7% SE-30 and 1.5% Carbowax 20M 6-ft column. All reactions were run at reflux and were irradiated. The reactions were continued until the reaction mixture gave a negative test with starch-potassium iodide paper. A description of the oxidation of 2,6-dimethyl-4-heptanol with NIS is given in detail. The other two reactions were performed in a similar manner.

Reaction of 2,6-Dimethyl-4-heptanol with NIS. Four milliliters of a CCl_4 solution containing 2,6-dimethyl-4-heptanol (1.57 mmol) and bromobenzene (0.93 mmol) was added to a 10-ml pear-shaped flask. To this solution was added 0.182 g (0.809 mmol) of NIS. The mixture was irradiated, heated at reflux, and stirred for 6 hr. Vpc analyses indicated a 39% yield of 3-methyl-1-isobutyltetrahydrofuran, a 3% yield of 2,6-dimethyl-4-heptanone, and 2% yields of 2-methyl-1-iodopropane and 3-methylbutanal.

Two reactions (with silver acetate added to reduce the decomposition of NIS by HI) produced 42 and 45% yields of the tetrahydrofuran product with the other products found in the 2-4% range. [The addition of silver acetate generally gave a small (5-7%) increase in the yield of tetrahydrofuran with no change in the percentage of the other products.]

Oxidation of Cyclopentanol with NIS. Five oxidations of cyclopentanol with NIS were performed. Vpc analyses of the reaction mixtures, after 3 hr, showed only trace amounts of cyclopentanone. The ω-iodopentanal was not found on the vpc. Evaporation of the CCl_4 solvent, after filtration of the reaction mixture, produced an oil. An nmr analysis of the oil showed a triplet at δ 9.61 (CHO) and 3.27 (ICH_2) and a complex multiplet at δ 1.6-2.0 ($CH_2CH_2CH_2$). A 2,4-dinitrophenylhydrazone derivative of the ω-iodoaldehyde gave a solid melting at 126-128°. (The 2,4-dinitrophenylhydrazone derivative[4] of the product obtained from the oxidation of cyclopentanol with HgO and I_2 melted at 127-128°.)

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Registry No. **1**, 611-69-8; **2**, 96-41-3; **3**, 108-82-7; NIS, 516-12-1.

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Intramolecular C-2 → C-1 Hydrogen Transfer Reactions during the Conversion of Aldoses to 2-Furaldehydes[1,2a]

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Sugar 1,2-enediols have been suggested as intermediates in acid-catalyzed dehydration reactions and alkaline degradation reactions, as well as in the interconversion of aldoses and related 2-ketoses[3,4] (the Lobry de Bruyn-Alberda van Eckenstein transformation). In previous experiments designed to test the importance of 1,2-enediols and related enolic structures as intermediates in dehydration reactions, sugars were converted to 2-furaldehydes in acidified deuterium oxide or in tritiated water.[5] The finding that D-xylose is converted in acidified, tritiated water to 2-furaldehyde which is devoid of carbon-bound isotope[5] suggests that 1,2-enediols, if formed, further react immediately. Otherwise significant isotope incorporation would have been detected at the aldehyde carbon atom of 2-furaldehyde as a result of aldose-ketose interconversion. It has recently been found, however, that D-glucose is converted to D-fructose in acidic solution *via* a reaction involving an intramolecular transfer of hydrogen from C-2 of D-glucose to C-1 of D-fructose.[6,7] In strong acid (2 *N* sulfuric acid), the transfer appears to be complete and involves an isotope effect (K_h/K_t) of 4.3. Thus, in this case, the data are more consistent with a reaction mechanism involving an intramolecular C-2 → C-1 hydride transfer rather than the more generally accepted one involving a 1,2-enediol intermediate. These data suggest that aldose-ketose interconversion could easily have occurred, as a result of hydride transfer reactions, during dehydration reactions and remained undetected during isotope acquisition experiments.

The purpose of the present work was to evaluate the importance of C-2 → C-1 hydride transfers during some typical dehydration reactions. This was studied by preparing D-xylose and D-glucose specifically tritiated on C-2 and converting them to respectively 2-furaldehyde (I) and 5-(hydroxymethyl)-2-furaldehyde (II) in acidified water. A determination of the amount of carbon-bound tritium on the aldehyde carbon (which corresponds to C-1 of the original aldose) of I and II would provide information on the extent of C-2 → C-1 transfer occurring during the dehydration reactions and, in addition, provide qualitative information on the extent of aldose-ketose interconversion occurring during the dehydration reactions.

