Anal. Calcd for $C_{11}H_{13}BF_4OS$: C, 47.15; H, 4.67. Found: C, 46.95; H, 4.50.

Reaction of **15** (0.2 g in 1 ml of DMSO-d_6) with 1 equiv of potassium *tert*-butoxide was observed directly by nmr. The AB pattern of the benzylic protons disappeared rapidly but there was no significant change in the chemical shift of the vinylic, SCH_3, or OCH_3 resonances of **15**. Attempts to isolate the product(s) of this reaction led only to the isolation of a sticky red solid which could not be recrystallized. Reaction of **15** with sodium hydride in dry THF in an inert atmosphere led to the immediate evolution of hydrogen, precipitation of $NaBF_4$, and formation of a dark red solution which, after evaporating at reduced pressure, gave a red oil which solidified on washing repeatedly with pentane. Analysis by tlc showed the presence of at least three components. Separation was unsuccessful, and the nmr of the crude product in $CDCl_3$ gave very broad signals which were uninformative as to structure.

***S*-Benzyl-*S*-methyl-*S*-phenacylsulfonium ylide (14)** was prepared from the corresponding sulfonium bromide salt by treatment with sodium hydride in THF.[24] The sulfonium bromide was prepared from benzyl methyl sulfide and phenacyl bromide in benzene.

Preparation of Sulfonium Salts 20.—Each of the salts was prepared from the corresponding sulfide by methylation with trimethyloxonium fluoroborate, as described above for **10**. The salts so obtained were recrystallized to analytical purity from absolute ethanol. The sulfides were in turn prepared by the reaction of the appropriate thiophenol under basic conditions (sodium ethoxide in ethanol) with the appropriate phenacyl bromide. The procedure used was typically as follows for the preparation of *p*-methylphenacyl phenyl sulfide. To a solution of 2.88 g (0.125 g-atom) of sodium metal in 250 ml of ethanol was added all at once 13.8 g (0.125 mol) of thiophenol. To this stirred solution was added 26.7 g (0.125 mol) of *p*-methylphenacyl bromide. The mixture was gently refluxed and stirred for 1 hr, during which time sodium bromide precipitated out. The cooled mixture was filtered and evaporated. The residual oil solidified on cooling and was recrystallized from hexane to give 26.3 g (87%) of product.

Determination of pK_a for Sulfonium Salts 20.—Aqueous solutions of each of the sulfonium salts were prepared using oxygen-free distilled water. These stock solutions were diluted accordingly with standard KOH and standard HBF_4 such that 8–10 solutions of a given salt at different pH were prepared, the net concentration of salt + ylide remaining constant. The pK_a value is expressed by the relationship pH = pK_a − log [salt]/[ylide] and a plot of pH *vs.* log [salt]/[ylide] should be linear and of unit slope. The relative amount of salt and ylide present at a given pH was determined spectrophotometrically, and a plot was made of pH *vs.* log [salt]/[ylide]. In each case, the slope was verified as unity. The pK_a was determined directly from the plot for the condition [salt] = [ylide].

Registry No.—**10**, 24806-67-5; **12**, 24310-06-3; **14**, 15876-09-2; **15**, 34881-62-4; **20a**, 34881-63-5; **20b**, 34881-64-6; **20c**, 33043-77-5; **20d**, 34881-66-8; **20e**, 34881-67-9; **20f**, 34881-68-0; **20g**, 33043-72-0; **20h**, 33192-02-8; **20i**, 33043-70-8; **20j**, 34881-71-5; **20k**, 33043-73-1; $PhCOCH_2S(Me)CH_2Ph \cdot BF_4$, 17069-29-3.

(24) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **33**, 70 (1968).

Mechanisms of Alkaline Hydrolysis of *p*-Nitrophenyl Glucopyranosides

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The alkaline hydrolysis of *p*-nitrophenyl-α- and -β-D-glucopyranosides has been studied by gas chromatographic, uv spectrophotometric, and nmr spectroscopic methods. The α anomer is hydrolyzed to a degradative product of D-glucose whereas the β anomer yields the degradative product of D-glucose and 1,6-anhydroglucopyranose. The formation of the degradative product of D-glucose and the detection of a free radical during the hydrolysis suggest the complexity of the over-all pathways for the alkaline hydrolysis of *p*-nitrophenyl glucopyranosides. *p*-Nitrophenyl-β-D-glucopyranoside is hydrolyzed by mixed mechanisms, C-2 oxyanion participation, and nucleophilic aromatic substitution. In alkaline media, *p*-nitrophenyl-α-D-glucopyranoside forms a Meisenheimer-type complex, 1,2-*O*-*p*-nitrophenylidene-α-D-glucopyranose, as the intermediate which undergoes hydrolysis.

