Note

Photochemical reactions of carbohydrates Part III*. The irradiation of D-galactose azine**

R. W. BINKLEY The Cleveland State University, Cleveland, Ohio 44115 (U. S. A.)

AND W. W. BINKLEY The New York Sugar Trade Laboratory, 37 Warren Street, New York, N. Y. 10007 (U. S. A.) (Received September 5th, 1969)

As a result of a continuing interest in the application of photochemical reactions to carbohydrate chemistry, we have studied the photochemistry of D-galactose azine (1). Our reason for selecting this azine system for study was the possibility that it would be photochemically converted into D-galactononitrile (2). Such a transformation seemed reasonable since the photolysis of aromatic aldazines in the presence of oxygen produces nitriles in high yield^{1,2}.

$$PhCH = NN = CHPh \qquad \frac{h\nu}{O_2} \qquad PhC \equiv N$$

Since sugar azines are readily obtained from sugars³, a photochemical conversion of an azine into a nitrile would provide a new and useful route for the synthesis of sugar nitriles. This paper presents the results of a photochemical investigation of 1.

Direct irradiation of 0.50 mmole of 1 in methanol under oxygen with a 450-watt Hanovia mercury-vapor lamp led to essentially complete disappearance of 1 after 2.0 h. Surprisingly, however, the i.r. spectrum of the crude reaction mixture showed no absorption in the nitrile region (4.4–4.6 μ m). In addition, analysis of the reaction mixture by t.l.c. in comparison with D-galactononitrile (2) showed that, although several photoproducts were formed, none of the expected nitrile 2 was present. A second irradiation, identical with the first but under nitrogen, also showed essentially complete decomposition of the starting material after 2.0 h, but no nitrile 2 was formed (i.r. spectrum, t.l.c.). Of the products formed by irradiation of 1 under nitrogen, only two appeared (by t.l.c.) to be the same as those formed during the similar irradiation under oxygen.

Thick-paper chromatographic analysis of the products from the irradiation made under oxygen led to the isolation of two sugars, identified as D-galactose (37%) and D-lyxose (23%). These two compounds were also isolated in 32% (D-galactose)

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and 14% (D-lyxose) yield from the irradiation under nitrogen. Control experiments showed that D-galactose azine (1) was stable in the absence of light under the conditions of reaction and isolation.

A possible mechanism for the formation of D-lyxose and D-galactose from the photolysis of D-galactose azine (1) is shown in Scheme I.



EXPERIMENTAL

General methods. — Solutions were evaporated below 50° under diminished pressure unless stated otherwise. Melting points were determined with a Fisher-Johns melting-point apparatus (Fisher Scientific Co., Pittsburgh, Pa.) and are uncorrected. X-Ray powder diffraction data give interplanar spacings, Å, for CuK α radiation. Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak.

Irradiation. — In each reaction the stirred solution of p-galactose azine (1) was irradiated at 20° with 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 irradiation and a slow stream of nitrogen was continued during photolysis. No filter was used. Solutions of the irradiation mixtures were evaporated below 30° under diminished pressure before chromatography. Specific information for each photolysis experiment is given in footnotes a-d of Table I.

Isolation. — In a typical thick-paper chromatogram, 70–150 mg lots of the irradiated reaction mixture in 2–3 ml of methanol were deposited on a sheet $(23 \times 53 \text{ cm})$ of Whatman No. 17 filter paper, which was developed at 20° with 150–180 ml of 85:15 (v/v) acetone-water. A strip (3 cm wide), cut from the lengthwise

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edge of the chromatogram, was sprayed with p-anisidine hydrochloride and was used as a guide in the location of the zones. The yields of materials recovered by water elution are given in Table I.

TABLE I

ZONE LOCATIONS AND YIELDS OF MATERIALS RECOVERED FROM THE THICK-PAPER CHROMATOGRAPHY OF IRRADIATED D-GALACTOSE AZINE

Zone	Zone location	Yields of recovered materials (mg)				Compound isolated
	(<i>cm</i>) ^{<i>e</i>}	Expt. A ^a	Expt. B ^b	Expt. C ^c	Expt. D ^d	
1	0.0-0.9	18.9	25.9	8.8	8.3	
2	0.4-1.3			11.7		
3	1.3-5.8	13.3	14.8	7.9	15.5	
4	5.2-7.0		7.7	8.1		D-Galactose azine
5	7.3-10.9	19.9	25.1	39.8	25.5	D-Galactose
6	13.8-16.9	4.4	3.5	4.6		
7	17.0-21.3	6.6	8.9	8.7	13.2	D-Lyxose
8	24.5-36.1	6.3	5.8	5.5	20.0	
9	36.7-13.5	10.5		4.9	13.0	
10	45.6-53.6	20.1	8.3		4.5	

^aIrradiated for 1.0 h, 80 mg of material in 400 ml of methanol, under nitrogen. ^bIrradiated for 2.0 h, 154 mg of material in 400 ml of methanol, under nitrogen. ^cIrradiated for 2.0 h, 308 mg of material in 400 ml of water, under nitrogen. ^dIrradiated for 2.0 h, 138 mg of material in 400 ml of methanol, under oxygen. ^eDistance from point of addition of adsorbate.

