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STERIC EFFECTS IN THE MASS SPECTRA OF THE STEREOISOMERS OF DECALIN-1,3-DIOL AND OF 1,3-DIMETHOXY-DECALIN†

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Abstract—The stereoisomers **1a–8a** of decalin-1,3-diol have been synthesized by LAH-reduction of *cis*- and *trans*-decalin-1,3-dione, respectively. With the exception of *trans*-decalin-1a,3e- and -1e,3a-diols, **7a** and **8a**, the stereoisomers have been isolated by column chromatography, and their configurations have been determined by ^{1}H-NMR, IR and chemical methods. It is shown by the aid of deuterated derivatives, that the elimination of H_2O, MeOH and CH_2O from the molecular ions of the stereoisomeric diols and di-O-methyl ethers, respectively, occurs predominantly by stereospecific reactions, if the ground state conformation of the molecule corresponds to the geometry of the transition state of the elimination reaction. The steric control of the fragmentations is greatly reduced, if conformational changes of the molecular ions have to occur prior to fragmentation. No clear steric effects are observed, if none of the conformations of the intact molecular ions corresponds to the transition state. These steric effects can be used to identify the various stereoisomers of decalin-1,3-diol and 1,3-dimethoxy-decalin by mass spectrometry.

In continuation of our studies on the steric effects in the mass spectra of cyclic and bicyclic polyol derivatives,[1] we synthesized the stereoisomers **1–8** of decalin-1,3-diol and investigated their mass spectrometric fragmentation. It is known, that large steric effects occur in the elimination of HOR (R = H,Me) from the molecular ions of cyclic diol derivatives and that the intensities of the corresponding fragment ions in the EI mass spectra, obtained by the usual conditions of analytical mass spectrometry, can be used for an identification of stereoisomers of cyclohexane-diol-derivatives.[2] In a previous publication it was shown, that similar steric effects are observed in the mass spectra of stereoisomeric decalin-1,4-diols and their O-Me derivatives.[3] Analogous mass spectrometric behaviour of cyclohexane-1,3-diols and of decalin-1,3-diols, respectively would therefore be expected. However, it has recently been observed, that the conformational mobility of the molecular ions has an influence on the stereochemical control of the elimination reactions.[4,5] Since the conformational mobility of the decalins is reduced, due to the presence of a second ring, it was of interest to see, whether steric effects are still observed in the mass spectra of decalin-1,3-diol derivatives and whether mass spectrometry can be used as an analytical tool for the identification of stereoisomers in this class of compounds.

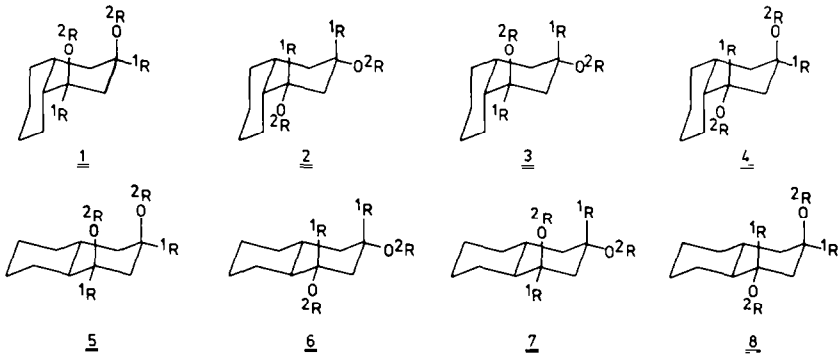
Synthesis and identification of compounds. The 8 stereoisomers of decalin-1,3-diol have not been described in the literature. The usual method of synthesis of cyclic alcohols is catalytic hydrogenation of the corresponding phenols. However, the mixture of aliphatic diols obtained from 1,3-dihydroxynaphthalene consisted mostly of the *cis* - decalin - 1,3 - diols **1a–4a** and only a small amount of diols **5a–8a** derived from *trans*-decalin had been formed. Therefore we chose reduction of *cis*- and *trans* - decalin - 1,3 - dione, respectively, by LAH to synthesize the 1,3-diols with the skeleton of *cis*- and *trans*-decalin. The same method, using LAD instead of LAH, gave the deuterated compounds **1c–8c**. No interchanges between the *cis*- and *trans*-decalin systems was observed. The decalin-1,3-diones[6] were obtained from 1 - acetyl - cyclohexene and sodium diethyl malonate via 4 - carbethoxy - *cis* - decalin - 1,3 - dione after hydrolysis and decarboxylation (Scheme 1).

The mixture of *cis* - decalin - 1,3 - diols obtained by reduction of the corresponding dione was analyzed by gas chromatography of the bis-trifluoracetates (Table 1). One isomer, **3a**, was formed in large amounts, while isomer **4a** was only a minor component of the mixture. Compounds **1a** and **4a** were isolated as pure compounds by repeated column chromatography (silica gel, acetone/benzene, 2:3, v/v), but, **2a** and **3a** were eluted as a mixture, from which pure **3a** was obtained by recrystallization from benzene. We did not succeed in isolating pure **2a**, therefore the mixture composed of 48% **2a** and 52% **3a** (by gas chromatography) was used for the mass spectrometric investigations. As the mass spectrum of pure **3a** and the composition of the mixture was known, the mass spectrum of **2a** could be calculated from that of the mixture by standard methods of quantitative mass spectrometric analysis of mixtures.[7]