In spite of the general agreement concerning mechanisms of acidic hydrolysis of aryl glucopyranosides,[1,2] alkaline hydrolysis of aryl glucopyranosides has not been successfully rationalized on the basis of generalized mechanisms. In particular, exalted rates of hydrolysis of *p*-nitrophenyl-α- and -β-D-glucopyranosides in alkaline media remain enigmatic.

Previous studies on the alkaline hydrolysis of aryl glucopyranosides[2,3] have shown that β anomers react by a process (Scheme I) which yields 1,6-anhydroglucopyranose (**1**) *via* neighboring C-2 oxyanion participation.[4,5] A trend toward the nucleophilic aromatic substitution (Scheme II) was noted as the electron-withdrawing character of substitutents increased.[6,7]

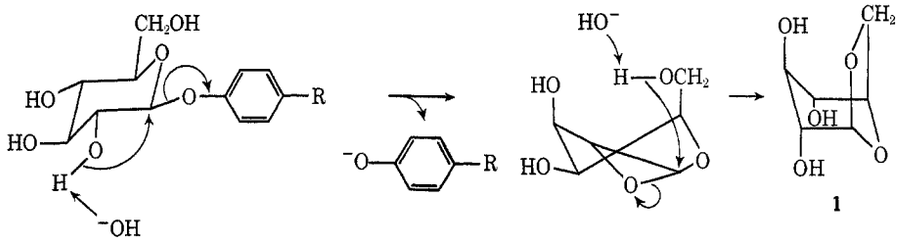
In the case of aryl-α-D-glucopyranosides, a nucleophilic aromatic substitution mechanism analogous to Scheme II was proposed.[8] This mechanism explains the fact that 1,6-anhydroglucopyranose is not formed when the α anomers are treated with alkali. However, it does not explain the formation of *p*-nitrophenol when the experiment is carried out with sodium methoxide in methanol. To resolve some of these uncertainties, the present work was undertaken. The knowledge concerning mechanisms of hydrolysis of *p*-nitrophenyl-α- and -β-D-glucopyranosides is desirable because they have been extensively used as substrates in the studies of α- and β-glucosidases.[9,10]

Results

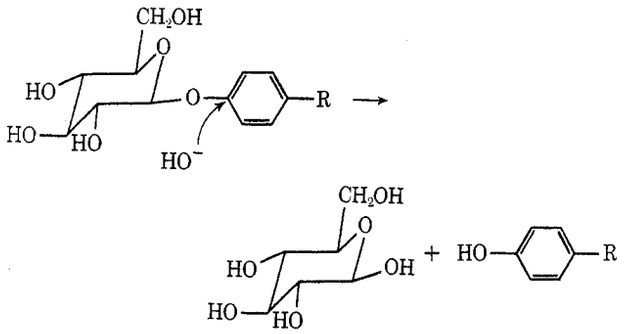
In the range of alkaline concentrations studied, the rate of *p*-nitrophenol liberation was first order in substrate concentrations until the hydrolysis is 50% completed. Figure 1 shows that the specific rate of alkaline hydrolysis of *p*-nitrophenyl-β-D-glucopyranoside (**3**)

(1) J. N. BeMiller, *Advan. Carbohyd. Chem.*, **22**, 25 (1967).
(2) B. Capon, *Chem. Rev.*, **69**, 407 (1969).
(3) C. E. Ballou, *Advan. Carbohyd. Chem.*, **9**, 59 (1954).
(4) E. M. Montgomery, N. K. Richtmeyer, and C. S. Hudson, *J. Amer. Chem. Soc.*, **65**, 3 (1943).
(5) A. Dyfverman and B. Lindberg, *Acta Chem. Scand.*, **4**, 878 (1950).
(6) C. M. McCloskey and G. H. Coleman, *J. Org. Chem.*, **10**, 184 (1945).
(7) R. C. Gasman and D. C. Johnson, *ibid.*, **31**, 1830 (1966).
(8) A. N. Hall, S. Hollingshead, and H. N. Rydon, *J. Chem. Soc.*, 4290 (1961).
(9) R. Heyworth and P. G. Walker, *Biochem. J.*, **83**, 331 (1962).
(10) M. V. Kelemen and W. J. Whelan, *Arch. Biochem. Biophys.*, **117**, 423 (1966).

