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Behaviour of arylalkylamines toward trimethyl borate as a gas-phase reagent

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Abstract

Gas-phase reactions of a number of arylalkylamines of general structure $R^1R^2C_6H_3CHR^3(CH_2)_nNR^4R^5$, where R^1 = H, F, NO_2, OH or OCH_3, R^2 = H or OH, R^3 = H or OH, R^4 and R^5 = H or CH_3 with the dimethoxyborinium ion, $(CH_3O)_2B^+$, *m/z* 73, obtained by electron ionization of trimethyl borate have been studied. Mass-analysed ion kinetic energy (MIKE) spectra of the $[M + 73]^+$ adducts, generated in a chemical ionisation source, together with MIKE spectra of some of their decomposition products, have been taken and interpreted. The interpretation is discussed in terms of structural features present in the neutral molecules, such as aliphatic chain length, methyl substitution at the amino group, presence of electron-donating or electron-withdrawing substituents in the aromatic ring and, finally, presence of a benzylic hydroxy group. The analysis of the results shows that the fragmentations of the adduct ions $[M + 73]^+$ are much more structurally sensitive than those for the $[M + 45]^+$ adducts previously observed with dimethyl ether, with the loss of methanol generating the most abundant ion only for three of the amines studied. The amino group is an important, but not always the dominant site of initial reaction, the exceptions being: (1) the aromatic ring, if substituted by activating substituents, and (2) a benzylic hydroxy group, if present in the structure. The 2-(4-nitrophenyl)-ethylamine constitutes the only exception to the general behaviour just described, because in that case the site of reaction of the electrophilic dimethoxyborinium ion is the oxygen atom of the nitro group. (Int J Mass Spectrom 203 (2000) 101–110) © 2000 Elsevier Science B.V.

Keywords: Arylalkylamines; Borinium ions; Chemical ionisation; Ion–molecule reactions; Trimethyl borate

1. Introduction

Arylalkylamines have been the subject of several recent studies, involving their reactions with both positive and negative chemical ionisation reagents [1,2] and the determination of their proton affinities [3]. The reactions of such amines with dimethyl ether in the gas phase have recently been investigated and have been shown to depend on the structural features of the substrates [4]. The $CH_3OCH_2^+$ adduct ions, $[M + 45]^+$, decompose mainly by loss of methanol, and the unimolecular decompositions of the resulting fragment ions indicate that a competition occurs between the amino group, aromatic ring, and benzylic hydroxy group, for the electrophilic attack. Trimethyl borate as a chemical ionization reagent has been the subject of a few recent publications, after the first description of its use in stereospecific reactions with diols and mono- and disaccharides [5]. The distinction of stereoisomers of 1,2-cyclopentanediol and 2,3-trinorbornanediol, based on the formation or absence

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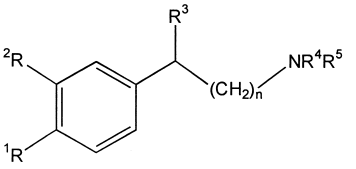
of a stable $[M + (CH_3O)_2B - CH_3OH]^+$ ion, has been reported [6]. The relative affinities of a group of substituted pyridines [7,8] have been determined by the kinetic and equilibrium methods, and have been found to correlate with the degree of steric hindrance caused by the substituents. Correlations between structural factors of quinones, such as functional group interactions and electron-withdrawing effects of substituents, and relative dimethoxyborinium ion affinities have been established [9]. Kenttamaa et al. have studied the reactions of dicoordinated boron cations with organic ethers [10], alcohols [11], long-chain carboxylic esters [12], and carbonyl compounds [13]. In the case of ethers, a mechanism involving the loss of two molecules of olefins is proposed to explain, eventually, the dehydration of these compounds. For carboxylic esters, the chain length, the degree of unsaturation, and the molecular weight of the ester could be derived from the mass to charge ratios of the primary and secondary ions generated in the reactions. Two competitive reaction pathways, that is abstraction of aldehyde and OH, have been observed for the adduct ions between aldehydes and ketones and the boron cation. Abstraction of part of the carbonyl compound as an aldehyde results in the formation of a boron cation product that is indicative of the location of the carbonyl bond. Abstraction of OH by the borocation yields a hydrocarbon product ion that contains the entire carbon skeleton of the aldehyde or ketone. The behaviour of biologically active organic molecules, which includes barbiturates [14], pilocarpine [15], and several others [16], toward trimethyl borate, has also been addressed. In the case of barbiturates, the $[M + (CH_3O)_2B]^+$ adducts dissociate by elimination of methanol upon collision induced dissociation (CID) and react by attachment of a molecule of trimethyl borate, generating structurally related ions at higher masses than the selected ions. For most of the other biologically active compounds studied, the most intense peak in the CID spectra of the $[M + 73]^+$adducts, is due to loss of a molecule of methanol. Recently, the synthesis of tricoordinated cyclic boron cations from reactions of dicoordinated borinium ions with neutral acetals has been described [17]. The group of arylalkylamines of general structure $R^1R^2C_6H_3CHR^3(CH_2)_nNR^4R^5$,shown in Table 1, contains several different nucleophilic functional groups, and includes a few biological amines active in neurotransmission. In the reactions of the same group of compounds with dimethyl ether we observed that the unimolecular decompositions of the $[M + 45]^+$ adducts are only structurally specific for the amines with a benzylic hydroxy group because, for most of the other amines, loss of methanol always generates the most abundant ion. The strong Lewis acidity of the dimethoxyborinium ion as compared with the $CH_3OCH_2^+$ ion, together with the well-known ability of boron to form quite strong bonds with other elements, in particular oxygen, prompted us to study the fragmentations of the adduct ions $[M + (CH_3O)_2B]^+$ generated in a chemical ionisation source by reaction of the amines with the dimethoxyborinium cation, obtained from electron ionization of trimethyl borate.

