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MECHANISMS OF MASS SPECTROMETRIC FRAGMENTATIONS: X*—INTERACTION BETWEEN REMOTE OR-GROUPS IN DECALIN-1,5-DIOLS AND THEIR DIMETHYL ETHERS

HANS-FRIEDRICH GRÜTZMACHER and KARL-HEINZ FECHNER
Institut für Organische Chemie der Universität Hamburg, 2-Hamburg 13, Papendamm 6,
West Germany

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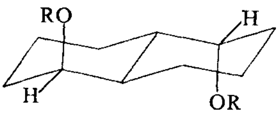
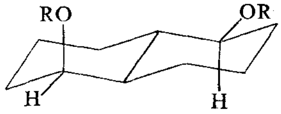
Abstract—The mass spectra of the five stereoisomers of decalin-1,5-diol and its dimethyl ether have been investigated. The differences in the mass spectra of stereoisomers I to III with a *trans*- decalin ring system are small. The differences are much larger in the mass spectra of the two isomers IV and V of the *cis*-decalin series and the elimination of CH_2O, formed by interaction between the two methoxy groups, from the molecular ion is only observed in the mass spectrum of Vb.

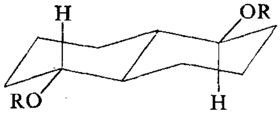
THE INTENSITY variation of $[M - H_2O]^{+\cdot}$, $[M - CH_3OH]^{+\cdot}$ and $[M - CH_2O]^{+\cdot}$ ions in the mass spectra of decalin-1,5-diol stereoisomers and the corresponding dimethyl ethers[1] follows the rules connecting molecular geometry and steric control of mass spectrometric eliminations, which have been observed in the mass spectra of monocyclic diols and their dimethyl ethers.[2,3] We now wish to report the observation of steric effects in the mass spectra of certain stereoisomers of decalin-1,5-diol derivatives, in which both OR groups are substituted at different rings of the molecule. A mixture of stereoisomeric diols (Ia to Va), obtained by catalytic hydrogenation (Raney-Ni, 170°C, 150 atm H_2) and vacuum distillation of the reaction product, was separated into the individual stereoisomers by column chromatography on silica gel (benzene/acetone in various amounts) with a purity greater than 90%. The stereoisomers were identified by n.m.r. spectra and gas chromatographic retention times.[4,5] The mass spectra of the free diols (Ia to Va) were obtained by direct insertion into a



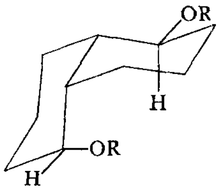
(Ia and Ib)



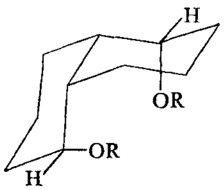
(IIa to IIc)



(IIIa and IIIb)



(IVa and IVb)



(Va to Vc)

(a) R = H
(b) R = CH_3
(c) R = CD_3

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* For Part IX, see Ref. 1.

Varian MAT SM-1B mass spectrometer (ion source temp. 120°C, electron energy 70 eV).

The diols were converted into the corresponding dimethyl ethers (Ib to Vb) and bistrideuteromethyl ethers (IIc and Vc) by standard procedures, and the mass spectra of these volatile derivatives were obtained by g.c./m.s. with a Varian MAT CH-4 instrument (ion source temp. 150°C, electron energy 70 eV). The prominent peaks of the spectra are given in Table 1. In the absence of any experiments with derivatives isotopically labelled at the decalin ring system, no details of the fragmentation mechanisms can be given. However, the genesis of the fragment ions can be easily imagined by analogy with the mass spectrometric fragmentations of monocyclic diols, decalin-1,4-diols and their derivatives.[1,2,3] The intensities of the molecular ions are surprisingly large, even in the series of dimethyl ethers. In the series of cyclic diols large molecular ion peaks have only been observed in the mass spectra of 1,2-diols, where cleavage of the C—C bond of the glycol group results in modified molecular ions with stabilisation of the positive charge and the radical electron by adjacent OR groups. In the molecular ions of decalin-1,5-diol a similar stabilisation can be achieved by double bond cleavages:

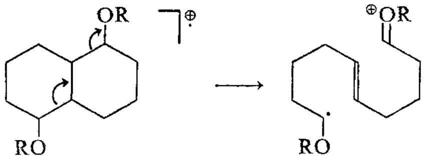

TABLE 1. INTENSITIES OF CHARACTERISTIC IONS IN THE MASS SPECTRA OF DECALIN-1,5-DIOLS AND THEIR DIMETHYL ETHERS (BASE PEAK UNDERLINED) ‰Σ_{39}

m/e	Ion	(Ia)	(IIa)	(IIIa)	(IVa)	(Va)
170	$[M]^{+\cdot}$	43,5	48,5	$\underline{80,0}$	18,7	77,0
152	$[M - H_2O]^{+\cdot}$	43,0	32,6	30,3	42,4	48,7
134	$[M - 2H_2O]^{+\cdot}$	$\underline{77,7}$	$\underline{88,2}$	50,9	55,4	105,2
123	C_9H_{15}	19,9	18,3	12,5	18,1	14,9
121	C_9H_{13}	8,8	11,9	14,7	9,0	16,9
119	C_9H_{11}	15,0	16,3	12,2	11,8	15,9
111	$C_7H_{10}OH$	30,0	35,3	38,4	22,6	23,6
108	C_8H_{12}	49,2	64,0	62,0	42,4	$\underline{112,4}$
84	C_5H_7OH	22,3	33,0	27,3	$\underline{130,0}$	20,3
		(Ib)	(IIb)	(IIIb)	(IVb)	(Vb)
198	$[M]^{+\cdot}$	19,1	11,1	16,8	5,1	7,0
168	$[M - CH_2O]^{+\cdot}$	0	0	0	1,3	10,0
166	$[M - CH_3OH]^{+\cdot}$	15,9	13,6	15,2	18,3	14,5
136	$[168 - CH_2O]^{+\cdot}$	1,3	1,3	1,0	2,0	8,9
134	$[M - 2CH_3OH]^{+\cdot}$	28,6	30,3	25,3	21,3	17,9
125	$C_7H_{10}OCH_3$	26,7	24,7	28,6	19,0	19,4
119	C_9H_{11}	9,5	11,6	10,1	10,9	7,5
111	$C_6H_8OCH_3$	26,7	22,7	26,9	24,5	22,1
108	C_8H_{12}	14,0	5,3	13,1	8,3	12,2
98	$C_5H_7OCH_3$	20,4	37,4	19,4	$\underline{78,7}$	54,0
84	$C_4H_8OCH_3$	68,6	64,6	56,4	57,9	$\underline{94,0}$
71	$C_3H_4OCH_3$	$\underline{75,0}$	$\underline{75,7}$	$\underline{86,4}$	74,1	79,9

A *synchronous* cleavage of the two bonds may be supported by equatorial orientations of both OR groups, analogous to a Grob fragmentation.[6] This would account for the particularly large intensities of the *m/e* 170 ions in the mass spectra of IIIa and Va. However, this effect is absent in the mass spectra of the corresponding dimethyl ethers (IIIb and Vb).

The two OR groups are held apart by the rigid bicyclic system in the *trans*-decalin-1,5-diols (Ia to IIIa) and the dimethyl ethers (Ib to IIIb). Consequently, fragmentation by interaction between both OR groups is not possible and the mass spectra of these stereoisomers are fairly similar. In the *cis*-isomer (IVa) and its dimethyl ether (IVb) however, one of the OR groups can approach the H atom of the second carbinol group, because this H atom and the OR group point into the hollow of the concave molecule. The dissociation energy of a C—H bond of a carbinol group is about 20 kcal/mol less than for a normal C—H bond:[7] therefore IVa and IVb may be expected to lose H_2O and CH_3OH easily, respectively, by transfer of the carbinol H atom to the OR group. However, this effect is not accompanied by an increased intensity of the corresponding fragment ions, and as appropriate deuterated derivatives are not available, a 'hidden stereochemistry'[8] of this elimination reaction cannot be detected.

In one of the conformations of stereoisomer V both OR groups approach each other in the hollow of the molecule. This is a favourable steric situation for H_2O elimination from the molecular ions of Va by interaction between both OH groups, and CH_2O from the molecular ions of Vb by interaction between both OCH_3 groups. Again the amount of pure Va isolated from the mixture was too small to allow any labelling experiments. However, metastable transitions show that the $[M - H_2O]^{+\cdot}$ ions are precursor ions for most of the other fragment ions, and the differences between the mass spectra of IVa and Va probably indicate a different structure for the $[M - H_2O]^{+\cdot}$ ions of both compounds. In the case of the dimethyl ether Vb a distinct $[M - CH_2O]^{+\cdot}$ ion peak is observed, which is completely shifted to $[M - CD_2O]^{+\cdot}$ in the mass spectrum of Vc. Furthermore, Vb is the only isomer of the decalin-1,5-diol dimethyl ethers which fragments by this reaction. This leaves no doubt that the elimination of CH_2O indeed occurs via transfer of a H atom from one CH_3O group to the other, as it has been observed in the mass spectra of *cis*-cyclohexane-1,4-diol and *cis*-cyclohexane-1,3-diol dimethyl ether.[3] This is the first example of a reactive interaction between two CH_3O groups in the molecular ions of a bicyclic diol derivative in which both substituents are attached to different rings. One can expect that this reaction will also occur in certain stereoisomers of other decalindiol dimethyl ethers, if the molecular geometry allows the two CH_3O groups to approach each other.

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