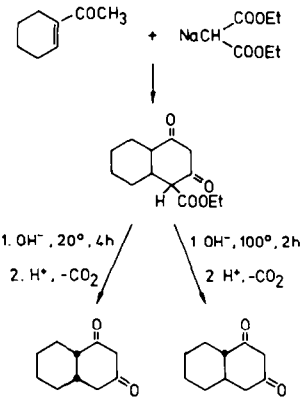
Similarly the mixture of diols obtained from *trans* - decalin - 1,3 - dione by reduction with LAH was analyzed by gas chromatography (Table 1). Only three peaks were observed in the gas chromatogram, and as was shown later by the ^{1}H-NMR and IR spectra, the peak with the retention time of 24.55 min was due to the bis-trifluoracetates of **7a** and **8a**. It was not possible to separate and isolate **7a** and **8a**, therefore a mixture of these isomers had to be used for the subsequent investigations. Isomers **5a** and **6a** were obtained as pure substances by repeated column chromatography (silica gel, benzene/acetone 3:1 v/v) of the bis-trimethylsilyl ethers of the mixture of the *trans*-diols and subsequent hydrolysis by boiling with aqueous methanol.

The stereochemistry of compounds **1a–8a** was determined by a combination of physical and chemical methods. The configuration of the carbon skeleton was

†Mechanisms of Mass Spectrometric Fragmentation Reaction—XVII. Part XVI: U. Neuert and H. F. Grützmacher, *Org. Mass Spectrom.* **11**, (1976) in press.



^1R	^2R							
H	H	1a	2a	3a	4a	5a	6a	7a	8a
H	D	1b	2b	3b	4b	5b	6b	7b	8b
D	H	1c	2c	3c	4c	5c	6c	7c	8c
H	CH_3	1d	2d	3d	4d	5d	6d	7d	8d
D	CH_3	1e	2e	3e	4e	5e	6e	7e	8e



Scheme 1.

Table 1. Gas chromatographic analysis of the mixtures of decalin-1,3-diols

cis-decalin-1,3-diols	1a	2a	3a	4a
r_t(min)	30,0	24,0	27,1	29,1
%	25	19	48	8
trans-decalin-1,3-diols	**5a**	**6a**	**7a + 8a**	
r_t(min)	21,8	19,9	24,6	
%	31	16	53	

known from the synthesis; **1a–4a** are derivatives of *cis*-decalin, while **5a–8a** are *trans*-decalin derivatives. This assignment facilitated the determination of the orientation of the hydroxy substituents, which could be deduced from the ^{1}H-NMR and IR spectra. It was known from the ^{1}H-NMR spectra of decalinols and decalin-1,4-diols,[8] that the width of the signal of the CH_2-groups at half-height decreases with the number of axial groups on the rings of the molecules and that the signal of the proton on the carbinol-C-atom appears at different δ-values for an axial and equatorial OH substituent. Similarly the stretching of the C–O bond gives rise to absorption bands in the IR spectra with different frequencies for decalinols with axial and equatorial OH groups, respectively.[9] The band of an axial OH substituent appears at 960–1020 cm^{-1}, while the same adsorption band is observed at higher frequencies for decalinols with equatorial OH groups. The relevant data of the ^{1}H-NMR and IR spectra of compounds **1a–8a** are presented in Table 2.

Only one signal of the carbinol protons was observed in the ^{1}H-NMR spectrum of **1a**. The IR spectrum of **1a** contained the C–O-adsorption band in the lower frequency region and showed some broadening of the bands due to intramolecular H-bonds. This identified **1a** as *cis*-decalin-1a,3a-diol with two axial OH groups. The ^{1}H-NMR spectra of **3a** and **4a** both contained two multiplets due to the carbinol protons, and both IR spectra showed bands of the C–O-stretching vibration in the lower and upper frequency region, respectively. Consequently an axial and an equatorial OH substituent is present in **3a** and **4a**. Therefore **2a**, which could not be isolated as a pure substance, is *cis*-decalin-1e,3e-diol with two equatorial OH groups.

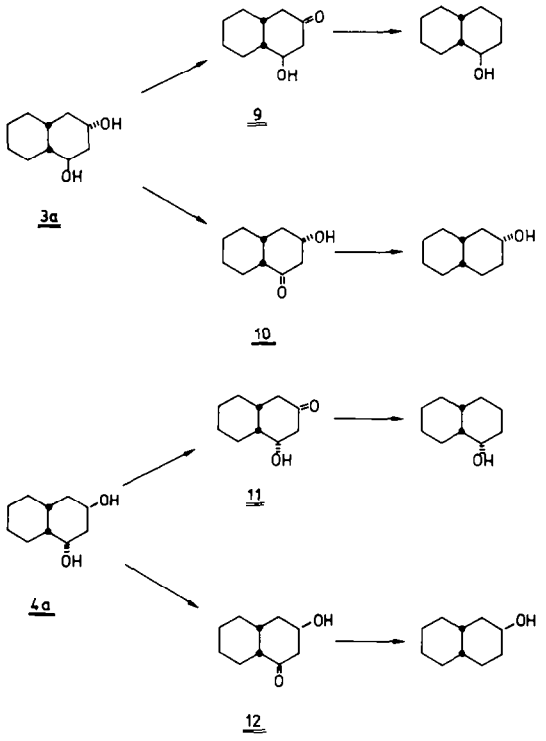
In the *trans* - decalin - 1,3 - diol series **5a** and **6a** gave only one multiplet signal of the protons on the carbinol-C atoms in the ^{1}H-NMR spectra, and therefore contain either two axial or two equatorial OH groups. It was easily seen from the width of the signal of the CH_2 groups in the ^{1}H-NMR spectra and from the location of the C–O bands in the IR spectra, that **5a** is *trans* - decalin - 1a,3a - diol with two axial OH groups and **6a** is *trans* - decalin - 1e,3e - diol with two equatorial OH groups, respectively. It follows that the mixture of **7a** and **8a** contain the remaining isomers of the *trans* - decalin - 1,3 - diol series with one axial and one equatorial OH substituent, in agreement with the location of the signals in the ^{1}H-NMR and IR spectra and the chromatographic behaviour of these isomers.

