Dry acetanilide (67.5 g.) is added to freshly distilled chlorosulfonic acid (290 g.) in the usual manner. After the reaction mixture has been poured into crushed ice and water, the precipitated p-acetaminobenzene sulfonyl chloride is centrifuged and washed three times with water in the centrifuge. The damp, crude acid chloride is then dissolved easily in ether (1000 cc.), separated from the aqueous layer, and washed with water until the washings no longer give a test for sulfate ion. Four 50-cc. portions of water are usually sufficient. After drying the ethereal solution over anhydrous sodium sulfate for one hour,[2] and filtering, the ether is removed by distillation. When approximately 300 cc. of ether remains, the acid chloride begins to separate, and benzene (1000 cc.) is added. After cooling in the icebox the crystals are transferred to the filter, washed with benzene (200 cc.), and dried *in vacuo* at room temperature. The average yield of several preparations was 70 g. of the colorless crystals of p-acetaminobenzenesulfonyl chloride, melting at 149°. An earlier preparation (m. p. 147–148°) had the same melting point after standing for seven months.

(2) Longer drying may cause the acid chloride to crystallize out, as it is less soluble in anhydrous ether.

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The Action of Titanium Tetrachloride on Benzylglucopyranoside Tetraacetates

BY E. V. PIEL[1] AND C. B. PURVES

Pacsu observed that in absolute chloroform solution titanium tetrachloride and a fully acetylated β-glycoside united to a less soluble, highly colored addition complex. The subsequent decomposition of this complex by water liberated the isomeric α-glycoside acetate in very high yield.[2] While using this reaction to prepare α- from β-benzylglucopyranoside tetraacetate, we noted that a small amount of starting material always could be recovered from the mother liquors of the product. As the yield of the crude, crystalline product was practically quantitative when the heating of the chloroform solution was not unduly prolonged, it was possible to follow the reaction by noting the amounts and the specific rotations of the various fractions (Table I). It was clear that the tetrachloride brought about an equilibrium containing the α- and β-forms of the acetylated glycoside in an approximate ratio of 9:1 and that this equilibrium could be experimentally reached from either side. Al-

(1) This article is based on a thesis submitted by Mr. Piel to the Faculty of the Massachusetts Institute of Technology in partial fulfilment of the requirements for the degree of S.B.
(2) Pacsu, *Ber.*, **61**, 1508 (1928); THIS JOURNAL, **52**, 2563, 2568, 2571 (1930).

though colored addition compounds were formed with tetraacetyl β-methylfructopyranoside,[3] with sucrose acetate or triacetyl β-glucosan,[4] the original materials were recovered unchanged. In these cases the titanium tetrachloride compound initially formed was apparently too stable to rearrange in the experimental conditions.

TABLE I
TITANIUM TETRACHLORIDE (1 MOLE) AND TETRAACETYL GLUCOPYRANOSIDE (1 MOLE) IN BOILING CHLOROFORM SOLUTION

Isomer used, g.	Reflux time, min.	Recryst. fractions		α-Isomer,[a] %
		G.	[α]D	
β, 20	30[b]	F(1) 14.7	− 52.2°	10[b]
		F(2) 4.5	30.0	
β, 20	75	F(1) 15	141.5	86
		F(2) 5	38.3	
β, 50	90	F(1) 42.5	142	93
		F(2) 2.8	2.5	
		F(3) 2.5	32	
β, 20	150[c]	F(1) 14.5	141.6	90
		F(2) 2.7	21	
α, 14	75	F(1) 9.4	141.2	91[d]
		F(2) 2.1	58.5	

[a] As % of the total crystalline product. [b] At 21° instead of at the b. p. Equilibrium was not nearly reached. [c] Too prolonged heating caused slight decomposition and reduced the yield. Fractional recrystallization of F(2) gave 0.5 g. of the pure β-acetate with a rotation of −51.8° in chloroform. [d] The total yield was only 86%. F(2) gave 0.2 g. of pure β-acetate with the correct rotation.

Attention to technical details made the α-benzylglucoside acetate readily available from acetobromoglucose in an over-all yield of 60%, the β-benzyl acetate[5] being an intermediate step. This was greatly superior to the earlier yield (11%) obtained by converting acetobromo to acetoiodoglucose and condensing the latter with benzyl alcohol in quinoline.[6]

Experimental

All rotations were made with sodium light in a 2- or 4-dm. tube at 20 or 21°.

Acetobromoglucose.—A solution made from recrystallized glucose pentaacetate, 50 g., and glacial acetic acid nearly saturated with hydrogen bromide, 75 cc., was kept at room temperature for two hours.[7] Most of the solvent was recovered by evaporation, bath 60° (20 mm.), fortified with hydrogen bromide and used again. Traces were removed from the residual sirup by the addition and evaporation, under diminished pressure, of dry toluene.[8] The recrystallized product was 85–90%.