Table 1
Arylalkylamines



n	R^1	R^2	R^3	R^4	R^5	Name
0	H	H	H	H	H	Benzylamine
1	H	H	H	H	H	2-phenylethylamine
2	H	H	H	H	H	3-phenylpropylamine
3	H	H	H	H	H	4-phenylbutylamine
1	F	H	H	H	H	2-(4-fluorophenyl)-ethylamine
1	NO_2	H	H	H	H	2-(4-nitrophenyl)-ethylamine
1	OH	H	H	H	H	Tyramine
1	OCH_3	H	H	H	H	2-(4-methoxyphenyl)-ethylamine
1	OH	H	H	CH_3	CH_3	Hordenine
1	OH	OH	H	H	H	Dopamine
1	OH	H	OH	H	H	Octopamine
1	OH	H	OH	CH_3	H	Synephrine
1	H	H	H	CH_3	H	2-phenyl-N-methylethylamine

2. Experimental

The arylalkylamines were commercially available and most of them were used without further purifica-

Table 2
Chemical ionization mass spectra of arylalkylamines upon reaction with trimethyl borate as reagent gas

	m/z value of the most abundant ion	M + 1	M + 73	M + 73 − CH_3OH
Benzylamine	108	100	1	<1
2-Phenylethylamine	122	100	11	7
3-Phenylpropylamine	136	100	22	a
4-Phenylbutylamine	150	100	6	1
2-(4-Fluorophenyl)-ethylamine	30	69	2	<1
2-(4-Nitrophenyl)-ethylamine	30	26	2	<1
Tyramine	138	100	20	18
2-(4-Methoxyphenyl)-ethylamine	122	62	3	<1
Hordenine	58	30	8	1
Dopamine	30	67	8	2
Octopamine	136	70	5	17
Synephrine	168	100	3	1
2-Phenyl-N-methylethylamine	44	70	12	14

[a] *m/z* value coincident with that of a major reagent gas ion

tion, in the form of their corresponding hydrochloride salts. The salts of 3-phenylpropylamine, 4-phenylbutylamine, and 2-phenyl-N-methylethylamine were recrystallized from acetone/hexane. Mass spectrometric measurements were performed with use of a Micromass Autospec Q mass spectrometer of *EBEqQ* geometry, equipped with a chemical ionization source. Trimethyl borate (Aldrich Chemical Co.) was used with ion source pressures selected in the range between about 7.5×10^{-6} and 7.5×10^{-5} torr, so as to maximise the intensity of the *m/z* 73 signal, and at a source temperature of 200 °C. The electron energy was 70 eV and the accelerating voltage 8 kV. Samples were introduced with an unheated direct insertion probe. The nature of the reagent gas ions and the composition of the reaction mixtures were analysed by means of the chemical ionisation mass spectra. The ions of mass-to-charge ratio corresponding to the relevant adducts formed with the alkylarylamines, were selected with the magnetic sector and their unimolecular fragmentations were analysed through scanning of the second electrostatic analyser of the mass spectrometer [18] (MIKES). The deuteration of the amines was performed by shaking their hydrochloride salts with D_2O at room temperature and drying under N_2, prior to reaction with trimethyl borate.

