Stereochemical Differentiation of Isomeric Trinorbornane-2,3- and Trinorbornane-2,5-diols by Chemical Ionization Mass Spectrometry

Tuula Partanen,* Mika Pykäläinen, Hannele Hulkkonen, Olli Savolainen and Pirjo Vainiotalo*
University of Joensuu, Department of Chemistry, PO Box 111, FIN-80101 Joensuu, Finland

Because stereoisomeric trinorbornane-2,3- and trinorbornane-2,5-diols cannot be distinguished under electron ionization, their differentiation was investigated under chemical ionization. The spectra were recorded using ammonia, isobutane, methane, acetone and trimethyl borate as reagent gas. Although all the stereoisomers could be identified, the differences between the *cis*-2,3-diols were minor. By contrast, the *trans*-2,3- and 2-*endo*-5-*endo*-diol isomers were easily differentiated from their corresponding stereoisomers. Stereochemical effects were greatest under isobutane, acetone and trimethyl borate chemical ionization. The collision-induced dissociation mass spectra of the $[M + NH_4]^+$ adduct ions also allowed most of the stereoisomers to be distinguished.

The stereochemical effects found for cyclic diols under chemical ionization (CI) have been intensively studied during the past two decades.[1-6] With the hydroxy group being one of the most important functional groups in biologically relevant molecules, cyclic diols are widely used as models of structurally more complex natural products that contain multiple hydroxy groups.[7] The mass spectrometric differentiation of stereoisomeric cyclic 1,2-diols is difficult to achieve by electron ionization (EI).[6,8] The greater proton affinity of *cis*-cyclopentane-1,2-diol relative to that of the *trans* isomer, however, allows the differentiation of these isomers under CI.[1,2] Cyclohexane-1,2-diols are more difficult to distinguish because a stabilized proton-bridge or chelate structure is formed for the *trans* isomer as well as the *cis* isomer owing to the conformational flexibility of the cyclohexane ring system and/or the vicinity of two hydroxy groups.[1,2] The rigid trinorbornane skeleton, in which substituents are fixed in a precisely known stereochemical position in the molecule, offers a convenient opportunity to examine the stereochemical interactions between functional groups. Much remains to be discovered, however, about the mass spectrometric behaviour of diols having trinorbornane skeleton. Only EI mass spectra have been published, and only for some derivatives.[8]

Many novel CI reagent gas systems have been developed for the study of isomeric compounds: acetone,[9] trimethyl borate,[10] methyl chloride,[11] formaldehyde dimethyl acetal[12] and methylene chloride,[13] for example, for the differentiation of isomeric alcohols. In particular, trimethyl borate ion and its complex ions react stereospecifically in the gas phase with *cis*-cyclopentane- and *cis*-cyclohexane-1,2-diol, allowing these isomers to be distinguished from the corresponding *trans* isomers.[10]

As a continuation of our studies on stereoisomeric bornane[6] and trinorbornane/ene[14] derivatives, we now examine the mass spectral behaviour of trinorbornane-2,3-diols (**1**–**3**) and trinorbornane-2,5-diols (**4**–**6**) (Scheme 1) under ammonia (proton affinity E_{pa}/kJ mol^{-1} = 854),[15] methane (551),[15] isobutane (802; 2-methylpropene),[16] acetone (823)[15] and trimethyl borate (TMB) CI. Our main aim was to find methods for their stereochemical differentiation.

Results and Discussion

The 70 eV EI mass spectra of isomeric trinorbornanediols have been recorded by Grützmacher and Fechner.[8] Although the ionized stereoisomeric compounds **1**–**6** give rise to identical spectra, the ionized positional isomers can be distinguished from each other (examples presented in Fig. 1). The molecular ion peak at *m*/*z* 128 occurs in the spectra of all the 2,3-diols (**1**–**3**) and also in the spectrum of the 2-*endo*-5-*endo*-diol **5**. From the abundances of the molecular ions, it can be concluded that the di-*endo* isomers (**2** and **5**) are always more stable than the respective di-*exo* and *trans* (*exo*–*endo*) isomers (**1** and **3**, **4** and **6**).

1 - 3 **4 - 6**

Compound	Isomer	Compound	Isomer
1	di-*exo*	**4**	di-*exo*
2	di-*endo*	**5**	di-*endo*
3	*trans* (*exo-endo*)	**6**	*trans* (*exo-endo*)

Scheme 1

Ammonia CI Mass Spectra.—In the ammonia CI mass spectra of the diols, the $[M + NH_4]^+$ ion peaks at *m*/*z* 146 were virtually the only peaks and, as such, the spectra were uninformative. However, the CID (collision-induced dissociation) mass spectra of the adduct ions revealed some stereochemical effects (Table 1).

The two *cis*-2,3-diols (**1** and **2**) gave rise to almost identical CID mass spectra and could be differentiated only with difficulty since their adduct ions decomposed similarly, mainly through the loss of ammonia and water giving rise to the ions at *m*/*z* 129 and 128, respectively. For the *trans* isomer **3**, elimination of NH_3 from the adduct ion was not observed, but rather the loss of water through an intramolecular substitution reaction (S_Ni).[6,17,18] In this respect, the 2,3-diols **1**–**3** decomposed in the same way as the corresponding bornane-2,3-diols.[6] In the case of the *cis*-bornane-2,3-diols, however, the loss of ammonia is far more favourable for the di-*endo* isomer than for the di-*exo* isomer due to steric crowding caused by the methyl groups at C-1 and -7 in the di-*exo* isomer. Although the $[M + NH_4]^+$ adduct ion is sterically more crowded for the 2-*endo*-3-*endo*-diol **2** than the 2-*exo*-3-*exo*-diol **1**, the steric hindrance caused by the hydrogen atoms is not large enough to cause a notable difference in the elimination of ammonia.

