CGC, MS and Theoretical Studies on the Transformation Mechanism of 3,4-Di-*O*-acetyl-1,5-anhydro-2-deoxy-D-*threo*-pent-1-enitol in Aqueous Solutions

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Heating 3,4-di-*O*-acetyl-1,5-anhydro-2-deoxy-D-*threo*-pent-1-enitol (per-*O*-acetyl-D-xylal) in water leads to a mixture of unsaturated compounds with cyclic, as well as open-chain structures. The mixture obtained was analysed by CGC and CGC–MS methods. The experimental findings were employed to model the mechanism of the transformation studied. In addition, the AM1 calculations were carried out in order to describe the elementary processes suggested. Full geometry optimizations performed for species found in the mixture made it possible to evaluate the thermodynamic characteristics of particular reactions. Next, the calculations for transition states afforded appropriate kinetic barriers. All computations were carried out for the gaseous phase as well as in aqueous solution. Both experimental and theoretical results are in good accordance with the mechanism proposed.

The 1,2-unsaturated derivatives of aldoses (glycals) are well known and can take part in a variety of selective addition reactions.[1-3] The *O*-acetyl derivatives of glycals undergo an intramolecular rearrangement giving 2,3-unsaturated products (pseudoglycals) with cyclic and open-chain structures. The rearrangement reaction has been studied by many chemists,[4-8] but the detailed mechanism is still unknown and some discrepancies await explanation.

It is worth mentioning that open-chain pseudoglycals are more reactive than cyclic ones. The condensation of 2-deoxy-D-pentose with purines and pyrimidines *via* open chain pseudoglycals has been the subject of great interest to many researchers, not only because of the importance of this group of compounds in biological phenomena, but also because of the challenging synthetic problems encountered.[9-11]

The present study was directed towards the CGC–MS analysis of the mixture obtained in the heated aqueous solution of per-*O*-acetyl-D-xylal† as well as the theoretical description of the transformation mechanism. For the latter purpose, *i.e.* the estimation of the thermodynamic and activation barriers of the elementary reactions, we employed the AM1 method including solvation effects (COSMO methodology).

Experimental

Reaction of Per-O-acetyl-D-xylal in Water.—Per-*O*-acetyl-D-xylal (0.5 mg) and water (0.5 cm^3) were heated at 310 or 373 K in reacti-vials for 5, 10 and 30 min, respectively. A portion (10 μl) of each reaction mixture was concentrated to dryness under nitrogen. The residue was conventionally *O*-acetylated with acetic anhydride–sodium acetate at 373 K for 1 h or *O*-trimethylsilylated with bis(trimethylsilyl)trifluoroacetamide (BSTFA)–pyridine at 373 K for 15 min.

Reaction of Per-O-acetyl-D-xylal in Aqueous Solution at Various pH *Values.*—Mixtures of per-*O*-acetyl-D-xylal (0.5 mg) and deionized water (pH ≈ 7) (0.5 cm^3) or aqueous acetic acid (pH ≈ 3.0 and ≈ 3.2) or aqueous sodium acetate solution (pH ≈ 7.9 and ≈ 8.2) were heated at 373 K in screw-capped glass vials for 30 min and after cooling, excess $NaBH_4$ (*ca.* 5 mg) was added and the mixtures were left for 2 h at room temperature. A portion (10 μl) of each mixture was concentrated to dryness under nitrogen and prepared for CGC analysis.

(E)-1,4,5-*Tri*-O-*acetyl*-2,3-*dideoxypent*-2-*enitol* (*Preparative Scale*).—A mixture of per-*O*-acetyl-D-xylal (1.5 g) and aqueous acetic acid (30 cm^3) (pH 3.0) was refluxed in a 100 cm^3 flask for 30 min and after cooling $NaBH_4$ (0.5 g) was added. After 2 h the excess of $NaBH_4$ was decomposed with acetic acid and the mixture purified by ion exchange chromatography (IR-120, IRA-400). It was next concentrated to dryness and the residue was conventionally acetylated with acetic anhydride–sodium acetate. The *O*-acetylated product was isolated by distillation at 454–458 K under reduced pressure (thick syrup, yield 49%). The CGC analysis of the distilled produced proved its 99% purity.

Diagnostic Microreactions.[12]—*Addition of bromine.* The sample (5 mg) was dissolved in chloroform (0.2 cm^3) and bromine (30 mm^3) was added, then after 3 h conditioning at room temperature the volatile components were removed under a nitrogen stream.

Selective reduction with $NaBH_4$ *in water.* The sample (5 mg) was dissolved in water (0.5 cm^3) and $NaBH_4$ (5 mg) was added. After 2 h conditioning at room temperature, acetic acid (10 μl) was added and the mixture then concentrated to dryness under a nitrogen stream. Next, 0.5 cm^3 of methanol was added and the sample was again concentrated to dryness.