3. Results and discussion

3.1. Chemical ionization mass spectra

In the adjustment of the source pressure to maximize the abundance of the *m/z* 73 ion, $(CH_3O)_2B^+$, two other reagent gas ions are observed at *m/z* 104, $(CH_3O)_3B^{\cdot +}$, with a relative abundance of ≅50%, and at *m/z* 177, $CH_3O[B(OCH_3)_2]_2^+$, with a lower abundance showing a tendency to increase slightly at a higher source pressure. The first two ions show up as (M − 1, M) signals with relative intensities of roughly 25:100, thus implying the presence of one boron atom. The third ion appears as (M − 2, M − 1, M) signals with relative intensities of roughly 6:49:100, confirming the presence of two boron atoms. Table 2 summarizes the relative abundances of the principal product ions formed upon reaction of the trimethyl borate ions with the arylalkylamines in the chemical ionization source of the mass spectrometer. The relative abundance of the adduct ions $[M + 73]^+$ ranges from 1% to 22% of the base peak and in general is higher than the abundance of the ions $[M + 41]^+$ which result from loss of methanol from the precursor $[M + 73]^+$ adduct ions.

Table 3
MIKE spectra of the $[M + 73]^+$ adduct ions of arylalkylamines

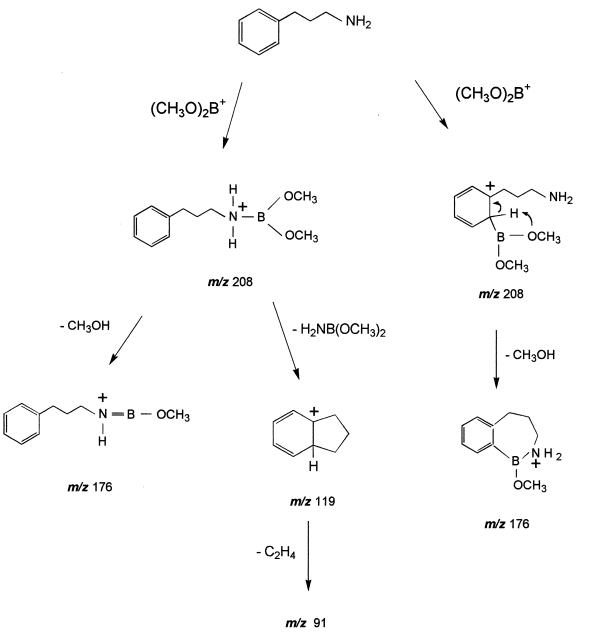
Benzylamine	$[M + 73 - CH_4]^+$ 50%	$[M + 73 - H_2NB(OCH_3)_2]^+$ 33%	$[M + 73 - CH_3^{\cdot}]^{\cdot +}$ 17%			
2-Phenylethylamine	$[M + 73 - H_2NB(OCH_3)_2]^+$ 67%	$[M + 73 - CH_3^{\cdot}]^{\cdot +}$ 17%	$[M + 73 - CH_3OH]^+$ 12%	$[M + 73 - C_6H_6]^+$ 2%	*m/z* 166 2%	
3-Phenylpropylamine	$[M + 73 - CH_3OH]^+$ 49%	$[M + 73 - H_2NB(OCH_3)_2]^+$ 31%	$[M + 73 - H_2NB(OCH_3)_2 - C_2H_4]^+$ 15%	*m/z* 180 5%		
4-Phenylbutylamine	$[M + 73 - CH_3OH]^+$ 64%	$[M + 73 - H_2NB(OCH_3)_2]^+$ 14%	$[M + 73 - NH_3]^+$ 13%	$[M + 73 - PhCH_2CH_2CHCH_2]^+$ 10%		
2-(4-Fluorophenyl)-ethylamine	$[M + 73 - H_2NB(OCH_3)_2]^+$ 39%	$[M + 73 - NH_3]^+$ 27%	$[M + 73 - CH_3OH - (CH_3)_2NH]^+$ 25%	$[M + 73 - CH_3OH]^+$ 6%	$[M + 73 - CH_3 - CH_2{=}NH]^+$ 3%	
2-(4-Nitrophenyl)-ethylamine	$[M + 73 - CH_2{=}NH]^+$ 96%	$[M + 73 - H_2NB(OCH_3)_2]^+$ 4%				
Tyramine	$[M + 73 - NH_3]^+$ 74%	$[M + 73 - H_2NB(OCH_3)_2]^+$ 11%	$[M + 73 - CH_3^{\cdot}]^{\cdot +}$ 7%	$[M + 73 - CH_3OH]^+$ 4%	*m/z* 132 2%	*m/z* 182 1%
2-(4-Methoxyphenyl)-ethylamine	$[M + 73 - H_2NB(OCH_3)_2]^+$ 68%	$[M + 73 - CH_3OH]^+$ 14%	$[M + 73 - NH_3]^+$ 10%	$[M + 73 - CH_3^{\cdot}]^{\cdot +}$ 8%		
Hordenine	$[M + 73 - (CH_3)_2NH]^+$ 75%	$[M + 73 - CH_3OH]^+$ 17%	$[M + 73 - (CH_3)_2NB(OCH_3)_2]^+$ 8%			
Dopamine	$[M + 73 - NH_3]^+$ 73%	$[M + 73 - H_2NB(OCH_3)_2]^+$ 22%	$[M + 73 - NH^3 - CH_3OH]^+$ 5%			
Octopamine	$[M + 73 - CH_3OH - OBOCH_3]^+$ 44%	$[M + 73 - CH_3OH]^+$ 14%	$[M + 73 - H_2O]^+$ 14%	*m/z* 126 14%	*m/z* 172 14%	
Synephrine	$[M + 73 - CH_3OH - OBOCH_3]^+$ 68%	$[M + 73 - H_2O]^+$ 17%	$[M + 73 - CH_3^{\cdot}]^{\cdot +}$ 10%	$[M + 73 - CH_3OH]^+$ 5%		
2-Phenyl-N-methylethylamine	$[M + 73 - CH_3OH]^+$ 54%	$[M + 73 - CH_3NHB(OCH_3)_2]^+$ 43%	$[M + 73 - C_6H_5CH_3]^+$ 3%			