In contrast to the 2,3-diols, all the 2,5-diols **4**–**6** could be distinguished by the CID method, although differences were not always large. Among the 2,5-diols **4**–**6**, only the di-*endo* isomer **5** was capable of forming an ammonium chelate structure with

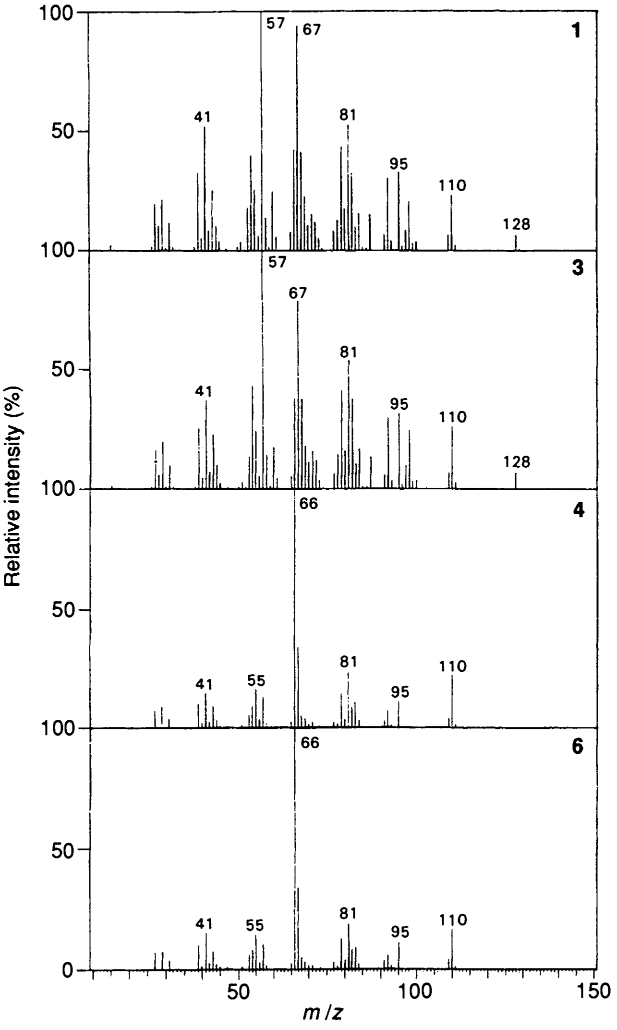


Fig. 1 70 eV mass spectra of compounds **1**, **3**, **4** and **6**

linear hydrogen bonds (Scheme 2). This chelate structure almost totally prevented the loss of water through $S_{N}i$ reaction (ion at *m*/*z* 128) and ammonia was eliminated instead (ion at *m*/*z* 129). For the di-*exo* and *trans* isomers **4** and **6**, we observed the intramolecular substitution reaction, and it was more favourable for di-*exo* isomer **4** than *trans* isomer **6**. The related monoalcohols, *exo*- and *endo*-trinorborneol, behave analogously: the ion due to the $S_{N}i$ reaction is far more abundant in the ammonia CI mass spectra of the *exo* isomer.[19]

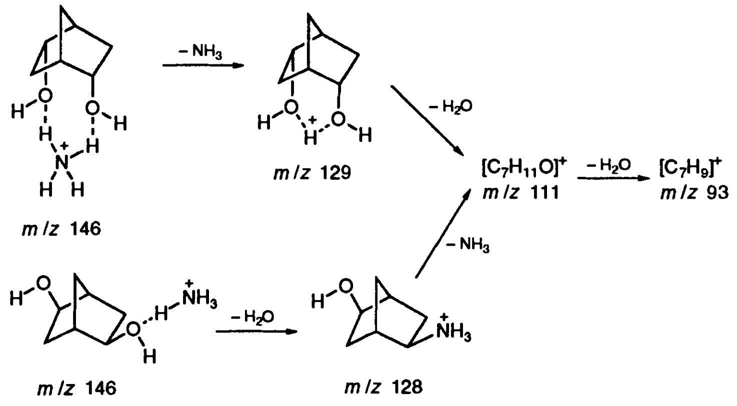
Table 1 Collision-induced dissociation mass spectra of the $[M + NH_4]^+$ ions generated from norbornanediols **1**–**6** by ammonia chemical ionization[a]

m/*z*	**1**	**2**	**3**	**4**	**5**	**6**
38	1.3	1.6	2.2	1.9	1.1	1.6
40	1.3	1,5	1.9	1.5	1.0	1.6
41	—	—	—	0.3	—	—
53	—	0.4	1.7	1.5	0.2	0.9
55	2.0	2.3	2.7	2.7	1.5	2.4
57	2.4	2.9	3.7	1.6	1.1	1.7
65	0.8	—	1.7	1.6	1.4	1.6
66	2.5	2.8	3.5	10.0	8.1	8.1
67	8.4	8.3	10.2	12.3	9.0	9.8
68	1.3	1.4	1.8	1.5	0.2	0.4
77	4.2	4.5	5.3	3.9	3.4	3.5
79	3.0	3.5	4.6	2.9	2.2	2.5
81	5.0	5.9	7.7	4.1	3.4	4.1
82	6.0	7.1	8.8	1.6	0.9	1.3
83	—	0.2	0.9	1.9	0.9	1.3
91	4.4	4.6	5.0	3.6	3.4	3.5
92	1.4	1.6	1.9	—	—	—
93	13.4	14.0	12.9	8.5	10.6	10.1
94	0.4	0.2	—	—	—	—
95	1.6	1.8	1.9	1.6	1.0	1.0
109	—	—	—	1.5	1.0	1.4
110	5.3	5.1	7.0	4.2	3.3	3.6
111	23.1	20.3	10.1	11.6	27.5	17.1
112	1.3	—	—	—	1.6	0.6
127	—	—	—	2.8	—	2.4
128	1.5	2.7	4.5	14.1	1.3	12.7
129	9.4	7.3	—	2.7	14.8	6.9
130	—	—	—	—	1.0	—

[a] Intensities are normalized to a total fragment ion abundance of 100. Data are not corrected for metastable peaks.

Methane CI Mass Spectra.—As a consequence of the highly exothermic protonation process under methane CI, all the $[M + H]^+$ ions at *m*/*z* 129 were unstable and decomposed readily through the loss of one or two water molecules. In addition, the spectra contained intense peaks at *m*/*z* 67 and 81. The spectra of the stereoisomeric compounds were never sufficiently different, however, to allow differentiation of the stereoisomers.