While it was obvious from the spectra of **3a** and **4a** (Table 2), that these *cis* - decalin - 1,3 - diols each have one axial and one equatorial OH group, it was not possible

Table 2. Characteristic signals in the ^{1}H-NMR-spectra and IR-spectra of **1a–8a**

	^{1}H-NMR -CH-OH (ppm)	^{1}H-NMR $-CH_2-$ (width, Hz)	IR -C-O-stretching (cm^{-1})	assignment
1a	3,57	25 ± 2	1003,1012	a, a
3a	3,67; 3,74	20 ± 2	1014,1062	a, e
4a	3,49; 3,57	18 ± 2	1002,1051	a, e
5a	3,97	31 ± 2	996,1016	a, a
6a	3,68	68 ± 4	1056,1065	e, e
7a + 8a	3,71; 3,95	38 ± 2	998,1018,1055	a, e

to determine definitely from the spectra the orientation of the OH groups at C-1 and C-3, respectively. Therefore **3a** and **4a** were transformed into decalinols of known stereochemistry by the sequence of reactions shown in Scheme 2.



Scheme 2.

Partial oxidation of **3a** by Jones reagent yielded the isomeric ketols **9** and **10** in a ratio of about 3:1, which were separated by column chromatography (silica gel, benzene/acetone 6:1, v/v). *cis* - Decalin - 1a - ol was isolated after Wolff–Kishner reduction of **9** as the only decalinol, while *cis* - decalin - 2e - ol was formed from ketol **10** by the same procedure. Hence **3a** is *cis* - decalin - 1a,3e - diol with an axial OH substituent at C-1 and an equatorial one at C-3.

Similarly a 1:1-mixture of ketols **11** and **12** was obtained from **4a** by partial oxidation with Jones reagent. The products of a Wolff–Kishner reduction of these ketols were *cis* - decalin - 1e - ol (from **11**) and *cis* - decalin - 3a - ol (from **12**), respectively. **4a** is therefore *cis*-decalin-1e,3a-diol.

Mass spectra. In Figs. 1 and 2 the mass spectra of **1a** and **5a** are shown as typical examples. As usual[3,10] the mass spectra of the stereoisomers are similar in appearance, although some variations in the ion intensities are present. However, with the exception of the intensities of the $[M-H_2O]^+$ ions, which will be discussed in the following section, it is difficult to establish that the differences in ion intensities are due to the influence of the geometry of the parent molecule on the fragmentation pathways.

The intensities of the molecular ions are small and the highest relative intensities were observed in the mass spectra of **1a** and **5a**. This effect could be due to a stabilisation of the molecular ions by an intramolecular H-bond[11] between the two axial OH groups of these compounds. However, a similar variation of molecular ion intensities was observed in the mass spectra of the methyl ethers **1d–8d**, again **1d** and **5d** giving the greatest values. Therefore another, still unknown effect is operating besides formation of an intramolecular H bond. The high mass region of the spectra is dominated by the peaks of the $[M-H_2O]^{+\cdot}$ ions and $[M-2xH_2O]^{+\cdot}$ ions at *m/e* 152 and *m/e* 134, respectively. The base peak at *m/e* 67 and most of the other peaks in the mass spectra are due to hydrocarbon ions. No complete mass shifts due to an incorporation of deuterium atoms was observed for these ions in the mass spectra of the deuterated derivatives **1b,c–8b,c**, therefore probably each of these ions was formed by more than one fragmentation reaction. Exceptions are the ions *m/e* 70 and *m/e* 73. The former ions, which are of especially large relative intensities in the spectra of the *trans*-derivatives **5a–8a**, are predominantly of the elemental composition C_4H_6O and their masses are shifted to *m/e* 71 in the mass spectra of the deuterated compounds **1b,c–8b,c**. Consequently these ions contain one OH group and one of the H atoms of the carbinol group, their structure being probably that of 1- or 2-hydroxybutadiene.

The elemental composition $C_3H_5O_2$ and the complete mass shifts by 2 m.u. in the spectra of **1b,c–8b,c** show, that the ions *m/e* 73 are dihydroxy allyl ions, which arise from the molecular ions by the typical fragmentation of cyclic alcohols.[12] The peak at *m/e* 73 is of diagnostic value, because ions of this type are only formed in the mass spectra of 1,3-diols. Therefore the decalin-1,3-diols can be distinguished from their positional isomers by this peak.

The mass spectrometric fragmentations are not very much altered by O-methylation of the decalin-1,3-diols, as was shown by the mass spectra of the 1,3 - dimethoxy - decalin **1d** and **5d** in Figs. 3 and 4.

Most of the intense ions in the lower mass region are

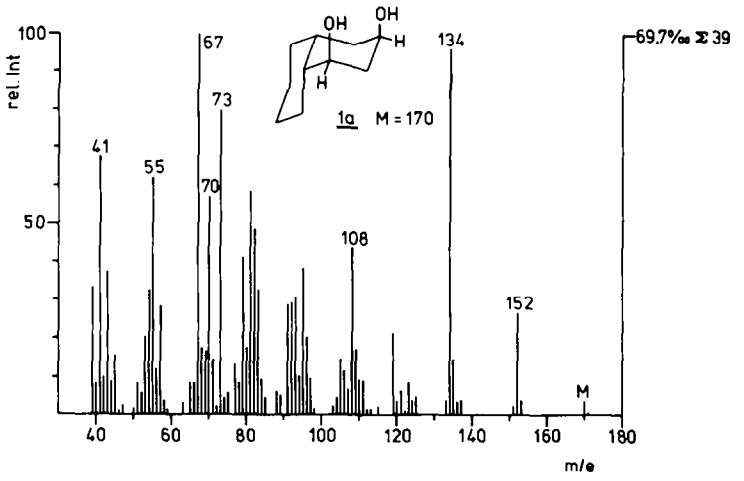


Fig. 1. 70 eV-mass spectrum of *cis*-decalin-1a,3a-diol **1a**.