Exhaustive reduction with Pd–H_2. The sample (5 mg) was dissolved in absolute ethanol (2 cm^3) and catalyst (10 mg; 5% Pd/C) was added. The mixture was reduced for 10 h with hydrogen, at room temperature. The catalyst was then removed and the residue concentrated to dryness under a nitrogen stream.

The components of each mixture, after exhaustive *O*-acetylation, were subjected to GLC using a Vega 6180 instrument equipped with a DB 23 fused silica column (60 m × 0.258 mm i.d.).

Mass spectra (EI-70 eV and CI-ammonia) were obtained with an HP 5890 mass spectrometer interfaced to a GC equipped with a glass capillary column coated with Carbowax 20M (25 m × 0.2 mm i.d.).

HPLC chromatograms were obtained with an HP 1090 instrument equipped with Nucleosil ODS column (10 cm × 4.6 mm i.d.) and UV detector (230 nm).

† Xylal = 1,2-dideoxy-*threo*-pent-1-enopyranose.

Table 1 Relative yields of the compounds after the rearrangement reaction of per-*O*-acetyl-D-xylal in an aqueous solution (pH 7) at 373 K

Per-*O*-acetyl derivative	Retention *t*/min	GC peak area (%)		
		5 min	10 min	30 min
5	5.5	3	9	15
4	9.5	3	5	—
3	9.7	80	60	3
α-6[a]	11.2	4	9	13
β-6[a]	12.1	6	11	14
8	15.7	4	6	55

[a] α or β relates to the anomeric form of the compound.

Calculations.—The AM1[13] calculations for per-*O*-acetyl-D-xylal and products of its transformation in water at 373 K were carried out using MOPAC93[14] and MOPAC6[15] packages. The choice of AM1 from among the four methods included in the packages was motivated by several reasons, such as accuracy in predicting molecular and some thermodynamic characteristics,[15,16] as well as widely tested methodology.[17]

The molecular mechanics force field incorporated into the SPARTAN v. 3.0 program package[18] was used for conformational analysis.

Unconstrained geometry optimizations of the molecules studied were performed using the EF[19] optimization procedure. The final gradient norm of the energy gradient was always less than 0.1 kcal mol^{-1} (1 cal = 4.184 J).

Three consecutive steps were taken for the location of the transition state on the reaction path. First, the 'saddle' calculations[20,21] led to the approximation of the saddle point structure. Next, the gradient minimization by the TS procedure[19] for this structure was carried out. Finally, force calculations were performed, always affording one and only one negative force constant. Force calculations were also carried out to evaluate changes in thermodynamic functions together with temperature (in harmonic approximation).[22]

In order to study solvent effects, the Conductor-Like Screening Model (COSMO)[23] incorporated into the MOPAC93 program package was applied both for minimum structures and saddle point configurations. The relative permittivity of water was taken as 55.3 (at 373 K).

All computations were carried out using an HP 730 work station or PC/487 computers.

Results and Discussion

Experimental Findings.—Heating per-*O*-acetyl-D-xylal in water at 373 K (initial pH of *ca.* 7) led to the formation of the mixture of the compounds (Table 1). The products were identified by the CGC–MS method and/or co-injection with standards after exhaustive acetylation of the reaction mixture. The GC of the mixture obtained after heating the title compound in water at 373 K shows six well-separated peaks. Identification of all the components is presented in order of GC elution.

4-O-*Acetyl*-1,5-*anhydro*-2,3-*dideoxypenta*-1,3-*dienitol* ($C_7H_8O_3$) (**5**). A possible structure of the compound (GC peak 1) was based on its molecular ion with *m*/*z* 140 (two double bonds responsible for rapid consumption of bromine). An analogous structure for a by-product of the reaction of per-*O*-acetyl-D-glucal in aqueous mercurium salt solution was proposed by Gonzales.[8]

4-O-*Acetyl*-D-*arabinal* (**4**). The compound (GC peak 2) was identified by co-injection with the authentic sample.

4-O-*Acetyl*-2,3-*dideoxy*-α- *and* -β-D-*pent*-2-*enopyranose* (*cyclic pseudoxylals;* **6**). The mass spectra obtained for both compounds (GC peaks 4 and 5) were identical: *m*/*z* 157 (M − CH_3CO), 140 (M − AcOH), 98 (M − AcOH − CH_2CO), 81 (M − AcOH − AcO), 80 (M − 2 × AcOH) and the molecular ion 200, which confirmed the structure of the compounds studied. A diagnostic reaction revealed bromine consumption.