Isobutane CI Mass Spectra.—The $[M + H]^+$ ions at *m*/*z* 129 decomposed less under isobutane CI than under methane CI and the fragment peaks at *m*/*z* 111 due to the loss of water were the only peaks of high intensity. Table 2 presents the partial isobutane CI mass spectra. The isobutane CI spectra allowed differentiation of the *trans*-2,3-diol **3** and 2-*endo*-5-*endo*-diol **5** from their respective stereoisomers. The $[M + H]^+$ ions generated from compounds **1**, **2** and **5** were stabilized by a linear proton-bridge, like that established in the protonated molecules of *cis*-cyclopentane-1,2-diol.[1] Since the extent of the stabilization was concluded to depend on the internal O$\cdots$O distance (Table 2), trinorbornane-2-*exo*-7-*syn*-diol was also



Scheme 2

Table 2 Partial isobutane chemical ionization mass spectra of trinorbornanediols **1–6** and trinorbornane-2-*exo*-7-*syn*-diol and calculated internal O ··· O distances

	Relative intensity of the ions				
Isomer	$[M + H]^+$	$[M - H]^+$	$[M + H - H_2O]^+$	$[M + H - 2 H_2O]^+$	Internal O ··· O distance/Å[a]
1 2,3-di-*exo*	100.0	12.9	96.0	5.4	2.63
2 2,3-di-*endo*	100.0	10.2	94.2	6.0	2.68
3 2,3-*trans*	6.3	9.0	100.0	9.3	3.50
4 2,5-di-*exo*	5.4	—	100.0	7.5	—
5 2,5-di-*endo*	36.7	1.1	100.0	4.8	3.62
6 2,5-*trans*	6.1	3.8	100.0	6.6	—
2-*exo*-7-*syn*	60.9	—	100.0	4.9	2.81

[a] Calculated by ALCHEMY II + III.

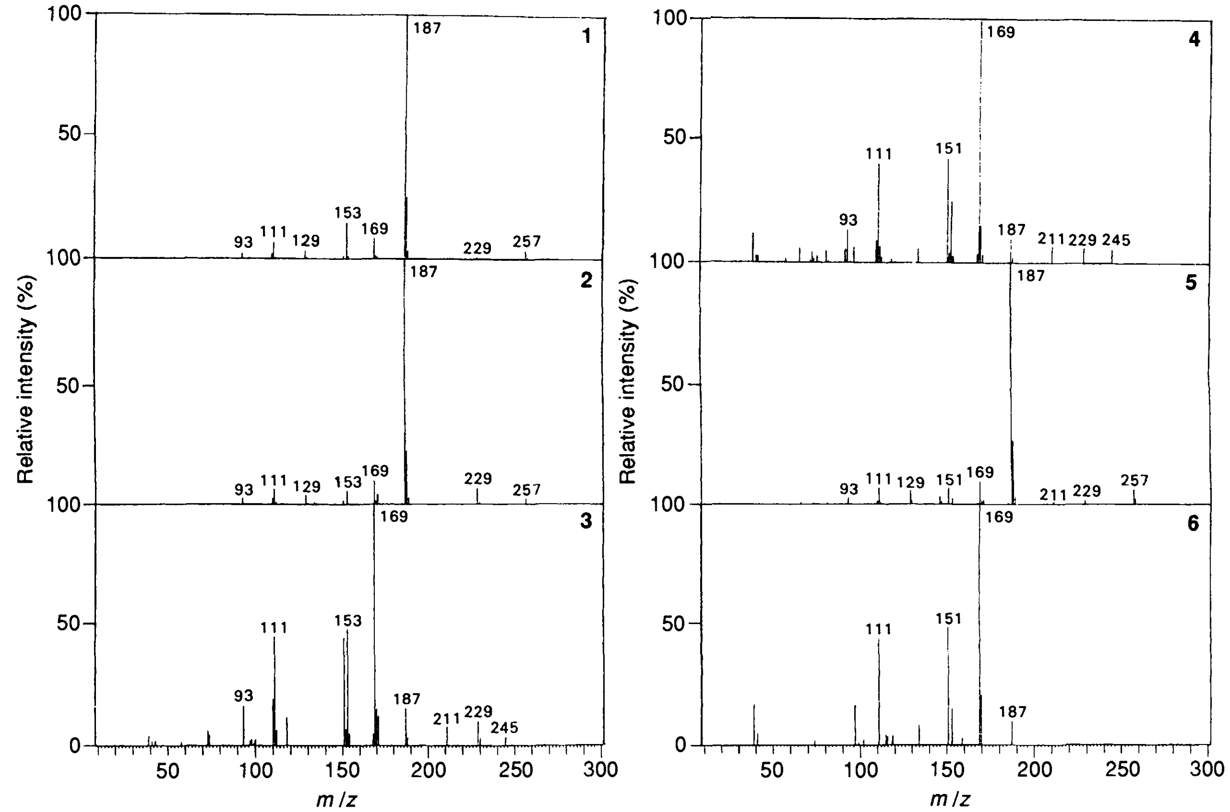


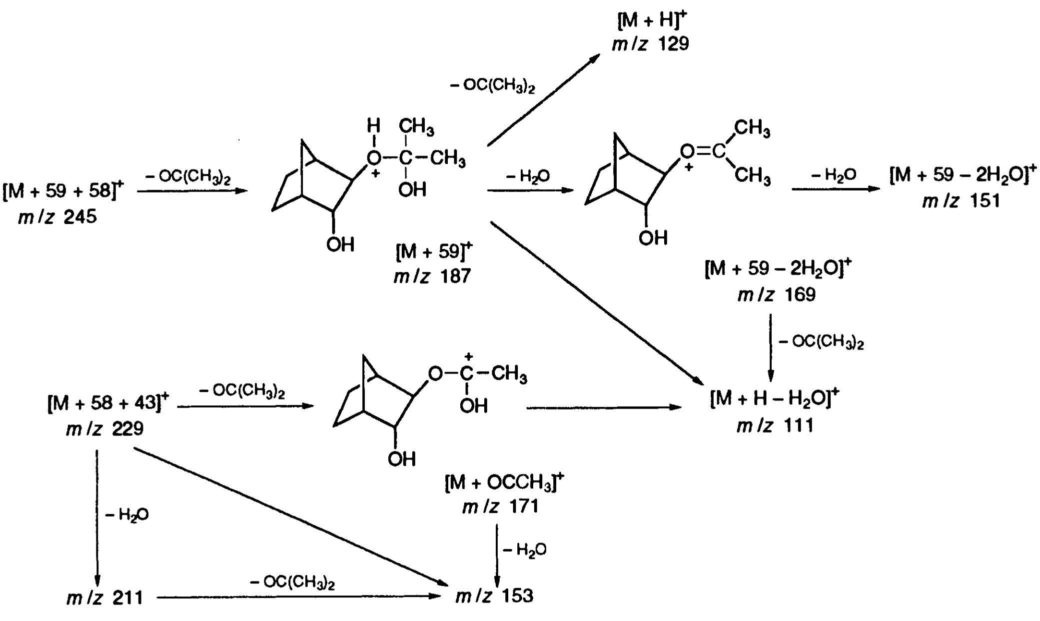
Fig. 2 Acetone chemical ionization mass spectra of compounds **1–6**