SCHEME I



SCHEME II



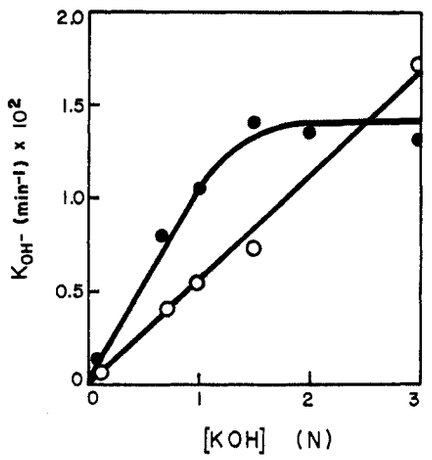


Figure 1.—Effect of hydroxide concentration on specific rates of hydrolysis of *p*-nitrophenyl-D-glucopyranosides for α anomer (●) and β anomer (○).

is first order with respect to hydroxide concentrations. For *p*-nitrophenyl-α-D-glucopyranoside (2), the linear relationship holds at low hydroxide concentrations but deviates at high concentrations, suggesting the formation of a kinetically significant intermediate. If one assumes that the alkaline hydrolysis of *p*-nitrophenyl-α-D-glucopyranoside proceeds *via* eq 1, the observed

$$2 + OH^- \underset{}{\overset{K}{\rightleftharpoons}} X \xrightarrow{k} P \qquad (1)$$

specific rate of alkaline hydrolysis (by equilibrium treatment) can be expressed by eq 2. K is the equilibrium

$$k_{OH^-} = \frac{kK[OH^-]}{1 + K[OH^-]} \qquad (2)$$

constant for the formation of the intermediate X, and k is the specific rate for the formation of product(s) P from X. The relationship describes the observed kinetic behavior; *i.e.*, at low hydroxide concentrations, k_{OH^-} is linearly related to $[OH^-]$ by $k_{OH^-} = kK[^-OH^-]$ whereas, at high hydroxide concentrations, k_{OH^-} is independent of $[OH^-]$ according to $k_{OH^-} = k$. Furthermore, the plot of $k_{OH^-}{}^{-1}$ *vs.* $[OH^-]^{-1}$ as shown in Figure 2 gives a straight line of intercept k^{-1} and slope $(kK)^{-1}$ from which k and K are estimated to be 1.55×10^{-2} min^{-1} and 4.17 mol^{-1}, respectively.

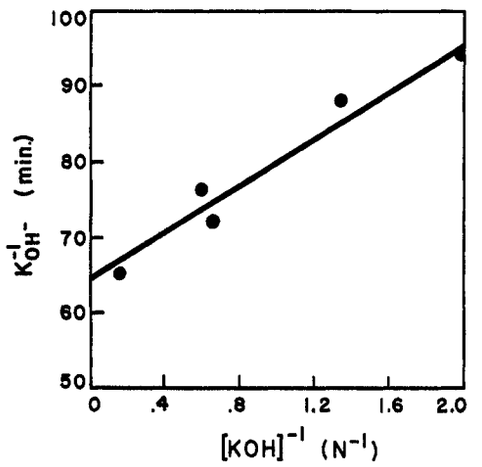


Figure 2.—Double reciprocal plot of specific rates of alkaline hydrolysis of *p*-nitrophenyl-α-D-glucopyranosides *vs.* hydroxide ion concentrations.

The results for *p*-chlorophenyl-α- and -β-D-glucopyranosides are shown in Figure 3. In these cases, the specific rates of alkaline hydrolysis are first order with respect to hydroxide concentrations and follow a linear relationship at low and high concentrations of base. These results again suggest that *p*-nitrophenyl-α-D-glucopyranoside is hydrolyzed by a mechanism different from other α derivatives or its β anomer.

Because of the presence of different mechanisms and the possibility of molecular rearrangement with subsequent degradation, kinetic studies alone do not provide sufficient information concerning mechanisms of alkaline hydrolysis. Alternative approaches were explored. An attempt was made to analyze hydrolysis products by gas chromatography, which has been used successfully for the analysis of glycoses and their derivatives.[11] Gas chromatographic analyses of hydrolysis products of *p*-nitrophenyl-α- and -β-D-glucopyranosides indicate that the α anomer is degraded by alkali to *p*-nitrophenol (retention time of 20.5 ± 1.0 min) and an unidentified major product (D with a retention time of 14.0 ± 1.0 min) which was shown to be the degradative product of D-glucose in alkaline solution. The work is in progress to isolate D for characterization. The β anomer yields, in addition to *p*-nitrophenol and D, 1,6-anhydroglucopyranose (retention time of 16.5 ± 0.5 min). Although D was not detected in the hydroly-

(11) (a) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Chem. Soc.*, **85**, 2497 (1963); (b) M. Bolan, and J. W. Steele, *J. Chromatogr.*, **36**, 22 (1968); (c) G. G. S. Button, K. B. Gibney, G. D. Jensen, and P. E. Reid, *ibid.*, **36**, 152 (1968).

