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**ALKALINE DEGRADATION OF CELLOBIOSE, 3,6-ANHYDROCELLOBIOSE,
3,6-ANHYDRO-4-O-METHYL-D-GLUCOSE, AND D-GLUCOSE**

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ABSTRACT

The title compounds were degraded in 0.099M oxygen-free aqueous NaOH at 25°, and sometimes 45°. Cellobiose degraded primarily to 3-deoxy-2-C-hydroxymethyl-D-pentonic ("isosaccharinic") acids, plus the series of 3- to 6-carbon 3-deoxyaldonic acids and glyceric acid also produced from glucose. No disaccharide acids indicative of a "stopping" reaction were formed. However, formation of 3,4-dideoxyhex-5-ulosonic acid from cellobiose indicates that elimination of OH-3, necessary for the "stopping" reaction, did occur, but that the glucosyloxy substituent at C-4 was also eliminated in the same reaction sequence. The major products from 3,6-anhydro-4-O-methyl-D-glucose and 3,6-anhydrocellobiose, 3-deoxy-D-hexonic acids and 3-deoxy-2-C-hydroxymethyl-D-pentonic acids, respectively, also indicate primary reaction sequences involving multiple substituent elimination. However, in contrast to cellobiose, 3,6-anhydrocellobiose also yielded a disaccharide product indicative of a "stopping" reaction. Mechanisms are proposed to account for the primary products of each substrate.

INTRODUCTION

Cellobiose (1) has often been used as a model compound for studies related to the alkaline degradation of cellulose.³⁻⁹ Cellulose is known to undergo both the "peeling" reaction and "stopping" (stabilization) reaction in dilute, oxygen-free

alkali.^{3,10-12} By analogy, the degradation of cellobiose might be expected to proceed partly by the peeling reaction and partly by the stopping reaction. Cellobiose does undergo the peeling reaction, but the products indicative of the stopping reaction have been reported to be absent,^{7,8} formed in trace amounts,⁵ or formed in substantial amounts⁴ in anaerobic alkaline degradations.

The mechanisms usually postulated for peeling and stopping are illustrated for cellobiose in Figure 1. One of our objectives was to further examine the degradation of cellobiose in dilute, oxygen-free alkaline solution, particularly to determine whether 3-deoxy-4-O-β-D-glucopyranosyl-D-arabino- (2) and -ribo-hexonic acids (3), the expected stopping reaction products, were formed in significant amounts. In addition, 3,6-anhydrocellobiose (4) was degraded under the same conditions. It was anticipated that degradation of 4 would yield more 2 and 3 than would cellobiose, somewhat analogous to enhanced formation of 3-deoxy-D-arabino- (5) and -ribo-hexonic acid (6) from 3,6-anhydro-D-glucose¹³ relative to D-glucose. However, the degree of enhancement was uncertain since degradation of 3-O-methyl-xylobiose reportedly does not yield the corresponding 3-deoxy-4-O-β-D-xylopyranosyl-D-erythro- and -threo-pentonic acids.¹⁴ The degradation of D-glucose, the elimination product from peeling of 1 or 4, was studied independently to assess its contribution to the product spectra. Degradation of 3,6-anhydro-4-O-methyl-D-glucose (7), a simple analog of 4, was also studied. Presumably, a study of 7 would parallel that of 4 but avoid the complication of the additional degradation products from glucose generated in degradations of 4.

RESULTS AND DISCUSSION

To minimize side reactions, degradations were run under mild conditions using oxygen-free 0.099M aqueous sodium hydroxide at

25°C or 45°C. The initial molar ratio of alkali to reducing sugar was 5:1. Reactions were monitored for alkali consumption (formation of acids) by titration and were considered complete when the alkali concentration remained constant. Degradation products were analyzed as their per-O-trimethylsilyl (TMS) derivatives by gas-liquid chromatography (glc) and glc in conjunction with mass spectrometry (glc-ms).

Degradation of D-glucose.

Product analyses for degradations of D-glucose are presented in Table 1. D-Glucose degraded primarily to the 3- to 6-carbon series of 3-deoxyaldonic acids plus glyceric acid.