(Z)- *and* (E)-4-O-*acetyl*-2,3-*didexoy*-D-*pent*-2-*enose* (cis *and* trans-*chain pseudoxylals;* **7** *and* **8**). The CGC–MS analysis indicates only one compound (GC peak 6) the identity of which was proved by co-injection with (*E*)-1,4,5-tri-*O*-acetyl-2,3-dideoxy-D-pent-2-enitol. The fragmentation ions obtained here were: *m*/*z* 170 (M − CH_2O), 140 (M − AcOH), 128 (M − CHOAc), 98 (M − AcOH − CH_2CO), 86 (M − CHOAc − CH_2CO) and the molecular ion 200. The fragmentation ions indicate the 4,5-di-*O*-acetyl-2,3-dideoxypent-2-enose structure which was also supported by the diagnostic reaction (no consumption of bromine). On the other hand, HPLC–UV studies carried out on the reaction mixture obtained immediately after heating of per-*O*-acetyl-D-xylal in water, also reveal the existence of the *Z*-isomer in the system studied (maximum at 204 nm).

The structures of both isomers were confirmed by CGC–MS analysis of products formed after the reduction of original unsaturated aldehydes with $NaBH_4$ as well as the H_2–Pd system.

The analysis of the relation between the initial pH of the solution and the *E*-isomer content revealed that the more acid the solution, the greater the amount of the *E*-isomer formed [pH; *E*(%): 3.0, 90; 3.2, 75; 7.0, 70; 7.8, 15; 8.2, 10].

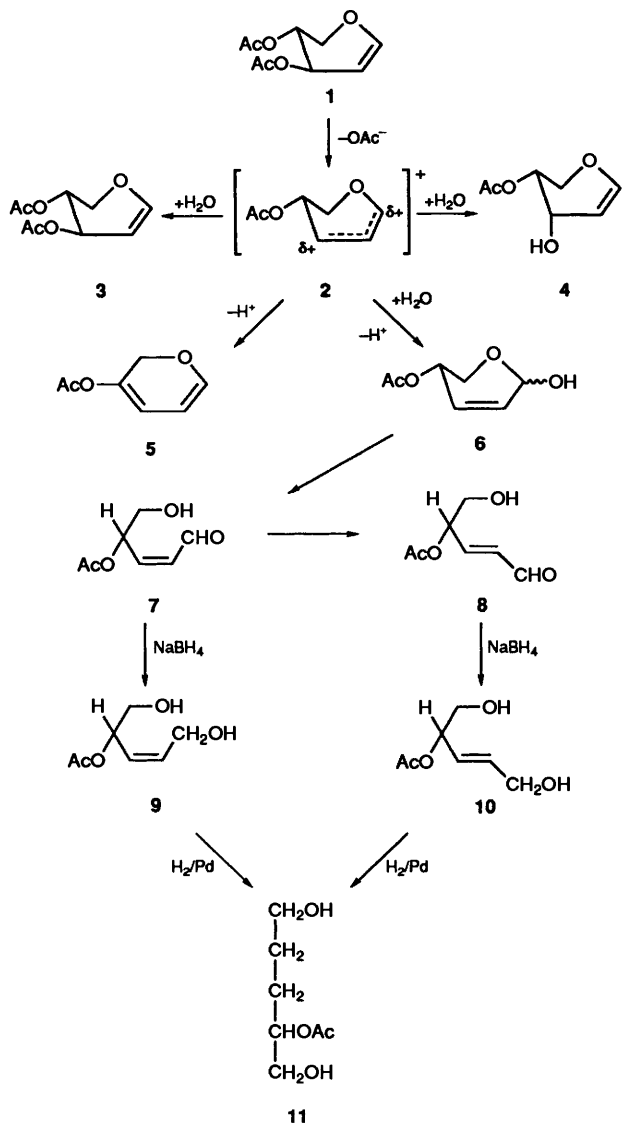
At the same time we did not find any influence of sunlight (suggested by Fraser-Reid)[5] on the content of *Z*- and *E*-isomers in the reaction mixture.

Proposed Mechanism (*Scheme* 1).—The first step of the reaction studied could be the heterolytic dissociation of the *O*-acetyl group bonded to C-3, leading to the formation of the allylic carbocation **2** (Scheme 1). A strong argument for the splitting of this particular bond involves the stabilization of the allyl-like carbocation structure **2** (calculated AM1 heats of the formation of carbocations after splitting the 3-C–O and 4-C–O bonds are 47.7 and 153.4 kJ mol^{-1}, respectively).