D-Glucose-2-^3H was prepared by converting D-fructose 6-phosphate to D-glucose 6-phosphate in tritiated water using phosphoglucose isomerase, followed by treating the resulting crystalline D-glucose 6-phosphate with alkaline phosphatase. This procedure was essentially the same as was used to prepare D-glucose-2-^2H.[8,9] That the D-glucose was tritiated only at C-2 is evident from the known[10,11] specificity of the enzyme, which produces, at equilibrium in tritiated water, only D-glucose-2-^3H 6-phosphate and D-fructose-*1*-^3H 6-phosphate, with no isotope being present at C-1 of the aldose. Further proof of this labeling specificty also observed in the past when the same procedure was used to prepare D-glucose-2-^2H,[8] which, from its nmr spectrum, was observed to be deuterated only at C-2. D-Xylose-2-^3H was prepared from D-glucose-2-^3H by converting the latter to 1,2-*O*-isopropylidene-D-glucofuranose followed by periodate oxidation to give 1,2-*O*-isopropylidene-D-xylo-1,5-dialdose-2-^3H. Reduction of the latter derivative with sodium borohydride gave 1,2-*O*-isopropylidene-D-xylofuranose-2-^3H, which was hydrolyzed to give chromatographically pure D-xylose-2-^3H.

D-Glucose-2-^3H was converted to II and a portion isolated as the crystalline bisether[12] oxybis(5-methylene-2-furaldehyde). The specific activity of the compound was 14% that of the starting sugar, indicating that each furan residue retained 7% of the radiochemical activity of the original D-glucose-2-^3H. A further portion of II was oxidized to 2-furoic acid which contained negligible activity indicating that all of the carbon-bound tritium was located on the aldehyde carbon of II. Considering the isotope effect involved for the conversion of D-glucose-2-^3H to D-fructose-*1*-^3H, approximately 30% of the dehydration reaction would involve hydride transfer if the reactant were protiated rather than tritiated.

D-Xylose-2-^3H was converted to I in acidified water in 33% yield. An aliquot of I was converted to the crystalline phenylhydrazone which contained 13% the activity of the starting sugar. Conversion of a further aliquot of I to 2-furoic acid which was radiochemically inert showed that all of the radiochemical activity was located on the aldehyde carbon of I.

The data collected established that intramolecular C-2 → C-1 hydrogen transfers occur during dehydration reactions, probably as a result of conversion of aldoses to ketoses as was established for the D-glucose to D-fructose conversion. It is noteworthy that analogous transfers in proceeding from 2-ketoses to aldoses have not yet been established in the case of chemical catalysis, and, for a complete assessment of the role and importance of reaction pathways involving intramolecular hydrogen shifts *vis-à-vis* 1,2-enediols, substantially more data will be required.

Experimental Section

Materials and Methods. Radiochemical activities were determined on a Packard Tri-Carb scintillation counter using a scintillant composed of two parts of a solution composed of 2 l. of toluene, 8.25 g of 2,5-diphenyloxazole (PPO), and 0.25 g of 1,4-bis-2-(4 methyl-5-phenyloxazole)benzene (Me_2POPOP), and one part of Triton X-100 (v/v). Ultraviolet spectra were obtained using a Coleman Model 124 recording double beam spectrophotometer. Thin-layer chromatography was performed using silica gel HF support with chloroform-methanol (95:5) as the eluent. Spots were visualized by uv light or by spraying with 10% ethanolic sulfuric acid followed by heating at 110° for 10 min. Paper chromatography was performed by the descending method using ethyl acetate-formic acid-acetic acid-water (18:1:3:4, v/v) as irrigant followed by visualization with aniline hydrogen phthalate spray reagent.[13] D-Glucose-2-^3H was prepared enzymatically as described in previous reports[6,7] and was diluted to a suitable level, as needed, with inert D-glucose, followed by recrystallization from water-ethanol.