investigated. According to calculations using the Alchemy II + III program, the distance between oxygen atoms in the 2-*exo*-7-*syn*-diol and in compounds **1–3** and **5** is favourable for the formation of a proton-bridge. However, in compound 3, the stereochemistry does not allow the formation of a linear hydrogen bond. In the case of compounds **1**, **2**, **5** and the 2-*exo*-7-*syn*-diol, the distance between the oxygen atoms correlated well with the intensity of the $[M + H]^+$ ions. When the linear proton-bridge could not form the protonated molecule was unstable and decomposed almost totally through the loss of water.

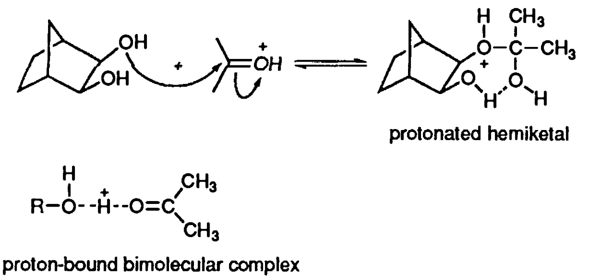
In the hope of finding greater differences between the isomeric compounds, we went on to measure the CID mass spectra of the $[M + H - H_2O]^+$ ions at *m*/*z* 111. Comparison of the CID mass spectra suggested that the structures of the dehydration products of five of the six protonated diols are identical; only 2-*exo*-5-*exo*-diol **4** gave rise to clearly distinct CID mass spectra. The similarity of the other CID mass spectra could be a consequence of a rupture of the trinorbornane framework during the collision activation in such a way that the stereospecificity of the molecules is lost.

Acetone CI Mass Spectra.—The acetone CI mass spectra are presented in Fig. 2 and the main reaction and fragmentation pathways in Scheme 3. For simplicity, only the ion structures of *trans*-2,3-diol **3** are included in the scheme. All six isomers could be distinguished, the differentiation of the *trans*-2,3-diol **3** and 2-*endo*-5-*endo*-diol **5** from their respective stereoisomers being especially easy.

For compounds **1**, **2** and **5**, the base peak was formed by the $[M + 59]^+$ adduct ion at *m*/*z* 187. This, together with the constant intensity of the adduct ion peaks at *m*/*z* 187 as the distance between the oxygen atoms changed (*cf.* intensity of the $[M + H]^+$ ion peaks under isobutane CI), can be explained by the hemiketal structure of the adduct ion (Scheme 4). Alcohols and ketones are known to react in the same way in the liquid phase,[20] and moreover, the ion–molecule reaction of protonated acetaldehyde and methanol results partly in a protonated hemiacetal product.[21] A proton-bound bimolecular complex structure for the $[M + 59]^+$ ion, which has previously been proposed for alcohols, does not explain the obtained spectra.[9] For compounds **1**, **2** and **5**, the formation of protonated hemiketal leads to a highly stable hydrogen-bonded



Scheme 3



Scheme 4

seven- or nine-membered chelate structure. Although the adduct ion formed from 2-*endo*-5-*endo*-diol **5** is sterically more hindered than the adducts of the *cis*-2,3-diols **1** and **2**, differences were not observed in the spectra.

For compounds **3**, **4** and **6**, the stability of the $[M + 59]^+$ adduct ion was low, since the ability to form an internal hydrogen bond was reduced or totally prevented. The loss of water from the adduct ion was favourable resulting in the $[M + 59 - H_2O]^+$ ion at *m/z* 169. The elimination of water is easily understood from the hemiketal structure of the adduct ion (Scheme 3), though it is also possible that the ion at *m/z* 169 originated from the reaction of acetone with the secondary fragment ion at *m/z* 111 formed from the protonated molecule. In the case of compounds **3**–**6**, the subsequent loss of water from the ion at *m/z* 169 gave rise to the ion at *m/z* 151 (Scheme 3).

The formation of the adduct ions $[M + 59 + 43]^+$ and $[M + 43]^+$ at *m/z* 229 and 171, respectively, was relatively favourable when the protonated acetone adduct had no opportunity to form the hydrogen-bonded seven- or nine-membered chelate structure. However, these adduct ions proved to be unstable and they decomposed to the ion at *m/z* 153. The mechanism for the formation of the ion at *m/z* 153 from the $[M + 43]^+$ adduct ion is not clear, as the loss of water can take place in several different ways. The difference in the abundance of the $[M + 43 - H_2O]^+$ ions for 2,3- and 2,5-diols nevertheless suggested two different mechanisms, and these were further studied by using deuteriated acetone as reagent gas. Since the hydrogen atoms located in the hydroxy groups were not exchanged for deuterium atoms, and since the $[M + OCCD_3]^+$ adduct ion lost H_2O, not HDO, it could be concluded that the reactant ion was not involved in the elimination. With only this information, however, it was impossible to assign precise structures to the ion at *m/z* 153.

TMB CI Mass Spectra.—Boric acid derivatives of the diols have been thoroughly investigated in the liquid phase.[22] 1,2-Diols react with boric acid and its esters to form cyclic complexes only when the two hydroxy groups in the diol are *cis* to each other. If such reactions were also to occur in the gas phase, they would be useful in the differentiation of stereoisomeric cyclic diols. In work done with stereoisomeric cyclopentane-1,2-diols, cyclohexane-1,2-diols and some mono- and di-saccharides under TMB–H_2O–CH_4 reagent gas mixture, Suming and co-workers[10] observed the formation of cyclic ion–molecule reaction products, especially with *cis*-diols. Their results encouraged us to examine the reaction of TMB with the trinorbornanediols **1**–**6**. To find the ideal reaction conditions, various reagent gas mixtures and concentration ratios were tested. The mass spectra of TMB, isobutane–TMB and methane–TMB plasma are shown in Fig. 3. In the following text, only the *m/z* values of the major ^{11}B isotope peaks are mentioned, these peaks are always accompanied by the corresponding isotopic peaks of ^{10}B. The plasma obtained with the reagent gas mixtures differed from the pure TMB plasma: first, with isobutane–TMB, the reactant ions of isobutane were present; second, with all reagent gas mixtures, the protonation reaction of TMB was favourable (leading to the ion at *m/z* 105); and third, the use of methane promoted the decomposition of TMB (intense fragment ion at *m/z* 73). Most of our subsequent measurements were made under reagent gas mixtures, since they proved to be more convenient for the filament. However, with all the reagent gas mixtures, and even under pure TMB, the observed ion–molecule reactions were the same, though for compounds **1**, **2** and **5**, the abundance of the product ions was strongly dependent on the reaction conditions.

