The Consecutive Loss of Two H_2O Molecules From Protonated 1,2- and 1,3-Cyclohexanediols in the Gas Phase: An Example for the Incidence of Skeletal Rearrangement in Chemical Ionization Mass Spectrometry†

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The consecutive dehydration of protonated molecules $[MH]^+$ of 1,2- and 1,3-cyclohexanediols (*cis* and *trans* isomers) by loss of two H_2O molecules has been investigated. Analysis of ^2H labelled compounds showed that loss of the first H_2O molecule represents a simple heterolysis, i.e. a dissociation without exchange of hydrogens between O—H and C—H bonds. Subsequent elimination of the second H_2O molecule in the process $[MH-H_2O]^+ \rightarrow [MH-2H_2O]^+$ followed several competing paths. The two major ones corresponded *formally* (with reference to an intact 6-ring skeleton) to 1,3- and 1,4-eliminations; in comparison, the alternative 1,2-elimination is only a minor route at most. At least for the 1,3-elimination, water loss from the $[MH-H_2O]^+$ ions is not direct, but is associated with skeletal rearrangement, most probably of the Wagner-Meerwein-type, effecting contraction of the 6- to a 5-membered ring.

INTRODUCTION

Chemical ionization mass spectra of *positionally* (and, more intriguingly, *configurationally*) isomeric cyclohexanediols can differ significantly in the degrees to which water molecules are lost consecutively from the protonated molecules $[MH]^+$ [2] Thus, in *trans*-1,4-cyclohexanediol the $[MH-2H_2O]^+$ fragments are formed in much smaller abundance from their $[MH-H_2O]^+$ precursors than in the *trans*-1,2- and especially the *trans*-1,3-diol, when mild ionization conditions are employed using isobutane as reagent gas (cf. also Figs. 1 and 3). At first sight, the particular ease of this second loss of H_2O in the 1,3- and also the 1,2-diols could be thought to reflect the formation of well-stabilized allylic carbenium ions *c* by a unimolecular 1,2-elimination (Scheme 1), i.e. a process that would give rise to merely *homo*allylic counterparts *e* of lesser stability in the 1,4-isomers. With such premises, the still greater relative ease of elimination in the 1,3- over that of the 1,2-diols (Figs. 3 and 4 and 1 and 2, respectively) could be ascribed to an additional effect, namely to proton abstraction from an *activated* site (vicinal carbenium ion centre) as compared with that from a non-activated one, located further away from the centre of ionic reactivity. Similarly in accordance with this, in the case of the 'activated' 1,3-diols, active participation of the electron-deficient centre and thus promotion of the process (an early adopted, empirically derived mechanistic concept in EIMS[3a,3b]) through double bond formation in the transition state for proton transfer should be possible, particularly in a non-concerted elimination, i.e. a two-step transfer/heterolysis sequence, although another recent attempt at classifying CI processes has been reported.[4] In contrast, in the 'non-activated' 1,2- and, even more so, in the 1,4-diols, direct charge participation as well as two-step routes would be precluded on such a basis, limiting the types of 1,2-elimination reaction channels to that of a concerted mode. Similar reasoning was recently applied in an attempt to explain analogous positional effects in the CI induced twofold loss of H_2O from $[MH]^+$ ions of more complex substrates,[5] including diterpene diols and related natural products.

Scepticism as to whether 1,2-elimination of water is a chief contributor to the unimolecular decomposition of closed shell cations formed by CI arises, however, in view of the fact that an analogous mode in EI was never demonstrated except for very short-lived (picoseconds) and, hence, highly energetic radical cations.[6] In CI fragmentation in particular, which *a priori* reflects electronic ground-state chemistry much more extensively than EI, reservations may exist with respect to those cases in which—as in the one mentioned above—only concerted 1,2-elimination paths appear feasible, for these are exactly the ones that are symmetry-forbidden and therefore accessible only to

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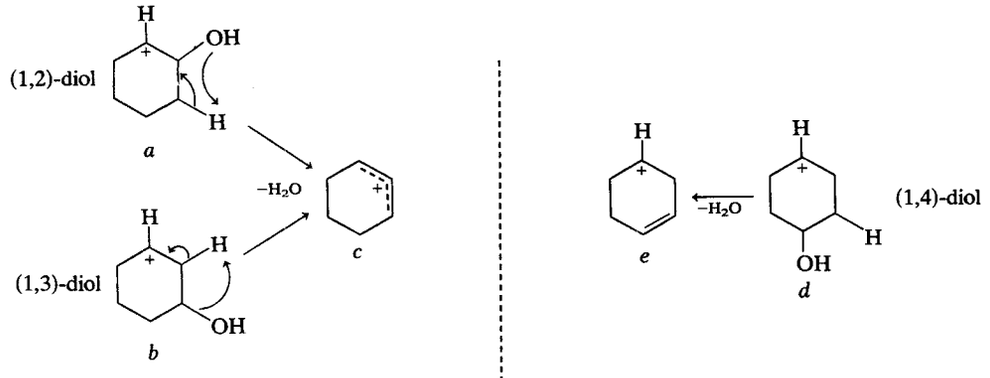


