Gas-phase interaction of Me_3Si^+ ions with *cis*- and *trans*-cyclohexanediols, their methyl ethers, and acetates

V. I. Kadentsev, N. G. Kolotyrkina,* A. A. Stomakhin, and O. S. Chizhov

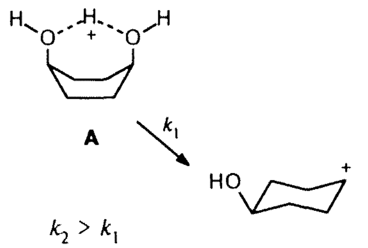
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

The effect of stereochemistry on the mechanism of gas-phase fragmentation of $[M+SiMe_3]^+$ ions was studied using *cis*- and *trans*-1,2- and -1,4-cyclohexanediols, their methyl ethers, and acetates as model compounds. The higher stability of the $[M+SiMe_3]^+$ ions is characteristic of *cis*-isomers of all the compounds examined, which is associated with chelation in the case of *cis*-cyclohexanediols and *cis*-methoxycyclohexanols and with the higher reactivity of *trans*-isomers due to anchimeric assistance of the methoxy and acetoxy groups. Dehydration is characteristic of the $[M+SiMe_3]^+$ ions formed from cyclohexanediols; both hydrogen atoms of the hydroxyl groups take part in the process, thus providing direct evidence of the chelation.

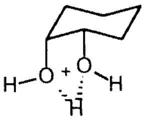
Key words: mass spectrometry, chemical ionization; tetramethylsilane; cyclohexanediols, acetates, methyl ethers; stereochemistry.

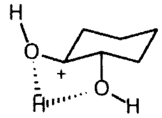
It is known[1] that protonated molecular ions $[M+H]^+$ (PMI) of *cis*-1,3- and 1,4-cyclohexanediols are more stable than those of the corresponding *trans*-isomers; this phenomenon is explained by chelate formation of type **A** in the case of *cis*-isomers (Scheme 1).

Scheme 1



Small differences in stabilities of the $[M+H]^+$ ions of *cis*- and *trans*-1,2-cyclohexanediols are due to very close values of free energies of formation of their chelate forms.





This paper examines the effect of stereoisomerism on the fragmentation of $[M+SiMe_3]^+$ ions, the analogs of PMI, of *cis*- and *trans*-1,2- and 1,4-cyclohexanediols (**1—4**), their OD-derivatives (**5—8**), methyl ethers (**9—16**), and acetates (**17—20**).

Experimental

The mass spectra were obtained with a Kratos MS-30 mass spectrometer (the energy of ionizing electrons was 200 eV, the temperature of the ion source was 150 °C). The constant pressure of the reagent gas (0.2 Torr) was maintained by an external manometer installed at the inlet system. Tetramethylsilane (Merck) was of 99.7 % purity. The samples were supplied through a direct inlet system (**1—8**, **17—20**) or a Carlo Erba Fractovap 4200 chromatograph equipped with a jet separator and a 2.5 m column (5 % SE-30 on Chromosorb W) at 100 °C; He was used as the carrier gas. The data on the preparation and purity of the compounds studied (**1—20**) were given previously.[2]

Results and Discussion

The interaction of *cis*- and *trans*-1,2- and -1,4-cyclohexanediols (**1—4**) with tetramethylsilane plasma results in $[M+SiMe_3]^+$ adducts, which dissociate to form $[M+SiMe_3-H_2O]^+$, $[M-OH]^+$, and $[M-OH-H_2O]^+$ fragments (Table 1). The $[M+SiMe_3]^+$ ions of the *cis*-isomers are more stable than those of the corresponding *trans*-isomers. An analogous effect has been observed in the protolytic reactions and it is caused by chelation effects. The difference in stabilities of the $[M+SiMe_3]^+$ ions of stereoisomeric 1,4-cyclohexanediols (**3** and **4**) is higher than that of 1,2-derivatives (**1** and **2**).