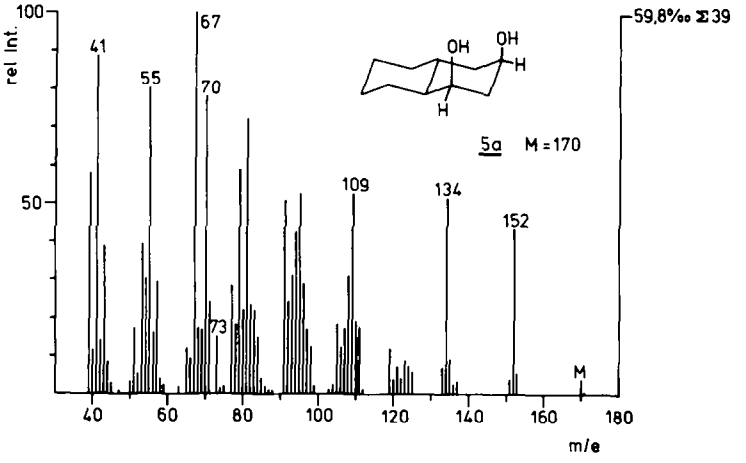


Fig. 2. 70 eV-mass spectrum of *trans*-decalin-1a,3a-diol **5a**.

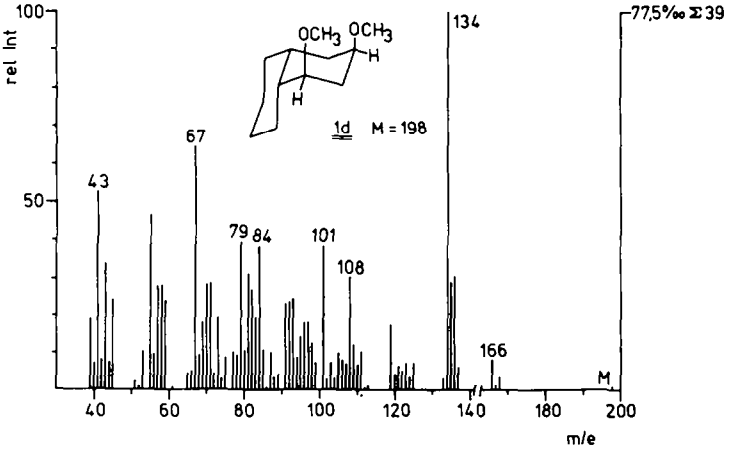


Fig. 3. 70 eV-mass spectrum of *cis*-1a,3a-dimethoxy decalin **1d**.

again of the hydrocarbon type, exceptions are the methoxybutadiene ions *m/e* 84 and the dimethoxy allyl ions *m/e* 101. The relative intensities of the latter ions are rather small in the mass spectra of the 1,3 - dimethoxy - *trans* - decalins, and it may be difficult to distinguish these compounds from their positional isomers by this peak, because small peaks at *m/e* 101 are also observed in the mass spectra of 1,4-dimethoxy decalins.[3] The high mass regions of the spectra contain peaks of the ions M^+, $[M\text{-}CH_3OH]^+$ and $[M\text{-}2xCH_3OH]^+$, as expected, at *m/e* 198, 166 and 134, respectively, and in the case of the isomers **1d**, **2d** and **5d** with a *cis*-orientation of the two

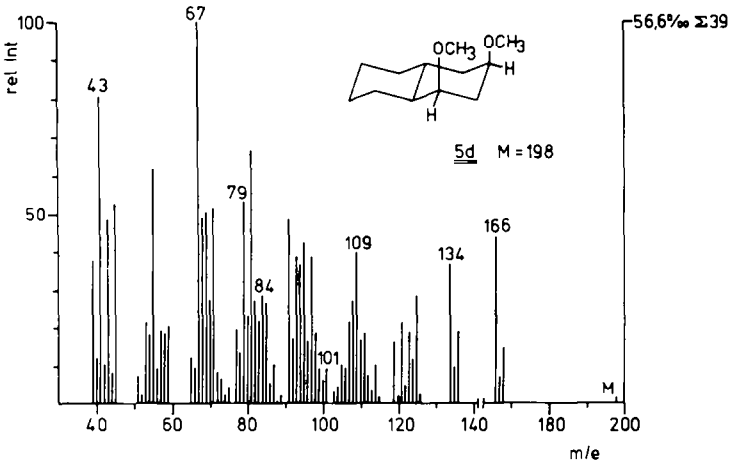


Fig. 4. 70 eV-mass spectrum of *trans*-1a,3a-dimethoxy decalin **5d**.

OMe groups, additional peaks of the ions $[M-CH_2O]^+$ and $[M-CH_2O-CH_3OH]$ at *m/e* 168 and *m/e* 136 were observed.

Steric effects on the elimination reactions. The relative intensities of the $[M-H_2O]^+$ ions in the mass spectra of **1a–8a** and the distribution of the ion current of these ions among the species $[M-H_2O]^+$, $[M-HDO]^+$ and $[M-D_2O]^+$ in the mass spectra of **1b,c–8b,c** is shown in Table 3.