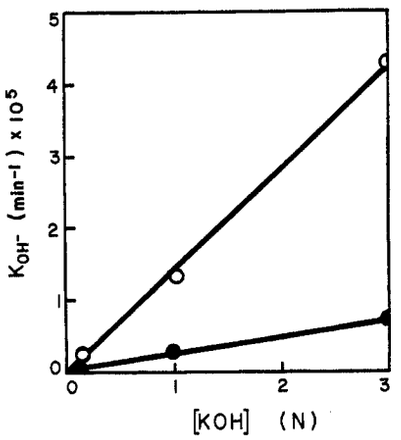
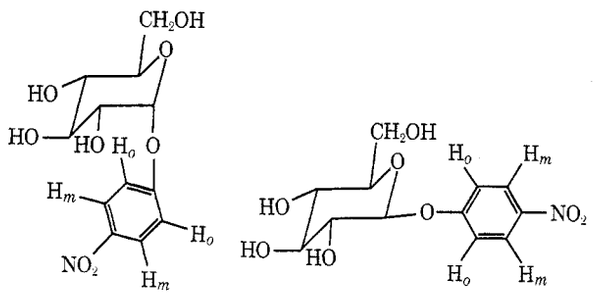


Figure 3.—Effect of hydroxide concentration on specific rates of hydrolysis of p-chlorophenyl-D-glucopyranosides for α anomer (●) and β anomer (○).

zate of phenyl-β-D-glucopyranoside, it was barely detectable in the hydrolyzate of p-chlorophenyl-β-D-glucopyranoside. None of three aryl-α-D-glucopyranosides yielded 1,6-anhydroglucopyranose. Both anomers produced small quantities of carboxylic acids such as lactic acid, suggesting the complexity of the degradative processes.

Nuclear magnetic resonance studies of alkaline hydrolysis provided unexpected results. p-Nitrophenyl-α-D-glucopyranoside (2) exhibits two pairs of aromatic protons: ortho protons (H_o) at δ 7.30 ppm (doublet, J = 9 cps) and meta protons (H_m) at δ 8.26 ppm (doublet, J = 9 cps). Immediately after the addition of 0.1 ml of 1.0 N NaOH, H_o and H_m split into a complex



2 3

multiplet centered at δ 7.20 ppm and a pair of doublets with a separation of 3.0 Hz. These signals broaden with time until complete disappearance. This is followed by the appearance of two new pairs of doublets corresponding to aromatic protons of p-nitrophenolate anion (Figure 4). By contrast, aromatic protons of p-nitrophenyl-β-D-glucopyranoside (3), H_o at δ 7.74 ppm (doublet, J = 10 cps) and H_m at δ 8.22 ppm (doublet, J = 10 cps), undergo broadening and disappearance without prior splitting (Figure 5). The reduction of aromatic nitro compounds by D-glucose in aqueous NaOH to produce amino aromatics is known;[12] however, p-aminophenol was not detected under these experimental conditions.

Decoupling experiments with 2 in aqueous NaOH were carried out. When the multiplet is irradiated, the signal at δ 8.26 ppm (H_m) turns into a singlet (Δf =

(12) H. W. Galbraith, E. F. Degering, and E. F. Hitch, *J. Amer. Chem. Soc.*, **73**, 1323 (1951).