Scheme 1

electronically excited species.[7] Furthermore, since 1,2-elimination of water in CI fragmentation has not yet been confirmed, nor rigorously sought, a detailed study of the H_2O elimination in cyclohexanediols by acid/base-type CI seemed to us desirable in order to subject this feasible, though not necessarily very likely mechanistic rationale to closer scrutiny. For that purpose, only the 1,2- and 1,3-diols were selected, because they satisfy the structural prerequisites discussed for the activation of corresponding abstraction sites better than the 1,4-isomers. Analogues, in which relevant sites are ^2H labelled, were subjected to CI analysis using a strongly acidic plasma (CH_4 as reagent gas), since—for uncovering positional origins of the H_2O molecules lost—pronounced differences in the abundance of second water loss rather than in the fragmentation patterns for the positional (and configurational) isomers were anticipated. Substantial discrepancies between the CI spectra quoted in Ref. 2 and those reported in this paper (Figs. 1–4) must be due to different experimental conditions other than source temperature (similar in both studies). As a result of GCMS rather than direct sample introduction, the formation of dimeric cluster ions of the $[2M+H]^+$ type is avoided in the present work due to the (controllable) larger excess of protonating reactant ions. These cluster ions are likely to contribute, in unknown degrees, to the $[MH-H_2O]^+$ and $[MH-2H_2O]^+$ ion current under investigation. Mildly protonating CI conditions (i-C_4H_{10} as reagent gas) were employed mainly for determining the ^2H incorporation rates achieved in the syntheses of the labelled compounds,[8] since appreciable $[MH]^+$ ions are obtained; under these conditions water loss from the $[MH-H_2O]^+$ ions is of minor importance.

RESULTS AND DISCUSSION

1,2-Cyclohexanediols

In none of the compounds studied (**1–10**, Scheme 2), does the initial loss of H_2O from the $[MH]^+$ ions involve hydrogen atoms from the ring positions, as is clearly indicated by the appropriate quantitative shifts of the $[MH-H_2O]^+$ peaks in the $CI(CH_4)$ spectra. Superficially, this can be accounted for by the operation of 'simple' heterolysis ejecting the protonated hydroxyl group. For compounds with a *trans*-configuration of the potentially interacting functional groups, neighbouring group participation of the free hydroxyl group in a gas phase S_Ni reaction is quite likely, however, but needs corroboration in order to be firmly established. Possibly due to such assisted heterolysis, the relative intensities of the $[MH]^+$, $[MH-H_2O]^+$and $[MH-2H_2O]^+$ ions in the *cis* series differ markedly from those of the *trans* isomers; however, this could also reflect differences in intramolecular stabilization of the $[MH]^+$ precursors by internal hydrogen bonding (cf. also Ref. 2). Uncertainty similarly prevails as to the structural stability of the *non-reactive* portion of the $[MH-H_2O]^+$ product ions, i.e. those ions that do *not* decompose further by the loss of a *second* H_2O molecule. If not already rearranged during (assisted) heterolysis, they may—as highly reactive carbenium ions *a*—rearrange readily into isomeric species of higher stability such as *f*, g or *h* (Scheme 3). This may occur either via a hydride shift (as found to be prevalent in unsubstituted cyclohexyl ions in solution[9]) into protonated cyclohexanones (*f*), or by Wagner-Meerwein-type ring contraction into protonated cyclopentanecarboxaldehydes (g), or (like in S_Ni assisted heterolysis) into protonated oxiranes (*h*) by

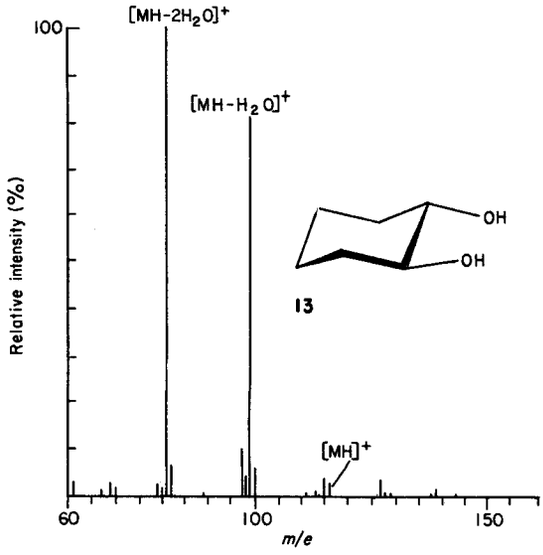


Figure 1. The $CI(CH_4)$ spectrum of *trans*-1,2-cyclohexanediol.