From the various fragmentations of intact molecular ions of cyclic diols forming $[M-H_2O]^+$ ions two reactions are distinguished by specific steric requirements of the transition states. The first one involves an OH group and the H atom bound to the C atom of the other carbinol group. As the dissociation energy of this C–H bond is about 20 kcal/mole lower than that of the C–H bonds of CH_2 groups in alkanes or cycloalkanes,[13] this H_2O elimination has the lowest activation energy. However, as OH group and H atom have to approach each other rather closely in the transition state, the H_2O elimination by this mechanism requires a *trans*-orientation of the two OH groups in cyclic 1,3-diols[2] (Scheme 3).

This steric condition is met by the decalin - 1,3 - diols **3a**, **4a**, **7a** and **8a**, each possessing one axial and one equatorial OH group. As there is an additional and energetically favoured reaction path for the H_2O elimination, compared to the other stereoisomers, one expects a larger intensity of the $[M-H_2O]^+$ ions in the mass spectra of **3a**, **4a**, **7a** and **8a**. Indeed, this effect was observed, although the effect is not very large in the case of the *trans* - decalin - 1,3 - diols and is not as clear as in the mass spectra of stereoisomeric decalin - 1,4 - diols.[3]

Scheme 3.

However, the different mechanisms of the H_2O eliminations from the molecular ions are easily seen from the ratio of $[M-H_2O]^+$ ions and $[M-HDO]^+$ ions in the mass spectra of the deuterated derivatives **1c–8c** (Table 3). About 80–83% of the H_2O molecules are lost by a 1,3-elimination from the *cis* - decalin - 1,3 - diols **3a** and **4a**, as is shown by the corresponding values of the loss of HDO from **3c** and **4c**, while less than 5% loss of HDO is observed in the mass spectra of **1c** and **2c**. A 1,3-elimination of HDO is not possible from the intact molecular ions of these isomers, but has to be preceded by cleavage of the hydroxylated ring. If in the mass spectra

Table 3. Relative ion intensities and deuterium retention of eliminations of water from molecular ions of decalin-1,3-diols (corrected for ^{13}C)

		1a	2a	3a	4a	5a	6a	7a + 8a
$[M-H_2O]^{+\cdot}$	% B *)	26,7	37,7	66,7	63,8	43,7	53,8	63,6
	% T**)	18,6	22,3	44,2	47,6	26,2	32,0	36,2
		1b	2b	3b	4b	5b	6b	7b + 8b
$[M-D_2O]^{+\cdot}$		90%	20%	-	-	90%	-	6%
$[M-HDO]^{+\cdot}$		10%	80%	>95%	>95%	10%	>95%	94%
		1c	2c	3c	4c	5c	6c	7c + 8c
$[M-HDO]^{+\cdot}$		-	-	83%	81%	9%	-	71%
$[M-H_2O]^{+\cdot}$		>95%	>95%	17%	19%	91%	>95%	29%

*) % base peak

**) % total ion current

of **3c** and **4c** the 1,3-elimination occurs to a similar percentage from ring opened molecular ions, at least 75% of the H_2O molecules are eliminated by a stereospecific process from the molecular ions of **3a** and **4a**. Similar results have been obtained from the mass spectra of decalin - 1,4 - diols.[3]

The steric control of the H_2O elimination is somewhat less in the mass spectra of the *trans* - decalin - 1,3 - diols **7a** and **8a**. The data of Table 3 indicate, that about 70% of the H_2O molecules are lost by a 1,3-elimination from the mixture of molecular ions of **7a** and **8a**, and more than 60% are lost by a stereospecific elimination from intact molecular ions. This slight reduction in the stereospecifity is probably due to the more rigid skeleton of the *trans* - decalin - 1,3 - diols.

The second specific mechanism of the H_2O elimination from molecular ions of cyclic diols corresponds to the formation of the H_2O molecules by interaction between the two OH groups (Scheme 4). In the case of intact

Scheme 4.

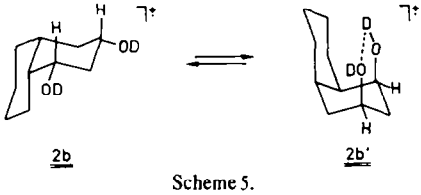
molecular ions of cyclic 1,3-diols, the short distance, which is a prerequisite for the elimination of H_2O by this mechanism, is only possible in isomers with a diaxial orientation of the 1,3-OH substituents. The occurence of this mechanism is easily established by elimination of D_2O in the mass spectra of the O-d_2 derivatives of diols.

The ground state conformations of the *cis* - decalin - 1,3 - diol **1a** and the *trans* - decalin - 1,3 - diol **5a** are convenient for this reaction. In the case of the *cis* - decalin - 1,3 - diol **2a** the required conformation of the transition state can be achieved by a chair-chair interconversion of the *cis*-decalin system. However, the ΔH_f of this conformation is certainly larger by some kcal/mols than that of the ground state conformation, because of severe 1,3-diaxal repulsions between the OH substituents and the fused second ring.[14] A rather short distance between the OH groups of the *trans* - decalin - 1,3 - diol **6a** is possible, if the hydroxylated ring adopts a boat conformation. But again this conformation of the molecular ion is energetically not favoured. In the case of the remaining isomers **3a**, **4a**, **7a** and **8a**, no conformation of the molecular ions has a sufficiently short distance between the OH groups.

