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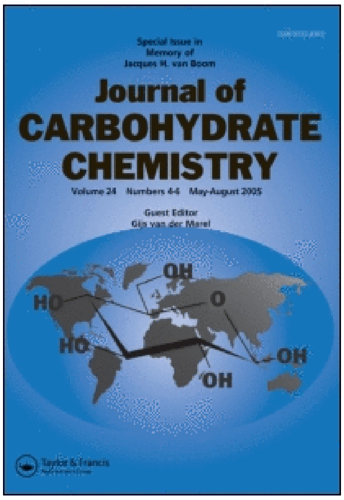

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Solvent-Free Thermal Dehydration of Pentitols on Zeolites[#]

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CONTENTS

[#] Dedicated to Professor Gérard Descotes on the occasion of the jubilee of his scientific career.

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ABSTRACT

Dehydration of D-arabinitol, ribitol, and xylitol at high temperature in the presence of molecular sieves without solvent in an argon atmosphere is described. Products arising after the dehydration–cyclization (cyclodehydration) reaction with retention or inversion of the configuration of asymmetric carbon atoms, were observed. Complete analytical separations of exhaustively O-acetylated reaction products were achieved by means of GC. The chemical structures of the compounds obtained were assigned using co-injection with standards.

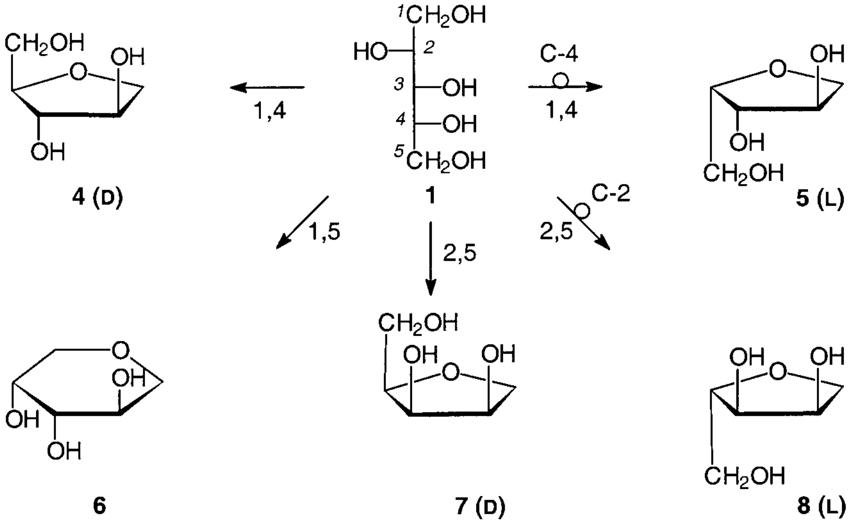
Key Words: D-Arabinitol; Ribitol; Xylitol; Dehydration–cyclization.

INTRODUCTION

Alditols undergo dehydration under different conditions. Most of them require treatment with strong acidic aqueous solutions (sulfuric acid,[1–3] and hydrochloric acid[4,5]) or hydrogen fluoride with a catalytic amount of formic or acetic acid,[6] or ion-exchange resins.[3,7] We previously described the solvent-free thermal dehydration of tetritols[8] and hexitols[9] in an argon atmosphere in the presence of a zeolite catalyst. We now report the behaviour of pentitols under the same conditions.

RESULTS AND DISCUSSION

Heating of pentitols in an argon atmosphere in the presence of 3 Å zeolites led to a mixture of monoanhydropentitols. The major compounds formed by dehydration of D-arabinitol (1) are presented in Sch. 1.