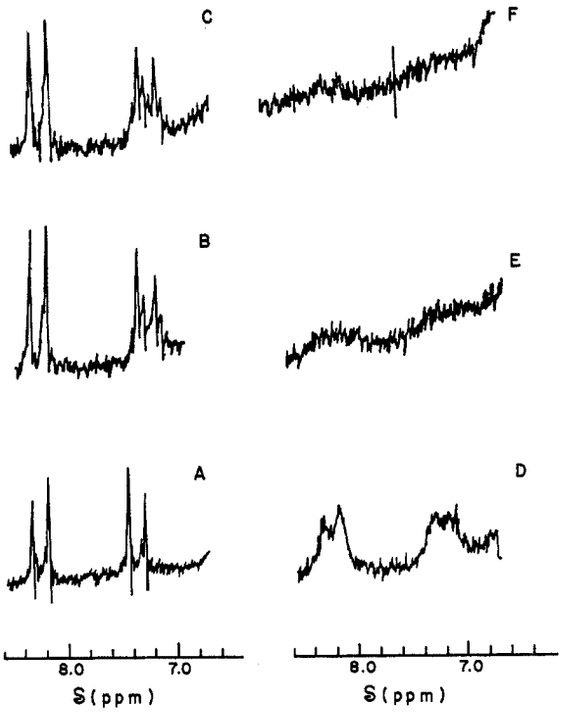


Figure 4.—Nmr studies of alkaline hydrolysis of p-nitrophenyl-α-D-glucopyranoside. 60-MHz spectra in H_2O were taken 0 (A), 6 (B), 12 (C), 16 (D), 22 (E), and 26 min (F) after the addition of NaOH.

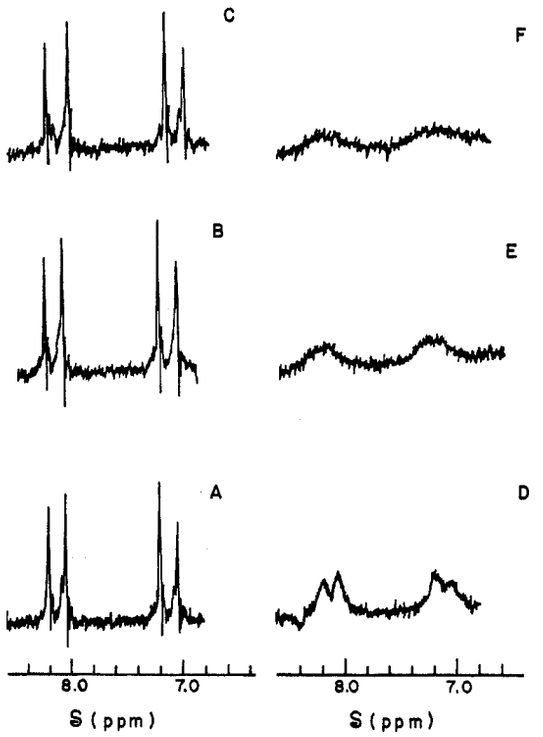


Figure 5.—Nmr studies of alkaline hydrolysis of p-nitrophenyl-β-D-glucopyranoside. 60-MHz spectra in H_2O were taken 0 (A), 12 (B), 24 (C), 40 (D), 45 (E), and 50 min (F) after the addition of NaOH.

100 Hz) and, when the low-field signal is irradiated, the multiplet (H_o) turns into a quartet (Figure 6).

The broadening and subsequent disappearance of nmr signals of aromatic protons are due to the formation of a paramagnetic species in the system. Figure 7 shows the esr signals corresponding to p-nitrophenoxyl

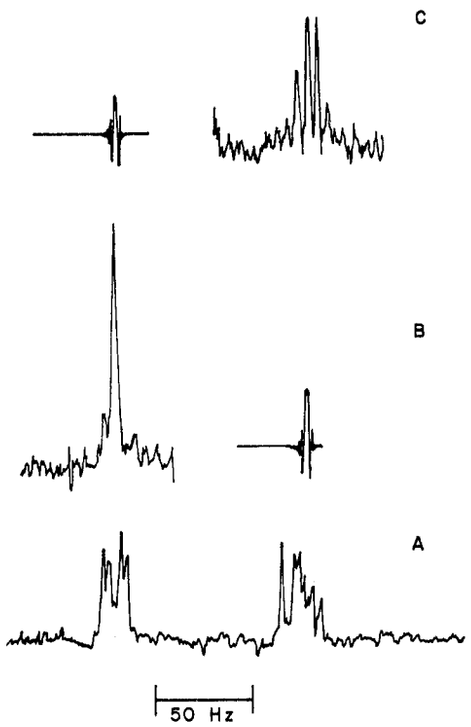


Figure 6.—Decoupling spectra (100 MHz) of aromatic region of *p*-nitrophenyl-α-D-glucopyranoside in NaOH before the irradiation (A) and irradiated at δ 7.30 ppm (B) and 8.26 ppm (C).

radical[13] which is formed by dissolving **2** in 1.0 *N* NaOH. Identical esr signals are also observed by dissolving **3** in 1.0 *N* NaOH or D-glucose and *p*-nitrophenol in 1.0 *N* NaOH.[14]

When the alkaline hydrolysis of **2** and **3** in NaOD (D_2O) and $NaOCH_3$ (CH_3OH) was studied by nmr spectroscopy, the following observations were made. (1) Nuclear magnetic spectra are not altered by replacing NaOH(H_2O) with NaOD(D_2O). (2) In $NaOCH_3$ (CH_3OH), **2** yields *p*-nitrophenol exclusively, whereas **3** produces *p*-nitrophenol and *p*-nitroanisol with an approximate ratio of 9:1.

