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# MECHANISM OF THE ELIMINATION REACTIONS IN $\alpha, \delta$ DIOLS AND THEIR HALOGENATED DERIVATIVES UNDER ELECTRON-IMPACT

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Abstract—Mass spectrometric investigations of  $\alpha$ , $\delta$  diols and their halogenated derivatives revealed the necessity of postulating a mechanism for both their elimination of water and of haloid acid. This mechanism proceeding via a transition state of larger ring-size than described for similar mono-functional aliphatic compounds was confirmed by deuterium labelling.

IN A PREVIOUS paper<sup>1</sup> we reported the mass spectrometric investigation of two hexitol derivatives, 1,3,4,6-tetrabromo-hexane-2,5-diol and 1,3,5,6-tetrabromo-hexane-2,4-diol. Interpretation of their spectra revealed that the mechanism for the loss of water from monofunctional aliphatic alcohols<sup>2</sup> could not be applied to their fragmentation. Similarly the elimination of haloid acid must also have a mechanism differing from that described for monofunctional alkyl halides.<sup>3</sup>

Several other hexanediol derivatives were synthesized to ascertain whether these differences are due to the bulky bromine atoms or if they generally occur in all diols having the hydroxyl groups in appropriate position.

The present paper reports the fragmentation pattern of hexane-2,5-diol and its derivatives in relation with these processes.

### RESULTS

The following compounds were investigated:\*

		R <sub>1</sub> CH	I2-CH-	CHR <sub>3</sub> -C	HR <sub>3</sub> CH-	$-CH_2R_1$		
			OR <sub>2</sub>			I		
	<b>(I)</b>	(Ia)	(II)	(IIa)	(III)	(IIIa)	(IV)	(IVa)
R <sub>1</sub>	Br	Br	Br	Br	Cl	Cl	н	н
$R_2$	н	D	н	D	H	D	Н	D
R3	Br	Br	Cl	Cl	Cl	Cl	Н	Н

Mass spectra (see Figs 1 to 10)

# DISCUSSION

# Elimination of water

As shown by the spectra obtained the loss of water and the consecutive processes play a very important role in the fragmentation of hexane-2,5-diol and its derivatives.

The rearrangement leading to the loss of water in monofunctional aliphatic alcohols is thought to occur preferably through a six-membered ring transition state, followed in many cases by the heterolytic fission of the bond in  $\beta$  position to the cation site formed.<sup>2</sup> Though the corresponding hydrogen in hexane-2,5-diols is activated, no abundant ions can be found having been formed via the above mechanism.

\* Compounds which do not fit this general formula are discussed separately in the text.









FIG. 3. Mass spectrum of 1,6-dibromo-3,4-dichloro-hexane-2,5-diol (11)







FIG. 5. Mass spectrum of 1,3,4,6-tetrachloro-hexane-2,5-diol (III).







FIG. 7. Mass spectrum of hexane-2,5-diol (IV) at 70 eV.













The principal processes shown by the spectra can only be interpreted if the hydrogen taking part in this rearrangement is assumed to come from the hydroxyl group and accordingly the elimination of water has to take place through a seven-membered ring transition state in this type of compound. Deuterium labelling showed that the rearranged hydrogen has belonged exclusively to the hydroxyl group.

Ions formed by the loss of water from the investigated diols have the same characteristics because of their common structure including a separated radical and cation site.<sup>4</sup> Fragmentation of the compounds investigated is governed mainly by the radical site.

The processes related to the elimination of water are represented in Scheme 1.

The extremely high abundance of the  $[M - H_2O - Br]$  ion in the spectra of I and Ia led to the supposition that its structure should be rather c2 than c1 or d, but in the spectra of II and IIa there was no difference between the intensities of ions c and d and thus the cyclization could not be proved. The high abundance may first be rationalized by the lesser tendency to lose hydrogen bromide (see below) and secondly by the more preferential loss of the secondary bromine atom.<sup>5</sup> The almost equal abundance of the ions c and d in the spectra of II and IIa may be interpreted on the assumption that the secondary position of chlorine equalizes the greater inclination of bromine to split off as an atom.

