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The solvent-free thermal dehydration of tetritols on zeolites☆

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Dedicated to Professor Zygfryd Smiatacz on the occasion of his 70th birthday

Abstract

A new alditol dehydration method at high temperatures, in the presence of molecular sieves without solvent in an argon atmosphere, is described. Investigations on tetritols have been carried out. Products arising after the intramolecular and intermolecular elimination of water, with retention or inversion of the configuration of asymmetric carbon atoms, were observed. Complete analytical separation of reaction products was achieved by means of GLC. The chemical structures of the compounds obtained were assigned using co-injection with standards, GLC–CIMS and GLC–EIMS analyses. Two intermolecular dehydration products of tetritols were isolated by HPLC and identified by ^{1}H and ^{13}C NMR spectroscopy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Alditols; D,L-Threitol; Erythritol; Thermal dehydration; Zeolites; Molecular sieves

1. Introduction

Several alditol dehydration methods are described in the literature. Most of them require treatment with strongly acidic aqueous solutions (sulfuric acid [1–3], hydrochloric acid [4,5], hydrogen fluoride with a catalytic amount of formic or acetic acid [6]), or ion-exchange resins [3,7]. Yields of products obtained depend on the reaction conditions and reactant structure. For example, erythritol in the presence of Amberlite 200 [7] gave only 1,4-anhydroerythritol, but in 50% aqueous sulfuric acid [2] 1,4-anhydroerythritol and 2,5-di-(1,2-dihydroxyethyl)-1,4-dioxan were obtained as a result of intra- and intermolecular elimination of water, respectively. Reaction of pentitols with concentrated hydrochloric acid in a sealed ampoule [4] afforded cyclic products with retained or inverted configuration at C-2 or C-4, as well as chlorodeoxy and dichlorodideoxy derivatives of pentitols and anhydropentitols. Heating of hexitols in 3 M sulfuric acid [3], hydrochloric acid [5] or in the presence of Amberlite IR-120 [3] gave mixtures of dianhydro- and 1,4-, 1,5- and 2,5-monoanhydrohexitols.

The newest anhydrohexitol syntheses involve treatment of alditols with anhydrous pyridinium chloride [8] or hydrogen on metallic catalyst [9].

☆ Part 1 in the series: Thermal dehydration of polyhydroxy alcohols.

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In this report, we describe a solvent-free thermal dehydration of tetritols in an argon atmosphere in the presence of a zeolite catalyst. Use of pure heterogeneous catalysts, such as clays and zeolites, in organic synthesis has received considerable attention in the past few years [10–12], mainly due to the minimum production of pollutant materials. This type of catalysis offers the possibility of performing efficient chemical transformations avoiding toxic reagents, large amounts of solvents and expensive purification steps. Zeolites, among others, are used as catalysts in dehydration reactions. During dehydration of monohydroxy alcohols on zeolites [13], alkenes and ethers are obtained, as a result of intra- and intermolecular elimination of water, respectively. Dehydration of diols [14] on zeolites afforded different kinds of products, depending on the structure of the reactant. Thus, 1,2-diols gave carbonyl compounds, unsaturated alcohols and dienes as a result of the pinacol rearrangement and 1,2-elimination reaction, respectively. 1,3-Diols gave carbonyl compounds, unsaturated alcohols, dienes and products of 1,3-diol fragmentation. The main reaction for 1,4- and 1,5-diols is dehydration–cyclization (cyclodehydration) leading to tetrahydrofuran and tetrahydropyran derivatives.

2. Results and discussion

Thermal dehydration of erythritol and D,L-threitol in the presence of zeolite LTA (1:1 molar ratio, SiO_2–Al_2O_3), in an argon atmosphere, in the temperature range 260–290 °C, gave complex mixtures of four groups of compounds. The products, after exhaustive O-acetylation, were analytically separated using capillary gas chromatography (GLC). Yields and retention times of per-O-acetylated products are listed in Table 1.