Discussion

The alkaline hydrolysis of aryl-β-D-glucopyranosides in which the aryl group and the C-2 hydroxyl group of D-glucopyranose are in the trans 1,2 configuration proceeds *via* Scheme I or Scheme II depending on the electron-withdrawing character of aryl substituents. Phenyl-β-D-glucopyranoside is hydrolyzed *via* Scheme I, whereas *p*-nitrophenyl-β-D-glucopyranoside is hydrolyzed *via* mixed mechanisms of Scheme I and Scheme II. This is consistent with the observation that *p*-nitrophenyl-β-D-glucopyranoside in alkali yields 1,6-anhydroglucopyranose and the degradative product (D) of D-glucose. In methanolic $NaOCH_3$, the *p*-nitrophenyl group is liberated as *p*-nitrophenol and *p*-nitroanisole.

No general mechanism is ascribed to alkaline hydrolysis of aryl-α-D-glucopyranosides. A mechanism analogous to Scheme II is implicated from the study

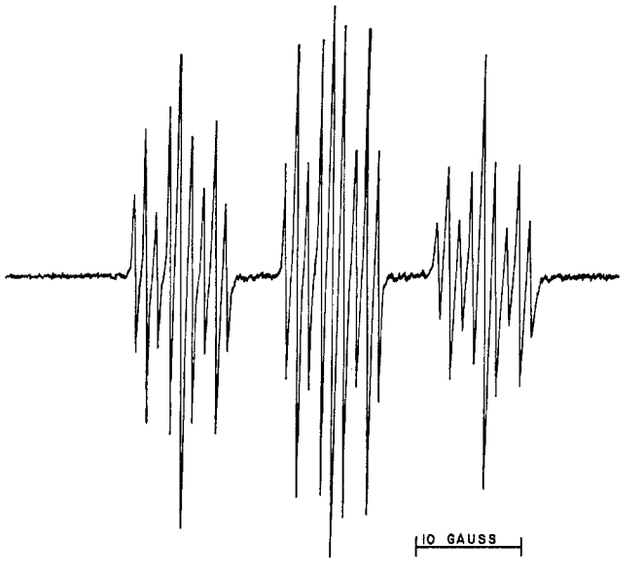


Figure 7.—Esr spectrum of *p*-nitrophenyl-α-D-glucopyranoside in NaOH. The spectrum was taken with a Varian Model E-9 esr spectrometer 10 min after dissolving 90 mg of *p*-nitrophenyl-α-D-glucopyranoside in 1.0 *N* NaOH solution (0.3 *M* solution).

of the effect of para substituents on the alkaline hydrolysis of aryl-α-D-glucopyranosides which exhibit a high positive reaction constant.[8] This mechanism is inconsistent with the formation of *p*-nitrophenol when *p*-nitrophenyl-α-D-glucopyranoside is hydrolyzed with $NaOCH_3$ in methanol. A mechanism involving nucleophilic substitution at the glucosyl carbon is considered unlikely for the *p*-nitro derivative because of the positive deviation of the *p*-nitro substituent from the Hammett plot[8] and the participation of the C-2 hydroxyl group in facilitating the alkaline hydrolysis of *p*-nitrophenyl-α-D-glucopyranoside (see below). The participation of the trans C-6 oxyanion in the alkaline hydrolysis of phenyl-α-D-galactopyranoside has been deduced from the formation of 1,6-anhydrogalactopyranose.[2] This mechanism is precluded because of the failure to detect 1,6-anhydroglucopyranose from *p*-nitrophenyl-α-D-glucopyranoside even after a prolonged alkali treatment.

The mechanism consistent with present experimental observations for *p*-nitrophenyl-α-D-glucopyranoside is presented in Scheme III.