TABLE 1

Products from D-Glucose and Cellobiose in 0.099M NaOH^a

Acid Product ^b	D-Glucose		Cellobiose	
	25°C	45°C	25°C	45°C
Lactic	56	59	33	27
Glyceric	5	2	3	2
3-Deoxytetronic	14	13	9	12
3,4-Dideoxypentonic (15)	--	--	5	3
3,4-Dideoxyhex-5-ulosonic (17)	--	--	5	3
3-Deoxy-D-pentonic (8)	3	2	4	4
3-Deoxy-D-hexonic (5 & 6)	22	24	11	11
3-Deoxy-2-C-hydroxymethyl-D-pentonic	--	--	30	38

^aFigures are percentages of total products observed, calculated from glc peak area. Very minor products are not included.

^bProducts identified by glc-ms as their per-O-trimethylsilyl derivatives with reference to known compounds when available.

Mechanisms have been proposed for the formation of lactic,¹⁵⁻¹⁷ 3-deoxytetronic,¹⁸ and 3-deoxy-D-hexonic acids (5 and 6)^{15-17,19} from D-glucose.

Although 3-deoxy-D-pentonic acids (8) have been reported as minor degradation products of glucose in oxygen-free aqueous sodium hydroxide,^{8,20} a mechanism has not been proposed for their

formation. A potential mechanism for formation of 8 from D-glucose²¹ is shown in Figure 2. Formation of D-fructose^{22,23} and subsequently the 3-hexulose (9, R = H) would precede a reverse aldol reaction to form a pentose and formaldehyde. The pentose would readily form 8¹⁵, analogous to the formation of 5 and 6 from glucose.^{16,17} Formation of pentoses in the early stages of the reaction of D-fructose with aqueous calcium hydroxide has been reported, and 8 is a degradation product of D-fructose in aqueous sodium hydroxide and calcium hydroxide solutions.²⁴ No attempt was made to detect formaldehyde, the resultant 1-carbon fragment in the proposed mechanism. Formaldehyde could potentially undergo formose- and Cannizzaro-type reactions,²⁵ thus making its detection difficult.

Thus far, a suitable mechanism for the formation of glyceric acid, a minor product from D-glucose, has eluded us.

At 25°C the degradation of D-glucose was complete in ca. 50 days and the 3-deoxyhexonic acids (5 and 6) accounted for only 22% of the degradation products. In contrast, under identical conditions, degradations of 3,6-anhydro-D-glucose (10) and 3-O-methyl-D-glucose (11) were complete in 6-7 days and 5 and 6 accounted for ca. 90% of the degradation products.²¹ To explain these results, ionization of hydroxyl groups in the alkaline medium must be considered. To form 5 and 6 from D-glucose OH-3 must be eliminated.¹⁶ However, the extent to which OH-3 exists as its conjugate base decreases the concentration of substrate capable of undergoing the β -elimination at C-3. Thus, in addition to the rate of degradation being decreased by ionization of OH-3, fewer 3-deoxy-hexonic acids are produced from D-glucose relative to 10 and 11. Instead, the reaction of D-glucose is directed primarily toward an initial rearrangement to D-fructose and a subsequent reverse aldol reaction to form 1,3-dihydroxy-2-propanone and glyceraldehyde, both of which form lactic acid,¹⁶ the major product from glucose.

Dianions of intermediate enediols, e.g., 12, have been proposed as critical intermediates in alkaline degradations of reducing saccharides, especially with respect to formation of 3-deoxyaldonic acids.²⁶⁻³¹ Presumably, the necessary elimination of hydroxide ion from C-3 requires additional coulombic assistance from a second anionic group in the molecule.^{30,31} However, the postulate^{26,30,31} that degradation of D-glucose to glucometasaccharinic acids requires a high enough alkalinity to convert the intermediate enediol to its dianionic form seems unwarranted. At the low alkali concentration ($< 0.1M$) used in this study, the monoanion of the enediol should be the dominant species.³⁰ However, the product distribution for D-glucose under these conditions (see Table 1) is remarkably similar to that reported for $8N$ NaOH at 100° .^{20,32} Thus, the relative importance of competing reactions must not change drastically between the two alkalinities.

An increase in temperature from 25 to $45^\circ C$ increased the rate of degradation of D-glucose by a factor of ca. 7 but had no important effect on the products or their relative proportions (Table 1).

Degradation of Cellobiose.