The products in groups A and B (Table 1) were identified by co-injection with standards, mass spectroscopy with chemical (GLC–CIMS) and electron (GLC–EIMS) ionization, in groups C,C′ and D,D′ by GLC–CIMS and GLC–EIMS analyses. None of the products in group D (D′) and only two of those in group C, with GLC retention times of 15.97 min (**5**) and 16.37 min (**7**), respectively, were isolated as their peracetates using HPLC and identified by GLC–CIMS analysis (Table 1), ^{1}H and ^{13}C NMR spectroscopy (Tables 2 and 3).

The HMBC (heteronuclear multibond correlation) spectra for compounds **5** and **7** indicate that they consist of two heterocyclic five-membered rings bonded via an oxygen bridge (ring X-O-ring Y). Theoretically, there are ten possible configurational isomers (Table 4). The simplicity of the NMR spectra for compound **7** (Tables 2 and 3) suggests that the molecule contains a symmetry element (C_2-axis or plane if free and sufficient speed of rotation around the bridged C–O bonds occurs). Thus, both five-membered rings of compound **7** must be identical. The value of vicinal coupling constant $J_{2,3}$ 5.1 Hz (Table 3) indicates a cis (erythro) [15,16] configuration of the vicinal H-2,H-3 system. These data correspond to structures **h** or **j** (pair of enantiomers) or **k** (meso form) (Table 4). The molecule of compound **5** is not symmetrical. Vicinal coupling constants $J_{2,3}$ 4.9 Hz (ring X) and $J_{2,3}$ 0.0 Hz (ring Y) (Table 3) indicate a cis (erythro) configuration of the vicinal H-2,H-3 system in one ring (X) and trans (threo) in the other ring (Y). These data suggest one of the four structures **d**, **e**, **f** or **g** (two pairs of enantiomers, Table 4).

In order to monitor the course of the process, we decided to control the concentration of products as a function of time and temperature of the transformation. The qualitative and quantitative results obtained in the transformation of erythritol and D,L-threitol are presented in Table 5.

The results obtained show that, during thermal dehydration in the presence of zeolites, tetritols undergo three types of reaction: inter- and intramolecular dehydration, and isomerization (inversion of configuration of C-2 or C-3) irrespective of the reaction conditions (temperature and reaction time).

The solvent-free thermal dehydration reaction of tetritols caused mainly intramolecular dehydration–cyclization leading to 1,4-anhydrotetritols with retention of configuration.

Dehydration reaction between two tetritol molecules led to two groups of compounds, formed with elimination of two or three water molecules (Tables 1 and 5, group D, D′ and C, C′, respectively), depending on the reaction conditions: temperature and reaction time. Concentrations of products in group D were higher at lower reaction temperatures (Table 5). Increasing the reaction temperature and prolonging the reaction time decreased the concentration of products in group D and simultaneously increased concentrations of products in group C (Table 5). These facts and GLC–CIMS analysis (Table 1) confirmed the transformation of some compounds in group D into compounds in group C by elim-

Table 1
GLC retention times and relative percentages of particular components of the product mixtures after thermal dehydration of tetritols on zeolites LTA at 290 °C for 4 h

Reactant	Per-*O*-acetyl derivative of	GLC peak [a]/group of isomers		Molecular weight [b]	GLC retention time (min)	Relative percentage [c]
Erythritol	1,4-anhydro-D,L-threitol	1	A	188	5.13	4.1
	1,4-anhydroerythritol	2			5.62	55.4
	erythritol	3	B	290	12.15	17.6
	D,L-threitol	4			13.05	traces
	products of intermolecular dehydration with the elimination of three water molecules	5	C	274	15.97	2.7
		6			16.01	2.4
		7			16.37	1.2
		8			16.66	2.8
		9			16.88	1.6
		10			17.23	2.0
		11			17.40	2.6
	products of intermolecular dehydration with the elimination of two water molecules	12	D	376	21.91	traces
		13			22.36	1.9
		14			22.97	1.0
		15			23.10	1.1
		16			23.59	0.7
		17			23.76	1.6
		18			24.33	1.0
D,L-Threitol	1,4-anhydro-D,L-threitol	1	A	188	5.13	84.3
	1,4-anhydroerythritol	2			5.62	2.6
	erythritol	3	B	290	12.15	traces
	D,L-threitol	4			13.05	3.0
	products of intermolecular dehydration with the elimination of three water molecules	19	C′	274	15.35	2.5
		20			15.60	1.9
		5			15.97	1.8
		6			16.01	1.5
	products of intermolecular dehydration with the elimination of two water molecules	21	D′	376	23.97	2.4