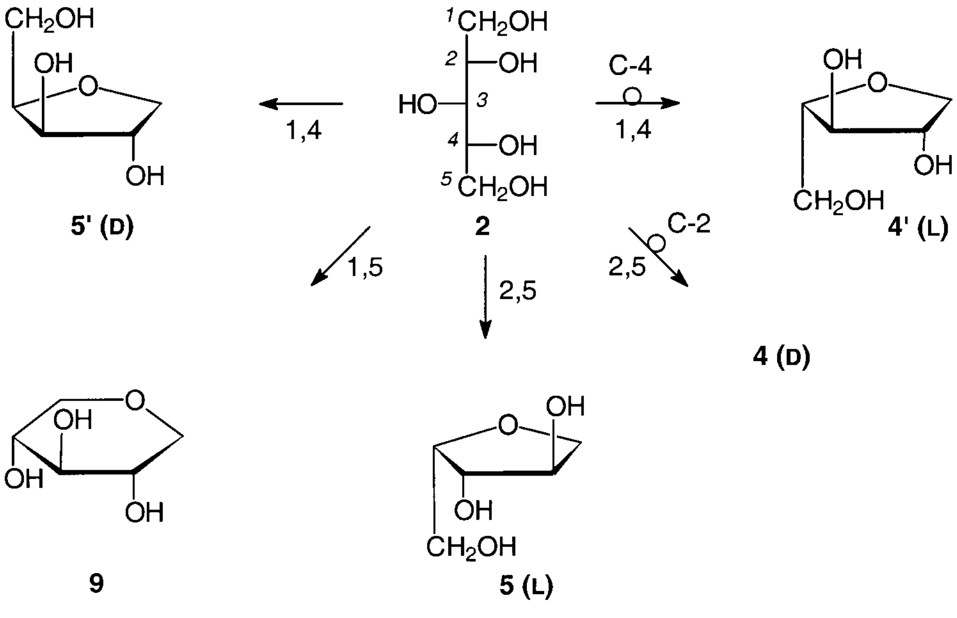
Scheme 1. Monoanhydropentitols formed by dehydration of D-arabinitol (**1**).

The 1,4- and 2,5-cyclizations of xylitol (**2**) and ribitol (**3**) led to pairs of enantiomers (racemic mixtures), because of substrates symmetry (Schs. 2 and 3).

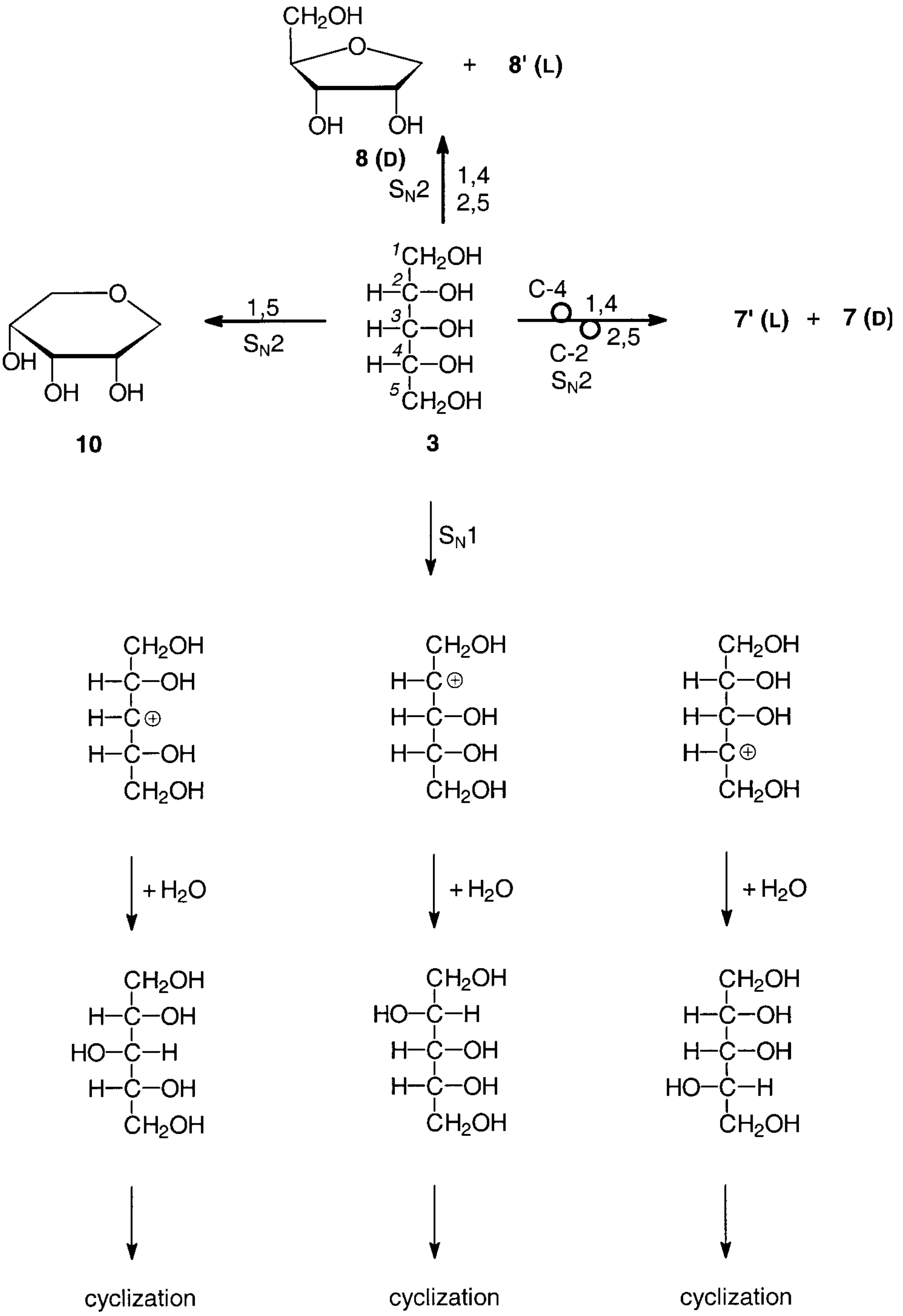
TLC and GC analyses of the mixtures obtained after dehydration of pentitols in the presence of 3 Å zeolites, as well as in the presence of mineral acids,[10,11] indicate that only monoanhydropentitols were formed due to an intramolecular dehydration. There were no traces of dianhydropentitols or products obtained by intermolecular dehydration. The monoanhydropentitols obtained were mostly five-membered ring products with retention of configuration of carbon atoms. Five-membered ring products with inverted configuration at C-2 or C-4 were formed in yields from traces to 14.9 % (see Table 2).