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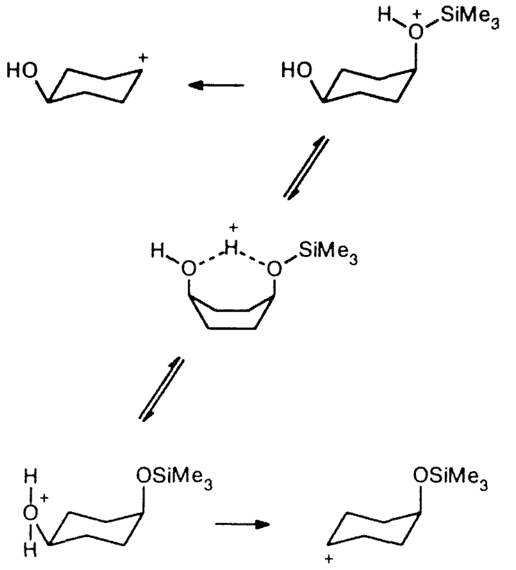
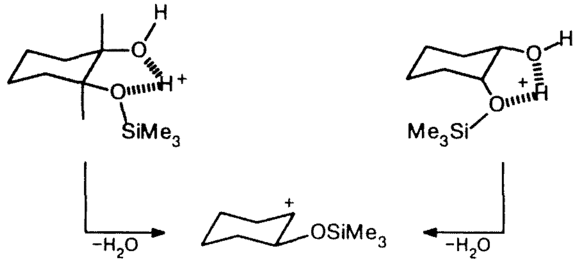
Table 1. Relative intensities of peaks in CI mass spectra of *cis*- and *trans*-1,2- and -1,4-cyclohexanediols **1—4** and their OD-derivatives **5—8**

Ion	*m/z*	I_{rel} (%) for			
		1,2-cyclohexanediols		1,4-cyclohexanediols	
		cis-(**1**)	*trans*-(**2**)	*cis*-(**3**)	*trans*-(**4**)
$[M+91]^+$	207	6.2	5.0	—	—
$[M+73]^+$	189	100	65.0	79.0	23.4
$[M+73-H_2O]^+$	171	96.0	100	19.9	13.8
$[M-OH]^+$	99	30.0	18.0	27.0	60.0
$[M-OH-H_2O]^+$	81	33.0	46.0	100	100
$Me_3SiOH_2^+$	91	62.2	33.0	64.0	26.6
		I_{rel} (%) for OD-derivatives			
		5	**6**	**7**	**8**
$[M+73]^+$	190	100	56.0	50.0	13.0
	191	75.0	28.0	75.0	16.0
$[M+73-D_2O(HDO)]^+$	171	116.0	100.0	19.0	14.0
$[M+73-H_2O(HDO)]^+$	172	35.0	30.0	9.5	11.0
$C_6H_{11}O^+$	99	21.0	18.0	16.0	42.0
$C_6H_{10}DO^+$	100	46.0	27.0	29.0	48.0
C_6H_9	81	30.0	46.0	100	100
C_6H_8D	82	5.0	7.0	20.0	30.0

Scheme 2



Scheme 3



That the chelation in the $[M+SiMe_3]^+$ ions is possible is manifested not only in their stability, but also in the degree of dehydration of these ions (Scheme 2).

The use of OD-derivatives of cyclohexanediols (**5**—**8**) (see Table 1) is evidence that both of the hydrogen atoms of the hydroxyl groups are involved in the elimination of a water molecule.

It was revealed that for *cis*- and *trans*-1,2-cyclohexanediols (**1** and **2**) this reaction proceeds very intensively (peaks of $[M+SiMe_3-H_2O]^+$ are of maximum abundance, see Table 1), which is direct evidence of formation of chelates in both *cis*-1,2- and *trans*-1,2-isomers (Scheme 3).

In the case of *cis*- and *trans*-1,4-cyclohexanediols, the stabilities of their $[M+SiMe_3]^+$ ions are significantly lower than those of the corresponding 1,2-isomers, which along with lesser intensities of the $[M+SiMe_3-H_2O]^+$ ions (19.9 and 13.8 %, respectively, see Table 1) indicates a decrease in the ability to form chelates of the former. The stability of the $[M+SiMe_3]^+$ ion of *trans*-1,4-cyclohexanediol, which is incapable of intramolecular chelation, is the lowest among the compounds studied. It should be noted that in the case of the 1,4-isomers, not only the hydrogen atoms of the hydroxyl group, but hydrogen atom of the cyclohexane ring also contribute significantly to the formation of the water molecule that is eliminated (see Table 1). Apparently, the reactions of intermolecular exchange can make a definite contribution to the generation of the ions at *m/z* 172.