[a] GLC peak and the corresponding compound have the same number.
[b] Determined by GLC–CIMS analysis.
[c] Calculated from GLC peak areas.

Table 2
^1H and ^{13}C chemical shifts (δ, ppm) of per-O-acetylated compounds **5** and **7** (in $CDCl_3$)

Compd		Appropriate hydrogen and carbon atoms									
		H-1	H-1′	H-2	H-3	H-4	H-4′	C-1	C-2	C-3	C-4
5	ring X	3.68	[a]	4.45	5.28	3.89	[a]	70.0	77.7	71.6	71.2
	ring Y	3.63	[a]	[a]	5.03	[a]	3.84	72.5	83.8	77.8	71.5
7		3.72	3.98	4.19	5.25	3.89	4.04	70.1	77.6	71.9	70.9

[a] 3.97–4.1ppm — multiplet containing signals of H-1′, H-4′ (ring X) and H-1′, H-2, H-4 (ring Y) protons.

Table 3
Coupling constants (J, Hz) of per-O-acetylated compounds **5** and **7**

Compd		Coupling constants						
		$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{2,3}$	$J_{3,4}$	$J_{3,4'}$	$J_{4,4'}$
5	ring X	8.8	7.6	7.1	4.9	5.1	2.9	10.5
	ring Y	10.0	1.9	[a]	0.0	3.9	0.0	10.7
7		9.0	6.1	6.3	5.1	5.4	3.9	10.9

[a] 3.97–4.1ppm — multiplet containing signals of H-1′, H-4′ (ring X) and H-1′, H-2, H-4 (ring Y) protons.

ination of the next water molecule. Identical EIMS spectra for compounds **5**–**8** in group C (Table 1) [characteristic fragmentation ions: *m*/*z* 69 (100%), *m*/*z* 129 (50%)] indicate that they are configurational isomers. The NMR spectra for compounds **5** and **7** showed that they consist of two heterocyclic five-membered rings bonded via an oxygen bridge and that configuration of all asymmetric carbon atoms (**7**, Tables 2 and 3) is retained or changed for one asymmetric carbon atom (**5**, Tables 2 and 3). Structures of all ring X-O-ring Y type products in groups C and C′ are presented in Tables 4 and 6. These products were formed in higher concentrations than others (Table 1). The other compounds in group C formed in lower yields (**9**–**11**, Table 1) could be 1,4-dioxane derivatives, because isomers (with the same dioxane ring) of the compound obtained by Haines and Wells [2] could undergo intramolecular dehydration in our reaction conditions. Molecular masses of the compounds studied were determined by CIMS, and the EIMS spectrum for compound **11**, with the greatest concentration in group C [characteristic fragmentation ions: *m*/*z* 69 (30%), *m*/*z* 154 (10%), *m*/*z* 189 (25%)], could confirm their 1,4-dioxane structure.

Survey of the studied reactions at different temperatures showed quite evidently that D,L-threitol undergoes intramolecular cyclization much more easily than erythritol [17]. Thus, concentrations of the intermolecular dehydration products obtained from D,L-threitol are lower than those from erythritol.