3.2. MIKE spectra

The most relevant fragmentations revealed by the MIKE spectra of the $[M + 73]^+$ adduct ions are presented in Table 3. A striking general observation is that the most abundant fragment ion formed strongly depends on the number of carbon atoms in the aliphatic chain, the nature of the substituents in the aromatic ring and the presence of a benzylic hydroxy group. Loss of methanol, for example, is only most abundant for the $[M + 73]^+$ adduct ions of 3-phenylpropylamine, 4-phenylbutylamine and 2-phenyl-N-methylethylamine, in contrast with that described for the $[M + 45]^+$ adduct ions from dimethyl ether as reagent gas. This can tentatively be explained by the fact that loss of methanol requires the cleavage of a B–O bond, known to be quite strong. The relative abundances presented in Table 3 also indicate a competition between the various fragmentation pathways available for each adduct ion, with the exception of 2-(4-nitrophenyl)-ethylamine, where 96% of the total fragment ion current is due to loss of CH_2=NH. The discussion of the results below will be focused on the effect of (1) the aliphatic chain length for unsubstituted amines, (2) the type of substituents on the aromatic ring and (3) the presence of a benzylic hydroxy group, on the fragmentation pattern observed for the $[M + 73]^+$adduct ions.

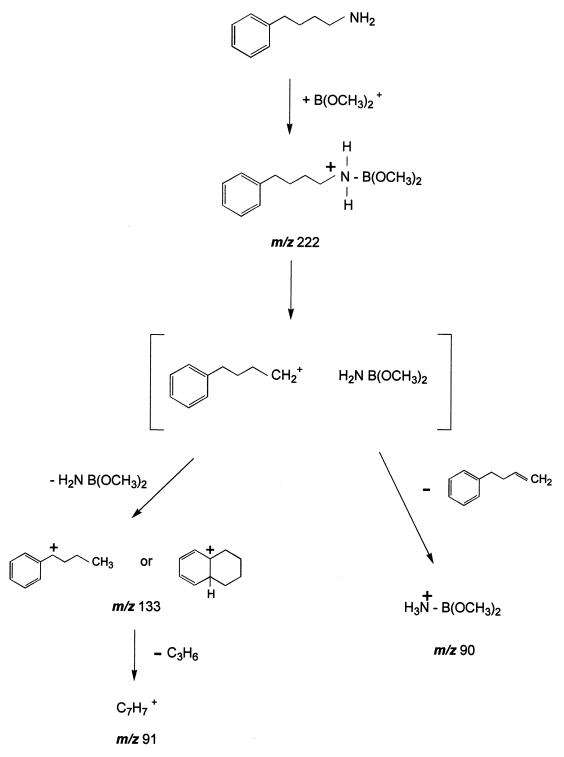
3.2.1. Unsubstituted arylalkylamines

With the exception of benzylamine, all the other unsubstituted amines including the secondary amine, form an adduct ion, $[M + 73]^+$, which decomposes essentially via two competing pathways: loss of methanol and loss of $H_2NB(OCH_3)_2$ (aminodimethoxyborane). The decreasing intensity of the peak due to loss of $H_2NB(OCH_3)_2$along the series of 2-phenylethylamine (67%), 3-phenylpropylamine (31%), and 4-phenylbutylamine (14%) is probably a consequence of the increasing stability of the quaternary ammonium ions that result from an initial attack of the amino group on the boron atom of the *m/z* 73 ion, a fact which is in agreement with the increasing gas-phase proton affinities previously determined [3]. An opposite trend is observed for the intensity of the peak



Scheme 1.