The dehydration reaction of D-arabinitol (**1**), xylitol (**2**), and ribitol (**3**) in the conditions studied also provides anhydro-products with inverted configuration of C-3, but five-membered and particularly six-membered cyclic products were formed in low yield. Three 1,5-anhydropentitols (**6**, **9**, **10**) and four 1,4-anhydropentitols (**4**, **5**, **7**, **8**) were formed and could be separated by GC. Six of them were identified as per-O-acetylated derivatives by co-injection with authentic samples. The per-O-acetylated derivative of **7** (or of its enantiomer **7′**, both give a single peak) was identified based on its mass spectrum (GC-MS).

Hudson and Barker[10] concluded from their results on the dehydration of pentitols in the presence of mineral acids that ribitol undergoes dehydration fastest, and D-arabinitol (≡D-lyxitol) is the least reactive. Our investigations suggested an alternative sequence of reactivity: Ribitol > D-Arabinitol > Xylitol which is in accordance with Baddiley's results.[12] Ribitol heated for 2 hr at 290°C in an argon atmosphere underwent dehydration without catalyst yielding mostly 1,4-anhydro-D,L-ribitol isolated in 45% yield as pure crystals. D-Arabinitol treated in the same conditions as ribitol but in the presence of 3 Å



Scheme 2. Major products formed by dehydration of xylitol (**2**, symbol prime refers to enantiomer).



Scheme 3. Simultaneous S_N1 and S_N2 mechanisms proposed for ribitol dehydration.

zeolites underwent dehydration in 95% yield. Xylitol underwent dehydration only in 42% in the same conditions as D-arabinitol. Longer reaction time 4 hr at 290°C improve the dehydration rate to 60% but further elongation of reaction time cased visible progression of decomposition. Additional amounts of zeolites strongly increased this process (Table 1).

Two major products of D-arabinitol dehydration, i.e., 1,4-anhydro-D-arabinitol (**4**) and 1,4-anhydro-L-xylitol (**5**) could not be separated by GC due to identical retention times and were identified by the Bock et al. procedure[3] (chemical shifts of carbon atoms were identical with those given in the literature[13]).

The composition of the mixtures after dehydration of the pentitols in the presence of 3 Å zeolites suggested that these reactions follow simultaneously S_N1 and S_N2 mechanisms as shown in Sch. 3 (for ribitol as an example).