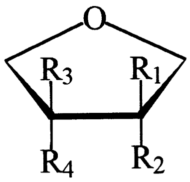
1,4-Anhydrotetritol, heated under the same conditions as tetritols, did not undergo intermolecular dehydration and only unchanged substrate was detected. These results suggest that the formation of **5** and **7** was possible only via intermolecular dehydration of tetritols in the first step of the reaction.

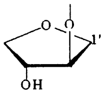
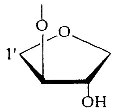
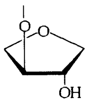
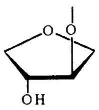
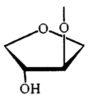
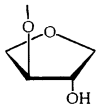
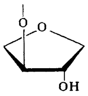
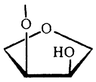
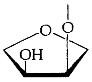
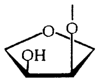
Tetritol isomerization and subsequent cyclodehydration afforded diastereoisomeric tetritols and the appropriate 1,4-anhydrotetritols.

Based on these results, we propose in Scheme 1 a pathway for the solvent-free thermal dehydration of tetritols in the presence of zeolites LTA (drawn for erythritol as an example).

Intramolecular dehydration–cyclization of tetritols on zeolites probably proceeds via an S_N2 mechanism, similar to acid-catalysed (sulfuric acid [3], hydrochloric acid [17]) alditol dehydration. Both isomerization and intermolecular dehydration of tetritols could be

Table 4
Structures and IUPAC names [a] of all theoretically possible configurational isomers having two heterocyclic five-membered rings bonded via an oxygen bridge



Structure	R_1	R_2	R_3	R_4	IUPAC name
a	OH	H	H		bis(1,4-anhydro-D-threitol) 2(*R*):2′(*R*) anhydride
b	H		OH	H	bis(1,4-anhydro-L-threitol) 2(*S*):2′(*S*) anhydride
c	OH	H	H		1,4-anhydro-D-threitol 1,4-anhydro-L-threitol 2(*R*):2′(*S*) anhydride
d	H		H	OH	1,4-anhydroerythritol 1,4-anhydro-D-threitol 2(*S*):2′(*R*) anhydride
e	H	OH	H		1,4-anhydroerythritol 1,4-anhydro-D-threitol 2(*R*):2′(*R*) anhydride
f	H		H	OH	1,4-anhydroerythritol 1,4-anhydro-L-threitol 2(*S*):2′(*S*) anhydride
g	H	OH	H		1,4-anhydroerythritol 1,4-anhydro-L-threitol 2(*R*):2′(*S*) anhydride
h	H		H	OH	bis(1,4-anhydroerythritol) 2(S):2′(*S*) anhydride
j	H	OH	H		bis(1,4-anhydroerythritol) 2(*R*):2′(*R*) anhydride
k	H		H	OH	bis(1,4-anhydroerythritol) 2(*R*):2′(*S*) anhydride

[a] *Pure Appl. Chem.*, 68 (1996) 1919–2008.

explained by the formation of carbocations as intermediates in the reaction. Formation of such carbocations in the presence of zeolites at high temperature is well known [14,18–20]. A detailed mechanism of the solvent-free thermal dehydration of tetritols in the presence of

Table 5
Relative percentages[a] of particular components of the product mixtures resulting after thermal dehydration of tetritols on LTA-type zeolites at various temperatures and reaction times

Reactant	Temperature (°C)	Time (h)	Products					
			1,4-AT[b]	1,4-AE[c]	Erythritol	D,L-Threitol	Products in group C (C′)	Products in group D (D′)
Erythritol	260	4	traces	7.2	84.9	traces	–	7.1
	270	2	–	8.5	90.9	traces	–	traces
		4	traces	23.5	62.0	1.9	traces	11.0
	280	2	traces	21.1	75.0	1.6	–	2.3
		4	3.4	41.3	21.0	traces	8.0	26.3
	290	1	traces	12.0	80.6	1.1	traces	6.1
		2	traces	13.3	62.2	1.4	traces	23.1
		3	2.6	38.8	21.7	1.8	9.6	25.5
		4	4.1	55.4	17.6	traces	14.5	7.7
		6	6.2	67.6	5.1	–	21.1	traces
D,L-Threitol	260	2	4.5	–	–	93.6	–	1.9
	270	2	11.5	traces	traces	82.1	traces	6.4
	280	2	52.4	traces	traces	40.3	2.3	5.0
		4	79.6	1.2	traces	6.2	2.6	10.4
	290	2	53.5	traces	traces	38.3	3.5	4.7
		4	84.3	2.6	traces	3.0	7.7	2.4