The different steric situation in the stereoisomeric decalin - 1,3 - diols is nicely demonstrated by the amount of D_2O lost from the molecular ions of the O-d_2 derivatives **1b–8b** (Table 3). No loss of D_2O was observed within the limits of error in the mass spectra of **3b** and **4b** and only about 6% in the mass spectrum of the mixture of **7b** + **8b**. In contrast to this the peak $[M-D_2O]^+$ dominates in the spectra of **1b** and **5b**, the percentages of D_2O elimination are *ca* 90%. A similar participation of the interaction of two OH groups in the elimination of H_2O was observed in the mass spectra of decalin - 1,4 - diols of appropriate geometry.[3] An interaction between the OH groups in these 1,4-diols is only posible, if the hydroxylated ring has a boat conformation. Obviously the necessity to change the conformation of the molecular ions prior to the H_2O elimination has no large effect on the course of the reaction in the case of the decalin - 1,4 - diols. A corresponding change of the conformation of the hydroxylated ring has to take place in the molecular ions of the *trans* - decalin - 1,3 - diol **6b** prior to elimination of D_2O, although the distance between the two OD-groups is still rather large. No elimination of D_2O was detected within the limits of error in the mass spectrum of **6b**, so a transition state with a suitable geometry for the interaction between the OH groups is not very likely for the molecular ions of **6a**.

The *cis* - decalin - 1,3 - diol **2a** is the other isomer, which has to change its ground state conformation to permit interaction between the two OH groups. In the mass spectrum of the O-d_2 derivative **2b** about 20% elimination of D_2O was observed besides loss of HDO. Hence in contrast to the results obtained from the mass spectra of decalin - 1,4 - diols the amount of H_2O lost from the molecular ions of decalin - 1,3 - diols by interaction of both OH groups is considerably reduced if a change of the conformation of the molecular ions is a prerequisite of this reaction.

The 20% loss of D_2O from molecular ions of **2b** can be explained in two ways. Firstly an equilibrium between the conformations **2b** and **2b'** prior to ionisation may be assumed in the gas phase of the inlet system and ions source of the mass spectrometer, and after ionisation only **2b'** loses D_2O.



Scheme 5.

In this case the ratio 4 of $[M-HDO]^{+\cdot}/[M-D_2O]^{+\cdot}$ should reflect the composition of the mixture at the equilibrium before ionisation, i.e. 80% **2b** and 20% **2b'**. The difference in energy between **2b** and **2b'** is not known, but has to be less than 1,5 kcal/Mol to account for the presence of 20% **2b'**. With respect to the steric repulsion between the axial substituents in **2b'** this is rather unlikely.

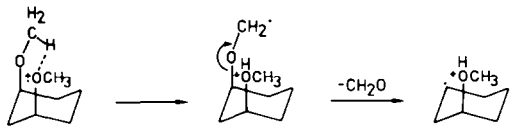
In the second explanation it is assumed, that nearly all molecules are in the conformation **2b** before ionisation, but that conformational changes take place in the molecular ions after ionisation. The transition state of D_2O elimination is not necessarily conformation **2b'**, because in the flexible *cis*-decalin system a short distance between both OH groups is already possible in a boat conformation. The excess energy implanted into the molecular ions during ionisation by 70 eV electrons is certainly large enough to activate these conformational changes, however changing the conformation has to compete with other fragmentation reactions with low activation energies. This accounts for the reduction in the amount of stereospecific loss of D_2O from **2b**, compared with the same reaction of **1b**. This explanation is in accord with stereospecific reactions in the mass spectra of stereoisomeric 4-t.-butyl- and 4 - methyl - cyclohexane - 1,3 - diols.[4,5]†

†It has been suggested by a referee, that in this case the ratio of $[M-HDO]^{+\cdot}/[M-D_2O]^{+\cdot}$ in the mass spectrum of **2b** should vary by reducing the energy of the ionizing electrons. Within the limits of error no such variations have been observed between 70 and 17 eV. Probably the energy distribution of the molecular ions is not sufficiently altered by this method to observe any effect on these processes with a low activation energy.

In the mass spectra of di - O - methyl ethers of cyclic diols, two elimination reactions were also observed which are controlled by the geometry of the molecular ions. The first one is a methanol elimination with a low activation energy, which involves an OMe group and the H atom of the other CH–carbinol group; analogous to Scheme 3, and which can take place in the 1,3 - dimethoxy - decalins **3d**, **4d**, **7d** and **8d**. For similar reasons as with the corresponding 1,3-diols one expects an enhanced intensity of the $[M–CH_3OH]^+$ ions in the mass spectra of **3d**, **4d**, **7d** and **8d**. However, as is seen by the data of Table 4, this enhancement is rather small.

Nevertheless the mass spectra of the deuterated derivatives **1e–8e** show the expected differences in the mechanism of the methanol eliminations. The molecular ions of **3d** and **4d** lose 76% MeOD and 72% MeOD, respectively, and those of **7d** + **8d** eliminate 65% MeOD, while only about 10% loss of MeOD was observed from the molecular ions of the other isomers, where no interaction between a MeOH group and a carbinol-CH group is possible in the intact molecular ions. Calculations based on these data show that about 70%, 63% and 57% of the elimination of methanol from **3d**, **4d** and **7d** + **8d**, respectively, occurs by a stereospecific process in intact molecular ions, in agreement with the extent of stereospecifity of this reaction in the mass spectra of 1,4 - dimethoxy - decalins[3] and dimethoxy cyclohexanes.[2]

The second reaction in the mass spectra of dimethoxycycloalkanes for which the steric control of the mechanism is known[2] corresponds to a loss of CH_2O from the molecular ions. The crucial step of this reaction is the transfer of a H atom from one MeO group to the second one. The short distance required by this transfer is only possible in a 1,3-dimethoxycycloalkane with both MeO substituents in an axial position (Scheme 6).



Scheme 6.