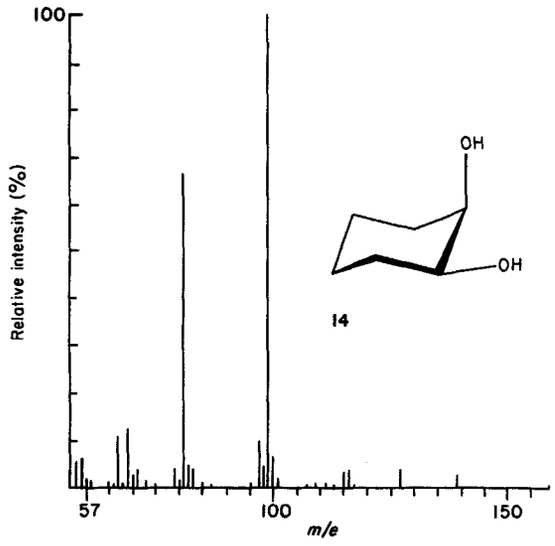
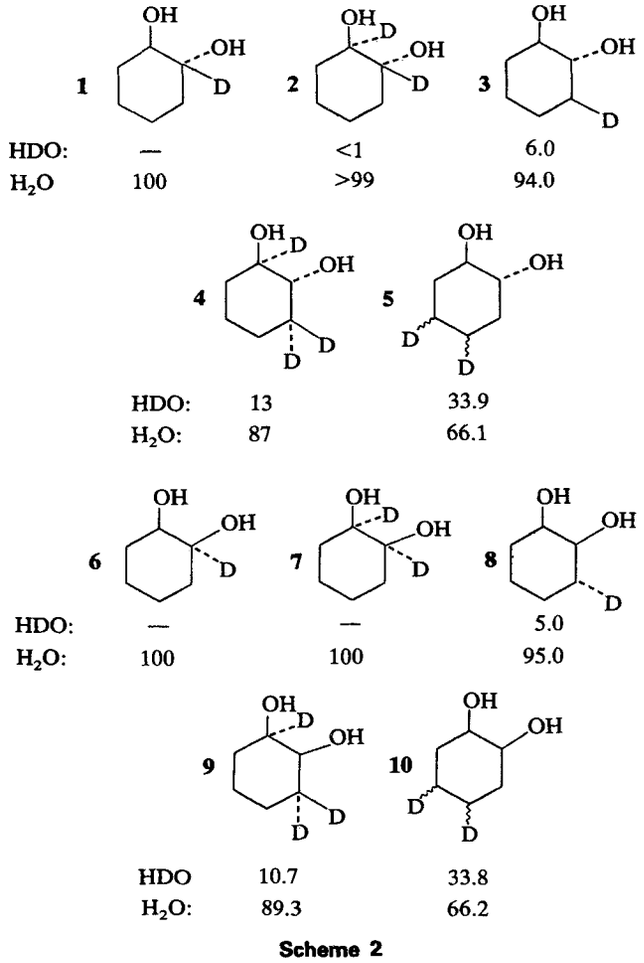


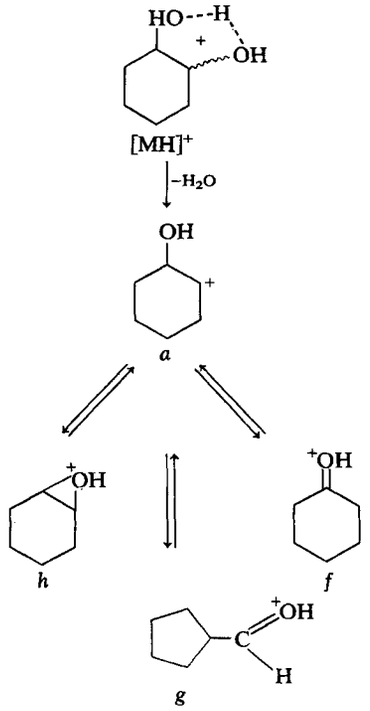
Figure 2. The CI(CH_4) spectrum of *cis*-1,2-Cyclohexanediol.

bond formation with ring closure. It is hoped that future collisional activation studies can resolve these ambiguities, at least in part.[10] In the subsequent *second* loss of H_2O from these intermediates i.e. $[MH-H_2O]^+ \rightarrow [MH-2H_2O]^+$, numerically only *one* C-bonded hydrogen atom becomes incorporated into the neutral particle lost. In accordance with a straightforward elimination scheme, the multiply ring labelled



Scheme 2

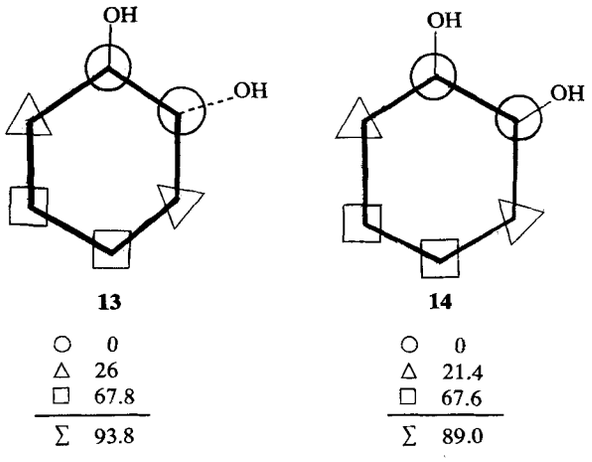
analogous (**2**, **4**, **5**, **7**, **9** and **10**) invariably show losses of H_2O and/or HOD, but *none* of D_2O, thus ruling out H/D-exchange between hydroxyl and carbon hydrogens befor the reaction occurs. Positionally, more than one H-atom is involved, however: whereas there are virtually no contributions from the two methine positions C-1 and C-2 (no loss of HOD in **1**,**2**, **6** and **7**), all four methylene groups, i.e. both pairs of equivalent positions C-3 (6) and C-4 (5), contribute strongly, albeit to uneven degrees (loss of H_2O/HOD in various ratios in compounds **3**–**5** and **8**–**10**). The variation of these contributions by the non-equivalent methylene positions in the $^2H_2$ labelled compounds again indicates that positional identities of the corresponding hydrogen atoms are maintained by and large; the different contributions by C-3(6) and C-4(5) thus reflect *at least two* distinct elimination routes rather