[a] Calculated from GLC peak areas.
[b] 1,4-AT = 1,4-anhydro-D,L-threitol.
[c] 1,4-AE = 1,4-anhydroerythritol.

Table 6
The identified and anticipated tetritol dehydration products with two five-membered rings bonded via an oxygen bridge.

Intermolecular dehydration between two molecules of	Products of tetritol intermolecular dehydration and next cyclodehydration			
	With retention of configuration		With inversion of configuration of one asymmetric carbon atom	
	GLC peak[a]	Structure[b]	GLC peak[a]	Structure[b]
Erythritol	7, 8	**h**, **j**, **k**	5, 6	**d**, **e**, **f**, **g**
D-Threitol	19	**a**	5, 6	**d**, **e**
L-Threitol	19	**b**	5, 6	**f**, **g**
D,L-Threitol	19, 20	**a**, **b**, **c**	5, 6	**d**, **e**, **f**, **g**

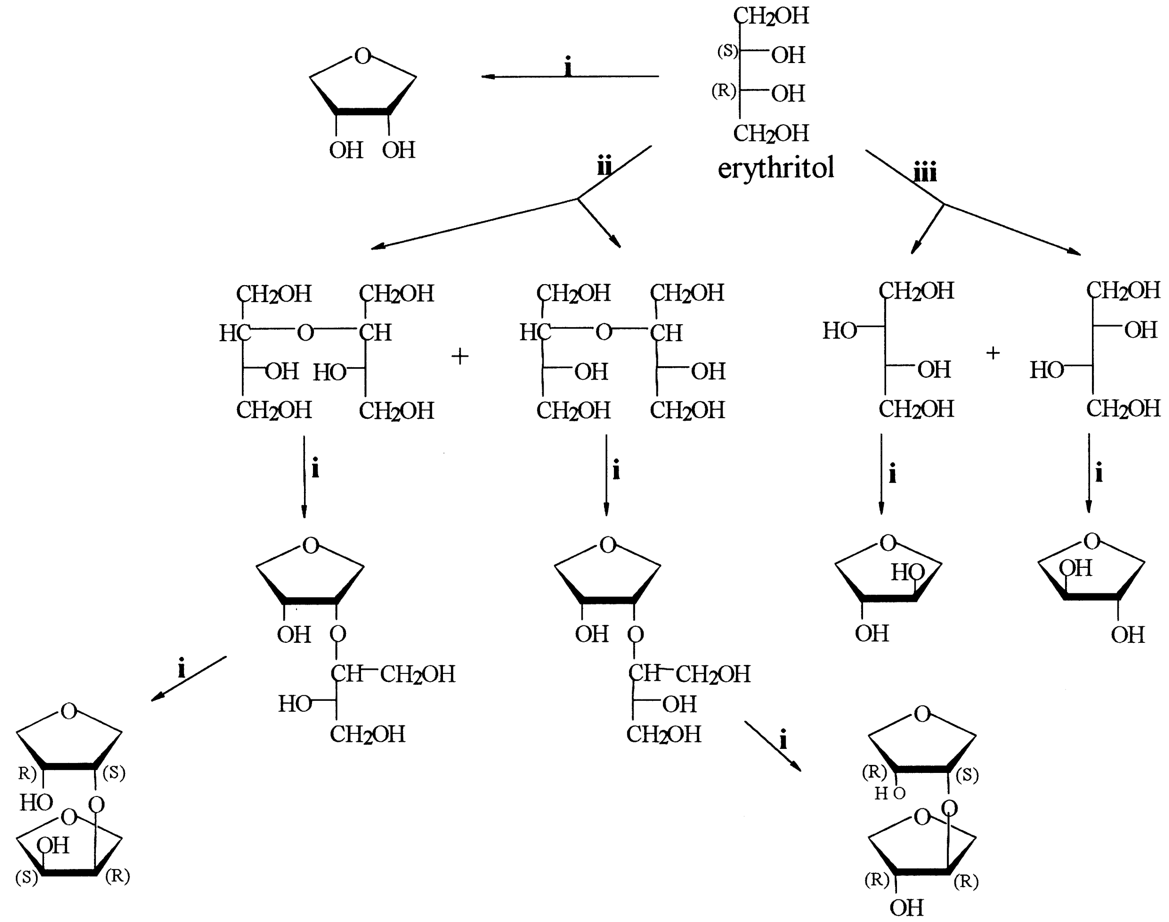
[a] GLC peak numbers are taken from Table 1.
[b] Structure notations are taken from Table 4.