The effect of sample concentration in the ion source was examined under pure TMB CI, with samples introduced by both direct inlet and from a gas chromatograph (GC). The appearance of the mass spectrum depended on the concentration of the sample, especially for compounds **1**, **2** and **5**, which are able to form seven- or nine-membered chelates. The spectra reported here were obtained for samples introduced *via* the GC.

The isobutane–TMB CI (isobutane source housing pressure 5×10^{-6} Torr) mass spectra are presented in Fig. 4. Again, the *trans*-2,3-diol **3** and 2-*endo*-5-*endo*-diol **5** could easily be distinguished from their respective stereoisomers. Scheme 5 illustrates possible reaction products of TMB reactant ions with the 2-*exo*-3-*exo*-diol **1**. The pathway common for all the compounds **1–6** was the reaction of the reactant ions at *m*/*z* 105 and/or 73 with the diol, giving rise to the ion at *m*/*z* 201. Except for compounds **3** and **5**, this ion was unstable and decomposed further by losing either water or methanol, giving rise to peaks at *m*/*z* 183 or 169, respectively. The elimination of water was especially favourable and the ion at *m*/*z* 183 even formed the base peak for compounds **3–6**. The difference in the intensities of the ion peak at *m*/*z* 169 in the spectra of the 2,3-diols **1–3** can be explained in terms of the formation of a five-membered ring structure by the *cis*-diols (Scheme 5), identically to cyclopentane-1,2-diols.[10] The spectra of the 2,5-diols **4–6** revealed, however, that the ion at *m*/*z* 169 must also have another structure because the cyclization reaction is possible only for the di-*endo* isomer **5** and the ion peak was intense for all the 2,5-diols. The ions at *m*/*z* 183 and 169 decomposed further giving rise to ions at *m*/*z* 111 and 93. These fragments can also be formed directly in the reaction of the *m*/*z* 73 reactant ion with the diols.

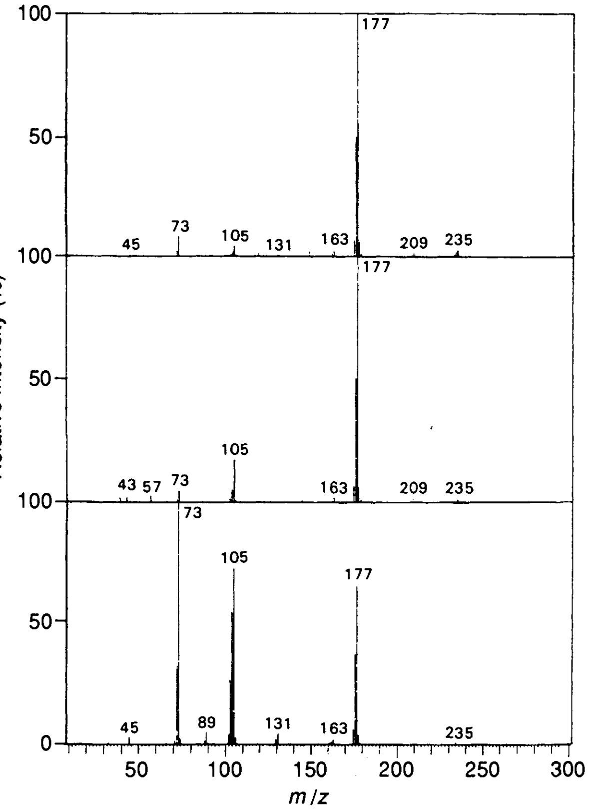


Fig. 3 Mass spectra of (*a*) trimethyl borate , (*b*) isobutane–trimethyl borate (isobutane source housing pressure 5 × 10^{-6} Torr), (*c*) methane–trimethyl borate (methane source housing pressure 5 × 10^{-6} Torr) plasma

For compounds **1** and **2**, the overwhelmingly favourable reaction pathway was the formation of the ion at *m*/*z* 241 having a seven-membered ring structure (Scheme 5). This same cyclization took place for compound **5**, in this case leading to a nine-membered ring, but it was less important than for compounds **1** and **2**. In this respect, the substitution reaction involving the elimination of two methanol molecules under TMB CI differs from the hemiketal formation observed under acetone CI. The other cyclization reaction under isobutane–TMB CI gave rise to the ion at *m*/*z* 227 and it was of equal importance for compounds **1**, **2** and **5**. Theoretically, the two above-mentioned cyclization reactions should also be possible for the *trans*-2,3-diol **3**, but no abundant ions at *m*/*z* 241 and 227 were observed. Most probably, the spatial arrangement of the hydroxy groups prevents the ring-closure reaction from taking place.

