Tetrahedron Letters No.39, pp. 3439-3442, 1970. Pergamon Press. Printed in Great Britain.

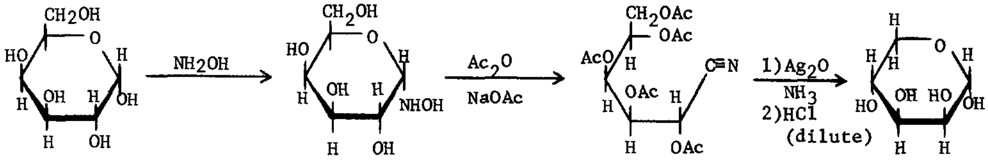
THE PHOTOLYSIS OF D-GALACTOSE OXIME. A PHOTOCHEMICAL WOHL DEGRADATION[1]

Wendell W. Binkley
The New York Sugar Trade Laboratory
37 Warren St., New York, N. Y. 10007

Roger W. Binkley
Department of Chemistry
The Cleveland State University, Cleveland, Ohio 44115

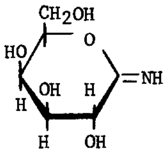
(Received in USA 9 July 1970; received in UK for publication 21 July 1970)

One of the important, classical methods for reducing the chain length of a carbohydrate by a one carbon unit is the Wohl degradation of the sugar oxime[2]. This reaction is illustrated below using D-galactose oxime (1) as the reactant. We have examined the photolysis of D-galactose oxime[3] (1) and N-D-galactopyranosylmethoxyamine (2), the methyl oxime of D-galactose, and have found that a degradation, similar to the Wohl degradation, takes place photochemically. This reaction, should it prove to be general, would provide an extremely mild method[4] for reducing the length of a carbon chain in carbohydrate systems.

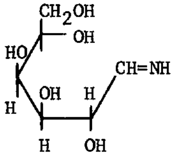


1 4 3

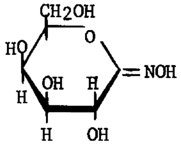
Direct irradiation of 1.00 mole of D-galactose oxime (1) in 400 ml methanol with a 450-W Hanovia mercury-vapor lamp results in complete disappearance of the starting material after 1.0 hr. Chromatography on powdered cellulose with acetone-water (85:15) separated the reaction mixture into two components. The slower moving, minor product (14%) was identified as D-lyxose (3) by tlc comparison with a known sample[5] and also by spectroscopic and mixture melting point comparisons of its tetraacetate with authentic α-D-lyxose tetraacetate. The major reaction product (81%) was



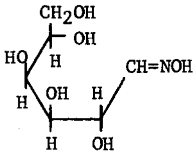
5



6



7



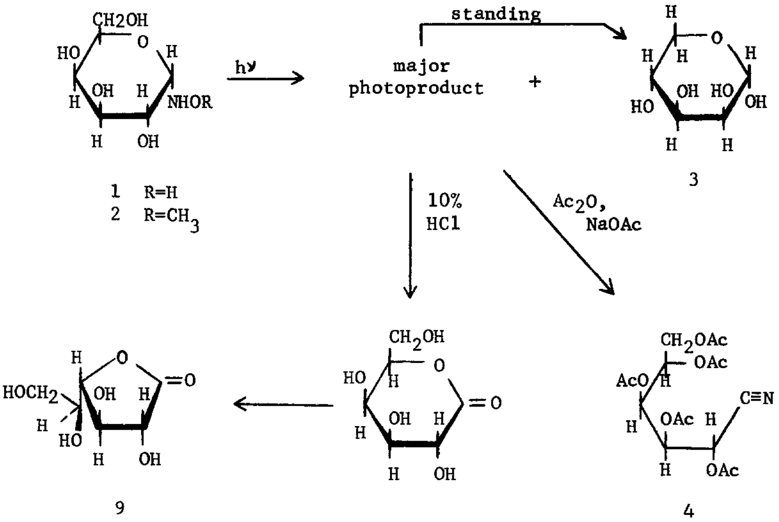
8

an unstable nitrogen-containing sirup which decomposed to D-lyxose on standing. The ir spectrum of the unknown photoproduct, immediately upon removal from the chromatography column, was similar to that of D-galactose oxime (1) except for a strong absorption which had developed at 6.05 μ (C=N)[6]. The nmr spectrum was too complex for simple interpretation and the photoproduct was too unstable for elemental analysis. It was possible, however, to convert this product into a stable derivative by acetylation, a reaction which gave D-galactononitrile pentaacetate[7] (4) in good yield (Scheme I). No nitrile absorption was present in the ir spectrum of the unacetylated photoproduct; in addition, acetylation caused the disappearance of the 6.05 μ band.

The presence of a C=N absorption in the infrared when combined with the fact that the galacto portion of the molecule was still intact after irradiation (as shown by acetylation to D-galactononitrile) suggested one of the four structures 5-8 for the unknown photoproduct. None of the four represented a known compound; in fact, for two of them (6 and 8) there was some doubt concerning the possibility of their existence since they would be likely to undergo immediate isomerization to cyclic structures[8,9] (which would show no 6.05 μ absorption).