Protonation of the primary hydroxyl groups at C-1 or C-5 in the ribitol molecule and intramolecular substitution by the hydroxyl groups at C-4 or C-2 give 1,4-anhydro-D,L-ribitol as the main product. Substitution of the protonated secondary hydroxyl group at C-2 or C-4 by an appropriate hydroxymethyl group yields 2,5-anhydro-D,L-arabinitol (**7** and **7′**). 1,5-Anhydroribitol (**10**) is formed as a result of the substitution of a protonated primary hydroxyl group by the other primary hydroxyl group of the molecule. The total concentration of the 1,4-anhydropentitols and the relative concentration of 1,4-anhydro-D,L-ribitol to 2,5-anhydro-D,L-arabinitol (5 : 1), strongly confirm that substitution at the primary carbon atom (with retention of configuration) by S_N2 mechanism is preferred. The presence of arabinitol (inversion of C-2 or C-4) and xylitol (inversion of C-3) and their dehydration products in the post-reaction mixture indicate the formation of secondary carbocations. These cations undergo intramolecular substitution faster than intermolecular substitution or elimination what can explain the lack of intermolecular dehydration products[8] or enols in the reaction mixture. The formation of some of the dehydration products of D-arabinitol or xylitol (Table 2) can be explained in the same manner. 1,4-Anhydropentitols obtained under the conditions used do not undergo further dehydration, also

Table 1. Composition of exhaustively O-acetylated mixture formed by dehydration of xylitol for 2 hr at 290°C with various amounts of 3 Å zeolites (xylitol : zeolites, w/w).

	Concentration (%) of products[a]	
Compound	(1 : 0.4)	(1 : 1)
9a[b]	3.2	5.6
6a	Trace	1.1
4a	13.7	35.0
5a	22.7	54.2
8a	Trace	Trace
7a	Trace	Trace
3a	—	Trace
1a	—	Trace
2a	58.0	3.2

[a] Concentrations were calculated from GC peak areas.

[b] Letter “a” refers to per-O-acetylated derivatives.

Table 2. GC Retention times and relative percentages[a] of compounds **1a–10a** in the exhaustively O-acetylated mixture after heating of pentitols in the presence of 3 Å zeolites at different temperature and times.

		D-Arabinitol			Xylitol				Ribitol				
Compound	Retention time (min)	280°C, 2 hr	290°C, 2 hr	Compound	290°C, 2 hr	290°C, 3 hr	290°C, 4 hr	Compound	260°C, 2 hr	270°C, 2 hr	280°C, 2 hr	290°C, 1 hr	290°C, 2 hr
9a	11.17	Trace	Trace	**9a**	3.2	2.6	3.7	**9a**	—	—	—	—	—
6a	11.75	5.0	7.2	**6a**	Trace	Trace	Trace	**6a**	Trace	Trace	0.9	0.9	1.0
4a	11.87	41.7	44.4	**4a + 4′a**	13.7	12.7	14.9	**4a + 4′a**	Trace	Trace	2.4	1.9	2.9
10a	12.09	Trace	Trace	**10a**	—	—	—	**10a**	1.7	3.8	7.0	6.5	7.0
5a	12.31	10.0	12.6	**5a + 5′a**	22.7	34.2	39.9	**5a + 5′a**	Trace	Trace	1.2	1.1	1.9
8a	12.95	10.4	11.4	**8a**	Trace	Trace	Trace	**8a + 8′a**	21.6	40.6	68.4	64.2	73.3
7a	13.41	16.4	18.1	**7a**	Trace	Trace	Trace	**7a + 7′a**	3.5	6.8	12.8	12.8	13.9
2a	16.38	Trace	Trace	**2a**	—	—	—	**2a**	72.6	47.9	6.9	11.6	Trace
1a	16.58	12.4	5.7	**1a**	—	—	Trace	**1a + 1′a**	0.6	0.9	0.5	0.9	Trace
3a	17.81	Trace	Trace	**3a**	58.0	49.0	40.5	**3a**	Trace	Trace	Trace	Trace	Trace

[a] Concentrations were calculated from GC peak areas.

heating of 1,4-anhydro-D,L-ribitol (**8** and **8′**) and 2,5-anhydro-D,L-arabinitol (**7** and **7′**) for 8 hr at 290°C left the unchanged substrates. Increasing of the zeolites amounts in relation to those of the alditol used accelerate the process of dehydration in all our experiments.

