7-Methoxy-2-(α-phenylethyl)-1-naphthoic Acid.—The lactone was hydrolyzed and reduced with activated zinc dust and alkali in the same way as described for IV. The yield from 13.4 g. of lactone was 13.1 g. (97%), m.p. 153–154.5°. An analytical sample prepared by vacuum sublimation melted at 155–155.5°. *Anal.* Calcd. for $C_{20}H_{18}O_3$: C, 78.4; H, 5.9. Found: C, 78.42, 78.49; H, 5.76, 5.81.

2′-Methoxy-9,10-dimethyl-1,2-benzanthracene.—The above naphthoic acid was cyclized with hydrogen fluoride, allowed to react with four equivalents of methyl Grignard, and heated to aromatize the molecule in much the same manner as described for its 7-methoxy isomer. Concentration of the 20:1 benzene:60–70° petroleum ether eluent from the chromatogram gave a first crop of 2.25 g. of product, m.p. 131–132.5°, and a second crop of 0.32 g., m.p. 128.5–130°. The total yield of 2.57 g. of product from 6.1 g. of naphthoic acid amounted to 45.7% of theory. A sample of melting point 131.0–132.5° was analyzed. *Anal.* Calcd. for $C_{21}H_{18}O$: C, 88.1; H, 6.30; CH_3O, 10.83. Found: C, 88.2, 88.1; H, 6.31, 6.45; CH_3O, 10.40, 10.69.

PHILADELPHIA 11, PENNA.

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH]

The Conversion of 1,4,6-Tri-*O*-benzoyl-2,3-*O*-(1-benzyloxybenzylidene)-β-D-fructofuranose to 1,4,6-Tri-*O*-benzoyl-2,3-*O*-(1-ethoxybenzylidene)-β-D-fructofuranose by Acidic Ethanol

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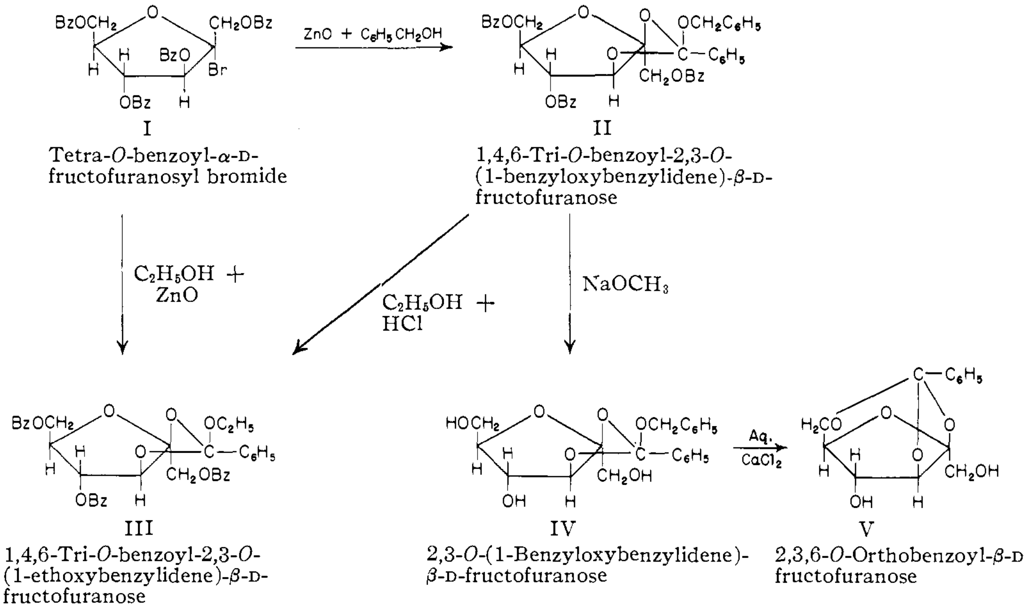
RECEIVED SEPTEMBER 23, 1955

The benzyloxy group in 1,4,6-tri-*O*-benzoyl-2,3-*O*-(1-benzyloxybenzylidene)-β-D-fructofuranose (II) is rapidly replaced by an ethoxy group through treatment with ethanol in the presence of a trace of acid. The product, 1,4,6-tri-*O*-benzoyl-2,3-*O*-(1-ethoxybenzylidene)-β-D-fructofuranose (III), was synthesized through the condensation of tetra-*O*-benzoyl-α-D-fructofuranosyl bromide (I) with ethanol in the presence of zinc oxide.