due to loss of methanol, which increases and reaches a maximum for 4-phenylbutylamine. This amine is also the only one to show a significant direct loss of NH_3 from the $[M + 73]^+$ adduct ion. These two observations, in particular that of the NH_3 loss, allow us to infer that the increasing intensity of the peak due to methanol loss, must be related to an increasing proportion of the initial reaction taking place at the aromatic ring, the remaining occurring at the amino group as shown in Scheme 1 for 3-phenylpropylamine. The $[M + 73]^+$ adduct ion of 4-phenylbutylamine is also the only one to generate an ion of $m/z = 90$ which is the result of the formation of an ion molecule complex between $H_2NB(OCH_3)_2$ and the phenylbutyl cation, which can decompose via two different pathways: loss of aminodimethoxyborane to give *m/z* 133 or abstraction of a proton from the cation to generate the ion $H_3NB(OCH_3)_2^+$ (*m/z* 90) (Scheme 2, Fig. 1). The formation of the latter ion for 3-phenylpropylamine is not observed. Instead, the ion resulting from the loss of $H_2NB(OCH_3)_2$ further decomposes by elimination of a molecule of ethylene, to give the stable ion *m/z* 91. The decrease of the



Scheme 2.

relative intensity of the peak due to loss of $CH_3NHB(OCH_3)_2$ from the $[M + 73]^+$ adduct of 2-phenyl-N-methylethylamine, as compared with the loss of $H_2NB(OCH_3)_2$ from that of 2-phenylethylamine, will be due to some steric hindrance caused by the methyl substitution at the amino group. Benzylamine behaves in a way that is quite different from that of the other three amines, particularly by showing

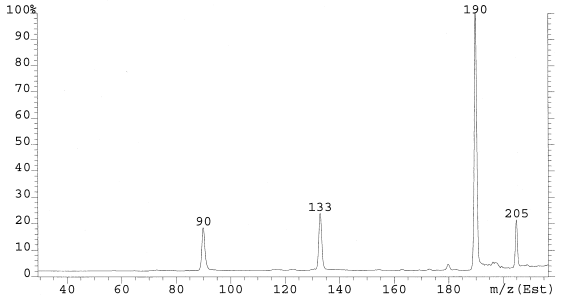


Fig. 1. MIKE spectrum of the $[M + 73]^+$ adduct ion of 4-phenylbutylamine.

loss of methane as the dominant fragmentation process. The MIKE spectra of the two $[M + 73]^+$ adducts formed with benzylamine and its amino dideuterated analogue are shown in Fig. 2. These spectra show that: (1) the peak at *m/z* 91 does not shift, but has a shoulder at *m/z* = 92 due to some H/D scrambling between the deuterated amino group and the aromatic ring, (2) the loss of $CH_3^{\cdot}$ is observed in both cases and shows no significant variation in its abundance, and (3) the peak at *m/z* 164 shifts to *m/z* 165 and 166, in the ratio 7:9, corresponding to losses of CH_3D and CH_4, respectively.

3.2.2. Arylalkylamines with substituents on the aromatic ring

The results presented in Table 3 for the arylalkylamines with an electron-withdrawing or electron-donating substituent in the aromatic ring show two competing fragmentations pathways: loss of aminodimethoxyborane and loss of ammonia or neutral amine. The only exception to this general behaviour is 2-(4-nitrophenyl)-ethylamine, in which most of the total fragment ion current (96%) is due to the ion $[M + 73 - CH_2{=}NH]^+$. The formation of this product ion can be rationalized in terms of an initial attack of the dimethoxyboron cation on the oxygen atom of the nitro group (Scheme 3) due to its very strong electrophilic character. The proposed mechanism also accounts for the elimination of methanol as the only significant loss from the $[M + 73 - CH_2{=}NH]^+$ ion as shown by its MIKE spectrum. The two fragmentation pathways mentioned above for all other substituted arylalkylamines, can be explained if two initial sites of reaction are considered: the aromatic ring (or substituent in the aromatic ring) and the amino group. In order to test the possibility of formation of an $[M + 73]^+$ adduct ion in which the boron atom is bonded to the phenolic hydroxy group, the hydroxy group of the amine hordenine has been deuterated and the MIKE spectrum of its $[M + 73]^+$ adduct ion recorded. The peak due to elimination of methanol is shifted up one mass unit and is not split up, indicating that no deuterium is incorporated in the neutral (Fig. 3). This observation is more consistent with reaction at the aromatic ring and not at the phenolic hydroxyl