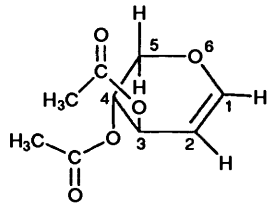
The carbocation can further be transformed in two ways, namely, by proton elimination or by the nucleophilic attack of a water molecule on C-1 or C-3 atoms. The former reaction should yield the 4-*O*-acetyl-1,5-anhydro-2,3-dideoxypenta-1,3-dienitol (**5**) as one of the final products (see Table 1 for the time-yield dependence).

Nucleophilic attack of a water molecule and subsequent proton elimination could occur at the C-1 or C-3 atoms of the carbocation. In the latter case D-xylal and the expected D-arabinal derivatives **3** and **4** were formed, which could next be transformed in the reverse reaction into the original carbocation. On the other hand, the addition of water to C-1 and subsequent proton elimination leads to the formation of α- or β-anomers of cyclic pseudoxylal **6**. If this process takes place the formation of both α- and β-anomers could have almost the same probability (see Table 1). The relative amounts of the reaction products formed by the nucleophilic attack of water on C-1 or C-3 depends primarily on the charge distribution over the crucial carbon atoms (C-1 and C-3). Net atomic charges on C-1 and C-3, equal to 0.36 and 0.01 for the aqueous phase, respectively, conformed qualitatively to the relative yields of products formed after nucleophilic attack on these atoms (27%, 3%, Table 1).

The main product in the exhaustively *O*-acetylated reaction mixture turned out to be the *E*-chain pseudoxylal, therefore, we suggest that the α- and β-anomers of cyclic pseudoxylals could be transformed into the isomeric *Z*-chain pseudoxylal



Scheme 1 Proposed mechanisms of transformation occurring in the course of the per-*O*-acetyl-D-xylal rearrangement reaction and the following reduction of chain pseudoxylals by using the $NaBH_4$ and H_2–Pd systems



in the ring opening reaction and *Z*–*E* isomerization is a process which closes the main reaction sequence.

Theoretical Arguments Supporting the Mechanism of the Transformation Studied.—Quantum chemistry calculations, carried out even on a semi-empirical level, should provide further insight into the rearrangement reaction. Thus, thermodynamic and kinetic barriers for each elementary process proposed were calculated. In order to obtain the characteristics mentioned above, conformational analyses were performed first, which assured the lowest conformation of molecules involved in elementary reactions. The AM1 optimized structures for starting geometries generated in the molecular mechanics force field are displayed in Fig. 1, whereas thermodynamic characteristics of elementary reactions for both gaseous and aqueous phases have been compiled in Table 2.

The values collected in Table 2 indicate the influence of the solvent on the overall thermodynamics. This effect is most obvious in the case of the initial elementary process (reaction 1). Since no saddle point was found here, $\Delta_r G$ should fully determine the behaviour of the title compound. For this particular reaction $\Delta_r G$ changes from 574.2 kJ mol^{-1} in the gaseous state to -2.4 kJ mol^{-1} in an aqueous solution. Indeed, per-*O*-acetyl-D-xylal could be distilled without decomposition under reduced pressure at *ca.* 450 K. On the other hand, the -2.4 kJ mol^{-1} value of $\Delta_r G$ indicates that the compound should dissociate spontaneously in an aqueous solution at 373 K.

Because of the strong influence of solvent on thermodynamic characteristics further discussion will be restricted to the aqueous phase exclusively. It is worth mentioning here, that most $\Delta_r G$ values are either negative (reactions 1, 8, 9, 10 and 11), or small positive numbers (reactions 4, 5, 12 and 13) (excluding these characteristics for the formation of **3** and **4**, which can be considered as the side products). This indicates that possible equilibria are moved towards products, which supports the possibility of transformations in the manner suggested. Only for the ring opening (reaction 6 and 7) is $\Delta_r G$ relatively high. The comparison of these characteristics with those of protonated cyclic pseudoxylals shows that for the latter system $\Delta_r G$ adopts relatively strong negative value (reactions 8 and 9). Being in accordance with experimental findings, this result suggests that the presence of H_3O^+ ions is necessary for progress of the process.

Further insight into the mechanism studied could be gained by calculations of kinetic barriers of the steps postulated. Full activation parameters, in both the gaseous phase and aqueous solution for the reactions considered, are given in Table 3 and the geometries of saddle point structures are presented in Fig. 2. The comparison of the data obtained for the gaseous and aqueous phases reveals a distinctly lower influence of the surroundings on the kinetic characteristics than the thermodynamic ones. Moreover, most of the barriers are easily passed as indicated by the $\Delta_r G^{\ddagger}$ values and by kinetic constants calculated for the aqueous phase on the basis of the theory of the transition state.[24] Only the free enthalpy of activation for the pseudoxylal ring opening reaction is extremely high (Table 3, reaction 3), suggesting that if this reaction were the bottle-neck step the final product [chain (*E*)-pseudoxylal] could not be observed experimentally (half-period equal to 8.1 10^{13} h). Considering the protonated molecule of cyclic pseudoxylal, however, the lowering of the activation barrier to 19.3 kJ mol^{-1} can be observed (reaction 4), which enables the overall process to be completed. It has been proved experimentally that in the course of the reaction, the neutral solution becomes acidic as the result of acetic acid formation.