Scheme 3. Isomerization of $(MH-H_2O)^+$.

than a single one preceded by H/D-exchange. Individual values for the specific contributions of the three types of non-equivalent ring positions are given in Scheme 4. They can be obtained from the (overall) H_2O/HOD ratios given in Scheme 2 for the losses in **1**–**10** by observing general symmetry relationships of difunctional cyclohexane derivatives, and by assuming equal probabilities for the protonation and heterolysis of either hydroxyl substituent in the *cis*-diol. In the *trans*-diol, such equal behaviour of both substituents is a necessary consequence of the special symmetry of this particular isomer.

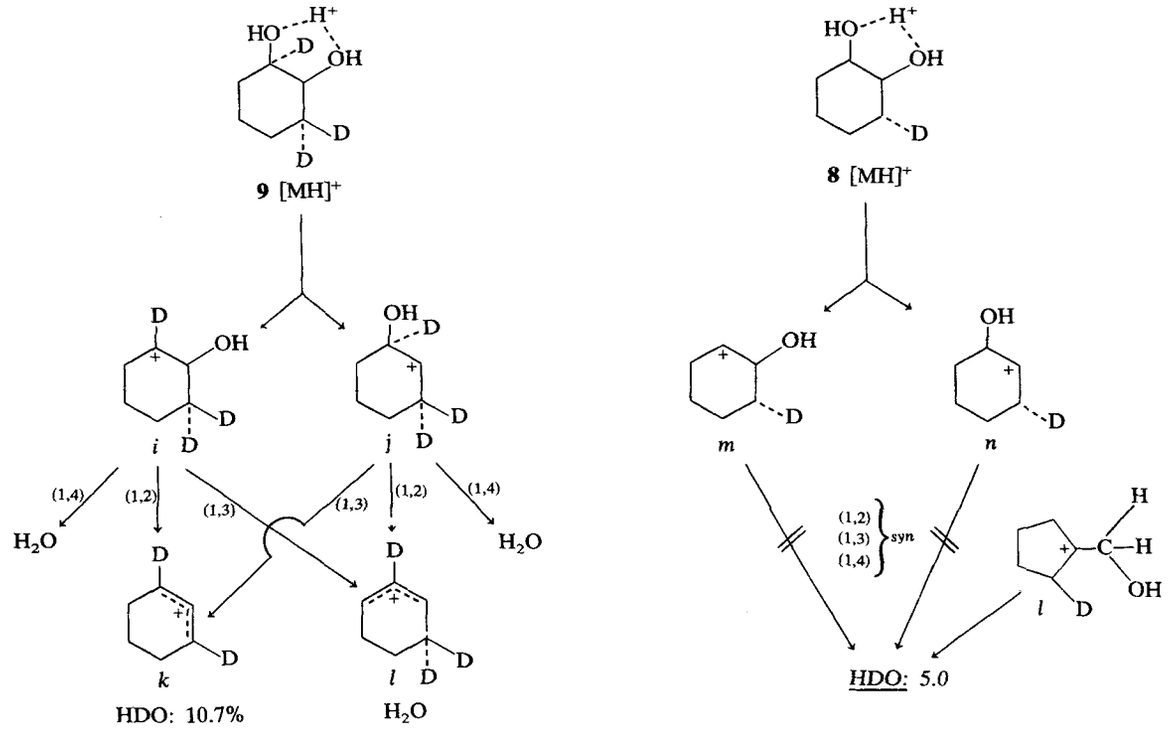
Direct 1,2-elimination. In addition to the above conclusion regarding the absence of statistical or partial equilibration of positions and, consequently, the operation of at least two distinct modes of elimation, three more conclusions as to mechanistic aspects can be