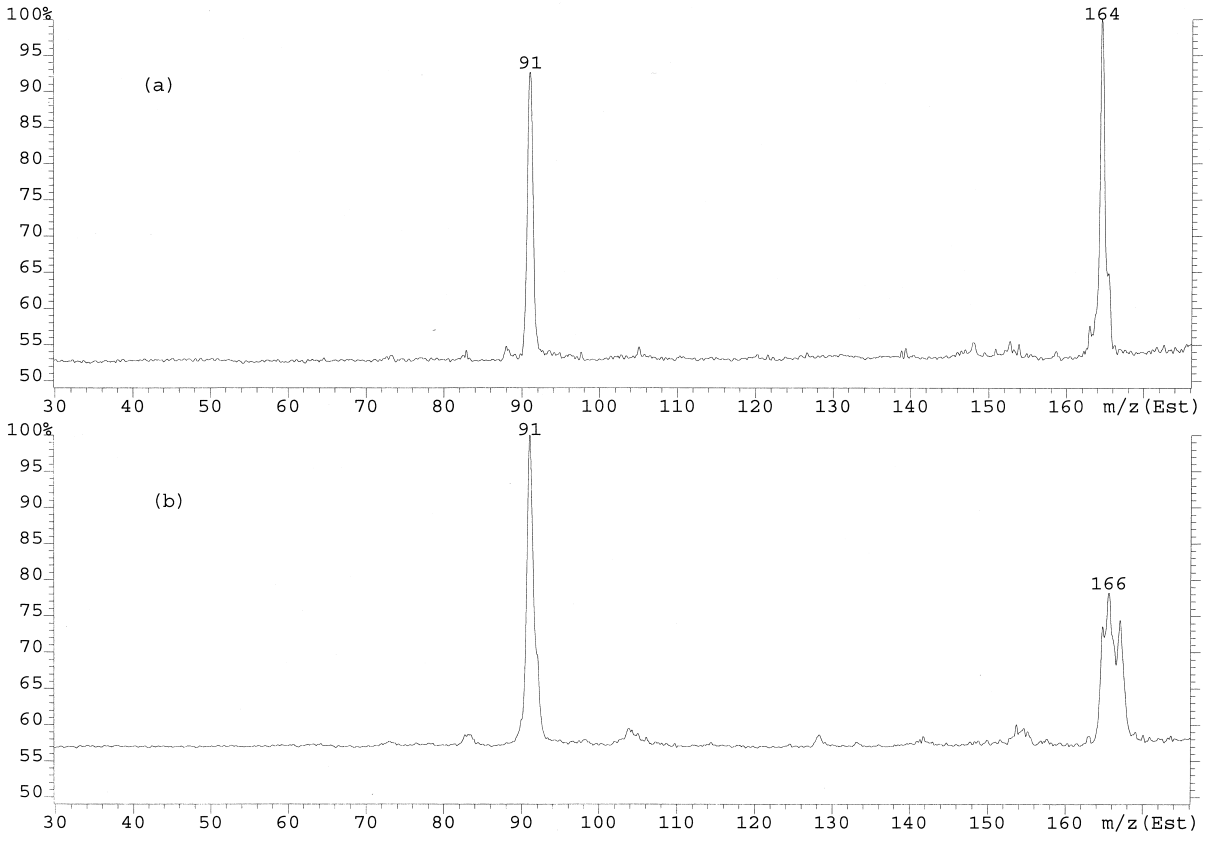
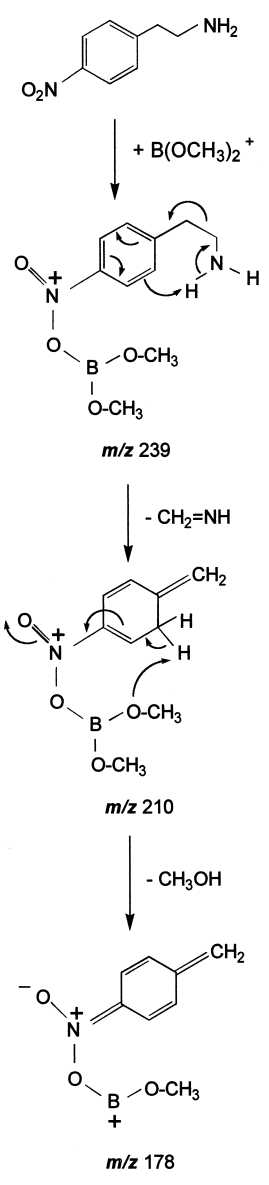


Fig. 2. (a) MIKE spectrum of the $[M + 73]^+$ adduct ion of benzylamine and (b) MIKE spectrum of the $[M + 73]^+$ adduct ion of benzylamine-d_2.