It can consequently be concluded that in solutions which are sufficiently acidic the bottle-neck step of the transformation studied should be the *Z*–*E* isomerization of chain pseudoxylal (Table 3). In the case of this reaction, the $\Delta_r G^{\ddagger}$ for the neutral compound and that protonated on the carbonyl oxygen atom, is equal to 144.4 and 122.6 kJ mol^{-1}, respectively. The lowering of the kinetic barrier after protonation could be explained in terms of the bond orders (see Table 4). One can observe that due to protonation, the C-1–C-2 bond assumes double bond character in part and, simultaneously, the lowering of the C-2–C-3 bond order can be observed which facilitates rotation around the latter bond. Hence, half-periods of the isomerization for neutral and protonated (*Z*)-chain pseudoxylal are equal to *ca.* 1.3×10^3 and 1.3 h, respectively. It is worth mentioning that in a heated aqueous solution of per-*O*-acetyl-D-

Table 2 Thermodynamic characteristics of the reactions considered in the transformation process of per-*O*-acetyl-D-xylal at 373 K

Reaction No.	Reaction	Gaseous phase				Aqueous phase			
		Δ_rH^a	Δ_rS^b	Δ_rF^c	K	Δ_rH	Δ_rS	Δ_rG	K
1	**1** ⟶ 2 + $CH_3CO_2^-$	663.0	238.3	574.2	3.86×10^{-81}	80.4	222.0	−2.4	2.17
2	**2** + $2H_2O$ ⟶ **3** + H_3O^+	106.8	−170.1	170.2	1.46×10^{-24}	−29.0	−151.1	27.4	1.46×10^{-4}
3	**2** + $2H_2O$ ⟶ **4** + H_3O^+	107.3	−185.2	176.4	1.98×10^{-25}	−27.7	−168.2	35.0	1.25×10^{-5}
4	**2** + $2H_2O$ ⟶ α-**6** + H_3O^+	75.0	−185.0	144.0	6.82×10^{-21}	−60.8	−169.0	2.2	4.92×10^{-1}
5	**2** + $2H_2O$ ⟶ β-**6** + H_3O^+	72.1	−184.1	140.8	1.91×10^{-20}	−61.0	−168.2	1.7	5.78×10^{-1}
6	α-**6** ⟶ **7**	57.0	28.5	46.4	3.18×10^{7}	37.9	7.5	35.1	1.22×10^{-5}
7	β-**6** ⟶ **7**	59.9	27.6	49.6	1.13×10^{-7}	37.9	6.7	35.4	1.10×10^{5}
8	α-**6**$^+$ ⟶ **7**$^+$	−7.1	17.6	−13.7	8.29×10^{1}	−7.5	19.2	−14.7	1.15×10^{2}
9	β-**6**$^+$ ⟶ **7**$^+$	−10.0	16.2	−16.0	1.74×10^{2}	−7.0	18.4	−13.9	8.84×10
10	**7** ⟶ **8**	−6.3	4.6	−8.0	1.32×10^{1}	−14.6	18.4	−21.5	1.03×10^{3}
11	**7**$^+$ ⟶ **8**$^+$	0.9	2.1	0.1	9.68×10^{-1}	−23.9	5.1	−25.8	4.10×10^{3}
12	**7**$^+$ ⟶ **9**	−28.3	4.5	−30.0	1.59×10^{4}	10.2	19.7	3.0	3.80×10^{-1}
13	**2** + H_2O ⟶ **5** + H_3O^+	162.5	−7.1	165.1	7.56×10^{-24}	6.7	10.0	2.9	3.93×10^{-1}

[a,b] kJ mol. [c] J mol^{-1} K^{-1}.