Helferich and his co-workers[1,2] have recently reported the condensation of amorphous tetra-*O*-benzoyl-α-D-fructofuranosyl bromide (I) with benzyl alcohol in the presence of zinc oxide as an acid acceptor to obtain a crystalline orthobenzoic acid derivative to which they assigned structure II, 1,4,6-tri-*O*-benzoyl-2,3-*O*-(1-benzyloxybenzylidene)-β-D-fructofuranose. On debenzoylation of this substance, they obtained 2,3-*O*-(1-benzyloxybenzylidene)-β-D-fructofuranose (IV) as a sirup which, under the action of aqueous calcium chloride, lost a molecule of benzyl alcohol to give a crystalline orthobenzoylfructofuranose; evidence indicated this latter compound to have the 2,3,6-structure V. A similar transformation in the D-ribopyranose series has more recently been reported by Fletcher and Ness[3] who found that 1,2-*O*-(1-benzyloxybenzylidene)-α-D-ribopyranose (VI) loses benzyl alcohol when treated with very weakly acidic, aqueous acetone to give 1,2,4-*O*-orthobenzoyl-α-D-ribopyranose (VII). These two transformations, IV → V and VI → VII, were *intra*molecular reactions, a free hydroxyl of the sugar itself taking part. However, if the hydroxyl groups were masked as, for instance, in II it is not unreasonable to suppose that an alkoxy group might be induced to replace the benzyloxy residue in an analogous *inter*molecular fashion. This has now been found to take place.



I
Tetra-*O*-benzoyl-α-D-fructofuranosyl bromide

II
1,4,6-Tri-*O*-benzoyl-2,3-*O*-(1-benzyloxybenzylidene)-β-D-fructofuranose

III
1,4,6-Tri-*O*-benzoyl-2,3-*O*-(1-ethoxybenzylidene)-β-D-fructofuranose

IV
2,3-*O*-(1-Benzyloxybenzylidene)-β-D-fructofuranose

V
2,3,6-*O*-Orthobenzoyl-β-D-fructofuranose

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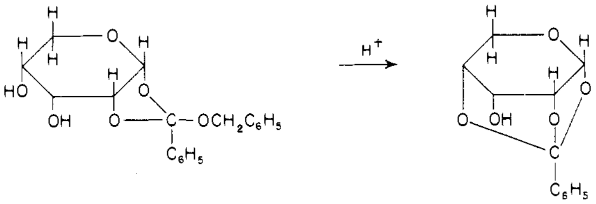
[1] B. Helferich and L. Bottenbruch, *Chem. Ber.*, **86**, 651 (1953).

[2] B. Helferich and W. Schulte-Hürmann, *ibid.*, **87**, 977 (1954).

[3] H. G. Fletcher, Jr., and R. K. Ness, THIS JOURNAL, **77**, 5337 (1955).



VI
1,2-*O*-(1-Benzyloxybenzylidene)-α-D-ribopyranose

VII
1,2,4-*O*-Orthobenzoyl-α-D-ribopyranose

When 1,4,6-tri-*O*-benzoyl-2,3-*O*-(1-benzyloxybenzylidene)-β-D-fructofuranose (II)[4,5] was dissolved in absolute ethanol and a trace of hydrogen chloride added, a rapid change took place and a crystalline product obtained in 69% yield. Analysis showed the substance to have the elementary composition of an ethyl hexoside tetrabenzoate. That the *ortho* structure had survived this treatment was evident from the fact that only three of the benzoyl groups could be removed by alkali. Further supporting evidence was obtained through condensation of tetra-*O*-benzoyl-α-D-fructofuranosyl bromide (I) with ethanol in the presence of zinc oxide—*i.e.*, a method analogous to that used for the preparation of II. The product of this condensation proved to be identical with that obtained earlier. It seems probable that the ring structure of the new tri-*O*-benzoyl-*O*-(1-ethoxybenzylidene)-D-fructose (III) is the same as that of the tri-*O*-benzoyl-*O*-(1-benzyloxybenzylidene)-D-fructose (II). Inspection of Table I shows that the rotation of the new substance (III) is quite close to those of the analogous derivatives prepared by Helferich. The configuration of C_2 of the dioxolane ring in both cases remains, of course, unknown. To the authors' best knowledge the present instance represents the first time that the intermolecular replacement of one radical by another has been observed in an orthoglycoside.

TABLE I

1,4,6-TRI-*O*-BENZOYL-2,3-*O*-(1-SUBSTITUTED-BENZYLIDENE)-β-D-FRUCTOFURANOSES

Radical	$[\alpha]_D$ (CHCl₃)
Methoxy	−0.99°[a]
Ethoxy	−2.3°[b]
n-Propoxy	−4.17°[a]
Cyclohexyloxy	−9.4°[a]
Benzyloxy	+5.8°[a]

[a] Helferich and Bottenbruch, ref. 1. [b] Present work.

It may be noted that if, as seems highly probable, the benzyl orthobenzoylfructose actually has the structure II which Helferich assigned it, this fact tends to support the assumption (based on rotation[1]) that the amorphous bromide I from which it was made is actually an α-D-halide since it is accepted that condensations such as I → II proceed by a neighboring group mechanism involving inversion of the configuration of C_2.