Preparation of D-Xylose-2-^3H. D-Glucose-2-H (100 g, specific activity = 1.0 μCi/mmol) was converted to 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose[14] (mp, mmp 108°) in 54% yield and then to 1,2-*O*-isopropylidene-D-glucofuranose,[14] which after recrystallization from ethyl acetate gave 25 g of material (mp, mmp 160°). This material was converted to syrupy 1,2-*O*-isopropylidene-D-xylo-1,5-dialdose-2-^3H by periodate oxidation,[15] and then reduced to 1,2-*O*-isopropylidene-D-xylofuranose with sodium borohydride.[15] The resulting syrupy material was dissolved in 100 ml of 0.1 *N* sulfuric acid and refluxed for 1 hr. After neutralization with barium carbonate, the resulting filtered solution was evaporated to dryness at reduced pressure to give a syrup which contained only D-xylose as evidenced by paper chromatography. To this syrup was added .5 g of inert D-xylose and sufficient water to produce a thick syrup, which slowly crystallized. The resulting crystalline D-xylose-2-^3H, which was isolated on a filter, washed with methanol, and dried *in vacuo*, had a specific activity of 2.42×10^{-2} μCi/mmol.

Conversion of D-Glucose-2-^3H to II. D-Glucose-2-^3H (200 g, specific activity = 0.916 μCi/mmol) was added to 2400 ml of 2 *N* sulfuric acid, and the solution was refluxed for 3.5 hr. The solution was extracted three times with chloroform and the extract was dried over anhydrous sodium sulfate and evaporated to dryness. The II contained by the residue was isolated by preparative thin-layer chromatography and identified by its chromatographic flow rate, which was identical with a standard sample, and from its uv spectrum (λ_{max} 278 mμ), which was identical with that of a standard sample. The overall yield of II was approximately 15 mg as determined from spectral measurements. Approximately half of this sample was converted to the oxybis(5-methylene-2-furaldehyde)[12] by heating at 100° for 2 hr. The resulting material (mp 113°) had a chromatographic flow rate and exhibited a uv spectrum identical with those of an authentic sample. This material, amounting to 5.7 mg, was counted and found to have a specific activity of 0.154 μCi/mmol. A further sample of II was converted to 5-(hydroxymethyl)-2-furoic acid,[8] which was purified by preparative thin-layer chromatography and had a thin-layer chromatographic flow rate and a uv spectrum identical with those of an authentic sample, amounted to 1.9 mg and had a specific activity of 8×10^{-3} μCi/mmol.

Conversion of D-Xylose-2-^3H to I. This conversion was made in 6 *N* sulfuric acid starting with 2.0 g of sugar (specific activity of 2.42×10^{-2} μCi/mmol) as described previously.[5] The 2-furaldehyde-^3H contained in 250 ml of distillate was identified by its ultraviolet spectrum which showed maxima at 227 and 278 mμ. Assuming a molar absorptivity of 16,000,[16] the absorbance at 278 mμ indicated a yield of 33%. The I in a 100-ml aliquot of the distillate was converted to 2-furaldehyde phenylhydrazone-^3H (mp, mmp 95°) which had a specific activity of 3.25×10^{-3} μCi/mmol. The I in a further 100 ml aliquot was converted to 2-furoic acid (mp, mmp 131°) which after purification by sublimation at 110° and 0.3 mm was found to be radiochemically inert.

Registry No.—I, 98-01-1; II, 67-47-0; D-xylose, 58-86-6; D-glucose, 50-99-7; 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose, 582-52-5; 1,2-*O*-isopropylidene-D-glucofuranose, 18549-40-1; oxybis(5-methylene-2-furaldehyde), 7389-38-0; 2-furaldehyde phenylhydrazone, 2216-75-3; 2-furoic acid, 88-14-2.

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Preparation and Characterization of Propiolyl Chloride

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Propiolyl chloride is the simplest of the acetylenic acid chlorides. We became interested in the compound, from the spectroscopic point of view, as part of a program to study the influence of conjugation and halogen substitution on the energies and stabilities of (π*, n) electronic states. While unsuccessful attempts to prepare propiolyl chloride have been reported,[1] brief mention is made in the chemical patent literature of its use in dye and plastics manufacture.[2]

The present communication describes a straightforward synthesis from propiolic acid and phosphorus pentachloride. The major product of the reaction is identified as

$$HC{\equiv}CCOOH + PCl_5 \longrightarrow HC{\equiv}CCOCl + POCl_3 + HCl$$

propiolyl chloride from spectroscopic and chemical evidence. The boiling point of the propiolyl chloride prepared in this way does not correspond to that of a compound prepared by pyrolysis of α,β-dichloropropionyl chloride, and claimed by Schaefer[2b] to be propiolyl chloride. Our product boils at 58–60° while Schaefer reports a boiling point in the range 72–75°.