In the spectra of IV and IVa the abundance of ions e and f, respectively, shows a reversal when changing the electron-energy from 70 eV to 20 eV. The phenomenon of the preferential loss of large vs. small alkyl chains in an  $\alpha$ -fission to a suitable functional group at high and low electron-energies, respectively, has been described<sup>6</sup> and commented upon<sup>7</sup> earlier. Although ion a formed from compound IV and IVa is similar to the molecular-ion of aliphatic ketones, the arguments used for explaining this behaviour<sup>6b</sup> could not be applied in the present case.

Firstly there is no significant further fragmentation which could be assigned to ion e (loss of the small alkyl group), whilst on the other hand ion f being an odd-electron ion, exhibits two main pathways for decomposition yielding ions g and i. The process takes place remote from the cation site; accordingly a primary charge-stabilization effect does not seem to play any role.

Only the one of the two reactions which leads to ion e yields a radical and an evenelectron ion. Cleavage on the side of the large alkyl chain results in no radical but a neutral molecule and an odd-electron ion. Accordingly the stability of the radicals themselves does not seem to be definitive. Consequently it may be assumed that in this case the radical site would be of deciding importance in governing the loss of small and large alkyl groups, respectively.

The abundances of the ions depicted in Scheme 1 are listed for compounds Ia, IIa, IIIa, IVa and V in Table 1.

Compound V was prepared to examine whether the ions depicted in Scheme 1 do or do not contain deuterium in the case of this compound.

$$\begin{array}{c} CH_3 - CD - CH_2 - CH_2 - CD - CH_3 \\ | & | \\ OH & OH \end{array}$$
(V)

As shown in Table 1 the deuterium content of ions e to i (Scheme 1) corresponds to their structure in the spectra of V.



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Ions			(a)			3	()			(c)				(q)					( <i>e</i> )	
spunoduc	m/e	$d_0$	$d_1$	$d_2$	m/e	$d_0$	$d_1$	$d_2$	m e	$d_0$	$d_1$	$d_2$	n e	$d_{0}$	$d_1$	$d_2$	m e	$d_0$	$q_1$	$d_2$
(Ia)	412				411		1	1	333	21.5	1	1		$R_1 = R_3$			319	2.5	1	
(IIa)	324	+			323	+		ł	245	2.67	l	i	683	2,9	l		231	3.1	0·7 <sup>b</sup>	1
(IIIa)	236	د.			235	+	i		201	0-95	1	1		$\mathbf{R_1}=\mathbf{R_3}$			187	5-46	1.85 <sup>b</sup>	
(IVa)	100	0.4	0.18	ł	66	0-49	l			$\mathbf{R_1} = \mathbf{H}$				$\mathbf{R_1} = \mathbf{R_3}$			85	17·3	ļ	1
Ś	100	I	0-29	0.34	66	1	0-34	1		$\mathbf{R_1} = \mathbf{H}$				$\mathbf{R_1} = \mathbf{R_3}$			85			17·2
Ions		0	Ų			C	()			<i>(y)</i>				<i>(i)</i>						
spunoduu	m e	$d_0$	$d_1$	$d_2$	m e	$d_0$	$d_1$	$d_2$	m e	$d_{0}$	$d_1$	$d_2$ 1	n e	$d_0$	$d_1$	$d_2$				
(Ia)	290	+	l	1	289	+	[	i	211	27·2	1	1	197	4.	l	1				
(IIa)	202	3.63			201	1	l	1	167	10-6	1	1	601	1.8	l	l				
(IIIa)	158	1.03	ļ		157	ļ			123	8·18	1	1	601	2·34	l	I				
(IVa)	56	26.9			55	2-77		1		$R_3 = H$			41	9.49	I	l				
Ś	56		28-7	ł	55		3-16			$R_3 = H$			41		6.03	1				
<sup>a</sup> Abundanc	tes are e:	xpresse	ed in ∑	% valu	es and	the int	ensities	of the	various	halogen	isotol	be bea	lks for	the same i	on are	sum	marize	d; ver	y small	inten-
ties are mark <sup>b</sup> These ion.	ed with s can be	a plus; consid	; <i>m/e</i> v. dered tc	alues a arise v	re giver via the	n for th dehydr	ie unlat atation	celled c	- M]	ruds I, II ·CH <sub>2</sub> R <sub>1</sub> ]	, III a + ion.	vl br (The	, resp(	ectively. dances are	correc	ted f	or <sup>13</sup> C (	contrik	oution.)	