 α -D-Lyxopyranose tetraacetate (3). — A mixture of D-lyxose (Nutritional Biochemicals Corp., Cleveland, Ohio) (1.00 g), powdered, fused sodium acetate (500 mg), and acetic anhydride (10 ml) was heated at 80° until all of the reactants had dissolved (15 min), and heating was continued for a total of 2 h at 80°. Partial removal of the solvents at 80° was achieved under diminished pressure, chloroform (20 ml) was added to the residue, and the mixture was shaken with saturated aqueous sodium hydrogen carbonate (10 ml) at 10° until all acetic anhydride had been removed. The dried (sodium sulfate) chloroform solution was evaporated, and resulting syrup crystallized spontaneously; yield 2.17 g. These crystals were recrystallized twice from 95% ethanol; m.p. 93–94°, $[\alpha]_D^{20}$ +25.1° (c 3.3, chloroform) [lit.⁴ m.p. 93–94°, $[\alpha]_{D}^{25} + 25^{\circ}$ (chloroform), method of preparation not given]; they were designated 3 lm (low melting); t.l.c. R_F 0.82 on silica gel developed with 100:1 (v/v) benzenetert-butyl alcohol; X-ray powder diffraction data: 9.87 vs, 7.54 vvs, 5.99 vs, 4.81 s, 4.62 m, 4.373 vs, 4.072 vs, 3.754 s, 3.559 s, 3.450 vs, 3.377 w, 3.207 m, 3.093 s, 2.996 mw, 2.895 m, 2.688 ms, 2.617 m, 2.528 mw, 2.467 mw, 2.412 m, 2.346 w, 2.300 mw, 2.191 m, 2.135 mw, 2.080 mw, 1.936 mw, 1.804 m, 1.637 mw.

In another acetylation of D-lyxose, performed in the same manner, the crystals formed in 95% ethanol had m.p. 113–114°, $[\alpha]_D^{20} + 25.0°$ (c 2.0, chloroform), and were designated 3 hm (high melting). The i.r. spectrum and t.l.c. mobility on silica gel of these crystals were identical with those of 3 lm: X-ray powder diffraction data of

3 hm: 9.87 vs, 7.57 vvs, 5.99 vs, 4.84 s, 4.61 m, 4.382 vs, 4.072 vs, 3.754 s, 3.570 s, 3.449 vs, 3.370 w, 3.220 m, 3.080 s, 2.988 mw, 2.898 m, 2.698 ms, 2.610 m, 2.535 mw, 2.464 mw, 2.406 m, 2.341 w, 2.292 mw, 2.186 m, 2.131 mw, 2.078 mw, 1.925 mw, 1.802 m, 1.637 mw.

Anal. Calc. for C₁₃H₁₈O₉: C, 49.06; H, 5.70. Found: C, 49.07; H, 5.71.

Recovery of unreacted D-galactose azine (1) from zone 4 of Experiment B. — Elongated prisms formed slowly in the residual syrup isolated from this zone (see Table I). These crystals were found to be identical with 1 (i.r., t.l.c., paper chromatography).

Isolation of D-galactose from zone 5. — The syrups recovered from this zone yielded elongated prisms having an i.r. spectrum, and R_F values on paper and powdered cellulose by t.l.c. identical with those for D-galactose. A methanolic solution of the residual syrups yielded golden-colored crystals. An aqueous-methanolic solution of these crystals afforded straw-colored crystals, m.p. 165–166° (mixed m.p. with D-galactose unaltered).

Isolation of D-lyxose tetraacetate (3) from zone 7. — The combined, residual syrups from zone 7 possessed R_F values on paper and powdered cellulose by t.l.c. identical with those for D-lyxose. A lot (40 mg) of these syrups was allowed to react with acetic anhydride (5 ml) and sodium acetate (50 mg) for 2 h at 80–90°. The work-up of the reaction mixture was the same as that used in the preparation of 3; yield 74 mg. An ethanolic solution of the resulting acetate, on nucleation with 3 hm, yielded 19 mg of prisms; the i.r. spectrum and t.l.c. R_F value on silica gel were identical with those of 3. Recrystallization from the same solvent, nucleating with 3 hm, afforded prisms, m.p. 112–113°; identical with α -D-lyxopyranose tetraacetate (3 hm) by mixed m.p. and X-ray powder diffraction.

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