Product analyses for degradations of cellobiose are presented in Table 1. Cellobiose degraded primarily to 2-C-hydroxymethyl-3-deoxy-D-pentonic (isosaccharinic) acids (13, Figure 1) and glucose; the latter subsequently degraded as described previously. In addition, 4-O- β -D-glucofuranosyl-D-fructose (cellobiulose) (14, Figure 1) was identified as a reactive intermediate.²¹ Thus, the primary reaction of cellobiose is adequately explained by the peeling sequence of reactions in Figure 1.

No disaccharide acid products (i.e., 2 or 3, Figure 1) were found in the cellobiose product mixture. This supports the earlier reports^{7,8} that the classical "stabilization" reaction is of negligible importance in the alkaline degradation of

cellobiose. Thus, in this respect, cellobiose is not a good model for cellulose.

3-Deoxy-D-pentonic acids (8) were minor products from cellobiose. One potential source of 8 is degradation of the glucose eliminated from cellobiose. However, the amount of 8 formed relative to that from glucose (Table 1) indicates that 8 must also be formed from cellobiose per se. A potential mechanism for the reaction,^{9,21} parallel to that for the formation of 8 from glucose, is shown in Figure 2.

3,4-Dideoxypentonic acid (15), another minor product from cellobiose, has been proposed to form from the 4-deoxy-D-2,3-hexodiulose (16)⁹ formed from the reducing glucose moiety in the peeling sequence (see Figure 1).

Formation of 3,4-dideoxyhex-5-ulosonic acid (17) from cellobiose can be explained by postulating the loss of both OH-3 and the C-4 glucosyloxy substituent from the reducing moiety, i.e., a double elimination. Thus, elimination of OH-3 from cellobiose (Figure 1) would yield the 3-deoxyglycosulose 18 in which base-catalyzed elimination of the C-4 glucosyloxy group is possible because it is beta to the C-2 carbonyl (Figure 3). Abstraction of the acidic proton at C-5 of the resultant 3,4-dideoxy-D-hex-3-enosulose (19) would yield the 3,4-dideoxyhex-2,4-dienose 20. Subsequent enol-keto tautomerizations and a benzil-benzilic acid type rearrangement would provide 17. Evidence for the formation of 17 in alkaline degradations of 3,4-di-O-methyl-D-glucose and -D-galactose has been presented, and an analogous mechanism was proposed for its formation.³³

The ramification of the double elimination reaction in cellobiose is that, in contrast to the classical concept of the stopping (stabilization) reaction (Figure 1), initial elimination of OH-3 from the reducing end unit does not ensure that stabilization of a 1,4-linked oligo- or polysaccharide toward peeling will result.

Degradation of 3,6-anhydro-4-O-methyl-D-glucose (7).

The key products identified for the degradation of 7 are reported in Table 2. The dominant products from 7 were isomeric 3-deoxy-D-hexonic acids (21), which were approximately 3.6 times as abundant as the isomeric 3-deoxy-4-O-methyl-D-hexonic acids (22 and 23), the anticipated products if only β -elimination from C-3 were involved in the degradation. The other primary identified products were lactic acid, 3-deoxy-D-pentonic acids (8), and 3,4-dideoxyhex-5-ulosonic acids (17).

A possible mechanism for formation of some of the key products is shown in Figure 4. Initial base-catalyzed elimination of the anhydride oxygen from C-3 of 7 would lead to 3-deoxy-4-O-methyl-D-erythro-hexosulose (24) which could undergo a benzil-benzilic acid type rearrangement to form the 3-deoxy-4-O-methyl-D-arabino- and -ribo-hexonic acids (22 and 23). Alternatively, 24 could undergo β -elimination of the methoxyl group at C-4 to form the 3,4-dideoxy-D-hex-3-enosulose (19). Compound 19 could react as shown in Figure 3 to form the ulosonic acid 17 or, being a vinyl ketone, undergo addition of hydroxide ion at C-4 to potentially form epimeric 3-deoxy-D-hexosuloses (25). Compound 25 could undergo a reverse aldol reaction to form D-glyceraldehyde and 2-hydroxypropenal, both of which can form lactic acid. Alternatively, a benzil-benzilic acid type rearrangement of 25 would yield the isomeric 3-deoxy-D-hexonic acids (21). Aspinall and Tam³³ earlier postulated an analogous mechanism to account for formation of 21 from 3,4-di-O-methyl-D-glucose. A similar mechanism also accounts for the formation of 3-deoxy-D-pentonic acid from alkaline degradation of 3,4-di-O-methyl-D-xylose.³⁴ Similarly, the formation of small amounts of 3-deoxy-D-hexonic acids (21) from alkaline degradation of 4-O-methyl-D-glucose³⁵ can be rationalized with this type of mechanism involving initial elimination of OH-3 to form 24 (see Figure 4).