Table 1<sup>a</sup>. Abundances of the ions from Scheme 1 in the spectra of the labelled compounds (Ia, IIa, IIIa and IVa)



FIG. 11. Mass spectrum of  $2,5-d_2$ -hexane-2,5-diol (V) at 70 eV.

It must be emphasized that the spectra of all  $\alpha, \delta$  diols found<sup>8</sup> exhibit the 'mechanism' described above for the loss of water; accordingly these reactions can be considered of general validity for these spectra.

# Elimination of haloid acid

The importance of the loss of haloid acid and the consecutive processes in compounds I to IIIa depends on the nature of the halogen atoms involved. As chlorine is more preferentially lost as haloid acid than bromine,<sup>5,9</sup> the processes described here are more important in the spectra of compounds II to IIIa containing chlorine.



FIG. 12. Mass spectrum of V at 20 eV

The loss of haloid acid from monofunctional alkyl halides is ascribed to proceed preferentially via a 1,3 elimination, i.e. through a five-membered ring transition state.<sup>3,9</sup> Although in compounds I to IIIa all hydrogens in appropriate positions are activated due to their tertiary nature, no abundant ions are found having been formed via this type of rearrangement.

The investigation of the deuterium labelled compounds Ia, IIa and IIIa indicated that the hydrogen taking part in this rearrangement belonged exclusively to one of the hydroxyl groups. If a 1,3 elimination mechanism would operate in this case, the halogen, expelled as hydrogen halide could be  $R_1$  as well as  $R_2$  but the spectra of II and IIa show unambiguously that only  $R_3$  takes part in this process.

Of the two  $R_3$  substituents in a  $\beta$  and  $\gamma$  position to one of the hydroxyl groups, respectively, the one in  $\beta$  position cannot be considered to be involved in the elimination reaction because of the lack of any abundant peaks corresponding to ions formed via the same sequence of reactions in the spectra of the isomeric 1,3,5,6-tetrahalo-hexane-2,4-diols.\*

The postulation that the elimination of haloid acid has to pass over a six-membered ring transition state in the case of these compounds, offers a coherent 'reaction mechanism' depicted in Scheme 2.

The considerable abundance of ion m in the spectra of I to IIIa, may be explained by the stabilizing effect of the presumably enolized keto group on the positive charge. The high abundance of ion s in the spectra of II to IIIa can be explained by the stability of the allylic structure formed. The abundance of ions j to s being formed after the loss of haloid acid, is collected in Table 2.

To ascertain whether the processes described above are of general validity for compounds containing hydroxyl and halogen functions in the appropriate position, compound VI was investigated.

$$HO--CH_2--CHBr--CHBr--CH_2-OH$$
(VI)

It can be seen that the fragmentation pattern of compound VI follows the rules outlined in this section. Accordingly the six-membered ring transition state can be postulated for the loss of haloid acid in compounds containing an hydroxyl group and a halogen in the  $\alpha, \gamma$  position.

#### EXPERIMENTAL

Mass spectra were obtained on a Varian MAT SM-1 mass spectrometer with the exception of the spectrum of compound I (see Ref. 1).

The operating conditions were: resolution 1500; electron energies 70 eV to 20 eV; accelerating voltage 8 kV; source temperatures 150°C (for compounds II, IIa, IV and IVa) and 250°C (for compounds Ia, III, IIIa, V and VI).

The following evaporation temperatures were used: compound Ia 55°C; II 30°C; IIa 60°C; III 50°C; III a 60°C; IV IVa and V *ca.* 5°C; VI 20°C.

