PHOTOCHEMICAL REACTIONS OF CARBOHYDRATES

PART V. THE PHOTOLYSIS OF CERTAIN SUGAR OXIMES A PHOTOCHEMICAL WOHL DEGRADATION*

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ABSTRACT

Ultraviolet photolysis of the oximes of D-galactose, D-mannose, D-glucose, D-ribose, D-arabinose, D-xylose, and D-lyxose, and also the *O*-methyl oxime of D-galactose, is reported. With the exception of D-glucose oxime (**4**), the photochemical process in each case leads to an iminolactone that spontaneously loses hydrogen cyanide to form a sugar one carbon shorter in chain length. Thus, D-galactose oxime (**1**) upon photolysis forms D-galactonoimino-1,5-lactone (**10**) in 81% yield and D-lyxose (**9**) in 14% yield. The unstable **10** decomposes on standing to give **9** and hydrogen cyanide. Ultraviolet irradiation of the oximes of D-ribose and D-arabinose gave the corresponding iminolactones only; D-xylonoiminolactone and D-threose were obtained from D-xylose oxime (**7**); D-threose was obtained in 18.0% yield from D-lyxose oxime (**8**). A mechanism for this photochemical process is proposed and discussed.

INTRODUCTION

Recent investigations[1] have led to a study of the light-induced reactions of sugar oximes, which are of particular interest for their role as intermediates in the Wohl degradation[2]. This study has shown that the Wohl degradation can be initiated via photochemical reaction.

RESULTS

Irradiation of D-galactose oxime (**1**) and of *N*-D-galactopyranosyl(methoxyamine) (**2**, D-galactose *O*-methyl oxime) led to the complete disappearance of the oximes after 1 h, and to the production of two chromatographically separable components. The minor component (14%) was identified as D-lyxose (**9**). The major one (81%) was an unstable nitrogen-containing syrup that decomposed on standing to

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give **9** in high yield. This syrup was deduced to be D-galactonoimino-1,5-lactone (**10**) from i.r. data; from acetylation and acid hydrolysis of the syrup, which gave D-galactononitrile pentaacetate (**11**) and D-galactono-1,4-lactone (**12**), respectively; and because the photolysis of **1** and **2** gave the same products. The photolysis of D-mannose oxime (**3**) proceeded as for **1**; however, the yields of iminolactone and pentose were significantly less. A different photochemical reaction occurred during the irradiation of D-glucose oxime (**4**), and only trace amounts of the iminolactone and pentose were formed. Chromatographic analyses of the products from the irradiation of D-ribose oxime (**5**) and D-xylose oxime (**7**) showed the probable presence of the corresponding iminolactones and tetroses; D-arabinose oxime (**6**), iminolactone, only; D-lyxose oxime (**8**), and tetrose (see Table I).

TABLE I

PRODUCTS FROM THE PHOTOLYSIS OF SUGAR OXIMES[a]

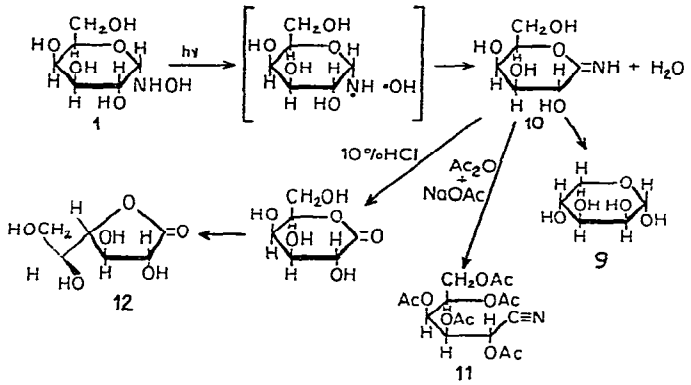
Compound		*Yields of irradiation products (%)*		
		Iminolactone	*Pentose*	*Tetrose*
D-Galactose oxime	(1)	81	14	
N-D-Galactopyranosyl(methoxyamine)	(2)	81	14	
D-Mannose oxime	(3)	33[b]	0	
D-Mannose oxime[c]	(3)		36[d]	
D-Glucose oxime	(4)	trace	trace	
D-Ribose oxime	(5)	22.7[b]		trace
D-Arabinose oxime	(6)	27.6[b]		0
D-Xylose oxime	(7)	14.8[b]		3.1[e]
D-Lyxose oxime	(8)	0.0		18.0[e]

[a]Acetylated immediately after photolysis. [b]Isolated as the peracetylated nitrile. [c]Acetylated after being kept for 14–21 days at 25°. [d]Isolated as the tetraacetate. [e]Isolated as the triacetate.