Table 3 Kinetic characteristics of elementary processes postulated for transformation of per-*O*-acetyl-D-xylal in water at 373 K calculated by AM1 in gaseous and aqueous phases

Reaction No.	Reaction	Gaseous phase				Aqueous phase			
		$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$	$\Delta G^{\ddagger c}$	k^d	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	k
1	**2** + H_2O ⟶ α-**6**$^+$	1.3	−0.8	1.7	3.33×10^{13}	23.4	−2.9	24.7	9.67×10^{9}
2	β-**6**$^+$ + H_2O ⟶ β-**6** + H_3O^+	6.3	−8.0	9.2	2.98×10^{12}	33.5	23.0	24.7	9.67×10^{9}
3	α-**6** ⟶ **7**	238.1	−4.6	240.2	4.86×10^{-21}	218.0	−8.0	221.0	2.37×10^{-18}
4	α-**6**$^+$ ⟶ **7**$^+$	16.3	0.4	16.3	1.10×10^{11}	18.8	−0.8	19.3	4.19×10^{10}
5	**7** ⟶ **8**	150.7	−0.8	151.1	1.46×10^{8}	151.6	20.3	144.0	1.44×10^{-7}
6	**7**$^+$ ⟶ **8**$^+$	143.5	−2.5	144.4	1.27×10^{-7}	126.0	9.2	122.6	1.43×10^{-4}
7	**7**$^+$ ⟶ a$^+$	21.3	4.6	19.6	3.80×10^{10}	36.6	4.8	34.8	2.38×10^{8}
8	**2** + H_2O ⟶ **5** + H_3O^+	111.7	−5.9	113.8	6.66×10^{-3}	91.2	8.0	88.3	9.10

[a,b] kJ mol^{-1}. [c] J mol^{-1} K^{-1}. [d] Calculated on the basis of transition state theory.[13] s^{-1} or s^{-1} dm^3 mol^{-1}.

Table 4 Chosen bond orders for neutral, protonated *Z*-chain pseudoxylal and acetoxonium cation in gaseous phase and aqueous solution

	Neutral		Protonated			
	Z-Chain	Pseudoxylal	*Z*-Chain	Pseudoxylal	Acetoxonium ion	
Bond	Gas	Aqueous	Gas	Aqueous	Gas	Aqueous
1-C–O	1.92	1.91	1.47	1.47	1.14	1.10
C-1–C-2	0.97	0.97	1.13	1.13	1.73	1.76
C-2–C-3	1.86	1.89	1.74	1.74	1.03	1.01

xylal the reaction was completed after *ca.* 30 min (see Table 1).

Additional Remarks Concerning the Proposed Mechanism (*Scheme 1*).—The analysis presented above supports the suggested mechanism entirely. However, calculations performed prompted us to make further corrections to the mechanistic proposal. Namely, the saddle point calculations carried out for reaction 6 (Table 3) indicates a strong tendency of the **7**$^+$ compound to transform into the cyclic acetoxonium cation gsa$^+$ (see Fig. 1).

Table 4 presents the orders for chosen bonds of neutral and protonated *E*-chain pseudoxylal and the gsa$^+$ cation. It is worth mentioning that only for the cyclic acetoxonium cation gsa$^+$, is the C-2–C-3 bond of a single bond character. On the other hand the only stable conformations of gsa$^+$ have the *trans* arrangement in the C(1)C(2)C(3)C(4) fragment. The calculations also showed that without any activation barrier, cation gsa$^+$ changes into the *E*-chain pseudoxylal after deprotonation. Furthermore, the activation barrier for the transformation of *Z*-protonated pseudoxylal **7**$^+$ into gsa$^+$ is equal to 34.8 kJ mol^{-1} for the process occurring in the aqueous solution, which indicates that the formation of the cyclic acetoxonium cation can proceed even at a very low temperature. It is also worth noting that because of the *trans* arrangement of the cyclic acetoxonium cation in the C(1)C(2)C(3)C(4) fragment during the reverse reaction (gsa$^+$ ⟶ protonated chain pseudoxylal) only the protonated *E*-pseudoxylal is formed. The mechanism of the *Z*–*E*-isomerization therefore proceeds *via* the formation of the transient cyclic acetoxonium cation (saddle point ts7; Fig. 2) rather than through the rotation around C-2–C-3 in the *Z*-chain pseudoxylal (saddle point ts5; Fig. 2).

To check theoretical predictions, rearrangement reactions were carried out at a relatively low pH (*ca.* 3) and low temperature (*ca.* 310 K). Taking into account the mechanism proposed, both the pH and temperature decrease should stop the formation of compound **5**. On the other hand, the increase of the hydrogen ion concentration should facilitate the formation of compound **8** only if the activation barrier for the process is