Suitable mechanisms for the formation of 3-deoxypentonic acid and glyceric acid from 7 have eluded us.

TABLE 2

Products from 3,6-Anhydro-4-O-Methyl-D-glucose (7) and
3,6-Anhydrocellobiose (4) in 0.099M NaOH at 25°C^a

Acid Products ^b	7 ^c	4
Lactic	17	28
Glyceric	1	3
3-Deoxytetronic	--	6
3,4-Dideoxypentonic (15)	--	1
3,4-Dideoxyhex-5-ulosonic (17)	6 ^d	--
3-Deoxy-D-pentonic (8)	8 ^e	2
3-Deoxy-4-O-methyl-D-hexonic (22 & 23)	11	--
3-Deoxy-D-hexonic (21)	40	11
3,4-Dideoxyhexonic	--	3
3-Deoxy-2-C-hydroxymethyl-D-pentonic (13)	--	39
3-Deoxy-4-O-(β-D-glucopyranosyl)-D-hexonic (2 & 3)	--	7 ^e

^aFigures are percentages of total products observed, calculated from glc peak areas. Very minor products are not included.

^bProducts identified by glc-ms as their per-O-trimethylsilyl derivatives with reference to known compounds when available.

^cTwo unidentified products accounted for 11 and 6% of the product mixture.

^dTentative. Incomplete resolution from the dominant unidentified product made quantitation difficult.

^eTentative identification.

Degradation of 3,6-Anhydrocellobiose (4).

Product analyses for degradation of 4 are reported in Table 2. In addition, glucose was formed in the reaction, but subsequently degraded. The major acidic products were isomeric 3-deoxy-2-C-hydroxymethyl-pentonic (isosaccharinic) acids (26), lactic acid, and isomeric 3-deoxy-D-hexonic acids (21). In contrast with cellobiose, degradation of 4 yielded a disaccharide product, tentatively identified as 3-deoxy-4-O-(β-D-glucopyranosyl)-D-hexonic acid (i.e., 2 and 3).²¹

Glyceric, lactic, 3-deoxytetronic, and 3-deoxy-pentonic acids could be formed from the glucose liberated from 4. Lactic acid, 3-deoxy-D-hexonic acids (21), glucose, and the 3-deoxy-4-O-(β-D-glucopyranosyl)-D-hexonic acids (2 and 3) could be formed from

4 as shown in Figure 4, by a mechanism analogous to that for degradation of 7.

The formation of the isosaccharinic acids (26) from 4 requires an alternate mechanism involving initial elimination of the glucosyloxy substituent from C-4 (Figure 5). Transformation of 4 to 3,6-anhydrocellobiulose (27) would lead to β -elimination of the glucosyloxy anion from C-4 to form the 3,6-anhydro-4-deoxy-D-hex-3-enulose (28). Abstraction of acidic H-5 from 28 would result in elimination of the anhydride oxygen from C-6 to form the 4,6-dideoxy-hex-3,5-dienulose (29). Nucleophilic addition of hydroxide to the conjugated system of 29 at C-6 and subsequent enol-keto tautomerization would yield the 3-deoxy-hex-2,3-diolose (30). A benzil-benzilic acid type rearrangement of 30 would yield the isomeric isosaccharinic acids 26.

Formation of substantial amounts of the isosaccharinic acids (26) from 3,6-anhydrocellobiose (4) but not from 3,6-anhydro-4-O-methyl-D-glucose (7) attests to the ability of the leaving group to direct the course of the reaction. The glucopyranosyloxy group of 4 would be expected to be a much better leaving group than the methoxy group of 7 and also better than the anhydride oxygen.

Isomeric 3-deoxy-D-hexonic acids (21) could also potentially form from 4 as shown in Figure 5. Nucleophilic addition of hydroxide to the intermediate enulose 28 at C-4 would yield epimeric 3,6-anhydro-D-hexuloses (31). Isomeric 3,6-anhydro-D-hexoses (32) which could be formed from 31 would readily yield the 3-deoxyhexonic acids 21.