1,3,4,6-Tetrabromo-1,3,4,6-tetradeoxy-allitol (I) was prepared according to the literature.<sup>10</sup>

1,6-Dibromo-3,4-dichloro-1,3,4,6-tetradeoxyallitol (II). A solution of 2,3:4,5-dianhydro-1,6-dibromo-1,6-dideoxy-galactitol<sup>10</sup> (2·7 g) in acetone (30 ml) was treated with concentrated hydro-chloric acid (5 ml) for 3 hrs at room temperature and then evaporated to 5 ml. The slurry was filtered and washed with water to yield a mixture of compound II and 1,6-dibromo-2,4-dichloro-1,2,4,6-tetradeoxy-D,L-mannitol (3·34 g, 97%, m.p. 117 to 119°C). This mixture was dissolved in ethyl

\* Gy. Horváth and J. Kuszmann, unpublished results.



$d_2$				this
$d_1$	0-47 4-9 1-92			ited by
$\begin{pmatrix} n \\ d_0 \end{pmatrix}$	0-44 1-93 0-74			illustra
m/e	228 184 140			tent is
$d_2$		$d_2$		n con
d <sub>1</sub>	0-07 8-16 8-75	$d_1$	2:45 11:4 27:8	uteriur
(m) d <sub>0</sub>	0-91 2-71 1-96	$d_0^{(S)}$	2:45 4:79 7:42	heir de
m/e	257 213 169	m/e	135 91 91	refore t
$d_2$		$d_2$		e; the
$d_1$	0.14	$d_1$	2·0 8·2 7·75	xchang
d <sub>0</sub> (f)	$\begin{array}{l} R_1=R_3\\ +\\ R_1=R_3 \end{array}$	$d_0^{(r)}$	2.0 2:49 2:82	deuterium e
m e	271	m/e	149 149 105	direct
$d_2$		$d_2$		to the
) d1	0-62 + 14	$d_1$		owing
d <sub>0</sub> (k	0. + + +	$q_{0}^{(b)}$	27·2 10·6 8·18	lly pure
m/e	271 227 183	m/e	211 167 123	. 1. otopica
+6 d2	3-9 4-6 1-89	$d_2$		s Table not is
$H_2R_1$	4·1 2·22 0·76	$d_1^{e}$		nner as IIa are
$d_0$		(0) q0	0·36 + 0·31	me ma a and I
[] m/e	337 249 205	m e	227 183 139	n the sa Is Ia, II
Ions Compounds	(Ia) (IIa) (IIIa)	Ions Compounds	(Ia) (IIa) (IIIa)	<sup>a</sup> Prepared ii <sup>b</sup> Compound

Table 2<sup>8</sup>. Abundances of the ions from Scheme 2 in the spectra of the labelled compounds (Ia, IIa and IIIa)

column. <sup>c</sup> See column  $d_0$  of ion n.



FIG. 13. Mass spectrum of 2,3-dibromo-butane-1,4-diol (VI).

acetate and was fractionated on a column of silicic acid (1000 g, carbon tetrachloride) with carbon tetrachloride-ethyl acetate 3:1 as solvent. Recrystallization of the residues of the combined and evaporated fractions from ether-light petroleum (b.p. 80°C) gave the pure allitol derivative II (0.65 g, 18.8%), m.p. 87 to 89°C,  $R_f$  0.55 (carbon tetrachloride-ethyl acetate 3:1), (Found: C, 20.79; H, 3.05; Br, 46.21; Cl, 20.63.  $C_6H_{10}O_2Br_2Cl_2$  requires C, 20.89; H, 2.92; Br, 46.35; Cl, 20.56%).

*Hexane-2,5-diol* (IV). Acetonylacetone (3.4 g) was treated in methanol (50 ml) with a solution of KBH<sub>4</sub><sup>11</sup> (5 g) in water (50 ml) at 0°C. After keeping the mixture overnight at room temperature it was stirred with Varian KS (H<sup>+</sup>) ion exchanger (120 ml) for 30 mins. The resine was filtered off, washed with methanol (50 ml) and the filtrate was evaporated. The residue was reevaporated three times with methanol and then distilled, b.p.<sub>25</sub> 132 to 134°C (3.0 g, 85%). Lit. 12 b.p.<sub>1</sub> 85 to 87°C.

Compounds Ia, IIa, IIIa and IVa were prepared by evaporation of the  $D_2O$  solution of the corresponding diols twice after having been heated for 30 mins in the steam bath.

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