Neither dilution of the isobutane–TMB reagent gas mixture (isobutane source housing pressure 7 × 10^{-6} Torr) with respect to TMB nor the use of methane–TMB reagent gas mixture (methane source housing pressure 5 × 10^{-6} Torr) intensified the

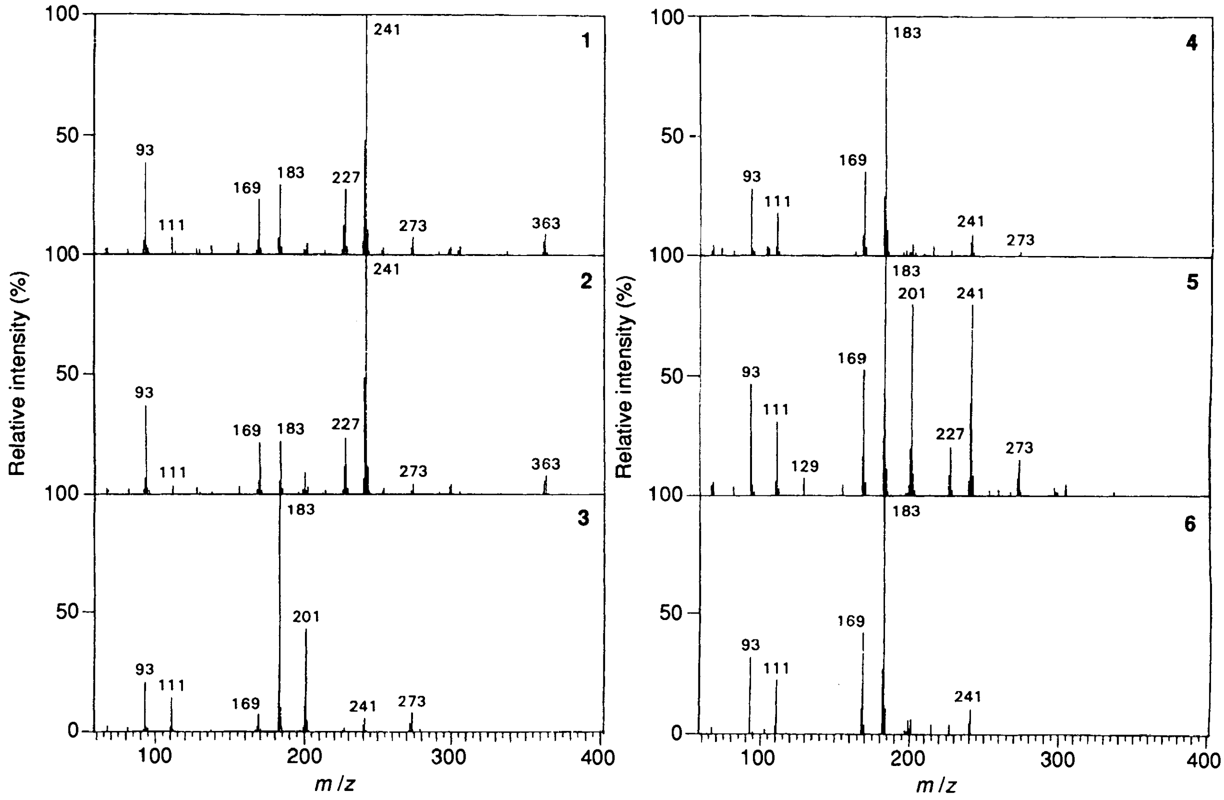
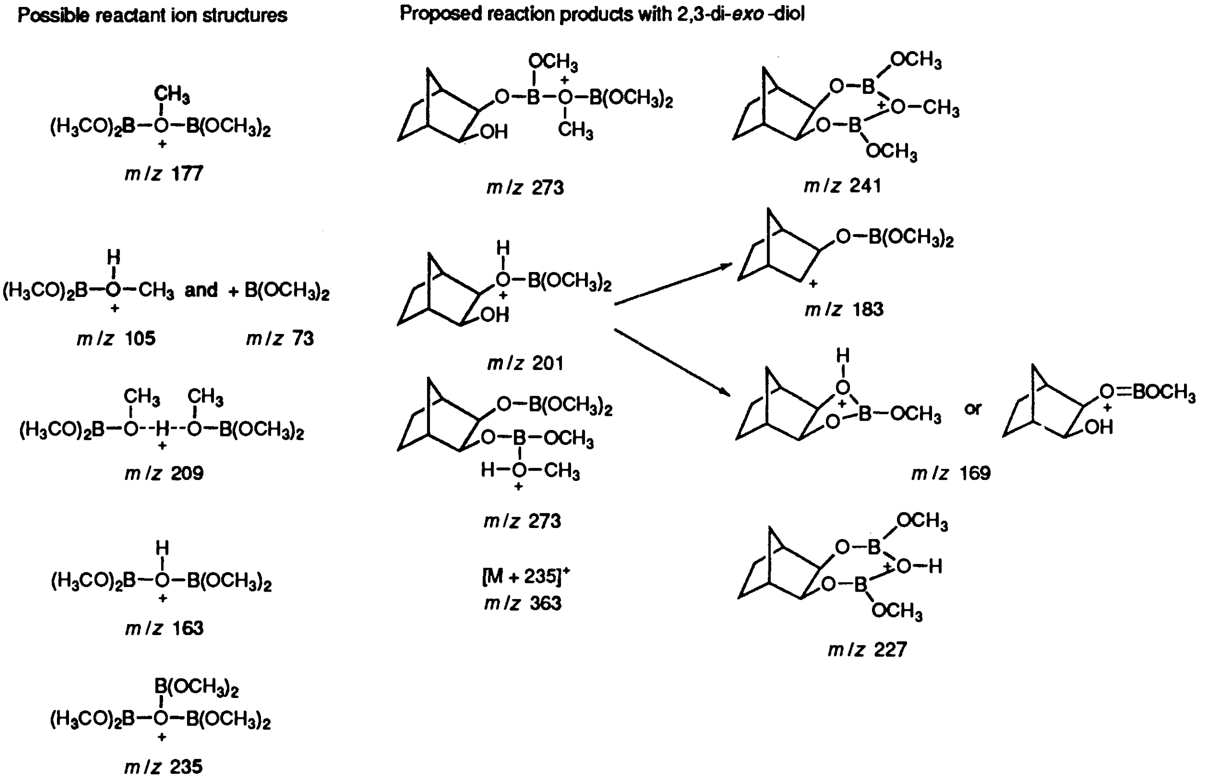
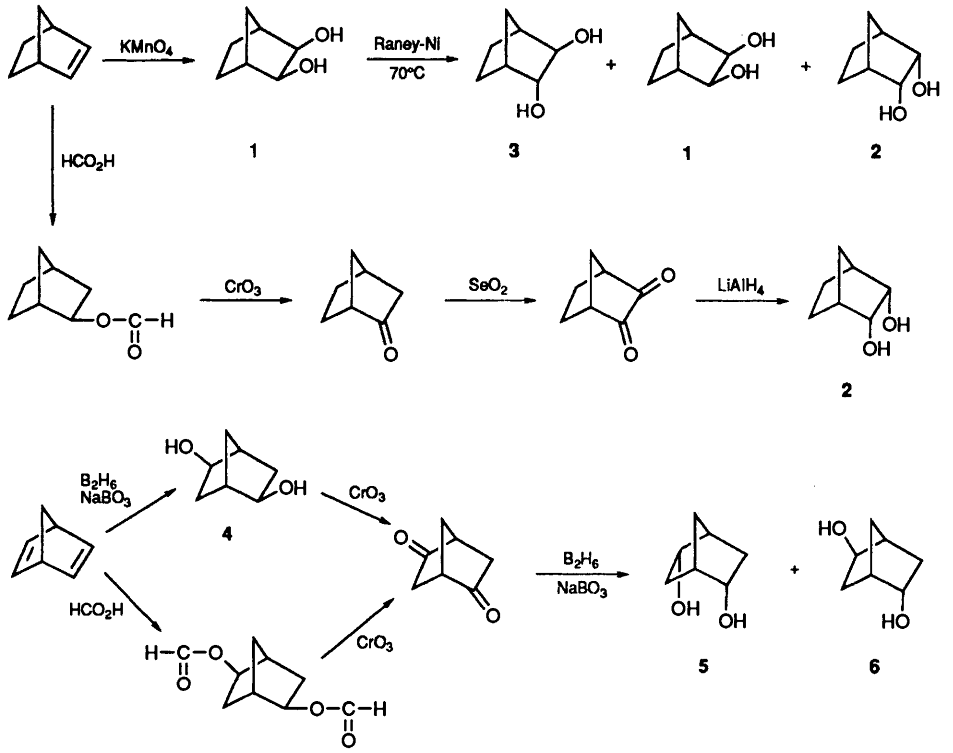