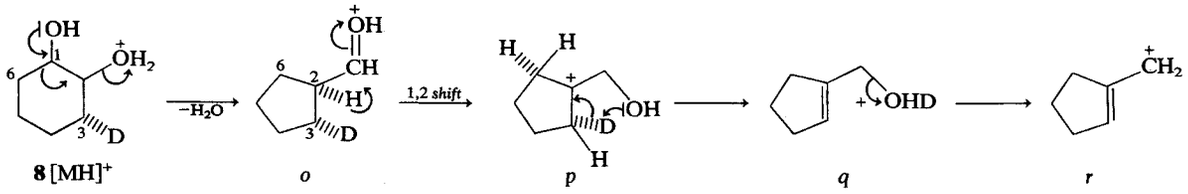
Scheme 4

drawn. (i) The relative configurations of the two hydroxyl groups affect the *extent* of total elimination quite markedly (cf. Figs. 1 and 2), yet are of little consequence to the relative amounts of hydrogen lost from the C-3(6) and C-4(5) methylene groups and hence, to the nature and relative amounts of the contributing processes that they reflect. It must be concluded, therefore, that for the two different stereoisomers the *reactive* populations of $[MH-H_2O]^+$ ions are structurally identical (irrespective of being homogeneous or not), and/or involve other common intermediates from which the same separate elimination routes can branch off. (ii) The fact that the sum of the individual contributions of the methylene positions is somewhat less than 100% (93.8 and 89.0% for the *trans*- and *cis*-diol, respectively) reflects the operation of a kinetic isotope effect either in the hydrogen abstraction step of H_2O elimination itself, or in some other rearrangement step involved in the overall process. (iii) Finally, the initial tentative rationale of 1,2-elimination with H abstraction, especially from charge activated sites is found to be *largely invalid* as far as the basic 1,2-type with intact 6-ring structures is concerned. The relevant findings do not, however, discredit the assumption of site activation by vicinal carbenium ion centres as a prerequisite of abstraction as such, e.g. in abstraction which involves—in analogy to EI—more favourable, larger transition states. That such direct 1,2-elimination does not indeed participate significantly, becomes readily apparent when the results of **8** and **9** are compared. In the latter, the (minor) loss of HOD (10.7%) certainly cannot result from direct 1,4-elimination (leading only to loss of H_2O), yet could very well correspond to direct 1,3- and/or 1,2-elimination modes (cf. Scheme 5; for energetic reasons, only abstraction possibilities from charge activated sites were considered without taking into account the ease of geometric accessibility). In contrast to **9**, both such direct 1,3- and 1,2-modes are, however, ruled out in **8** as appreciable contributors (HOD loss still around 5% in spite of containing only one label), since due to the double *trans* relationship between the label and *both* hydroxyl groups, HOD elimination cannot take place except after skeletal rearrangement. By stereospecific labelling the existence of direct elimination routes and the integrity of the 6-membered ring can thus be sought after in a cursory manner.

Formal 1,3-elimination. In order to account for the bulk of the elimination from the 3(6) methylene group (which is more than 20% of the total water loss according to Scheme 4), a preceding skeletal rearrangement must be invoked that leads to loss of the



Scheme 5



Scheme 6

rigid, non-interactive *trans* geometry between the hydroxyl groups and two of these (four) methylene hydrogens in the *cis* series. As depicted in Scheme 6 for compound **8**, ring contraction by a Wagner-Meerwein-or, more specifically, a pinacol-type rearrangement, would satisfy this condition. Moreover, it would simultaneously provide a suitable activation of the abstraction site and a geometrically feasible, 5-membered transition state, if it is followed by a single 1,2-hydride shift ($o \rightarrow p$).

This mechanistic scheme of a rearrangement induced (as opposed to direct) 1,3-elimination represents a plausible, though not yet sufficiently established rationale for all the observed facts. Stereochemical discrimination against originally *trans* positioned deuterium in the 3-position is, at the latest, overcome in the second (hydride transfer) step, by which—in analogy to an S_Ni reaction in racemization—an sp^2 centre is generated at C-2, thus rendering both the ^1H and ^2H atoms at C-3 equally accessible. On this basis, the observation of approximately 5% HOD elimination from **8** would represent merely one-quarter of the total indirect 1,2-elimination (two abstraction sites in each of the 3- and 6-positions); considering isotope effects, this result is in very good agreement with the 21% of Scheme 3 (Δ-values) calculated for the *cis* isomer. Accordingly, the *trans*-diol **3**, in which direct 1,3-HOD elimination could conceivably occur involving one of the hydroxyl groups (C-1 and *cis* with respect to the label at C-3), in fact, only a little more than 6% (Scheme 2) of a direct 1,3-elimination is observed. This is exactly what would be expected since such a direct route was discounted above.

Observations that lend additional support to this intervention of ring contraction pertain to the CI fragmentation of 2(6)-methyl substituted cyclohexanones and -heptanones. These compounds lose $CH_3CH{=}O$ from $[MH]^+$ (ejection of C-2(6) and the methyl substituents together with the carbonyl oxygen from C-1), and, interestingly, also H_2O, in abundances that are dependent upon the degree of substitution at C-2(6), which would facilitate skeletal rearrangement quite decisively[11] (cf. also Ref. 4). Furthermore, it is worth mentioning that protonated unlabelled cyclopentanecarboxaldehyde, the intermediate (cf. *o*) of the proposed Scheme 6, shows likewise an abundant loss of H_2O (base peak), when this compound is subjected to CI under identical conditions. It may be also recalled that ring contraction of this type has been shown to play an important role in the chemistry of related alicyclic compounds in the condensed phase.[12]

Formal 1,4-elimination. As is borne out by Scheme 4, the greater portion (*c.* 68% both in *cis* and *trans*) of the second H_2O loss involves H abstraction from the C-4(5) methylene groups, i.e. follows—at least formally—a 1,4-elimination route. As opposed to the above 1,3-elimination, a *direct* route with conservation of the original 6-ring structure is, in the absence of stereospecific labelling of the 4(5)-position, not to be *a priori* discounted. Further experiments are required, however, to elaborate the mechanism of such reactions.

