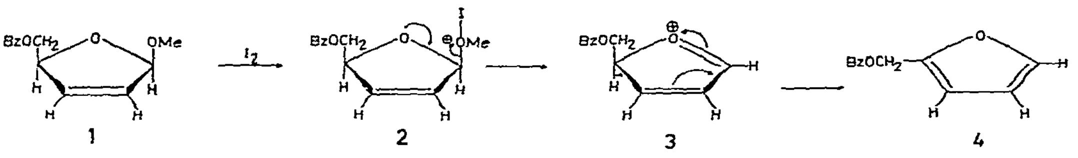
Note

Conversion of methyl 5-*O*-benzoyl-2,3-dideoxy-β-D-*glycero*-pent-2-enofuranoside into a furan derivative in the presence of iodine

R. G. S. Ritchie and W. A. Szarek
Department of Chemistry, Queen's University, Kingston, Ontario (Canada)

(Received December 14th, 1970)

A program in this laboratory is concerned with the addition of pseudohalogens (prepared *in situ* by the reaction of the appropriate silver salts with iodine) to unsaturated carbohydrates. Additions have already been achieved to a pyranoid derivative possessing an endocyclic double bond[1] and to furanoid derivatives possessing exocyclic double bonds[2,3]. In an effort to extend these studies to furanoid derivatives having endocyclic double bonds, methyl 5-*O*-benzoyl-2,3-dideoxy-β-D-*glycero*-pent-2-enofuranoside[4,5] (**1**) was initially treated overnight at 0° with freshly prepared silver nitrite and iodine in dry ether; only one product was formed, which was found to be identical with authentic furfuryl benzoate (**4**). The reaction of silver nitrite with iodine generates the pseudohalogen, nitryl iodide[1,6] (NO_2I). When the unsaturated sugar **1** was added to a preformed solution of nitryl iodide in acetonitrile at −23°, a complete conversion into the furan derivative **4** was observed after 30 min. With iodine nitrate[3,7] (obtained by treating silver nitrate with iodine) in acetonitrile at −20°, compound **4** was the predominant product formed in 15 min. However, with this pseudohalogen, there were also formed trace amounts of two other components (t.l.c.). It was finally shown that treatment of **1** with an equimolar amount of iodine only, in dry ether at room temperature, gave a quantitative yield of compound **4** in less than 20 min.



A possible mechanism for the formation of furfuryl benzoate (**4**) from (**1**) is one occurring through **2** by the path shown (**2**–**4**). A number of other, comparable, decomposition reactions have been reported recently. Thus, treatment of methyl 5-*O*-benzoyl-2,3-di-*O*-*p*-tolylsulfonyl-β-D-ribofuranoside with sodium iodide and zinc dust in *N*,*N*-dimethylformamide for 1.5 h at 170° gives initially the unsaturated sugar **1**, but, if heating is continued, furfuryl benzoate (**4**) is formed; compound **1** was completely converted[4] into furfuryl benzoate when the unsaturated sugar was heated with aqueous acetic acid for 5 min at 65°. When 1,3,5-tri-*O*-acetyl-2-chloro-2-deoxy-D-arabinose was distilled at 150°/0.5 torr, some decomposition occurred to give 2-acetoxymethyl-4-chlorofuran[8]. An analogous type of aromatization reaction was observed[9] with 1,2,3,5-tetra-*O*-acetyl-4-thio-D-ribofuranose, in the presence of both an acid and a base, to give 2-acetoxymethyl-4-acetoxythiophene.

It has been reported previously[1,10] that another 2,3-unsaturated sugar of the alkene type, methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside, is unreactive toward some pseudohalogens. The lack of reactivity may possibly be due to the electron-withdrawing properties of the anomeric center. Horton *et al.*[11] have found also that this alkene reacted with nitrosyl chloride below room temperature, but that the product decomposed to regenerate the starting alkene on attempted isolation. In view of these results, and the work described in the present report, it appears that the addition of pseudohalogens is not a practical procedure for the stereospecific introduction of nitrogen functions into 2,3-unsaturated sugars. Other addition reactions of compound **1** are being investigated, and the results will be reported separately.