Fig. 4 Isobutane–trimethyl borate (isobutane source housing pressure 5 × 10^{-6} Torr) chemical ionization mass spectra of compounds **1–6**



Scheme 5



Scheme 6

stereochemical effects. However, whereas the spectra of compounds 3, 4 and 6 remained more or less unchanged under the different reaction conditions, the spectra of compounds 1, 2 and 5 varied considerably with the reagent gas mixture. For compound 1, 2 and 5, the ion peak at *m*/*z* 241 due to cyclization reaction was most abundant under isobutane–TMB CI (isobutane source housing pressure 5 × 10^{-6} Torr). The other cyclic product ion at *m*/*z* 277 was most abundant under methane–TMB CI, but at the same time, the ion at *m*/*z* 93 formed the base peak in the spectrum. When the isobutane–TMB reagent gas mixture was diluted (isobutane source housing pressure 7 × 10^{-6} Torr), the ion peaks at *m*/*z* 129, 111 and 93 increased in intensity.

Experimental

Synthesis.—The synthetic routes leading to trinorbornane-2,3- and trinorbornane-2,5-diols are presented in Scheme 6.

Trinorbornane-2-*exo*-3-*exo*-diol (**1**) was prepared from trinorborn-2-ene by $KMnO_4$ reduction according to a published procedure.[23] Trinorbornane-2-*endo*-3-*endo*-diol (**2**) was obtained through a four-step synthesis comprising formylation of trinorborn-2-ene,[24] Jones oxidation to trinorbornan-2-one,[24] SeO_2 oxidation to trinorcamphorquinone[25] and finally reduction with $LiAlH_4$.[26] Both of the obtained diols **1** and **2** were purified by column chromatography (55 g silica gel 60, 0.5 g diol, diethyl ether as eluent). Raney nickel isomerization of the di-*exo* isomer (**1**) yielded a 5:1:61 mixture of trinorbornane-2,3-diols **1**, **2** and **3**.[27] The *cis* isomers (**1** and **2**) were converted to acetonides, and pure *trans* isomer **3** was isolated according to Heyns *et al.*[27] and purified by sublimation. Hydroboration–oxidation of trinorborna-2,5-diene yielded a 19:5:1 mixture of trinorbornane-2-*exo*-5-*exo*-diol **4**, *trans*-trinorbornane-2,5-diol **6** and trinorbornane-2-*exo*-6-*exo*-diol.[28] Trinorbornane-2-*exo*-5-*exo*-diol **4** could be isolated, because it proved to be more soluble in water and at the same time more insoluble in the Na-dried diethyl ether than were the other isomers. Diol **4** was further purified by sublimation. For the syntheses of trinorbornane-2-*endo*-5-*endo*-diol (**5**) and *trans*-trinorbornane-2,5-diol (**6**), the above-mentioned mixture of trinorbornane-2,5-diols was converted to trinorbornane-2,5-dione by Jones oxidation. [29] The same diketone was obtained by formylation of trinorborna-2,5-diene followed by Jones oxidation.[24] Hydroboration–oxidation of trinorbornane-2,5-dione yielded a 4:1 mixture of trinorbornane-2-*endo*-5-*endo*-diol (**5**) and *trans*-trinorbornane-2,5-diol (**6**); as well, small amounts of trinorbornane-2-*exo*-5-*exo*-diol (**4**) were obtained as a side-product.[28] Pure diols **4**, **5** and **6** were obtained after column chromatography of the mixture (100 g silica gel 60, 0.65 g diol, Na-dried diethyl ether as eluent).

The purity of the compounds was checked with a Carlo Erba Fractovap 4160 GC using chemically bonded fused silica NB-20M column (length 25 m, i.d. 0.32 mm, phase layer 0.20 μm). All isomers were separated and the order of elution was **1**, **2**, **5**, **4**, **6** then **3**.

Mass Spectrometry.—The mass spectra were recorded on a JEOL JMS-D 300 mass spectrometer equipped with a combined EI/CI ion source and connected to a JEOL JMA-2000H data system. Typical source conditions were: temperature 443 K, electron energy 70 eV for EI and 200 eV for CI, accelerating voltage 3 kV, ionization 300 μA. Samples were introduced *via* the GC and/or through a direct inlet system at 295–363 K. The reagent gas flow was adjusted by monitoring the source housing pressure (8×10^{-6} Torr).* The isobutane–TMB and methane–TMB reagent gas mixtures were prepared by allowing the isobutane or methane to flow so that the source housing pressure was 5×10^{-6} or 7×10^{-6} Torr. The supplementary TMB reagent gas was introduced through a heated inlet system at 363 K, and the gas flow was adjusted so that the total source housing pressure was 8×10^{-6} Torr. The CID mass spectra were measured using linked scans at constant B/E, with helium led into the first field-free region so that transmission of the main beam was 33%. To ensure identical experimental conditions, the spectra of all ions with the same mass value but generated from different compounds were recorded one after the other without adjustment of the instrumental parameters.