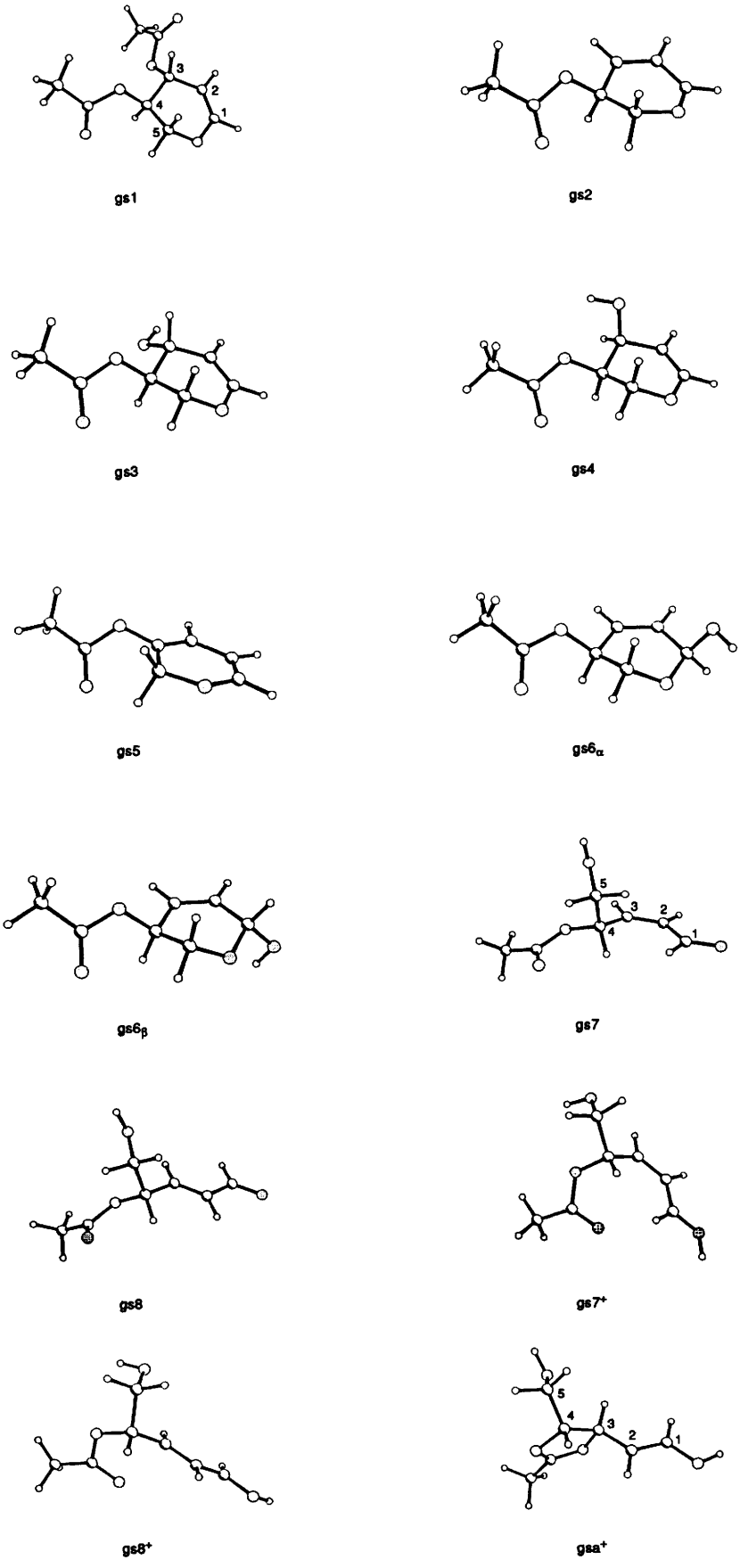


Fig. 1 Minimum structures (calculated for the aqueous phase) of the compounds considered in the per-*O*-acetyl-D-xylal rearrangement process. The carbon atoms are presented by shadowed, the oxygen atoms by dotted and the hydrogen atoms by empty circles. gsx, symbols: gs = ground state, x = 1–8 corresponds to the compounds **1–8** in Scheme 1, + = protonated compound, gsa^+ = acetoxonium ion.