EXPERIMENTAL

General methods. — I.r. spectra (film) were recorded with a Beckman IR-5A spectrophotometer. N.m.r. spectra were recorded at 60 MHz in chloroform-*d* with tetramethylsilane as the internal standard. U.v. spectra were measured in ether with a Unicam SP-800B spectrophotometer. Thin-layer chromatography (t.l.c.) was performed with Silica Gel G as the adsorbent, and 3:1 (v/v) petroleum ether (b.p. 60–80°)–ethyl acetate as the developing solvent. The developed plates were air-dried, sprayed with 5% ethanolic sulfuric acid, and heated at about 150°.

*Treatment of methyl 5-O-benzoyl-2,3-dideoxy-β-*D-glycero*-pent-2-enofuranoside* (**1**) *with silver salts and iodine.* — Methyl 5-*O*-benzoyl-2,3-dideoxy-β-D-*glycero*-pent-2-enofuranoside (**1**) was prepared from methyl β-D-ribofuranoside by the method of Géro *et al.*[4], and purified by column chromatography on silica gel*; after chromatography the unsaturated sugar had the same physical constants as those reported by Lemieux *et al.*[5] for compound **1**. The reactions with silver nitrite and iodine, and with silver nitrate and iodine, were performed in the dark as described previously[1,2]. The progress of the reaction was followed by t.l.c. The reaction mixture was filtered, and the filtrate was washed with aqueous sodium thiosulfate solution until the iodine color had disappeared. The washed solution was dried (sodium sulfate) and concentrated to a syrup. In all cases the syrupy product had i.r., n.m.r. and u.v. spectra identical with those of authentic furfuryl benzoate (**4**).

A quantitative yield of furfuryl benzoate was also obtained when compound **1** was treated with an equimolar amount of iodine only, in dry ether at room tempera-

---

*Occasionally prolonged contact with silica gel led to decomposition.

ture; the conversion was complete when the reaction mixture was examined (t.l.c.) after 20 min.

ACKNOWLEDGMENTS

The authors thank the National Research Council of Canada for financial support of this work and for a Bursary awarded to one of us (R. G. S. R.), and Professor J. K. N. Jones for his interest and encouragement.

REFERENCES

1 W. A. Szarek, D. G. Lance, and R. L. Beach, *Chem. Commun.*, (1968) 356; *Carbohyd. Res.*, 13 (1970) 75.
2 W. A. Szarek, J. S. Jewell, I. Szczerek, and J. K. N. Jones, *Can. J. Chem.*, 47 (1969) 4473.
3 J. S. Jewell, R. G. S. Ritchie, W. A. Szarek, and J. K. N. Jones, to be published.
4 J. Hildesheim, J. Cléophax, and S. D. Géro, *Tetrahedron Lett.*, (1967) 1685; J. Cléophax, J. Hildesheim, and S. D. Géro, *Bull. Soc. Chim. Fr.*, (1967) 4111.
5 R. U. Lemieux, K. A. Watanabe, and A. A. Pavia, *Can. J. Chem.*, 47 (1969) 4413.
6 A. Hassner, J. E. Kropp, and G. J. Kent, *J. Org. Chem.*, 34 (1969) 2628.
7 L. Birckenbach and J. Goubeau, *Ber.*, 67 (1934) 1425; D. H. Ball, A. E. Flood, and J. K. N. Jones, *Can. J. Chem.*, 37 (1959) 1018; J. E. Kropp, A. Hassner, and G. J. Kent, *Chem. Commun.*, (1968) 906.
8 J. Kuszmann and P. Sohár, *Carbohyd. Res.*, 14 (1970) 415.
9 R. L. Whistler and D. J. Hoffman, *Carbohyd. Res.*, 11 (1969) 137.
10 J. S. Brimacombe, J. G. H. Bryan, T. A. Hamor, and L. C. N. Tucker, *Chem. Commun.*, (1968) 1401.
11 E. L. Albano, D. Horton, and J. H. Lauterbach, *Carbohyd. Res.*, 9 (1969) 149.