EXPERIMENTAL

General Methods

Melting points were determined on a Thomas-Hoover capillary apparatus which was calibrated with known compounds. Polarimetric measurements were made on a Perkin-Elmer 141 MC polarimeter. Tlc was performed on microscope slides coated with Silica Gel G

(Brinkman Instruments, Inc.) using anisaldehyde-sulfuric acid-acetic acid reagent³⁶ for component detection. Paper chromatography was performed on Whatman No. 1 paper using ethyl acetate-acetic acid-water (3:1:1, vol) for development and alkaline silver nitrate reagent³⁷ for component detection.

Pmr spectra were determined on a Varian A-60A spectrometer at normal probe temperature using tetramethylsilane as an internal standard in CDCl₃ and DMSO-d₆ solutions.

Glc was conducted on a Varian Aerograph 1200-1 chromatograph equipped with a hydrogen flame-ionization detector and a Honeywell Electronic 16 recorder with a Disc integrator. Analyses were performed on a column (5 feet x 0.125-inch o.d., stainless steel) of 5% SE-30 on 60-80 mesh Chromosorb W using N₂, 10 mL min⁻¹; column, 80 + 240°C at 4° min⁻¹; injector, 230°C; and detector, 250°C.

Mass spectra were determined on a Du Pont Instruments 21-491 spectrometer interfaced with a Varian Aerograph 1440 gas chromatograph. Glc separations were performed as described above except that helium (UHP, Matheson Gas Products) was used as the carrier gas.

Benzyl 4',6'-O-Benzylidene-β-cellobioside (33)

Hepta-O-acetyl-α-cellobiosyl bromide³⁸ was condensed with benzyl alcohol in a modified Koenigs-Knorr reaction³⁹ to give benzyl hepta-O-acetyl-β-cellobioside⁴⁰ which was deacetylated with methanolic sodium methoxide⁴¹ to produce benzyl β-cellobioside (59%), m.p. 190-191°C (5:1 EtOH-MeOH, vol), $[\alpha]_D^{22} - 34.2^\circ$ (c 1.14, H₂O). [Lit.⁴² m.p. 187°C, $[\alpha]_D - 35.5^\circ$ (H₂O)].

Powered anhydrous zinc chloride (35 g), benzaldehyde (70 mL), and powdered benzyl β-cellobioside (17 g) were allowed to react in a sealed flask with mechanical shaking for 48 hours. The mixture was poured into cold aqueous 10% sodium hydrogen sulfite (1 L) with stirring. After 30 minutes stirring, the precipitate was filtered, washed with cold 10% sodium hydrogen sulfite and cold water, rinsed with petroleum ether (b.p. 30-60°C), and dried in

vacuo at 50°C for 24 hours. The yield of **33** was 12.8 g (62%), m.p. 191-193°C, $[\alpha]_D^{22} -46.6^\circ$ (c 1.08, MeOH). [Lit.⁴³ m.p. 191°C, $[\alpha]_D^{20} -47.0^\circ$ (MeOH)].

Benzyl 4',6'-O-Benzylidene-6-O-p-toluenesulfonyl- β -cellobioside (34)

A solution of compound **33** (12 g) in anhydrous pyridine (60 mL) was cooled to 5°C. After addition of p-toluenesulfonyl chloride (4.83 g, 1.1 equivalents) to the solution, it was allowed to come to room temperature and react for 48 hours with stirring. The reaction was quenched by addition of water. After dilution with chloroform, the solution was washed with water, cold 10% hydrochloric acid, and water; dried (calcium chloride); and concentrated in vacuo to a white solid. Crystallization from ethanol-methanol (4:1, vol) yielded **34** (10.2 g, 66%); m.p. 159°C (decomposition), $[\alpha]_D^{22} -33.7^\circ$ (c 1.01, MeOH).

Anal. Calc. C₃₃H₃₈O₁₃S: C, 58.8; H, 5.7; S, 4.8. Found: C, 58.7; H, 5.6; S, 4.8.

Pmr data for **34** (Me₂SO - d₆): τ 2.0 - 2.7 (14 H; broad multiplets; benzyl, benzylidene, and toluenesulfonyl aromatic protons), 4.38 (1 H, singlet, benzylidene methine proton), and 7.60 (3 H, singlet, toluenesulfonyl methyl group).