Experimental[6]

1,4,6-Tri-*O*-benzoyl-2,3-*O*-(1-ethoxybenzylidene)-β-D-fructofuranose (III) from 1,4,6-Tri-*O*-benzoyl-2,3-*O*-(1-benzyloxybenzylidene)-β-D-fructofuranose (II).—A solution of 0.80 g. of 1,4,6-tri-*O*-benzoyl-2,3-*O*-(1-benzyloxybenzylidene)-β-D-fructofuranose[1] in a mixture of 4 ml. of dry dioxane and 1 ml. of absolute ethanol was treated with 0.094 ml. of 1.81 *N* absolute ethanolic hydrogen chloride. After 20 minutes the reaction mixture was concentrated *in vacuo* at room temperature. Ethanol (10 ml.) was added and the mixture warmed to *ca.* 45° to effect solution. On cooling, crystallization was spontaneous, giving 0.50 g. (69%) of product melting at 119–122°. After two recrystallizations from ethanol, the product (0.35 g., 48%) showed a double melting point 113–115°, 126–127°. Two more recrystallizations, seeding with the lower-melting form, gave needles of m.p. 113–114° and $[\alpha]^{20}D$ −1.5° (CHCl₃, *c* 0.69).

Anal. Calcd. for $C_{36}H_{32}O_{10}$: C, 69.22; H, 5.16; 3 C_6H_5CO, 50.48; 4 C_6H_5CO, 67.31. Found: C, 69.36; H, 5.19; C_6H_5CO (alkaline method), 47.4, 52.9.

Another recrystallization from ten parts of absolute ethanol provided needles of m.p. 126–127° and $[\alpha]^{20}D$ −2.0° (CHCl₃, *c* 0.92).

Anal. Calcd. for $C_{36}H_{32}O_{10}$: C, 69.22; H, 5.16; C_2H_5O, 7.21. Found: C, 69.09; H, 5.08; C_2H_5O, 7.13.

It was eventually found that either form of the material could be obtained by appropriate seeding. The lower-melting form obtained from II melted at 113–115° when mixed with the lower-melting product from I (see below). The higher melting forms from the two sources melted at 126–127° when mixed. A mixture of the two forms melted at 125–127°.

1,4,6-Tri-*O*-benzoyl-2,3-*O*-(1-ethoxybenzylidene)-β-D-fructofuranose (III) from 1,3,4,6-Tetra-*O*-benzoyl-D-fructose *via* Amorphous Tetra-*O*-benzoyl-α-D-fructofuranosyl Bromide (I).—A procedure similar to that which Helferich and Bottenbruch[1] employed for the synthesis of the analogous benzyloxy-, cyclohexyloxy-, *n*-propoxy- and methoxybenzylidene derivatives was used. Ten grams of 1,3,4,6-tetra-*O*-benzoyl-D-fructose[7] was dissolved in 100 ml. of dry benzene and 30 g. of Drierite added. The mixture was cooled in an ice-bath and a stream of dry hydrogen bromide passed in during a period of 15 minutes. After standing at room temperature for 1.5 hours the reaction mixture was freed of excess hydrogen bromide by passing a stream of dry air through it for 2 hours. The whole was then added to a mixture of 23 ml. of absolute ethanol, 30 ml. of dry benzene, 20 g. of Drierite and 6 g. of zinc oxide which had previously been shaken for 1.5 hours. The entire reaction mixture was shaken for 19.7 hours and then filtered through a bed of Super-Cel. When the filtrate was concentrated *in vacuo* to a sirup and the latter dissolved in 100 ml. of absolute ethanol, crystallization was spontaneous giving 5.21 g. (50%) of material melting at 125–127°. Recrystallization from twelve parts of absolute ethanol gave, with little loss, pure 1,4,6-tri-*O*-benzoyl-2,3-*O*-(1-ethoxybenzylidene)-β-D-fructofuranose melting at 126–127°. Careful recrystallization from twenty parts of absolute ethanol and seeding with the lower-melting form described above gave, with negligible loss, material melting at 114–115° and rotating $[\alpha]^{20}D$ −2.3° (CHCl₃, *c* 0.69). The sample used for the determination of the rotation was recovered and found to melt at 127–128°.

Acknowledgments.—We wish to thank Mr. Harry W. Diehl for assistance in one of the preparations. Analyses were carried out in the Institute's Microanalytical Laboratory under the direction of Dr. W. C. Alford.

BETHESDA, MARYLAND

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(4) It may be noted, in passing, that attempts to cleave the benzyl-oxygen linkage in this substance with hydrogen in the presence of palladium have thus far failed. A similar failure was encountered in the case of 1,2-*O*-(1-benzoyloxybenzylidene)-α-D-ribopyranose (VI, see ref. 3).

(5) While benzoyl chloride in pyridine solution converts 1,2-*O*-(1-benzyloxybenzylidene)-α-D-ribopyranose (VI) to tri-*O*-benzoyl-β-D-ribopyranosyl chloride (ref. 3) Helferich and Bottenbruch[1] reported a normal benzoylation of 2,3-*O*-(1-benzyloxybenzylidene)-β-D-fructofuranose (IV) to the corresponding tribenzoate II. In the course of the present research II, dissolved in pyridine, was treated with two moles of benzoyl chloride at room temperature. No change was observed in the rotation of the solution over the course of 46 hours and the starting material was recovered in 84% yield.

(6) All melting points are corrected.

(7) P. Brigl and R. Schinle, *Ber.* **67**, 127 (1934).