Carbohydrate Research, 208 (1990) 273–275
Elsevier Science Publishers B.V., Amsterdam

Note

Some studies concerning the dimerization of 2,3-*O*-isopropylidene-L-erythrose

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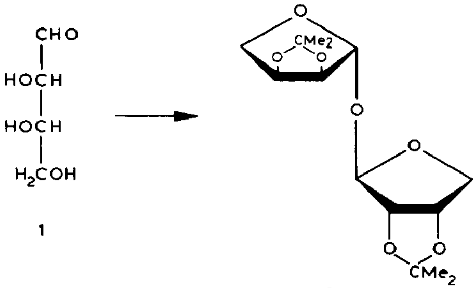
(Received April 9th, 1990; accepted for publication, June 5th, 1990)

Recently, I reported the slow dimerization of a sample of 2,3-*O*-isopropylidene-L-erythrose (**1**) to form 2,3-*O*-isopropylidene-β-L-erythrofuranosyl 2,3-*O*-isopropylidene-β-L-erythrofuranoside (**2**) over many years[1]. New preparations of **1** have now been kept as long as three years without change, which would indicate that there is no autocatalysis involved. Moreover, when the original storage flask was ground into a fine powder and mixed with **1**, there was still no detectable conversion of **1** to **2**, even after nine months, so it was unlikely that the glass surface catalyzed the reaction. A further group of tests were performed with a large number of substances in use in this laboratory at the time that the original sample of **1** was stored. Disaccharide **2** was observed in tubes containing ferric chloride, with traces of **2** also appearing in the tubes containing ferric sulfate or mercuric chloride. These salts also catalyzed the slow hydrolysis of the isopropylidene group of **1**.



1

2

Because the original filtrate[1] had unfortunately been discarded, it was not possible to test for the presence of elements such as iron, and so it may never be known what caused the original dimerization. However, it appeared of some interest to develop the ferric chloride-catalyzed conversion of **1** to **2** into a useful synthetic procedure. This reaction could be performed by addition of ferric chloride to the neat syrup (**1**), or to a solution of **1** in an inert solvent, such as dichloromethane. Yields of **2** were between

0008-6215/90/$03.50

20–25% in both cases. The amount of ferric chloride had to be kept relatively low to prevent the competing hydrolysis of the isopropylidene groups and formation of intractable brown substances. Usually, the Lewis acid constituted about 10% by weight of the amount of the sugar derivative, *e.g.*, 50–60 mg of anhydrous ferric chloride to 600 mg of **1**. The reactions performed in the solvent proceeded much faster (16–24 h) than the reactions carried out in the neat syrup (4–6 days).

In order to keep the reaction mixtures dry and to remove water liberated during the dimerization, Davison molecular sieve type 3A or 4A was added when the reaction was performed in dichloromethane; the yields of **2** doubled to 40–45%. However, this result did not appear to be related solely to the desiccant properties of the molecular sieve, for when Drierite (anhydrous calcium sulfate) was used in place of the molecular sieve, the reaction yields dropped to below 10%. This suggested that the molecular sieve may be acting as a kind of promoter for this dimerization. The reaction was generally performed for 16–24 h, since less time (6–10 h) gave lower yields (~30%), and longer periods did not change the yields significantly. Attempts to convert **1** to **2** in refluxing 1,2-dichloroethane gave low yields (10–20%). The reaction did not occur in acetone, in which ferric chloride is readily soluble.

Substitution of boron trifluoride ethyl etherate for ferric chloride resulted in lower yields of **2** (32–33%); however, it made no difference if molecular sieve was present or not, which suggests that the mechanism of reaction is different.

A number of attempts were made to remove the isopropylidene groups from **2** with hydrolytic procedures commonly used with other oligosaccharides. In every case where conditions were strong enough to remove the blocking groups, the disaccharide linkage was also cleaved to form L-erythrose.

EXPERIMENTAL

General methods. — Methods, instrumentation, and t.l.c. were described in the previous paper[1]. 2,3-*O*-Isopropylidene-L-erythrose (**1**) was prepared from either D-gulono-1,4-lactone[2] or D-ribono-1,4-lactone[3].

Synthesis of **2**. — To a mixture containing anhydrous $FeCl_3$ (50 mg), molecular sieve type 3A beads (~1 g), and dry dichloromethane (5 mL), was added a solution of **1** (600 mg) dissolved in dichloromethane (5 mL). The mixture was stirred at room temperature for 18 h, filtered, and the solvent was evaporated. The residue was dissolved in chloroform and chromatographed in a column (18 × 2 cm) of silica gel (Baker, 60–200 mesh) with 99:1 (v/v) chloroform–methanol as eluent. Evaporation of the fractions containing **2** afforded a white solid (358 mg), which crystallized from methanol–water to give 247 mg (44%) of **2**, m.p. 116–117.5°. Admixture of **2** from the previous work[1] gave no depression of the melting point (m.m.p. 116–118°), and the i.r. spectra were also identical.

An alternative workup of the aforementioned reaction mixture involved dilution with 1,2-dichloroethane, treatment with aqueous $NaHCO_3$, filtration, washing, and drying of the organic solution, and chromatography. However, yields of **2** were the same. For example, the reaction yielded 244 mg (43%) of **2**, m.p. 116.5–118°.

REFERENCES

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