Benzyl 3,6-Anhydro-4',6'-O-benzylidene- β -cellobioside (35)

Compound **34** (7.2 g) was allowed to react in 0.4N methanolic sodium methoxide (40 mL) for 24 hours at 20°C. The solution was neutralized with Amberlite IRC-50 (H+) and concentrated in vacuo to a thin sirup. The sirup was crystallized from absolute ethanol to yield **35** (4.1 g, 74%); m.p. 156-157°C, $[\alpha]_D^{22} -132^\circ$ (c 0.75, CHCl₃).

Anal. Calc. C₂₆H₃₀O₁₀: C, 62.1; H, 6.0. Found: C, 62.1; H, 5.9%.

Pmr data for **35** (CDCl₃): τ 2.4-2.8 (10 H, multiplet, benzyl and benzylidene aromatic protons), and 4.48 (1 H, singlet,

a sirup, $[\alpha]_D^{25} = 15.2^\circ$ (c 3.12, H₂O). [Lit.48 $[\alpha]_D^{18} = -17^\circ$ (c 0.7, H₂O)].

Alkaline Reactions

Solutions of sodium hydroxide (0.099M) were prepared with deionized, boiled water and were thoroughly purged with nitrogen. Reactions were conducted in glass bottles sealed with airtight rubber septa and were initiated in a nitrogen atmosphere. The initial ratio of equivalents of alkali to moles of reducing sugar was 5:1. A water bath maintained constant temperature (25 or 45°C).

Samples were withdrawn from the reactions with a nitrogen-purged syringe and titrated with sulfuric acid (0.01N) to the phenolphthalein endpoints (pH 8). Solutions of only sodium hydroxide, treated in the same manner, were analyzed in parallel with the degradation reactions; in no case was any change in alkali concentration detected.

Acid products were analyzed by glc and glc-ms as their per-O-trimethylsilyl derivatives. The neutralized reaction samples were concentrated in vacuo to dryness. The product mixture from a 5-mL sample was dissolved in dimethylsulfoxide (0.3-0.4 mL, silylation grade) and treated with Tri-Sil Concentrate (0.3 mL) (Pierce Chemical Co.) with mechanical shaking for 10-16 hours. Samples for glc or glc-ms analysis were taken from the upper layer of the resulting two-layer (liquid-liquid) mixture. When lactonization was desired, the product mixture was dissolved in a minimum of distilled water, one drop of concentrated hydrochloric acid was added, and the mixture was concentrated to dryness prior to derivatization.

To gage the stability of some of the acid products, the sodium salts of cellobionic, 3-deoxy-D-arabino-hexonic (5), and 3-deoxy-2-C-(hydroxymethyl)-D-erythro-pentonic acids were treated with 0.099M NaOH for 49 days at 25°C. In addition, it has been

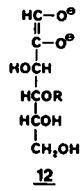
reported^{49,50} that, except for epimerization to the ribo-isomer (6), 5 was undegraded in 5% NaOH at 170°C after 7 hours.

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Cut 1.

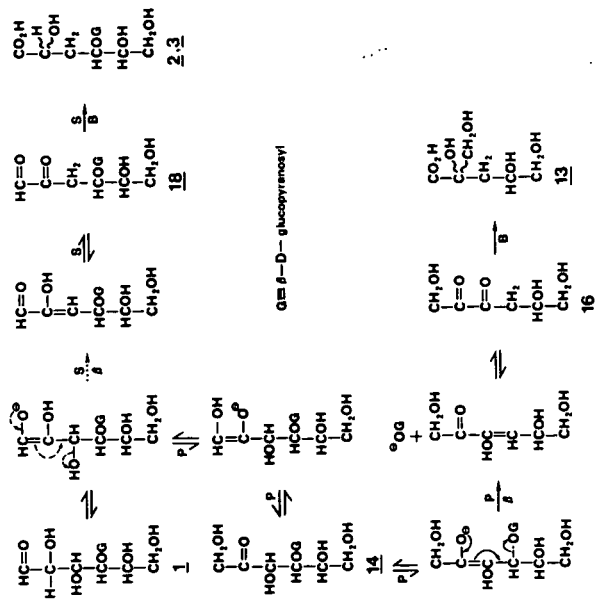


Figure 1. Possible mechanisms for anaerobic alkaline degradation of cellobiose^{3,5}: β , β -elimination; B, benzil-benzilic acid type rearrangement; P, peeling sequence; S, stabilization sequence.