zeolites is being studied and will be discussed later.

3. Experimental

General methods.—Commercial erythritol (Aldrich Chemical), D,L-threitol (Sigma Chemical) and 3 Å molecular sieves (Polish Chemical, Gliwice) were used. All reactions were conducted under normal pressure of dry argon. Wood's alloy as a heating bath was used, and the temperature of the bath was measured. Molecular sieves (3 Å) were desiccated before use at 250 °C for 5 h. Evaporation was performed under reduced pressure.

All reactions were monitored by thin-layer chromatography (TLC) on Kieselgel 60 F254 Silica Gel plates (E. Merck, 0.20 mm thickness). The spots were detected by spraying with 5% ethanolic H_2SO_4 and charring. Column chromatography was carried out with Kieselgel 60 Silica Gel (E. Merck, smaller than 200 mesh). GLC separation of per-O-acetylated derivatives of all compounds was carried out with a VEGA 6180 (Carlo Erba) gas chromatograph equipped with a DB 23 fused silica capillary column (60 m × 0.258 mm I.D.) and flame ionization detector (FID). Hydrogen was used as a carrier gas. The running conditions were: initial temperature 140 °C, increase 4 °C/min to 160 °C, 6 °C/min to 200 °C, 8 °C/min to 240 °C, final hold 10 min, detector temperature 260 °C. GLC–MS analyses were carried out using a Finnigan MAT 95 mass spectrometer linked to a VARIAN 3400 gas chromatograph equipped with a DB 23 fused silica capillary column (60 m × 0.258 mm I.D.) and helium as a carrier gas. The temperature of the ion source in EI was 250 °C, in CI it was 200 °C. An electron beam of 70 eV was used for EI and isobutane was used for CI. The scan from m/z 0 to m/z 500 took 1 s. HPLC analytical analyses of per-O-acetylated compounds were performed using a VISTA 5500 (VARIAN) HPLC chromatograph equipped with a Kromasil C8 column (5 μm; 4.6 × 250 mm; Eka-Nobel, Sweden). Solvent system: 11:39 MeCN–water and 0.1% TFA with constant flow rates of 1 mL/min. Detection of products was carried out with a UV detector at λ 220 nm.



Scheme 1. Proposed pathways for the dehydration products obtained from erythritol: (i) intramolecular dehydration (1,4-cyclization); (ii) intermolecular dehydration; (iii) isomerization; *one of the three possible structures (**h**, **j**, **k**, Table 4); **one of the four possible structures (**d**, **e**, **f**, **g**, Table 4).

