Stereochemical Effects in Mass Spectrometry: Preferential Formation of Bromonium Ions from *trans*-Substituted 1,1′,2,2′-Polyalkyl-2,2′-dibromodiethyl Ethers

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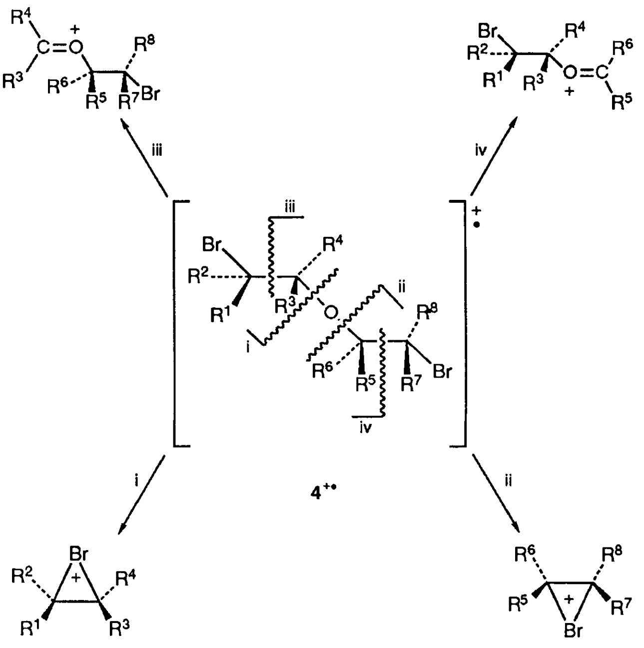
The relative abundance of bromonium ions in the electron ionisation mass spectra of acyclic 1,1′,2,2′-polyalkyl-2,2′-dibromodiethyl ethers is enhanced by *trans* stereochemistry of the alkyl groups.

The bromination of alkenes is of fundamental importance in organic chemistry.[1] Cyclic bromonium ion intermediates usually play key roles in this reaction, especially in non-polar solvents.[2,3] A variety of mass spectrometric measurements[4,5] have established that many simple bromonium and other halonium ions are stable species in the gas-phase; indeed, $\overline{CH_2CH_2Br}^+$, **1**, has even been employed as a reagent ion in chemical ionisation mass spectrometry.[6] Recent molecular orbital calculations indicate that **1** is 6 kJ mol^{-1} more stable than CH_3CH^+Br ($\longleftrightarrow CH_3CH{=}Br^+$), **2**, with an energy barrier of *ca.* 100 kJ mol^{-1} towards interconversion of **1** and **2**.[7] In contrast, $^+CH_2CH_2Br$, **3**, was not found to lie in a potential energy well, but to represent a transition state at a much higher energy (*ca.* 125 kJ mol^{-1}) than **1** or **2**.[7] Other MO calculations have suggested that the structure of homologous bromonium ions varies with the substitution pattern of the alkyl groups attached to the two carbon atoms of the ring in **1**: unsymmetrical substitution causes distortion of the symmetrical structure of **1**, resulting in a longer C–Br bond to the more heavily substituted carbon atom.[8]

The 70 eV 4 kV electron ionisation mass spectra of 1,1′,2,2′-polyalkyl-2,2′-dibromodiethyl ethers, **4**,[9] contain prominent peaks corresponding to $C_nH_{2n}Br^+$ bromonium ions. These ions may be considered to arise by fragmentation of the molecular ion *via* routes (i) or (ii), see Scheme 1. The combined abundances of these bromonium ions typically amounts to 18–45% of the total ion current in the mass spectra of **4**.



4a; $R^1, R^2, R^3, R^4, R^5, R^7 = H; R^6, R^8 = CH_3$ (*sym*)-*cis*
b; $R^1, R^2, R^3, R^4, R^5, R^8 = H; R^6, R^7 = CH_3$ (*sym*)-*trans*
c; $R^1, R^3 = H; R^2, R^4, R^5, R^6, R^7, R^8 = CH_3$ *cis*-(*sym*)
d; $R^1, R^4 = H; R^2, R^3, R^5, R^6, R^7, R^8 = CH_3$ *trans*-(*sym*)
e; $R^1, R^3, R^5, R^7 = H; R^2, R^4, R^6, R^8 = CH_3$ *cis-cis*
f; $R^1, R^3, R^5, R^8 = H; R^2, R^4, R^6, R^7 = CH_3$ *cis-trans*
g; $R^1, R^4, R^5, R^7 = H; R^2, R^3, R^6, R^8 = CH_3$ *trans-cis*
h; $R^1, R^4, R^5, R^8 = H; R^2, R^3, R^6, R^7 = CH_3$ *trans-trans*
i; $R^1, R^3, R^5, R^8 = H; R^2, R^4 = CH_3; R^6, R^7 = C_2H_2$ *cis-trans*
j; $R^1, R^4, R^5, R^8 = H; R^2, R^3 = CH_3; R^6, R^7 = C_2H_5$ *trans-trans*

Scheme 1†

Table 1 Relative abundance of ions corresponding to the fragmentations (i) and (ii) in the mass spectra of **4**