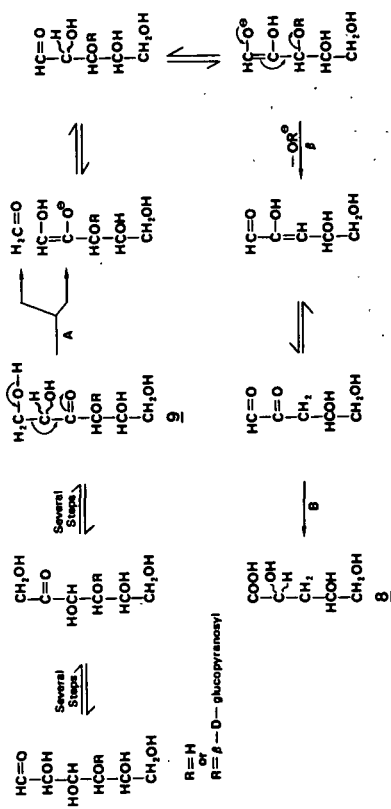


Figure 2. Possible mechanism for formation of 3-deoxy-D-pentonic acids (8) from D-glucose or cellobiose: A, reverse aldol reaction; B, β -elimination; B, benzil-benzilic acid type rearrangement.

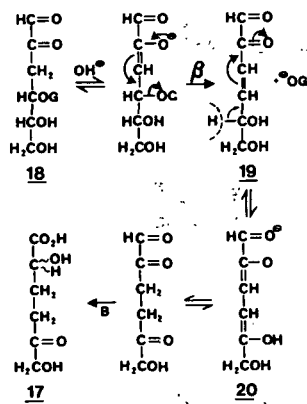


Figure 3. Possible mechanism for formation of 3,4-dideoxy hex-5-ulosonic acid (17) from cellobiose; see Figure 1 for intermediate 18.

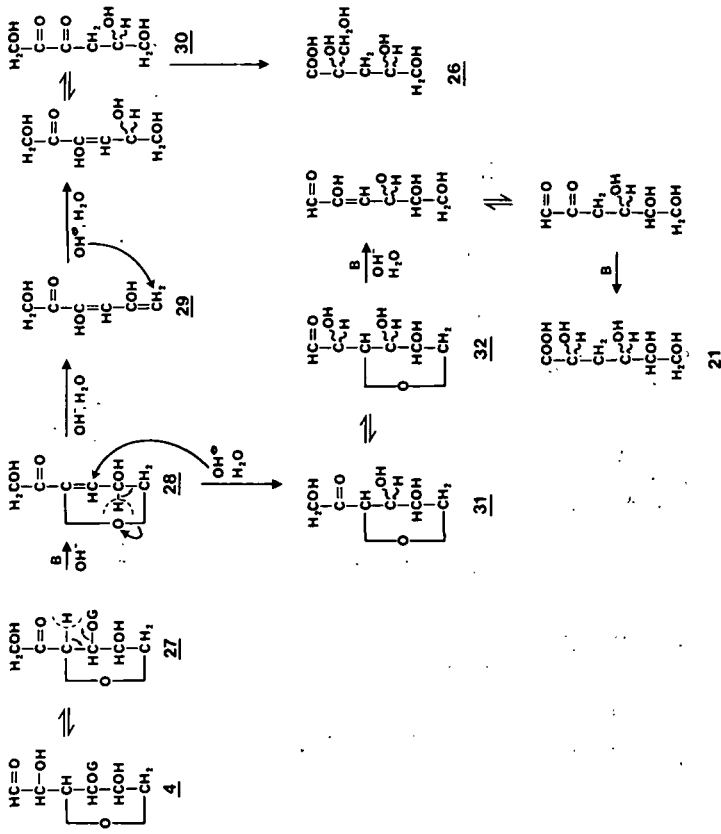


Figure 5. Possible mechanisms for formation of 3-deoxy-2-C-hydroxymethyl pentonic (isosaccharinic) acids (26) and 3-deoxy-D-hexonic acids (21) from 3,6-anhydrocellobiose.