1,3-Cyclohexanediols

In order to test the original hypothesis of direct 1,2-elimination in an even more favourable case, *cis*- and *trans*-1,3-cyclohexanediol were included in this investigation. As stated at the outset of the discussion, the 1,3-diols should be structurally better disposed for a direct 1,2-route than the 1,2- and, especially, the 1,4-isomers. As shown in Figs. 3 and 4, the two 1,3-diols lose two molecules of H_2O with still greater ease than their 1,2-counterparts under identical conditions. Stereochemical differences between the *cis* and *trans* isomers are largely cancelled out under these circumstances. In turn, to probe selectively for direct and, hence, stereospecific elimination routes, two diastereotopically labelled analogous, **11** and **12** (Scheme 7) with ^2H in the 2-position as the relevant potential abstraction site, were synthesized and analysed. As before in the 1,2-diols, loss of the first H_2O molecules involves no label at all, whereas the second water loss does (HOD losses around 10% of total secondary loss). In principle, the observed loss of 11.9% HOD from **11** would allow for an appreciable 1,2-contribution of up to 23.8%; however, the 7.7% elimination of HOD in **12** demonstrates unambiguously that the greater portion (15.4%) of this contribution must be due to a skeletal rearrangement

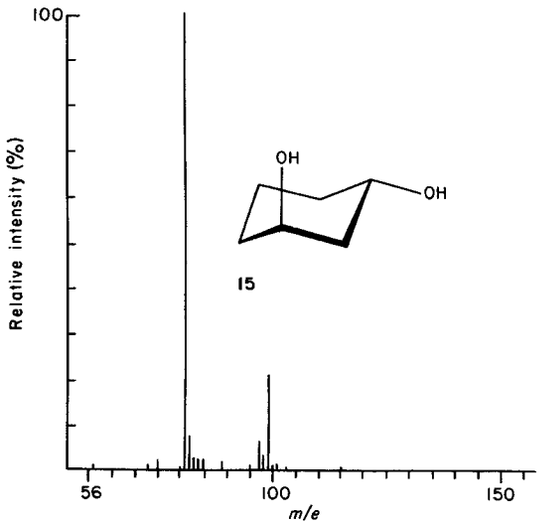


Figure 3. The CI(CH_4) spectrum of *trans*-1,3-cyclohexanediol.

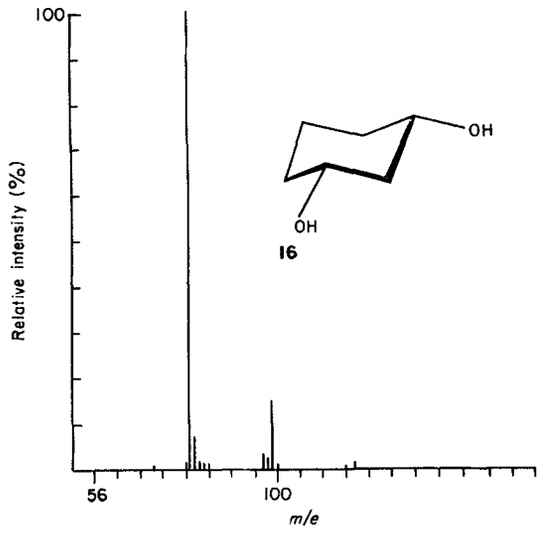
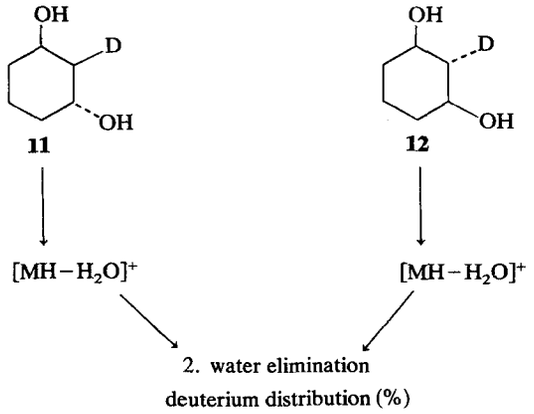


Figure. 4. The CI(CH_4) spectrum of *cis*-1,3-cyclohexanediol.

similar to those observed for the 1,2-isomers, since the label is *trans* positioned with respect to both hydroxyl groups and is hence inaccessible. Skeletal rearrangement of the proposed ring contraction type (Scheme 6, ion *o*) could again account for this lack of stereospecificity, as long as it is preceded or accompanied by a 1,2-hydride transfer, this time from C-2 to C-1(3). The remaining, major route for elimination of the H_2O molecule may be due to a 1,4-process as was found for the 1,2-isomers. However, no concrete evidence is available at present, and will have to be furnished by a special detailed study of this system. Should such a route prove operative, as would not be surprising, the directly resulting 3-hydroxycyclohexyl carbenium ion would indeed represent a very pausible intermediate for straightforward elimination of water. It would provide an easily accessible abstraction site (originally C-4(6)) already activated without any rearrangement.



deuterium distribution (%)

