

The Nitration of Tetraacetyl- β -Phenyl Glucoside

BENGT LINDBERG

Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

In experiments dealing with the transformation of β -glucosides into α -glucosides, a glucoside of a nitrophenol was needed. Hurd and Bonner¹ have prepared tetraacetyl- β -*p*-bromphenyl glucoside by direct bromination of the phenyl glucoside in acetic acid. Analogously, tetraacetyl- β -phenyl glucoside could be nitrated with concentrated nitric acid in acetic acid. The yield was almost quantitative but the resulting product was a mixture of the ortho and para derivatives, which could be fractionated by recrystallization. Tetraacetyl- α -phenyl glucoside was treated in the same way, but in this case it was not possible to isolate any crystalline substances from the sirupy mixture obtained.

The structure of the substances obtained on nitration of tetraacetyl- β -phenyl glucoside was proved by comparison with authentic samples of tetraacetyl- β -*o*-nitrophenyl glucoside and the corresponding *p*-derivative, which were prepared according to Glaser and Wulwek². For tetraacetyl- β -*o*-nitrophenyl glucoside Glaser and Wulwek report the rotation + 53° (chloroform) and the melting point 158—159°*. Montgomery, Richtmeyer and Hudson³, who prepared the substance by a modification of the Helferich and Schmitz-Hillebrecht fusion procedure, report the rotation + 45° and the melting point 150

—152°. The substance prepared by the two independent methods in this laboratory, rotated + 45° and melted at 158—159° (corr). The most probable explanation of this discrepancy is that Montgomery, Richtmeyer and Hudson obtained the pure substance but in a low-melting modification, and that the specific rotation reported by Glaser and Wulwek is incorrect (even the recalculated value). The present author, however, has never been able to isolate a low-melting modification of this compound.

Experimental. Tetraacetyl- β -phenyl glucoside (5 g) was dissolved in a mixture of acetic acid (40 ml) and acetic anhydride (2 ml). Almost dry nitric acid, b. p. 86°, (5 ml) was added and the mixture allowed to stand at room temperature. After an hour it was poured into ice water (1000 ml) containing sodium acetate (20 g). The white precipitate was filtered and dried (5.5 g). Separation of the ortho derivative was effected by recrystallization from hot ethanol. After four recrystallizations pure tetraacetyl- β -*o*-nitrophenyl glucoside (2.7 g) was obtained. $[\alpha]_D^{20} + 45^\circ$. M. p. 158—159°. It showed no m. p. depression with an authentic sample of tetraacetyl- β -*o*-nitrophenyl glucoside.

The mother liquors were concentrated and the residue recrystallized several times from a mixture of water and acetic acid when pure tetraacetyl- β -*p*-nitrophenyl glucoside (0.3 g) was obtained. $[\alpha]_D^{20} - 41^\circ$. M. p. 174—175°. It showed no m. p. depression with an authentic sample of tetraacetyl- β -*p*-nitrophenyl glucoside.

The new mother liquors were evaporated and the residue thoroughly mixed and dried. The product (1.8 g) showed a rotation of — 7.5°. Assuming that this mixture consists of the *o*- and *p*-derivatives, the total yield of *ortho* and *para* nitrophenyl glucosides was 70 % and 30 % respectively.

* The rotations reported in this paper had been calculated incorrectly. The above value is recalculated from the data given by the original authors. Cf. Helferich and Peters. *J. prakt. Chem.* [2] 138 (1933) 283, footnote 1. Cf. also ref. 3.