In accord with this mechanism distinct peaks of $[M–CH_2O]^{+\cdot}$ ions at *m/e* 168 were observed in the mass spectra of **1d** and **5d**, and were completely absent in the spectra of **3d**, **4d** and **7d** + **8d** (Figs. 3 and 4 and Table 4). A small ion current persists at *m/e* 168 in the mass spectra of **2d** and **6d** after corrections for the contribution of ^{13}C containing ions to this *m/e*-value, but the corrected relative intensities of 1.6% and 2.3%, respectively, are too small to prove the formation of $[M–CH_2O]^{+\cdot}$ ions. If at all, a small amount of these ions may be formed in the mass spectrum of **2d**. Again the necessity of the molecular ions to change their conformation before the fragmentation reduces the probability of this fragmentation pathway drastically.

It is of interest to note that the intensity variation of the $[M–2xH_2O]^+$ and $[M–2xCH_3OH]^+$-ions in the mass spectra of **1a–8a** and **1d–8d** is quite different from that of the $[M–H_2O]^+$ - and $[M–CH_3OH]^+$-ions (Table 5).

Table 4. Relative ion intensities and deuterium retention of eliminations from molecular ions of 1,3-dimethoxy decalins (corrected for ^{13}C)

		1d	2d	3d	4d	5d	6d	7d + 8d
$[M-CH_3OH]^{+\cdot}$	%B*)	8,4	11,6	16,6	16,2	43,8	42,1	68,4
	%T**)	6,5	9,2	12,2	12,4	24,7	23,4	38,7
$[M-CH_2O]^{+\cdot}$	%B*)	4,0	(1,6)	-	-	14,9	(2,3)	-
	%T**)	3,1	(1,2)	-	-	8,4	(1,2)	-
		1e	2e	3e	4e	5e	6e	7e + 8e
$[M-CH_3OD]^{+\cdot}$		12%	8%	76%	72%	13%	12%	65%
$[M-CH_3OH]^{+\cdot}$		88%	92%	24%	28%	87%	88%	35%

*) % base peak

**) % total ion current

Table 5. Relative intensities of $[M–2xH_2O]^+$ and $[M–2xCH_3OH]^+$ ions

		1a	2a	3a	4a	5a	6a	7a + 8a
$[M - 2x\ H_2O]^{+\cdot}$	%B*)	96,0	44,6	24,9	32,2	51,8	59,0	60,2
	%T**)	66,9	29,5	16,5	24,0	31,0	35,0	34,2
		1d	2d	3d	4d	5d	6d	7d + 8d
$[M - 2xCH_3OH]^{+\cdot}$	%B*)	100,0	60,9	44,3	49,8	36,9	38,8	36,7
	%T**)	77,5	48,1	32,8	38,9	20,9	21,6	20,8

*) % base peak

**) % total ion current

Large intensities of $[M-2xH_2O]$- or $[M-2xCH_3OH]^{+\cdot}$ ions were found in the mass spectra of isomers with relatively small intensities of the primary fragment ions of $[M-H_2O]^{+\cdot}$ or $[M-CH_3OH]^{+\cdot}$ and *vice versa*. This indicates, that many of the primary fragment ions decompose rapidly by loss of a second H_2O or MeOH molecule. However, most of the $[M-2xH_2O]^{+\cdot}$ and $[M-2xCH_3OH]^{+}$ ions in the mass spectra of **1c–8c** and **1e–8e**, respectively, retain both D atoms and consequently are formed by sterically unspecific processes. This result is in keeping with the Quasi-Equilibrium-Theory of mass spectrometry, because the sterically controlled eliminations from the molecular ions of cyclic diol derivatives are reactions with low activation energies. Hence molecular ions with a large excess energy react rapidly with a low selectivity and the excess energy is large enough for a further decomposition of the primary fragment ions, while molecular ions with a small excess energy form with a higher selectivity stable fragment ions by low energy processes.

CONCLUSION

The investigation of the mass spectrometric fragmentations of the stereoisomeric decalin - 1,3 - diols **1a–8a** and 1,3-dimethoxydecalins **1d–8d** with the aid of deuterated derivatives demonstrates, that the molecular ions of these compounds decompose by stereospecific elimination reactions similar to the fragmentation of molecular ions of cyclohexane - 1,3 - diol and its derivatives. Obviously the extent of stereospecific elimination is not influenced very much by the attachment of a second saturated ring, if the ground state conformation of the decalin - 1,3 - diol corresponds to the spatial arrangement of the transition state of the elimination reaction. However, contrary to cyclohexanediols and decalin - 1,4 - diols or their O-Me derivatives, the amount of ions formed by stereospecific eliminations is reduced drastically if conformational changes of the molecular ions are required before the fragmentation. The difference in the ion intensities and in the incorporation of D labels into the ions formed by elimination of water or methanol can be used to distinguish between the stereoisomers of decalin - 1,3 - diol and 1,3 - dimethoxy decalin by mass spectrometry.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were taken in KBr pellets with a Perkin-Elmer 137 spectrophotometer. NMR spectra were measured on a 60 MHz NMR spectrometer Varian T 60 in $(CD_3)_2SO$-soln using TMS as internal reference. Gas chromatograms were obtained with a Perkin-Elmer F6 and Varian MAT 111 gas chromatograph using 50 m QF 1 capillary columns (130°, 1 ml/sec He).