	11	12
HDO	11.9	7.7
H_2O	88.1	92.3

Scheme 7

CONCLUSION

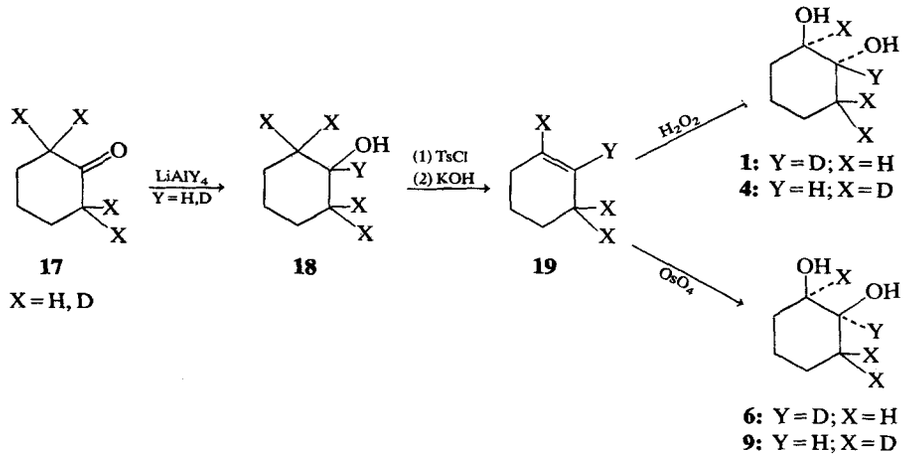
In conclusion, it can be stated that even under optimized structural conditions, as in the 1,3-isomers, 1,2-elimination of H_2O represents, is insignificant compared with the dominating routes of Cl induced H_2O elimination from the $[MH-H_2O]^+$ ions of the diols studied. In the cases of the 1,2-diols the processes of normal 1,3- and 1,4-elimination channels can be discerned by extensive ^2H labelling which, when stereospecific, permits the discovery of skeletal rearrangement. For the 1,4-elimination the absence of stereospecific labelling information does not permit any deductions as to the intermediacy of skeletally rearranged ions. Therefore, any assumptions about the true mechanism of this route can serve only as tentative working hypotheses for additional studies. Like collisional activation experiments, these may aim directly at establishing definite ion structures for specific intermediates rather than doing so indirectly by uncovering their genesis and the positional origins of their atoms when formed from their precursors. An extension of the present study in this direction may also be appropiate, since the mechanisms of elimination of simple neutrals, such as H_2O, from simple closed shell models (like the protonated alicyclic diols in Cl) may be important. Water elimination as a 'simple' process in open shell systems in EIMS has probably been studied more extensively than any other elimination process.[13] This may be especially relevant, if firmly established, in the current discussion of the principles governing by which mechanisms closed and open shell ions fragment in the mass spectrometer.[14]

EXPERIMENTAL

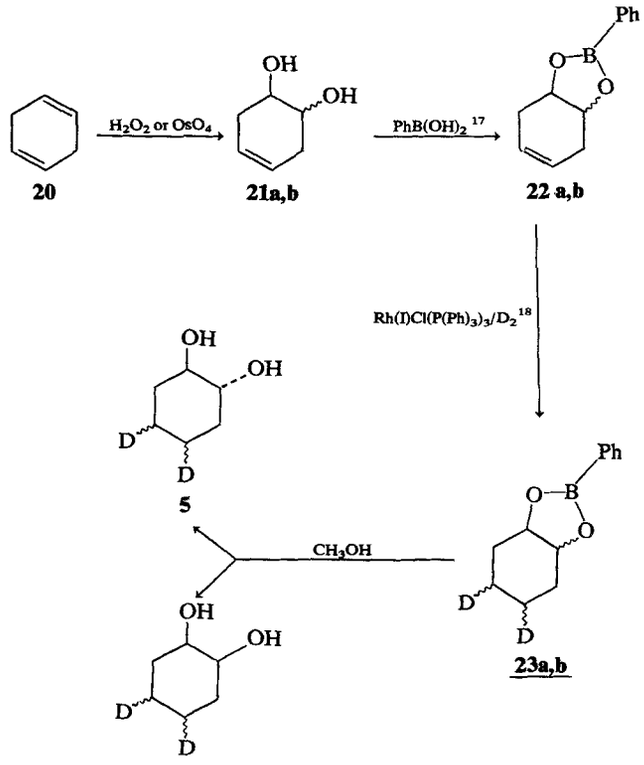
Synthesis of cyclohexanediols (general discussion of routes)

Trans-1,2-Cyclohexanediol (**13**) was obtained from cyclohexene by oxidation with H_2O_2 following a routine procedure. The *cis* isomer (**14**) was also obtained from cyclohexene, using *N*-methylmorpholine *N*-oxide in the presence of catalytic amounts of OsO_4 as the oxidizing agent.[15]

The preparation of the mono- and trideuterated analogues **1**, **4**, **6** and **9** followed routes generally outlined in Scheme 8. The *di*deuterated analogues **2** an **7** were readily accessible in a one-step procedure by $NaBD_4$ reduction of 1,2-cyclohexanedione according to Dale;[16] **5** and **10** required several steps as shown in Scheme 9, with 1,4-cyclohexadiene (**20**) serving as starting material. For symmetry reasons deuteration of **22a** to **5** can occur from the front and back with equal probability. The same is true for the deuteration of **22b** to **10** due to the configurational flexibility of the *cis* fused ring system of the substrate.