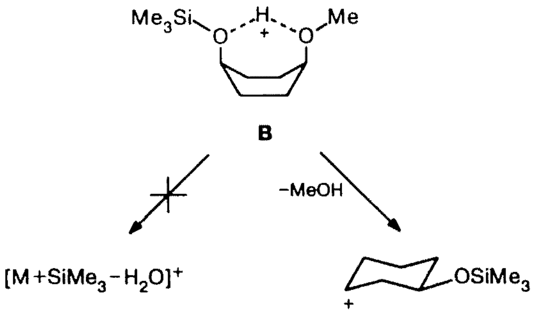
Heterolysis with the elimination of the OH-group is characteristic of 1,4-cyclohexanediols. The $[M-HO]^+$ ions thus formed eliminate the H_2O molecule affording $[M-OH-H_2O]^+$ ions, *m/z* 81, whose peaks are the most abundant in the spectra.

In the mass spectra of cyclohexanediols, peaks of the $[Me_3SiOH_2]^+$ ions, *m/z* 91, are also present; they are more intense for the *cis*-isomers, as in the case of cyclopentanediols.[3,4]

In going to the stereoisomeric pairs of 2- and 4-methoxycyclohexanols (**9**—**12**), the stability of ions of adducts is somewhat lower; however, as is true for cyclohexanediols, these ions are more stable for *cis*-isomers, and the greater difference in stability is typical for 1,4-isomers (analogously to that observed for cyclohexanediols).

Elimination of water from the $[M+SiMe_3]^+$ ions is suppressed; however, elimination of methanol is observed, the latter apparently being caused by the formation of chelate of the **B** type (Scheme 4).

Scheme 4



As can be expected, this process is the most intense in *cis*- and *trans*-2-methoxycyclohexanols **9** and **10** (Table 2). Localization of the $SiMe_3^+$ ion at the methoxyl group can be accompanied by the generation of $Me_3SiO^+(H)Me$ ions (*m/z* 105) characteristic of methyl ethers.[5]

Processes of elimination of neutral molecules of Me_3SiOH and, to a lesser extent, of Me_3SiOMe, are the dominating fragmentation pathways for the $[M+SiMe_3]^+$ adducts for methoxycyclohexanols, which is in accord with the assumption[6] on the preferable elimination of the less basic molecules.

As in the case of cyclohexanediols, the generation of the $[M-OH-MeOH]^+$ ions (*m/z* 81) is the most characteristic of 4-methoxycyclohexanol (peak at *m/z* 81 is the most prominent in the spectra of **11** and **12**, see Table 2).

For the $[M+SiMe_3]^+$ adducts for *cis*- and *trans*-1,2--and -1,4-dimethoxycyclohexanes, only heterolysis affording $[M-OMe]^+$, $[M-OMe-MeOH]^+$, and $Me_3SiO(H)Me$ ions is characteristic (Table 3). The $[M+SiMe_3]^+$ ions of *cis*-isomers (**13** and **15**) are somewhat more stable than the corresponding *trans*-analogs (**14** and **16**), and the greater difference is observed for *cis*- and *trans*-1,4-dimethoxycyclohexanes.

Previously,[7] we did not detect the ability of the Me_3Si^+ ion to form intermolecular chelates with any functional groups. Therefore, the most likely explanation of higher stability of *cis*-isomers **13** and **15** is the higher rate of fragmentation of the $[M+SiMe_3]^+$ ions of *trans*-isomers due to the possibility of the intramolecular nucleophilic assistance of the methoxy group in the dissociation of the carbon—oxygen bond (Scheme 5).

Table 2. Relative intensities of peaks in CI mass spectra of *cis*- and *trans*-2-methoxy- and -4-methoxycyclohexanols **9**—**12**

Ion	*m/z*	I_{rel} (%) for			
		2-methoxycyclohexanols		4-methoxycyclohexanols	
		cis-(**9**)	*trans*-(**10**)	*cis*-(**11**)	*trans*-(**12**)
$[M+73]^+$	203	80.0	25.4	14.0	1.0
$[M+73-MeOH]^+$	171	33.0	40.0	3.0	—
$[M-OH]^+$	113	100	100	22.9	80.5
$[M-OH-MeOH]^+$	81	24.0	74.0	100	100
$Me_3SiO^+(H)Me$	105	—	23.8	18.7	34.0