Acknowledgements

Funding by the Academy of Finland is gratefully acknowledged.

References

1 J. Winkler and F. W. McLafferty, *Tetrahedron*, 1974, **30**, 2971.
2 F. J. Winkler and D. Stahl, *J. Am. Chem. Soc.*, 1979, **101**, 3685.
3 R. Wolfschütz, H. Schwarz, W. Blum and W. J. Richter, *Org. Mass Spectrom.*, 1978, **13**, 697.
4 B. Munson, B. L. Jelus, F. Hatch, T. K. Morgan, Jr. and R. K. Murray, Jr., *Org. Mass Spectrom.*, 1980, **15**, 161.
5 P. Ashkenazi, W. Blum, B. Domon, A. L. Gutman, A. Mandelbaum, D. Müller, W. J. Richter and D. Ginsburg, *J. Am. Chem. Soc.*, 1987, **109**, 7325; Y. Klopstock, P. Ashkenazi, A. Mandelbaum, D. Müller, W. J. Richter and D. Ginsburg, *Tetrahedron*, 1988, **44** 5893; P. Ashkenazi, B. Domon, A. L. Gutman, A. Mandelbaum, D. Müller, W. J. Richter and D. Ginsburg, *Isr. J. Chem.*, 1989, **29**, 131.
6 T. Partanen, P. J. Mälkönen, P. Vainiotalo and J. Vepsäläinen, *J. Chem. Soc., Perkin Trans. 2*, 1990, 777.
7 M. Blanc-Muesser, J. Dafaye, R. L. Foltz and D. Horton, *Org. Mass Spectrom.*, 1980, **15**, 317.
8 H. F. Grützmacher and K. H. Fechner, *Tetrahedron*, 1971, **27**, 5011; H. F. Grützmacher, *Suomen Kemistilehti*, 1973, **A46**, 50.
9 G. Wang, Y. Sha, Z. Xu and J. Pan, *Anal. Chem.*, 1985, **57**, 2283; M. Vairamani, K. V. Siva Kumar and G. K. Viswanadha Rao, *Ind. J. Chem.*, 1992, **31B**, 9.
10 H. Suming, C. Yauzu, J. Longfei and X. Shuman, *Org. Mass Spectrom.*, 1985, **20**, 719.
11 T. Keough, *Org. Mass Spectrom.*. 1984, **19**, 551.
12 Ya-P. Tu, Y.-Zu Chen, Su-N. Chen, M.-L. Wang and Z.-Z. Jing, *Org. Mass Spectrom.*, 1990, **25**, 9.
13 Ya-P. Tu, G.-Yu Yang, Yu-H. Liu, S.-N. Chen and Y.-Zu Chen, *Org. Mass Spectrom.*, 1991, **26**, 645.
14 P. Vainiotalo, *Ann. Acad. Sci. Fenn., Ser. A2*, 1985, **204**; T. Partanen, P. Vainiotalo, G. Stájer, G. Bernáth and K. Pihlaja, *Org. Mass Spectrom.*, 1990, **25** 615; T. Partanen, P. Vainiotalo, G. Stájer, G. Bernáth, G. Göndös and K. Pihlaja, *Rapid Commun. Mass Spectrom.*, 1993, **7** 1121; T. Partanen, P. Vainiotalo, G. Stájer, G. Bernáth and K. Pihlaja, *Org. Mass Spectrom.*, 1994, **29**, 126; T. Partanen, P. Vainiotalo, G. Stájer and K. Pihlaja, *J. Heterocycl. Chem.*, in press.
15 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, suppl. 1.
16 J. W. Keister, J. S. Riley and T. Baer, *J. Am. Chem. Soc.*, 1993, **115**, 12613.
17 J.-C. Tabet, in *Fundamentals of Gas Phase Ion Chemistry*, ed. K. R. Jennings, Kluwer Academic Publishers, Dordrecht, 1991, p. 355.
18 J. B. Westmore and M. M. Alauddin, *Mass Spectrom. Rev.*, 1986, **5**, 381.
19 F. O. Gülacar, F. Mermoud, F. J. Winkler and A. Buchs, *Helv. Chim. Acta.*, 1984, **67**, 488.
20 A. Streitwieser, Jr. and C. H. Heathcock, *Introduction to Organic Chemistry*, Macmillan, New York, 1989, p. 379.
21 G. G. Dolnikowski, T. G. Heath, J. T. Watson, J. H. Scrivens and C. H. Rolando, *J. Am. Soc. Mass Spectrom.*, 1990, **1**, 481.
22 *Rodd's Chemistry of Carbon Compounds*, ed. S. Coffey, vol. 1, part D, Elsevier, Amsterdam, 1965, p. 25, and references cited therein; A. I. Vogel, *Elementary Practical Organic Chemistry, Part 2: Qualitative Organic Analysis*, Longmans, London, 1966, p. 87; T. W. Greene, *Protective Groups in Organic Synthesis*, Wiley-Interscience, New York, 1981, pp. 70 and 86.
23 H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, 1954, **76**, 5400.
24 D. C. Kleinfelter and P. von R. Schleyer, *Org. Synth.*, 1973, coll. vol. 5, 852.
25 K. Alder, H. K. Schäfer, H. Esser, H. Krieger and R. Reubke, *Liebigs Ann. Chem.*, 1955, **593**, 23.
26 K. Alder and H. Wirtz, *Liebigs Ann. Chem.*, 1956, **601**, 138.
27 K. Heyns, G. Rüdiger and H. Paulsen, *Chem. Ber.*, 1972, **105**, 1019.
28 R. T. Hawkins, R. S. Hsu and S. G. Wood, *J. Org. Chem.*, 1978, **43**, 4648; G. W. Kabalka, P. P. Wadgaonkar and N. Chatla, *J. Chem. Educ.*, 1990, **67**, 975.
29 J. Meinwald, J. K. Crandall and P. G. Gassman, *Tetrahedron*. 1962, **18**, 815.

Paper 4/02017K
Received 5th *April* 1994
Accepted 6th *May* 1994

---

* 1 Torr = 133.322 Pa.