In two of these four possible structures (5 and 6) the nitrogen-oxygen bond was cleaved during reaction; thus, if N-D-galactopyranosylmethoxyamine (2) gave the same reaction product on photolysis as did D-galactose oxime (1), structures 7 and 8 could be eliminated from consideration. Irradiation of 2 produced a reaction which was identical to the reaction of 1 conducted under the same conditions; that is D-lyxose and the unknown photoproduct were formed in the same yields as before (Scheme I). This result effectively eliminated structures 7 and 8 as possibilities for the photoproduct.

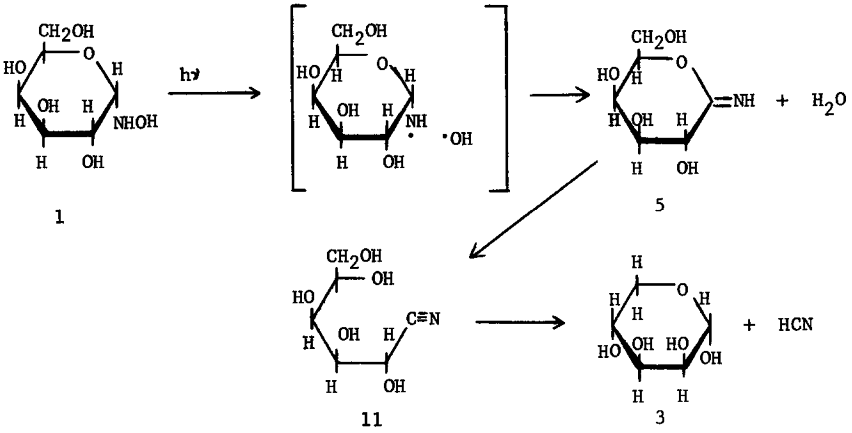
The results from the photolysis of N-D-galactopyranosylmethoxyamine (2) when combined with the questionable existence of compound 6, clearly pointed to the iminolactone 5 as the photoproduct. Elimination of 6 as a possibility and final confirmation of 5 as the reaction product was achieved by hydrolysis of the photoproduct in 10% HCl to D-galactono-1,4-lactone (9), Scheme I. Photolysis of D-Galactose Oxime (1) and Reactions of the Major Photoproduct



identical with an independently obtained sample of 9. Compound 6 would have hydrolyzed to D-galactose.

We would like to suggest the sequence of steps shown in Scheme II as a possible explanation for the reactions which result from the irradiation of D-galactose oxime (1). The crucial step in the initial portion of this proposed process is the photochemical fragmentation of the nitrogen-oxygen bond. Although this type of photochemical N-O cleavage has not been widely observed previously, a similar process has been reported in at least one instance[10]. The latter portion of this reaction sequence begins with the ring opening of D-galactonoimino-1,5-lactone (5) to its tautomeric form, D-galactononitrile (11). This ring opening to give 11 is followed by loss of hydrogencyanide to form D-lyxose. The spontaneous loss of hydrogen cyanide from a sugar nitrile has been observed previously for D-gluconitrile[11]. In connection with the mechanism of this reaction it is worthwhile to note that the photochemical decomposition of benzoylperoxide in the presence of D-galactose oxime (1) (through a pyrex filter so that 1 absorbs no light) causes no change in 1. This fact argues against a photo-initiated radical process.

Scheme II. Proposed Mechanism For Photochemical Reaction of D-Galactose Oxime (1)



ACKNOWLEDGEMENTS: The authors are grateful to Dr. J. W. LeMaistre for helpful discussion of this work. One of us (RWB) wishes to thank the National Science Foundation (Grant No. GP 16664) for support of this research.

REFERENCES

1. Paper IV in a series on Photochemical Reactions of Carbohydrates.
2. A. Wohl, *Ber.*, **24**, 994 (1891); **26**, 730 (1893).
3. The question of the structure of sugar oximes in solution is a complex one (see B. Capon, Chem. Rev. **69**, 458 (1969)). We have pictured the structure of D-galactose oxime as 1 to be consistent with the lack of C=N absorption in the ir and in analogy with the structure of the parent sugar.
4. "Mild" in this case refers to room temperature and the absence of acids, bases, and other catalytic or reactive species.
5. Nutritional Biochemicals Corporation, 26201 Miles Road, Cleveland, Ohio 44128.
6. K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Cal., 1962, p 38.
7. V. Deulofeu, M. L. Wolfrom, P. Cattaneo, C. C. Christman, and L. W. Georges, *J. Amer. Chem. Soc.*, **55**, 3488 (1933).
8. M. L. Wolfrom, A. Thomposon, and L. W. Georges, *J. Amer. Chem. Soc.*, **54**, 4091 (1932).
9. R. Kuhn and W. Kirschenlohr, *Ann. Chem.*, **600**, 126 (1956).
10. N. A. Lebel, T. A. Lajiness, D. B. Ledlie, *J. Amer. Chem. Soc.*, **89**, 3076 (1967).
11. P. E. Papadakis, *J. Amer. Chem. Soc.*, **64**, 1950 (1942).