group, because in the latter case loss of CH_3OD and CH_3OH would be expected, assuming that the hydrogen atom involved in the methanol loss originates from the atom to which the dimethoxyboron cation becomes bonded and that some H/D exchange would occur. The peak due to elimination of dimethylamine is shifted up one mass unit and contains a "shoulder" at *m/z* 193, indicating that prior to dimethylamine elimination, deuterium scrambling involving the aromatic ring has occurred (Fig. 3). Contrary to that observed for the $[M + 45]^+$ adduct ion from dimethyl ether, the preferred site of reaction of not only hordenine but also tyramine with the dimethoxyborinium ion is the aromatic ring because the MIKE spectra show that loss of NH_3 [or $(CH_3)_2NH$] is the most abundant fragmentation channel of the adduct ions. This marked preference, as compared with the unsubstituted amines, can be explained by an increase in the electron density of the ring due to the presence of electron-donating substituents. 2-(4-methoxyphenyl)-ethylamine is an exception, because in this case loss of $H_2NB(OCH_3)_2$ yields the most abundant ion. The presence of a methoxy group on the ring may render the approach of the bulky dimethoxyborinium ion more difficult, which will favour the attack on the amino group. Dopamine, with the aromatic ring more activated than tyramine, consequently has a slightly higher tendency for the initial reaction to take place on the aromatic ring, which becomes evident from adding up the relative abundances of two of its decomposition products: the one arising from loss of NH_3 and the other from the consecutive loss of NH_3 and CH_3OH.



Scheme 3.

3.2.3. Substituted arylalkylamines with a benzylic hydroxy group

The dominant fragmentation pathway of the adduct ion formed between the dimethoxyborinium ion and octopamine and synephrine is loss of methanol followed by loss of O=$BOCH_3$ (Scheme 4, for octopamine). Although, in terms of the mass-to-charge ratio of the product ion formed, this consecutive loss is equivalent to a single loss of $HOB(OCH_3)_2$, there is evidence in favour of the first hypothesis: for both compounds the MIKE spectra of the $[M + 73]^+$ adduct ions contain a peak due to elimination of methanol, and those of the $[M + 73 - CH_3OH]^+$ product ions a peak due to elimination of O=$BOCH_3$. These observations are interpreted in terms of an initial attack of the dimethoxyborinium ion on the benzylic hydroxy group, the driving force for the decompositions observed being not only the formation of a strong boron-oxygen bond, but also the formation of a resonance-stabilized product ion as shown in Scheme 4. The formation of a similar product ion but with an initial attack of the boron cation on the amino group, followed by proton migration from the amino group to the hydroxy group, would explain the loss of water also shown by the MIKE spectra of the $[M + 73]^+$ adduct ions of these two compounds. The absence of fragmentation pathways leading to the loss of NH_3 (for octopamine) and CH_3NH_2 (for synephrine) and loss of amino-dimethoxyborane indicates that for these two amines, a competition for the dimethoxyborinium ion exists between the amino and benzylic hydroxy group, but not with the aromatic ring. The proximity of these two groups and the possibility of formation of hydrogen bonds between the oxygen atom of the methoxy group and either the amino or hydroxy group, could account for the obvious preference of initial site of reaction at these two nucleophilic centers.

4. Conclusions

The arylalkylamines used in this study react with the dimethoxyborinium ion, $(CH_3O)_2B^+$, to generate $[M + 73]^+$ adduct ions, whose fragmentation pathways are strongly dependent on the structural features of the substrate, namely: (1) aliphatic chain length for the unsubstituted amines; (2) type of substituents on the aromatic ring; and (3) presence of a benzylic hydroxy group. Contrary to that observed for the unimolecular decompositions of the $[M + 45]^+$ adduct ions formed by reaction of the arylalkylamines with dimethyl ether, in which loss of methanol leads