Mass spectra were measured on a Varian MAT CH4 mass spectrometer at an electron energy of 70 eV, electron trap current 40 μA, ion source temp. *ca.* 200°. The decalin - 1,3 - diols were introduced into the ion source by a vacuum lock and direct insertion probe, the 1,3-dimethoxydecalins were measured by a heated inlet system (150°). The exact masses of selected ions was determined with a Varian MAT SM 1B mass spectrometer by the peak matching technique using PFK as reference. Experimental and calculated values of the ion masses agreed within 3 ppm to the assumed elemental composition of the ions.

cis - Decalin - 1,3 - diols **1a–4a**. *cis* - Decalin - 1,3 - dion[6] (18.7 g) in THF was reduced with 10% excess LAH. The crude product consisted of an octalinol as a main product and of *cis* - decalin - 1,3 - diols (*ca.* 40%). The crude mixture was used without any purification for column chromatography on silica gel and elution with acetone/benzene = 2/3 (V/V). The fractions containing the octalinol were discarded. The remaining fractions yielded **1a** (1.72 g) m.p. 182°, and **4a** (0.50 g) m.p. 147°, after recrystallization from benzene, and were obtained together with 4.13 g of a mixture of **2a** and **3a**. By recrystallization of this mixture from benzene **3a** (1.71 g), m.p. 168°, was obtained. The combined benzene solns from the recrystallization of **3a** were evaporated to give about 2 g of a mixture of **3a** and **2a** (52%: 48%).

trans - Decalin - 1,3 - diols **5a–8a**. LAH-reduction (10% excess) of *trans* - decalin - 1,3 - dion[6] (21.4 g) in THF gave a crude product, from which a mixture of **5a–8a** (16.7 g) was obtained by column chromatography on silica gel and elution with acetone/benzene = 2/3 (V/V). The bis-TMS ether of the diols were obtained from the mixture by reaction with N - bis - TMS - acetamide, dilution with H_2O and extraction with n-hexane.[15] The resulting mixture was separated by column chromatography on silicagel and elution with acetone/benzene = 1/3 (V/V) into three fractions. Each fraction was purified by column chromatography using the same conditions as before. After evaporation of the solvent the residual oil of each fraction was redissolved in water/MeOH 1/1 (V/V) and heated under reflux for 1 hr. By evaporation to dryness and recrystallization from EtOH **5a** (2.63 g) m.p. 189°; **6a** (1.45 g) m.p. 155°; and a mixture of **7a** and **8a** (4.61 g) were obtained.

1,3 - *Dimethoxy - decalins* **1d–8d**. The individual isomers of the diols **1a–6a** and the mixtures of **2a** + **3a** and **7a** + **8a**, respectively, were dissolved in CH_2Cl_2 (30 ml/g diol) and methylated by the CH_2N_2/BF_3/ether complex.[16] After the usual work up of the mixture the 1,3-dimethoxydecalins were purified by vacuum destillation.

Decalin - 1,3 - diol - bis - trifluoracetates. For gas chromatographic analysis the mixtures of the diols were transformed into the corresponding trifluoracetates by dissolving in trifluor-acetic acid anhydride (*ca.* 10 times in excess). After 5 min most of the anhydride and of trifluor-acetic acid was removed by vacuum destillation and the residues used for gas chromatography.

Deuterated derivatives. The decalin - 1,3 - diols - 1,3 - d_2 **1c–8c** were synthesized by the same methods as **1a–8a**, using LAD for the reduction.

Deuterium content (by mass spectrometry)

1c	99% d_2;	1% d_1;		**5c**	96% d_2;	4% d_1;	
2c + **3c**	98.5% d_2;	1.5% d_1;		**6c**	98% d_2;	2% d_1;	
3c	99% d_2;	1% d_1;		**7c** + **8c**	98% d_2;	2% d_1;	
4c	99% d_2;	1% d_1;					

The 1,3 - diemthoxydecalins - 1,3 - d_2 **1e–8e** were obtained from the correspondingly deuterated diols by O-methylation as described before. The decalin - 1,3 - diol - O - d_2 derivatives **1b–8b** were obtained by dissolving **1a–8a**, respectively, in a small amount of THF and adding D_2O (99.9% deuterium) in a very large excess. After mixing for 1 hr the solns were evaporated to dryness and the residues introduced into the mass spectrometer after preconditioning of the instrument with D_2O. Deuterium content (by mass spectrometry) 95% d_2; 5% d_1.

Partial oxidation of **3a**. **3a** (856 mg) in THF was oxidized by Jones reagent analogous to the method of Bec *et al.*[17] A mixture of 360 mg (~ 42%) of ketols **9** + **10** was obtained, which was separated into 276 mg **9** and 82 mg **10** by column chromatography on silica gel and elution with acetone/benzene = 1/6 (V/V); **9** m.p. 54°; **10** m.p. 18° after recrystallization from benzene.

Wolff–Kishner-reduction of **9**. From the Wolff–Kishner-reduction of **9** (276 mg) by standard procedures,[18] 77 mg (28%) of decalin - 1a - ol were obtained after purification by column chromatography (silica gel, acetone/benzene = 1/2 (V/V)) and identified by comparison of its IR spectrum with that of an authentic sample.

Wolff–Kishner-reduction of **10**. Decalin - 2e - ol 25 mg (31%) was obtained from **10** (82 mg) and identified by the same methods.

Partial oxidation of **4a**. By the methods mentioned for the oxidation of **3a** a mixture of ketols **11** + **12** (132 mg; 49%) was obtained from **4a** (269 mg), which was separated into **11** (68 mg), m.p. 93° and **12** (63 mg), m.p. 103° after recrystallization from benzene.

Wolff–Kishner-reduction of **11**. As described above the reduction of **11** (68 mg) gave decalin-1e-ol (30 mg; 45%; after purification), which was identified by its IR spectrum.

Wolff–Kishner-reduction of **12**. After reduction and purification, as described before, decalin-2a-ol (23 mg; 36%) was obtained from **12** (63 mg) and identified by its IR spectrum.

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