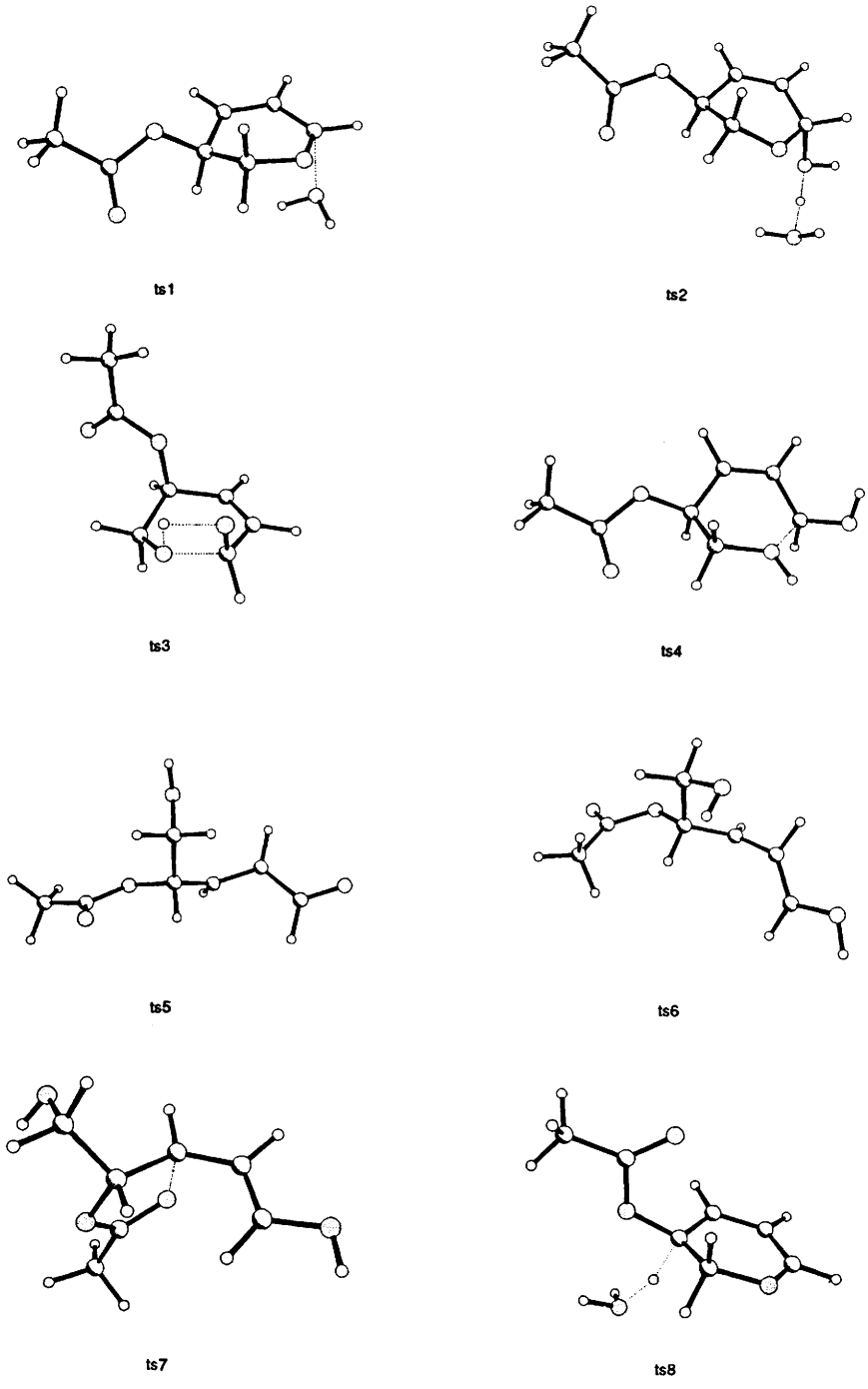


Fig. 2 Saddle point geometries (calculated for the aqueous phase) for chosen elementary processes in the reaction mechanism. The carbon, oxygen and hydrogen atoms are presented as in Fig. 1. Dotted lines represent the bonds which are formed and broken in the course of the reaction; tsx, symbols: ts = transition state, x = 1–8 corresponds to the number of reactions in Table 3.

distinctly lower than that for formation **5**. The reaction mixture obtained under conditions described above contained mainly *E*-chain pseudoxylal, which fully confirms the results of theoretical calculations.

Conclusions

The compilation of the experimental findings with the results of theoretical calculations concerning both thermodynamics and kinetics of the system studied enabled us to make the proposed mechanism of transformations more reliable. Some experimental observations, such as the catalytic role of hydrogen cations were explained by the AM1 calculations.

The theoretical approach assumed in this paper showed the unquestionable importance of solvent–solute interactions. The effect turned out to be most visible in the case of thermodynamic characteristics. In general, the higher the charge separation as the result of the process, the stronger the change in $\Delta_r G$ relative to the gaseous phase (*e.g.* reaction 1, Table 2).

The results obtained cannot be considered final in this matter. The COSMO methodology took into account only the energy effects connected with the relaxation of the solute molecule in the field generated by the solvent. This does not consider changes created in the solvent itself by introducing the solute molecule, which, for example, could be taken into account in a supermolecular model. It is therefore difficult to say how far

the results obtained are accurate in the quantitative sense. Nevertheless, even the relatively simple approach presented in this paper affords an insight into the reactivity and energetics in this important (both from the model as well as practical point of view) class of reactions.

Acknowledgements

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