DISCUSSION

The presence of the appropriate iminolactone and/or pentose or tetrose in the products from the u.v. irradiation of eight aldose oximes has led us to propose the following mechanism for the photochemical reaction of oximes (Scheme 1, illustrated with **1**). This mechanism describes the reaction process as being initiated by photochemical homolysis of the N–O bond in the oxime (hydroxylamine) system, followed by transfer of a hydrogen atom from carbon to oxygen, resulting in the formation of water and D-galactonoimino-1,5-lactone (**10**). Supporting the proposal for such a reaction process is the report[3] of an analogous type of reaction observed in a heterocyclic system that is quite different.

Although the major photoproduct (**10**) appears to result directly from the photochemical rupture of the N–O bond, the minor product from photolysis of **1** arises as a result of a nonphotochemical, tautomeric ring-opening of **10** to form D-galactononitrile, which by loss of hydrogen cyanide yields D-lyxose (**9**). Spontaneous loss of hydrogen cyanide from a sugar nitrile is a known reaction[4].



The possibility existed that the reactions observed in the photolysis of **1** were, in fact, resulting from a chain-reaction process that was light-initiated. In an experiment designed to test this possibility, azobis(2-methylpropiononitrile) was decomposed in the presence of **1**. The oxime was quantitatively recovered from this reaction mixture. A similar decomposition of benzoyl peroxide in the presence of **1** also gave no reaction; thus, it is unlikely that a free-radical chain-reaction is responsible for the transformation of oxime to iminolactone.

The photochemical shortening of the carbon chain of sugars by one carbon atom offers the advantages of a reaction occurring at room temperature in a neutral solvent without the addition of catalytic species or reagents to the reaction mixture. Irradiation of the D-galactose oximes (**1** and **2**) produced **9** in high yields. Reactions competing with the photochemical Wohl degradation in the photolysis of the other hexose oximes (**3** and **4**) were complex, and prevented production of a single photoproduct in significant yield. Of the four pentose oximes, only D-lyxose oxime participated in photochemical chain-shortening to any meaningful extent; D-threose was obtained in 18.0% yield. In the case of the sugar oximes, the usefulness of the photochemical process suffers primarily from the wide variation of product yields, and this process cannot be considered to be a general one for the stepwise shortening of the carbon chain of sugars.

EXPERIMENTAL

General procedures. — In each reaction, the oxime (1.00 mmole) in 300 ml of methanol was irradiated at 25°, with constant stirring, with the light from a 450-watt Hanovia, high pressure, quartz, mercury-vapor lamp that had been lowered into a water-cooled, quartz immersion-well. Prepurified nitrogen was passed through the solution for 1 h prior to the irradiation, and a slow stream of nitrogen was continued during photolysis. Methanol was evaporated from the irradiation mixture at 30°. Acetylation of the residual syrups, from the irradiation mixtures and recovered adsorbates from cellulose-column chromatography, was achieved by the action of acetic anhydride (5 ml) and powdered, fused sodium acetate (200–300 mg) until the dissolu-