That the formation of the intermediate which is in a rapid equilibrium with **2** and hydroxide ion is supported by the linear relationship between $k_{OH^-}{}^{-1}$ and $[OH^-]^{-1}$. Thus, the rate of alkaline hydrolysis of **2** is first order in base at low hydroxide ion concentrations and zero order in base at high hydroxide ion concentrations. The nature of the intermediate is characterized by nmr studies. The change in the aromatic region of the nmr spectrum of **2** upon the addition of NaOH suggests the formation of a Meisenheimer complex[15-18] of the type **4** in which the two ortho protons (H_o) become nonequivalent due to the restricted rotation when the ring is formed. The involvement of the C-2 hydroxyl group in the formation of **4** is deduced from following observations. (1) A molecular model

(13) K. Umenoto, Y. Deguchi, and T. Fujinaga, *Bull. Chem. Soc., Jap.*, **36**, 1539 (1963).

(14) Under the identical condition (30°), D-glucose in NaOH does not yield a radical, but on boiling an esr signal is detected. See also C. Lagercrantz, *Acta Chem. Scand.*, **18**, 1321 (1964).

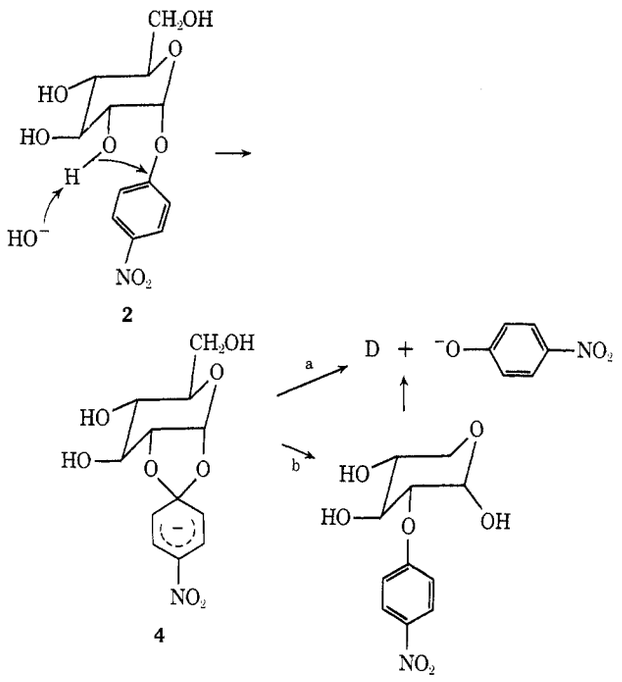
(15) J. Meisenheimer, *Justus Liebigs Ann. Chem.*, **323**, 205 (1902).

(16) K. L. Servis, *J. Amer. Chem. Soc.*, **87**, 5495 (1965).

(17) M. R. Crampton and V. Cold, *J. Chem. Soc. B*, 893 (1966).

(18) C. A. Fyfe, *Can. J. Chem.*, **47**, 2331 (1969).

SCHEME III



indicates that the C-2 hydroxyl oxygen is approximately 2.8 Å away from C-1 of the aryl ring when the aryl ring of *p*-nitrophenyl-α-D-glucopyranoside exists in a syn configuration with respect to the pyranose ring as in **2**. (2) The aromatic protons of *p*-nitrophenyl-β-D-glucopyranoside whose aryl ring exist in an anti configuration with respect to pyranose ring as in **3** do not exhibit nmr splitting upon the addition of NaOH. (3) A comparison of rates of the alkaline hydrolysis of *p*-nitrophenyl-α-D-glucopyranoside and its 2-deoxy derivative indicates that the C-2 hydroxyl group facilitates the liberation of *p*-nitrophenol.[19]

The exact nature of the release of *p*-nitrophenolate anion from **4** *via* a or b is not known. *p*-Nitrophenyl-α-D-glucopyranoside in alkaline solution yields *p*-nitrophenoxy radical[20] when the hydrolysis is approximately 50% completed. The radical is also formed immediately upon mixing D-glucose with *p*-nitrophenol in aqueous NaOH. It is likely that the radical formation is the consequence rather than the cause of the alkaline liberation of the *p*-nitrophenyl group. Recently Horton and Luetzow[21] observed the O-migration of the *p*-nitrophenyl group prior to its release. This is in agreement with the formation of **4**, which is hydrolyzed *via* pathway b of Scheme III.[22]

Experimental Section

Melting points were determined on a Fisher-Johns hot stage apparatus. Optical rotations in aqueous solutions were measured with a Perkin-Elmer Model 141 polarimeter. Ultraviolet spectra were taken with a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra were obtained with Varian Associates T-60 and XL-100 instruments. Chemical shifts are reported on the δ scale, parts per million (ppm) downfield from sodium 3-(trimethylsilyl)-1-propanesulfonate. Adjustments of pH were made with a Radiometer TTTlc. Phenols were obtained from Eastman Organic Chemicals. 1,6-Anhydroglucopyranose, mp 175–176.5°, was synthesized by Rayle Chemical Ltd., Edmonton, Alberta. Chromosorb W (AW-DMCS treated, 80–100 mesh) and XE-60 were purchased from Chromatographic Specialties Ltd. Tri-sil, *p*-nitrophenyl-α-D-glucopyranoside, mp 214–215°, [α] +210 (*c* 0.88), and *p*-nitrophenyl-β-D-glucopyranoside, mp 170–171°, [α] −96.4 (*c* 1.07), were products of Pierce Chemical Co.