EXPERIMENTAL

General Methods

^1H and ^{13}C NMR spectra were recorded at 25°C with a Varian Mercury spectrometer at 400 and 100 MHz, respectively, with Me_4Si as internal standard. Assignments were based on homonuclear decoupling experiments, and homo- and heteronuclear correlation. Optical rotations were measured with a JASCO J-20 polarimeter. Elemental analyses were made with Carlo Erba apparatus. Commercial D-arabinitol, ribitol and xylitol (Aldrich Chemical Co.) and molecular sieves type 3 Å (Polish Chemical Co., Gliwice) were used. All reactions were conducted under normal pressure of dry argon. Wood's alloy as a heating medium was used. Molecular sieves type 3 Å before use were desiccated at 250°C for 5 hr. Evaporation was performed under reduced pressure. All reactions were monitored by thin-layer chromatography (TLC) on Kieselgel 60 F_{254} 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). GC separation of per-O-acetylated derivatives of all compounds was carried out by a VEGA 6180 (Carlo Erba) Gas Chromatograph equipped with 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.

The standard compounds 1,4-anhydro-D-arabinitol,[10] 1,4-anhydro-D,L-xylitol,[14] 1,4-anhydro-D-ribitol,[15] 1,5-anhydroxylitol,[16] 1,5-anhydro-D-arabinitol[17] and 1,5-anhydroribitol[18] were conventionally acetylated by using acetic anhydride–sodium acetate prior to GC.

General Procedure for Dehydration Reaction

Pentitol and 3 Å molecular sieves were placed in a quartz apparatus, which was purged with argon for 30 min. Then the reaction mixture was heated in an argon atmosphere at various temperature for various time. After cooling to room temperature 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 mixture was concentrated to a thick syrup under a nitrogen stream and exhaustively O-acetylated with Ac_2O in the presence of catalytic amounts of anhydrous NaOAc over 1 hr at 100°C, after which the per-O-acetylated products were analysed by GC.

Dehydration of D-Arabinitol

D-Arabinitol (**1**, 0.5 g) and 3 Å molecular sieves (0.5 g) were placed in a quartz apparatus. Then the reaction mixture was heated at 280°C or 290°C for 2 hr.

Dehydration of Xylitol

Xylitol (**2**, 0.6 g) and 3 Å molecular sieves (0.6 g) were placed in a quartz apparatus. Then the reaction mixture was heated at 290°C for 2, 3, or 4 hr.

Dehydration of Ribitol

Ribitol (**3**, 0.6 g) and 3 Å molecular sieves (0.6 g) were placed in a quartz apparatus. Then the reaction mixture was heated at 260°C, 270°C, or 280°C for 2 hr and at 290°C for 1 or 4 hr.

1,4-Anhydro-D,L-ribitol (8). Ribitol (**3**, 0.38 g) was placed in a quartz apparatus, which was purged with argon for 30 min. Then the reaction mixture was heated in an argon atmosphere at 290°C for 2 hr. After cooling to room temperature the crude post-reaction mixtures was dissolved in hot isopropyl alcohol. The solution was cooled and the precipitate was filtered to give 1,4-anhydro-D,L-ribitol (0.15 g, 45% yield) [m.p. 74–75°C, $[\alpha]_D$ 0° (*c* 0.97, H_2O); ^1H NMR (D_2O): δ 3.66 (1H, dd, $J_{1,2}$ 5.2 Hz, $J_{1,1'}$ 10.3 Hz, H-1), δ 3.81 (dd, 1H, $J_{5,5'}$ 10.4 Hz, $J_{4,5}$ 2.6 Hz, H-5), δ 3.82 (dd, 1H, $J_{1',2}$ 2.8 Hz, H-1′), δ 3.88 (m, 1H, $J_{2,3}$ 7.2 Hz, H-2), δ 4.08 (dd, 1H, $J_{4,5'}$ 4.2 Hz, H-5′), δ 4.11 (dd, 1H, $J_{3,4}$ 5.0 Hz, H-3), δ 4.30 (m, 1H, H-4); ^{13}C NMR (D_2O): δ 62.46 (C-5), δ 72.11 (C-2), δ 73.69 (C-3), δ 73.28 (C-1), δ 82.65 (C-4)].

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