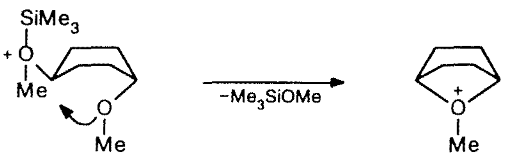
Table 3. Relative intensities of peaks in CI mass spectra of 1,2- and 1,4-dimethoxycyclohexanes **13**—**16**

Ion	*m/z*	I_{rel} (%) for			
		1,2-dimethoxycyclohexanes		1,4-dimethoxycyclohexanes	
		cis-(**13**)	*trans*-(**14**)	*cis*-(**15**)	*trans*-(**16**)
$[M+73]^+$	217	8.0	3.0	5.6	<1.0
$[M-OMe]^+$	113	100	100	37.8	80.0
$[M-OMe-MeOH]^+$	81	30.0	35.0	100	100
$Me_3SiO^+(H)Me$	105	—	—	60.0	30.0

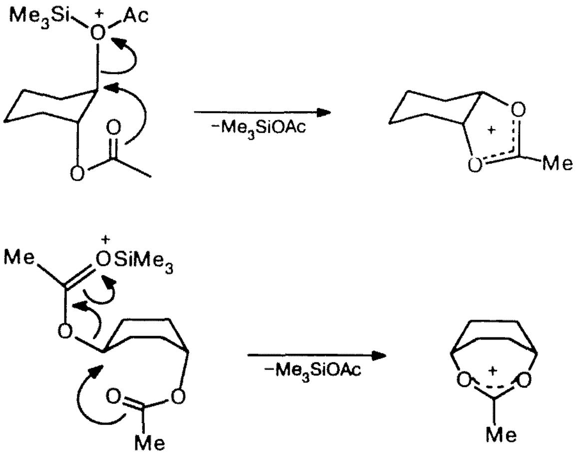
Table 4. Relative intensities of peaks in CI mass spectra of 1,2- and 1,4-diacetoxycyclohexanes **17—20**

Ion	m/z	I_{rel} (%) for			
		1,2-diacetoxycyclohexanes		1,4-diacetoxycyclohexanes	
		cis-(**17**)	*trans*-(**18**)	*cis*-(**19**)	*trans*-(**20**)
$[M+73]^+$	273	100	15.0	100	19.5
$[M-OAc]^+$	141	27.0	100	38.0	100
$[M-OAc-AcOH]^+$	81	11.0	10.0	11.0	12.0
$[M+73-AcOH]^+$	213	—	—	10.0	5.0

Scheme 5



Scheme 6



The insignificant contribution of the assistance of the methoxyl group in 1,2-*trans*-isomer (**14**) is apparently due to the high-energy transition state of the reaction in the formation of a three-membered ring. It seems unlikely that the higher stability of ions of adducts to the *cis*-dimethoxycyclohexanes results from the chelation, although the Me_3Si^+ ion is capable of interacting with two nucleophilic centers[8] and this explanation cannot be totally rejected.

The behavior of cyclohexanediol acetates confirms the first assumption. In the reaction with Me_3Si^+, they give adducts $[M+SiMe_3]^+$ (ions of relatively high abundance), and *cis*-isomers **17** and **19** give more stable ions than *trans*-isomers **18** and **20**. As expected, the effect of assistance of the acetates is greater than in the case of the methyl ethers.

The major fragmentation pathway of the $[M+SiMe_3]^+$ adduct is the generation of the $[M-OAc]^+$ ions (m/z 141). The $[M-OAc-AcOH]^+$ and $[M+SiMe_3-AcOH]^+$ ions are also formed to a small extent and are observed only for the 1,4-isomers.

It is of note, first of all, that differences in stabilities of *cis*- and *trans*-1,2-diacetoxycyclohexanes (**17** and **18**) are practically the same as for 1,4-isomers (**19** and **20**) and achieve a large value (Table 4). This apparently indicates that the higher stability of the *cis*-isomers is associated not with their involvement in chelation, but rather with the higher reactivity of *trans*-isomers, the fragmentation of which is favored by the anchimeric effect (Scheme 6) analogous to that observed for a series of esters[9] and *O*-acetyl derivatives of dianhydrohexopyranoses.[10]

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