carbonyl-oxygen, a significant portion of the charge may prefer to reside on the ether-oxygen and the expulsion of bromine is favored over the McLafferty rearrangement.

Another similarity in the spectra of β-bromoethyl benzoates containing electron-withdrawing groups and β-bromoethyl acetate is the presence of moderately intense peaks at *m/e* 106 and 108 of about equal intensity. These peaks correspond to the molecular ion of vinyl bromide or its elemental equivalent and most likely arise from a McLafferty rearrangement with charge retention by the olefinic portion. This reaction indicates that the charge in the molecular ion prefers to be away from the carbonyl group.

* In an earlier paper McLafferty and Wachs reported that the McLafferty rearrangement of substituted butyrophenones showed a positive ρ-value.[14] This behavior is usually interpreted to mean that a given reaction is aided by electron-withdrawing groups. An explanation for the positive ρ-value might be related to large differences in ionization potentials and smaller differences in appearance potentials for the $[M - C_3H_6]^{+\cdot}$ ions. The net result would be a lower activation energy for the formation of $[M - C_3H_6]^{+\cdot}$ ion from butyrophenones containing an electron-withdrawing group. See reference 15 for a similar explanation of the phenomena observed for benzophenones and related systems.

EXPERIMENTAL

Mass spectra

The mass spectra were measured with a Varian MAT CH-5 mass spectrometer and results were occasionally checked with a Varian MAT CH-7 mass spectrometer. The solid samples were introduced by means of a direct insertion probe. The ionizing energies are nominal and were monitored by means of a digital voltmeter. The trap current was stabilized at 20 micro amps.

Compounds

The substituted 2-bromoethylbenzoates were prepared in the following manner: About 0·03 mole of the appropriately substituted benzoyl chloride was heated on a steam bath overnight with an excess of 2-bromoethanol. Ether was added and the reaction mixture was washed with sodium bicarbonate solution and water. The ether layer was dried over magnesium sulfate and the ether was evaporated at reduced pressure. The compounds were purified by gas chromatography.

The ethylene ketals were prepared as follows: A mixture of 0·05 mole ketone in 50 ml benzene, 10 ml ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid ($\leq 0{\cdot}2$ g) was heated at reflux for 12 hrs. The water formed was collected in a Dean-Stark trap. After a saturated potassium carbonate solution was added, the layers were separated and the benzene layer washed with sodium bicarbonate solution and dried over magnesium sulfate. The benzene was evaporated to yield the ketal. The benzophenone ethylene ketal was purified by gas chromatography. The acetophenone ethylene ketal was purified by recrystallization from ether/petroleum ether m.p. 60 to 62°, literature[17] 60 to 61° m.p.

Benzoic acid $^{18}O_2$ was prepared by a modification of the procedure of Ponticorve and Rittenberg.[18] Benzotrichloride (2·7 g) and $H_2{}^{18}O$ (0·5 g) were heated at reflux for 48 hrs. The product was filtered and washed with petroleum ether and water to yield 1·0 g of benzoic acid-$^{18}O_2$ (95% $^{18}O_2$). The labeled benzoic acid esters were prepared as follows: Benzoic acid-$O_2{}^{18}$ (25 mg) was treated with thionyl chloride (4 fold excess). The excess thionyl chloride was evaporated at reduced pressures. To the benzoyl chloride-^{18}O was added a four fold excess of the alcohol and the solution was heated on a steam bath. The esters were purified by gas chromatography. The ester contained 85% ^{18}O.

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