	Fragmentation				
	(i)		(ii)		
Compound	*m/z*	RA[a]	*m/z*	RA[a]	$x = \frac{RA^a(i)}{RA^a(ii)}$
4c	135/137	85	163/165	96	0.89
4d	135/137	118	163/165	72	1.64
4i	135/137	199	163/165	144	1.38
4j	135/137	198	163/165	47	4.24

[a] Relative abundances measured from peak heights in 70 eV, 4 kV spectra recorded on a KRATOS MS 80 double-focusing mass spectrometer operating at a source temperature of *ca.* 200 °C. These data are normalised to a value of 100 units for the base peak; the quoted RAs represent the sum of the individual abundances of ions containing ^{79}Br and ^{81}Br isotopes. In the cases of **4a** and **4b**, formation of the unsubstituted bromonium ion (*m/z* 107/109) was very strongly favoured over production of the dimethylated homologue (*m/z* 135/137). In such circumstances, the variation in the ratio (x = 9.4 and 10.5, respectively) may not be significant.

Table 2 Relative abundances of ions corresponding to the fragmentations [(i) + (ii)] and [(iii) + (iv)] in the mass spectra of **4**

	Fragmentation				
	(i)/(ii)		(iii)/(iv)		
Compound	*m/z*	RA[a]	*m/z*	RA[a]	$y = \frac{RA^a[(i)+(ii)]}{RA^a[(iii)+(iv)]}$
4e	135/137	199	179/181	172	1.16
4f	135/137	178	179/181	123	1.44
4g	135/137	199	179/181	138	1.46
4h	135/137	198	179/181	95	2.07

[a] See Table 1 for the significance of this footnote.

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† These bromoethers were prepared by addition of bromine to a 2 : 1 mixture of the appropriate epoxide and alkene in pentane at −78 °C.[9] The upper left- and lower right-hand portions of **4** originate from the epoxide and alkene respectively. *Cis* and *trans* refer to the stereochemistry of the substituents within each of the two bromoethyl groups when the appropriate C–Br and C–O bands are antiperiplanar; the expression *sym* denotes a case in which all four substituents in a particular bromoethyl group are identical. The assignment of the stereochemistry of the bromoethers was based on the assumption that opening of both the bromonium ion and the epoxide rings occurs with inversion of configuration. Only one diastereoisomer (or, in the case of **4e–4j**, a single pair of diastereoisomers differing only in relative stereochemistry at C1 and C1′) could be detected by ^1H and ^{13}C NMR spectrometry. All the bromoethers were racemic mixtures of enantiomers, but a single enantiomer is depicted for clarity. Similarly, the relative stereochemistry at C1 and C1′ is neglected for simplicity; although **4e–4j** are actually mixtures of two diastereoisomers, each of the fragmentations (i)–(iv) yields product ions having structures that are not influenced by the relative stereochemistry of C1 and C1′.

Two trends in the relative abundance of ions derived *via* routes (i) and (ii) indicate that production of *trans*-1,2-dialkyl bromonium ions occurs more readily than formation of their *cis*-stereoisomers.

First, in systems in which non-isomeric bromonium ions are produced, the ratio, x, of the abundances of ions formed *via* routes (i) and (ii), respectively, is enhanced in cases involving formation of a *trans*-1,2-dialkylbromonium ion *via* route (i), see Table 1. Thus, the abundance of $\mathrm{CH_3\overline{CHCHBr}CH_3^+}$ is greater, when compared to the abundance of $\mathrm{CH_3CH_2\overline{CHCHBr}CH_2CH_3^+}$, if the two methyl substituents have *trans*-stereochemistry (**4j**, x = 4.24) rather than *cis*-stereochemistry (**4i**, x = 1.38). Similarly, the relative abundance of $\mathrm{CH_3\overline{CHCHBr}CH_3^+}$ is greater, compared to that of $\mathrm{(CH_3)_2\overline{CCBr}(CH_3)_2^+}$, in the spectrum of **4d** than in that of **4c** (x = 1.64 and 0.89, respectively).

Secondly, in systems in which routes (i) and (ii) lead to isomeric bromonium ions, the ratio, y, of the combined bromonium ion abundance relative to the total abundance of bromo-oxonium ions formed *via* routes (iii) and (iv) is also increased when *trans*-bromonium ions can be produced, see Table 2. Thus, for **4e**, **4f**, **4g** and **4h**, in which the pairs of methyl groups have *cis-cis, cis-trans, trans-cis* and *trans-trans* orientations, respectively, the corresponding values for y are 1.16, 1.44, 1.46 and 2.07.

Assuming that the assignment of the stereochemistry of the bromoethers is correct, all of these data are consistent with the interpretation that dissociative ionisation of **4** yields cyclic bromonium ions. Moreover, production of bromonium ions having *trans*-1,2-disubstitution patterns appears to be kinetically and/or thermodynamically more favourable than formation of their *cis*-isomers. This preference for forming *trans*-1,2-dialkylbromonium ions possibly reflects steric effects, which can exert a significant influence on the kinetics and thermodynamics of bromonium ion formation.[3,7]

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