Carbohydrate Research, 85 (1980) C5–C6
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Preliminary communication

Epoxidation with triphenylphosphine and diethyl azodicarboxylate: epoxide derivatives of sucrose

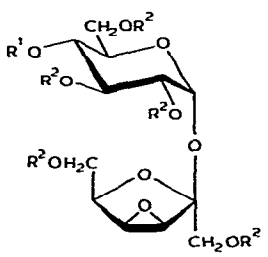
R. D. GUTHRIE*, IAN D. JENKINS, and RYOHEI YAMASAKI
School of Science, Griffith University, Nathan, Queensland 4111 (Australia)

(Received August 1st, 1980; accepted for publication, August 14th, 1980)

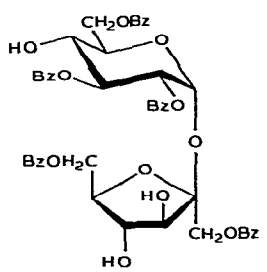
We have recently reported on the use of the triphenylphosphine (TPP)–diethyl azodicarboxylate (DEAD) system for the synthesis of 3,4-epoxides (oxiranes) of methyl α- and β-D-tagatofuranosides[1] in high yield from the appropriate methyl D-fructofuranosides. The novel feature of the reaction was that no protection of the 1- and 6-hydroxyl groups was necessary in the one-step reaction.

The "sucrose epoxide" **1** (α-D-glucopyranosyl 3,4-anhydro-β-D-tagatofuranoside) would be an extremely useful intermediate for the synthesis of sucrose derivatives modified in the D-fructosyl moiety, particularly at C-4′. Epoxide **1** has been prepared, but only as its hexaacetate (**2**) in ~8% yield in six steps from sucrose[2]. Compound **2** has been shown[3] to undergo ring-opening at C-4′ with azide ion, to yield a product having the sucrose configurations.

The results of experiments[4] with methyl α-D-glucopyranoside implied that, for sucrose, some protection of the hydroxyl groups in the sucrose part of the molecule would be necessary. Indeed, with DEAD–TPP in $HCONMe_2$, sucrose itself gave a mixture of as-yet-uncharacterized products.



1 $R^1 = R^2 = H$
2 $R^1 = R^2 = Ac$
3 $R^1 = H, R^2 = Bz$



4

0008-6215/80/0000–0000/$ 02.25,

Sucrose 2,3,6,1′,6′-pentabenzoate (**4**), which can be prepared in a one-pot reaction directly from sucrose[5], would appear to be a good starting-material for the synthesis of **1**, as it has the required, *trans*-diol grouping at C-3′ and C-4′. The isolated hydroxyl group on C-4 should not interfere (on the basis of our previous experience with methyl D-fructofuranosides[1]). By analogy with those systems, the product should have the required, D-*lyxo* configuration.

Treatment of compound **4** with 2.5 equivalents of the DEAD–TPP reagent in $HCONMe_2$ overnight at room temperature gave a 62% yield of a penta-*O*-benzoyl epoxide, characterized as its monoacetate. The structure of this epoxide was demonstrated to be **3** by deacylation with methanolic ammonia, followed by peracetylation to yield compound **2** {$[\alpha]_D$ + 69.9° ($CHCl_3$), lit.[2]* +70.2°}. The free epoxide† **1** obtained by deacylation of **3**, was crystalline, m.p. 179° (from ethanol), $[\alpha]_D$ +78.4° (H_2O); ^{13}C-n.m.r. data (D_2O): 104.5 (C-2′), 92.1 (C-1), 77.5 (C-5′), 73.7 and 73.3 (C-3,5), 71.9 (C-2), 70.4 (C-4), 64.3 (C-6′), 61.5 and 61.1 (C-6,1′), and 57.3 and 56.3 p.p.m. (C-3′,4′). 2,3,6-Tri-*O*-benzoyl-α-D-glucopyranosyl 3,4-anhydro-1,6-di-*O*-benzoyl-β-D-tagatofuranoside (**3**), a syrup, had $[\alpha]_D$ +50.9° ($CHCl_3$); ^{13}C-n.m.r. data ($CDCl_3$): 103.0 (C-2′), 90.3 (C-1), 74.9 (C-5′), 73.7 (C-3), 71.3 and 71.0 (C-2,5), 69.8 (C-4), 65.8 (C-6′), 63.9 and 62.7 (C-6,1′), and 56.4 and 54.8 p.p.m. (C-3′,4′).

Thus, compound **1** is available from sucrose in three steps with an overall yield, in our hands§, of ~26%.

REFERENCES

1 R. D. Guthrie, I. D. Jenkins, and R. Yamasaki, *Chem. Commun.*, (1980) in press.
2 R. Khan, M. R. Jenner, and H. Lindseth, *Carbohydr. Res.*, 65 (1978) 99–108.
3 M. R. Jenner, Ph.D. Thesis, University of London, 1976.
4 G. Grynkiewicz, *Pol. J. Chem.*, 53 (1979) 2501–2525.
5 T. Ogawa and M. Matsui, *Carbohydr. Res.*, 56 (1977) C1–C6.

*R. Khan, personal communication, has informed us that the $[\alpha]_D$ value reported for compound **2** in ref. 2 is incorrect.

†All new compounds had satisfactory elemental analyses.

§In ref. 5, a yield of 87% of compound **4** was reported. In our hands, the yield was consistently ~50%.