tion of the reactants was completed (30–60 min) and an additional h of heating at the same temperature. Solvents were evaporated off under diminished pressure at 80–85°; the residual acetic anhydride was removed by evaporation of ethanol (5 ml) from the residue. The latter, mixed with 10 ml of benzene, was added at the top of a column (2.3 × 15 cm) of 27 g of acetone-washed mixture of 5 parts (by wt.) of a hydrated magnesium acid silicate (Magnesol, manufactured by the Westvaco Chemical Division of the Food Machinery and Chemical Corp., South Charleston, West Virginia) with 1 part Celite No. 535 (produced by Johns–Mansville Corp., New York, New York), prewetted with 10 ml of benzene. The chromatograms were developed with 60 ml of 50:1 or 135 ml of 100:1 (v/v) benzene–*tert*-butyl alcohol. Zones were detected with a 1% solution of potassium permaganate in 10% sodium hydroxide. Components were recovered from the adsorbent with acetone. T.l.c. was performed on cellulose (~160 μm thick) on polyester sheets (Eastman Kodak Co., Rochester, New York) with 85:15 (v/v) acetone–water as the developer and *p*-anisidine hydrochloride as the indicator.

Unacetylated residual syrups from the photolysis reactions were placed on a column (215 × 80 cm) of cellulose powder that was slurry-packed in 85:15 acetone–water and conditioned by the successive percolation of 500 ml of 80:20 acetone–water and 500 ml of 85:15 acetone–water prior to addition of the adsorbate. The chromatograms were developed with 1,000 ml of 85:15 acetone–water, the column effluent being collected in 20-ml fractions.

Chromatography of the products from irradiation of hexose oximes. — *A.* D-*Galactose oxime* (**1**). T.l.c. indicated the presence of a fast-moving component near the solvent front, followed by a substance having the same mobility as D-lyxose, and a component near the origin. The first substance detected in the effluent from the cellulose column (fractions 15–17) was a syrup, isolated in 81% yield, that showed strong i.r. absorption at 6.05 μm. Acetylation of this material yielded a crystalline substance which, after two recrystallizations from ethanol, had a m.p. 138–139° and was found to be identical by i.r. and n.m.r. spectroscopy, and by m.p., with D-galactononitrile pentaacetate (**11**, lit.[5] m.p. 138–139°), mixed melting point with **11** was unaltered. When this syrup (fractions 15–17) was refluxed with 10% hydrochloric acid for 1 h immediately after being recovered from the column, the cooled solution extracted with ether, and the ether evaporated, a crystalline material identical with authentic D-galactono-1,4-lactone (**12**) was obtained. Finally, after being kept for 2 days at 20–25°, this syrup decomposed to D-lyxose.

The second product to appear in the effluent (fractions 20–25) from the cellulose column possessed the same mobility on powdered cellulose as D-lyxose. Acetylation of this substance gave crystalline α-D-lyxose tetraacetate (**13**), recrystallized from 95% ethanol; m.p. 92–93° (lit.[6] m.p. 93–94°); the mixed m.p. with **13** was unaltered.

B. N-D-*Galactopyranosylamine* (**2**). This analysis was identical with that described for the chromatography of the irradiation mixture from D-galactose oxime.

C. D-*Mannose oxime* (**3**) *acetylated immediately after irradiation.* T.l.c. of these irradiated products (before acetylation) showed a major, fast-moving component

near the solvent front followed by a minor component having a mobility identical to that of D-arabinose, and other major components near the origin. Column chromatography of the acetylated irradiation products revealed the presence of a major zone (40.8% of the recovered adsorbate) at the top of the column and a minor zone (5.5% of recovered adsorbate) in the middle section. Another major zone (33.2% of recovered adsorbate) was located in the lower portion of the column; nucleation with D-mannononitrile pentaacetate (**14**) of this zone yielded crystals, m.p. 91–92° (recrystallized from ethanol) (lit.[7] m.p. 92–93° for **14**), mixed m.p. with **14** was unaltered.

D. D-*Mannose oxime* (**3**) *acetylated after irradiation products were kept for 14–21 days at 25°*. T.l.c. of these irradiated products showed a major component having a mobility identical to D-arabinose, followed closely by another major component, and a major component near the origin. Column chromatography of the acetylated irradiation products showed a zone in the upper portion of the column (42.4% of the recovered adsorbate). A zone found in the middle of column (36.0% of the recovered adsorbate) yielded crystals, m.p. 94–95° (recrystallized from ethanol) whose mixed m.p. with β-D-arabinose tetraacetate was unaltered. A zone (21.6% of the recovered adsorbate) isolated from the lower portion of the column also yielded crystals which were not identified.