Semi-preparative HPLC separations were performed using a VISTA 5500 (VARIAN) HPLC chromatograph equipped with a Kromasil C8 column (5 μm; 16 × 250 mm; Eka-Nobel, Sweden). Solvent system: 3:22 MeCN–water and 0.1% TFA with constant flow-rates of 7 mL/min. The products were detected using a UV detector at λ 226 nm. The ^{1}H, ^{13}C, HSQC (heteronuclear singlequantum correlation) and HMBC (heteronuclear multibond correlation) spectra for per-O-acetylated compounds were recorded in $CDCl_3$ using a VARIAN Unity Plus 500 spectrometer. Chemical shifts were measured relative to residual solvent signal at 7.27 and 77.0 ppm for ^{1}H and ^{13}C, respectively. HSQC [21] and HMBC [22] spectra were performed with pulsed-field gradient. The HSQC spectrum was acquired in phase-sensitive mode with broadbond ^{1}H decoupling in spectral windows of 3043 and 12,570 Hz for ^{1}H and ^{13}C, respectively. Data were collected in a 1024 × 150 matrix and processed in a 2K × 1K matrix. The HMBC spectrum was acquired in absolute value mode in the spectral windows 3043 and 9679 Hz for ^{1}H and ^{13}C, respectively. Data were collected in a 1536 × 128 matrix and processed in a 2K × 1K matrix. All ^{13}C NMR signals were assigned through C–H correlated spectra.

Dehydration of D,L-*threitol.*—D,L-Threitol (1 g) and 3 Å molecular sieves (0.4 g) were placed in a quartz apparatus, which was purged with argon for 30 min. The reaction mixtures were then heated in an argon atmosphere, over a temperature range of 260–290 °C. After cooling to room temperature (rt), the crude post-reaction mixtures were dissolved in hot MeOH, and TLC analyses were made in a solvent mixture of 3:2:1 Et_2O–$CHCl_3$–MeOH. A small portion of each product was concentrated under a nitrogen stream to a thick syrup and exhaustively O-acetylated with Ac_2O in the presence of catalytic amounts of anhyd NaOAc over 1 h at 100 °C, after which the per-O-acetylated products were analysed by GLC and GLC–MS. Preparative separation of the crude post-reaction mixture (0.75 g), obtained after dehydration of D,L-threitol (1 g) at 290 °C for 4 h, in an argon atmosphere in the presence of molecular sieves (0.4 g), was performed on a silica gel column with 3:2:1 EtOAc–$CHCl_3$–MeOH as an eluent. Oily 1,4-anhydro-D,L-threitol (0.35 g, 46%) was obtained, R_f 0.46 in the solvent system 3:2:1 Et_2O–$CHCl_3$–MeOH. Products of intermolecular dehydration of D,L-threitol were not isolated.

Dehydration of erythritol.—Erythritol (1 g) was dehydrated, with 3 Å molecular sieves (0.4 g), in an argon atmosphere, and analysed by GLC and GLC–MS, as described above. Preparative separation of the crude post-reaction mixture (0.58 g), obtained after dehydration of erythritol (1 g) at 290 °C for 6 h in an argon atmosphere, in the presence of molecular sieves (0.4 g), was performed on a silica gel column with 5:3:2 Me_2CO–EtOAc–$CHCl_3$ as eluent. The fraction containing the largest amounts of intermolecular dehydration products was exhaustively O-acetylated with Ac_2O in pyridine for 24 h at rt and then separated by high-performance liquid chromatography. Per-O-acetylated compounds **5** and **7** were obtained as syrups in very low yields, R_f 0.51 in the solvent system 3:2:1 Et_2O–$CHCl_3$–MeOH, GLC retention times 15.97 and 16.37 min, respectively. NMR data are given in Tables 2 and 3.

Dehydration of D-*threitol.*—D-Threitol (0.24 g) was dehydrated in the presence of 3 Å molecular sieves (0.1 g) and then analysed by GLC as described for D,L-threitol. Intermolecular dehydration products (**19**, **20**, Table 6) were distinguished and identified.

Dehydration of 1,4-anhydro-D,L-*threitol.*—1,4-Anhydro-D,L-threitol (0.3 g) was dehydrated and analysed by GLC under the same conditions as described above. No reaction was observed and no intermolecular dehydration product was detected.

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