Scheme 8



Scheme 9

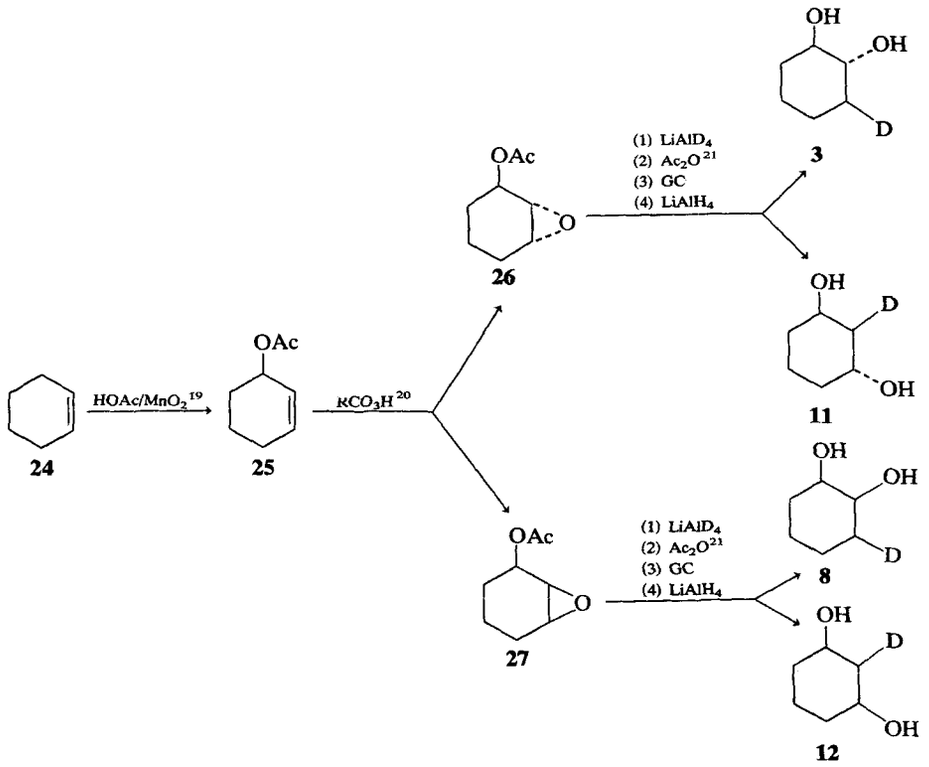
The stereospecifically labelled 1,2-diols **3** and **8** were also obtained from cyclohexene along with the isomeric 1,3-diols **11** and **12**, employing allylic oxidation (Scheme 10). Standard procedures, for which references are given in the scheme, were used with slight modifications. The constitution and configuration of all products has been established by extensive spectroscipic investigations (especially by 270 MHz ^{1}NMR spectroscopy). Details of the synthesis of the compounds as well as their structure elucidation are available on request.

The following deuterium incorporations (measured by CI using i-C_4H_{10} as reagent gas, *vide infra*) were attained by these syntheses: 99% d_1 for **1**, **3**, **6**, **8**, **11**, **12**; 99% d_2/1% d_1 for **5** and **10**; 81% d_2/17% d_1 for **2** and **7**; 94% d_3/4% d_2/1% d_1 for **4** and **9**.

GCCIMS measurements

The CI spectra discussed in this work were produced by subjecting individual samples to GCMS analysis rather than direct introduction, regardless of whether they represented mixtures or pure compounds. In preliminary experiments, direct sample introduction had proven unmanageable as far as good reproducibility of spectra is concerned (cf. Ref. 8). This appeared to be due, at least in part, to the hard-to-control formation of $[2M+H]^+$ cluster ions, whose fragmentation seems to overlap with that of the $[MH]^+$ ions (cf. also p. 699). In GCMS analysis this undesirable effect is easily suppressed by using capillary columns and accordingly small sample loads (*c.* 50 ng). Since due precision of isotopic distribution measurements of the precursor and fragment ions is generally a prerequisite in comparative studies of isomers of any kind, GCCIMS appears especially appropriate. By this technique identical CI conditions (source and sample temperature, reagent/sample ratios, etc.) are more easily maintained for all compounds to be compared, than by delivery of samples from the condensed phase by means of a probe rod.

The GCMS system used consisted of a Carlo Erba Fractovap 2101 AC gas chromatograph and a Finnigan 3200 mass spectrometer, operated in conjunction with an Incos data system. Details of the GCMS system have been reported earlier.[22] For analysis of the (underivatized) diols, glass capillaries (20 m × 0.33 mm) were coated with SE-54. GC conditions were kept constant throughout the series of experiments (carrier gas: 0.5 mbar helium; oven temperature: 140 °C). CH_4 and i-C_4H_{10} of the highest available purity (grades N 55 and CH 35, respectively, L'Air Liquide, Geneva, Switzerland) served as CI reagent gases. Filament current, electron energy and ion source temperature were maintained at 200 μA, 140 eV and 120 °C, respectively. Since glass capillaries effect partial separation of components of differing deuterium content of a labelled sample, spectra can be selected from continuous scans, which represent higher isotope incorporation than average. Due to the constant GC conditions, exact correlations of the CH_4 and i-C_4H_{10} runs become possible. Thus, single CH_4



Scheme 10

and i-C_4H_{10} spectra can be selected and meaningfully compared, that correspond exactly as to retention values and thus to identical label enrichment.[22]

Acknowledgement

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