E. D-*Glucose oxime* (**4**). T.l.c. of the irradiated products from **4** indicated the probable presence in minute proportion of a component migrating near the solvent front, followed by a product having a mobility identical with that of D-arabinose; the major products of the irradiation remained near the origin. Column chromatography of the acetylation products from the irradiation of **4** showed two major zones (75.3% of the recovered adsorbate) located at and near the top of the column. Two minor zones appeared near the middle of the column, the lower zone yielding crystals (23% of the recovered adsorbate). Two minute zones (1.5 % of the recovered adsorbate) were found in the pentose tetraacetate–hexononitrile pentaacetate region in lower section of the column.

Chromatography of the products from the irradiation of the D-*pentose oximes.* — *F.* D-*Ribose oxime* (**5**). T.l.c. of the irradiated products from **5** showed the probable presence of a major component migrating near the solvent front, followed by a substance having the mobility of D-ribose, together with a major component(s) near the origin. Column chromatography of the irradiation products after acetylation revealed a zone(s) near the top of the column (41.4% of the recovered adsorbate). A zone located just above the middle of the column (11.2% of the recovered adsorbate) yielded crystals after nucleation with β-D-ribopyranose tetraacetate. A zone detected just below the middle of the column (30.7% of the recovered adsorbate) yielded crystals, m.p. 68–69° (recrystallized from 95% ethanol) [lit.[8] m.p. 71–72° for D-ribononitrile tetraacetate (**15**)]; mixed m.p. with authentic **15** was unaltered. Rechromatography of the residual syrup from this zone yielded additional **1**. A minor zone was detected in the tetrose triacetate section of the column.

G. D-*Arabinose oxime* (**6**). T.l.c. of the irradiated products from **6** gave results essentially the same as those obtained with the irradiated products from **5**. Column

chromatography of the acetylated products from the irradiation of **6** afforded a chromatogram similar to that obtained from irradiated **5** after acetylation. A zone (27.6% of the recovered adsorbate) located near the middle of the column yielded crystals, m.p. 119–120° (recrystallized from ethanol) [lit.[9] m.p. 120–121° for D-arabinononitrile tetraacetate (**16**)]; the mixed m.p. with **16** was unaltered.

H. D-*Xylose oxime* (**7**). T.l.c. of the irradiated products from **7** indicated the probable presence of two products migrating near the solvent front, followed by a product having the mobility of D-xylose, and a major component(s) near the origin. Column chromatography of the irradiation products after acetylation gave results similar to those obtained from acetylated **5**. A zone detected just above the middle of the column (9.0% of the recovered adsorbate) yielded crystals, after nucleation with β-D-xylose tetraacetate. A zone located just below the middle of the column (28.4% of the recovered adsorbate) was rechromatographed, and two major zones were obtained. The upper zone (14.8% of the originally recovered adsorbate) yielded crystals, m.p. 78–79° (recrystallized from ethanol) [lit.[10] m.p. 81–82° for D-xylononitrile tetraacetate (**17**)]; the mixed m.p. with **17** was unaltered. The lower zone (3.1% of the adsorbate originally recovered) yielded crystals on nucleation with D-threose triacetate (**18**), m.p. 114–115° (recrystallized from ethanol) [lit.[11] m.p. 113–114°, 117–118°]; the mixed m.p. with **18** was unaltered.

I. D-*Lyxose oxime* (**8**). T.l.c. of the irradiated products showed a major component near the solvent front and another major one near the origin. A minor component having the mobility of D-lyxose was noted also. Column chromatography of the acetylated irradiation products from **8** gave a major zone at the top of the column (34.4% of the recovered adsorbate) and another major zone just below the middle of the column (37.8% of the recovered adsorbate). A zone just above the middle of the column (14.5% of the recovered adsorbate) yielded crystals after nucleation with α-D-lyxose tetraacetate. Rechromatography of the lower major zone afforded one major zone (18% of the originally recovered adsorbate), which gave crystals after nucleation with D-threose triacetate, m.p. 115–116°; the mixed m.p. with **18** was unaltered.

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