Synthesis of Aryl-α- and -β-D-glucopyranosides.—Phenyl-α-D-glucopyranoside, mp 160–161°, $[\alpha]_D$ +179 (*c* 1.25), and *p*-chlorophenyl-α-D-glucopyranoside, mp 195–197°, $[\alpha]_D$ +59.3 (*c* 2.23), were synthesized by the condensation of penta-*O*-acetyl-β-D-glucopyranose[23] with phenol or *p*-chlorophenol in the presence of $ZnCl_2$[24] followed by O-deacetylation.[25] Phenyl-β-D-glucopyranoside, mp 176–177°, $[\alpha]_D$ −67.5 (*c* 1.03), and *p*-chlorophenyl-β-D-glucopyranoside, mp 179–179.5°, $[\alpha]_D$ −96.4 (*c* 1.08), were synthesized by the condensation of penta-*O*-acetyl-β-D-glucopyranose with phenol or *p*-chlorophenol in the presence of *p*-toluenesulfonic acid[26] followed by O-deacetylation.

Gas Chromatographic Analysis of Hydrolysis Products.—An F & M Model 402 gas chromatograph (Hewlett-Packard) equipped with a recorder Model 7101B (Moseley) and a Disc integrator Model 229 (Moseley) was used for the product analysis. Aryl-α- or -β-D-glucopyranoside (0.5 g) was dissolved in 30 ml of 0.1 *N* NaOH and incubated at 40°. At time intervals, an aliquot (0.5 ml) of the reaction mixture was withdrawn and neutralized with HCl. The hydrolyzate was evaporated to the dryness and trimethylsilated with 0.5 ml of Tri-sil.[27] The trimethylsilyl derivative (5 μl) was injected into the glass U-shaped column (6 ft × 0.125 in.) packed with 3.8% (w/w) XE-60 on Chromosorb W (AW-DMCS treated, 80–100 mesh). The injection temperature was 290° and the analysis (column temperature) was carried out isothermally at 150°. Products were detected by a hydrogen flame detector (270°). Occasionally, mannitol was added as the internal standard.

Spectrophotometric Determination of Rates of Hydrolysis.—*p*-Nitrophenyl-α- or -β-D-glucopyranoside (8×10^{-5} *M*) was dissolved in a KOH solution (ionic strength of the solution was maintained at $\mu = 0.3$ *M* with KCl) and placed into a Beckman DB spectrophotometer equipped with a recorder, a scale expander, and a thermostat circulator maintained at 40 ± 0.5°. Rates of hydrolysis were followed at 400 nm. For *p*-chlorophenyl-α- or -β-D-glucopyranoside (1.6×10^{-3} *M*) and phenyl-α- or -β-D-glucopyranoside (1.6×10^{-3} *M*), rates of hydrolysis were followed at 300 and 285 nm, respectively. The observed pseudo-first-order rate constants (k_{obsd}) were calculated from plots of log $[A_\infty - A_0)/(A_\infty - A_t)]$ *vs.* time (*t*) as usual. After substraction of the first-order rate constant for spontaneous hydrolysis (k_0), the observed rate constant gives the second-order rate constant for alkaline hydrolysis (k_{OH^-}).[28]

Nuclear Magnetic Resonance (Nmr) Spectroscopic Studies of Hydrolysis.—The hydrolysis of *p*-nitrophenyl-α- or -β-D-glucopyranoside (4.4×10^{-2} *M*) in 0.1 *N* NaOH (H_2O), 0.1 *N* NaOD (D_2O), or 0.1 *N* $NaOCH_3$ (CH_3OH) was followed in a Varian nmr spectrometer T-60 or XL-100. Sodium 3-(trimethylsilyl)-1-propanesulfonate or tetramethylsilane was used as the internal standard for aqueous or methanol solution, respectively.

Registry No.—**2**, 3767-28-0; **3**, 2492-87-7.

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