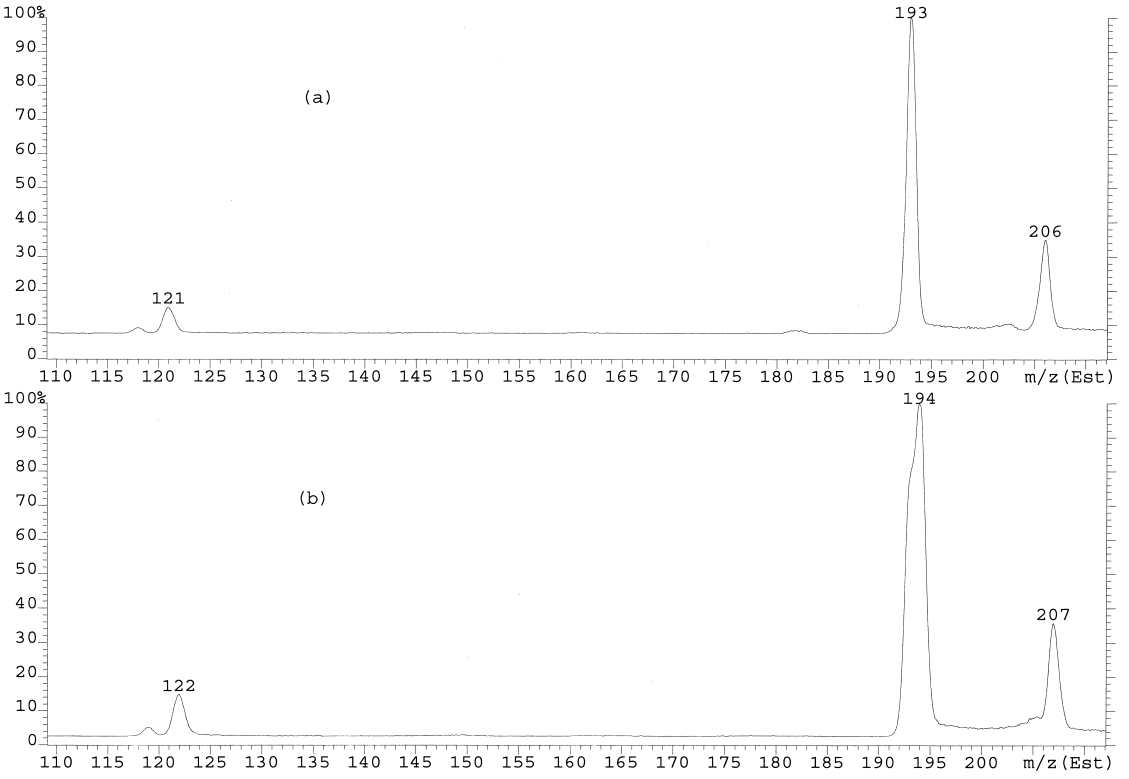
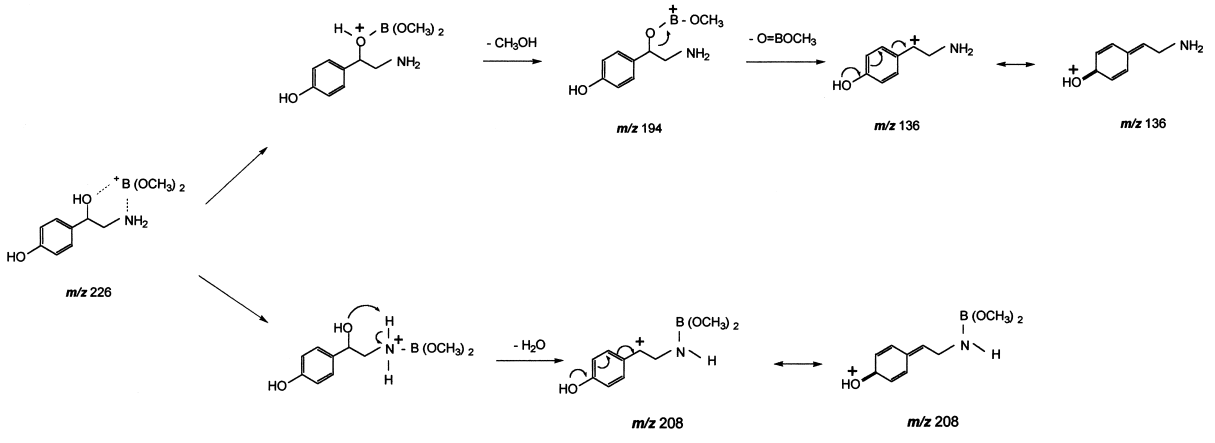


Fig. 3. (a) MIKE spectrum of the $[M + 73]^+$ adduct ion of hordenine and (b) MIKE spectrum of the $[M + 73]^+$ adduct ion of hordenine-d_1.

to the most abundant ion, the direct loss of methanol from the presently studied $[M + 73]^+$ adduct ions is only for a few cases the dominant pathway, in particular for some of the amines which are not substituted on the aromatic ring and do not have a benzylic hydroxy group. This tentatively can be explained by the fact that loss of methanol requires cleavage of a B–O bond, which is known to be quite



Scheme 4.

strong. The presence of activating substituents in the aromatic ring increases the probability of initial attack on the ring by the electrophilic reagent ion. In fact, the main decomposition pathway for the $[M + 73]^+$ ions of the substituted amines is loss of ammonia or an amine. A benzylic hydroxy group, whenever present, becomes the preferred site of initial reaction, followed by losses of water or methanol and $O{=}BOCH_3$. In conclusion the dimethoxyborinium ion has proven to be a much more selective reagent ion than the methoxymethyl cation from dimethyl ether, because the unimolecular decompositions of the $[M + 73]^+$ adduct ions formed are substantially more dependent on the different structural features of the arylalkylamines studied.

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