(3) Pacsu and Cramer, *ibid.*, **59**, 1059 (1937).
(4) Hurd and Cantor, *ibid.*, **60**, 2677 (1938).
(5) Slotta and Heller, *Ber.*, **63**, 1024 (1930).
(6) Helferich and Gootz, *ibid.*, **62**, 2788 (1929).
(7) Fischer, *ibid.*, **44**, 1898 (1911).
(8) *Cf.* Compton, THIS JOURNAL, **60**, 396 (1938).

Tetraacetyl - β - benzylglucopyranoside.—Acetobromoglucose, 110 g., redistilled benzyl alcohol, 265 cc., dry ether, 250 cc., and dry silver oxide, 60 g., were shaken together till the liquid was bromide free.[9] After filtration and evaporation of ether, the excess benzyl alcohol was recovered for the next run by distillation, bath 95–100° (0.1 mm.). A still head lagged with asbestos tape and at least 1 cm. in diameter, together with efficient cooling (ice water) of condenser and receiver, was necessary. The slightly impure product (75%) after complete purification from alcohol had specific rotations of −53.2° in chloroform and −46.7° in dioxane (c, 4.0).

Deacetylation gave pure β-benzylglucopyranoside, m. p. 122° (corr.), with rotations of −56.3° in water, −59.5° in dioxane (c, 2.0) and −57.6° in methyl alcohol (c, 1.5).

Tetraacetyl-α-benzylglucopyranoside.—The β-isomer, 20 g., titanium tetrachloride, 9 g. (1 mole), and pure chloroform, 200 cc., were heated under reflux for seventy-five minutes and the crude product was isolated by Pacsu's methods.[2] Recrystallization from 100 cc. of hot alcohol gave a first fraction of 15 g. and a second fraction, after dilution of the mother liquors with water, of 5 g., the rotations in chloroform being 141.5 and 38.3°, respectively. As those of the pure α- and β-isomers were 144.8 and −53.2°, the α-contents of the two fractions were 99 and 47%, corresponding to an average of 86% for the α-isomer. In a duplicate rearrangement of 153 g. of the β-tetraacetate, the second fraction, 15 g., was twice recrystallized from alcohol and gave 5 g. of the pure starting material with the correct levorotation of −52.8°. Other experiments are summarized in Table I.

Pure tetraacetyl-α-benzylglucopyranoside, m. p. 111°, had rotations of 144.8° in chloroform and 146.0° in dioxane (c, 2.5). Deacetylation gave the pure α-benzyl glycoside with rotations of 133.5° in water, 152° in dioxane (c, 2.5) and 150.3° in methyl alcohol, m. p. 122° corr.

(9) Such syntheses have been improved by the addition of Drierite [Kreider and Evans, THIS JOURNAL, **58**, 1661 (1936)].

Benzoylformic Acid from Styrene

BY CHARLES D. HURD, R. W. MCNAMEE AND FRANK O. GREEN

Oxidation of mandelic acid with potassium permanganate is the usual method[1] of synthesizing benzoylformic acid. Yields of 50 to 72% are attained. In place of mandelic acid it has been found that styrene (phenylethylene) may be oxidized in satisfactory yields to benzoylformic acid according to the equation

$$3C_6H_5CH{=}CH_2 + 8KMnO_4 \longrightarrow 3C_6H_5COCOOK + 8MnO_2 + 5KOH + 2H_2O$$
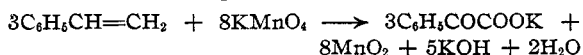
The commercial availability of pure styrene makes

(1) Acree, Am. Chem. J., **50**, 389 (1913); Hurd and Raterink, THIS JOURNAL, **56**, 1349 (1934); Hurd and McNamee, Org. Syntheses, **16**, 89 (1936).

this an economical source of benzoylformic acid, whereas mandelic acid is much more expensive. It was established also that crude styrene, which was obtainable from "Drip Oil"[2] by fractional distillation, might be used also in this synthesis.

For some of the work, styrene was prepared by pyrolysis of cinnamic acid.[3] In other experiments, technical styrene[4] was used. This was vacuum distilled before use to remove the inhibitor (p-t-butylcatechol) and the polymers. From 3.5 g. of this distilled styrene, 8 g. of styrene dibromide, m. p. 72°, was obtained by reaction with bromine in carbon tetrachloride. The purity of this styrene, therefore, was at least 90%, and probably higher.

Styrene was concentrated from "Drip Oil"[5] for the oxidation experiments by fractionation through an efficient column. The fraction taken, b. p. 141–142°, was about one-half styrene because 2.78 g. of it yielded 3.56 g. of styrene dibromide.

Oxidation of Styrene of 90–100% Purity.—Eighteen grams (0.173 mole) of styrene and 9 g. (0.225 mole) of sodium hydroxide were shaken with 100 cc. of water in a 2-liter flask fitted with an air condenser. To this mixture was added in six portions a hot (70°) solution of 75 g. (0.474 mole) of potassium permanganate in 1500 cc. of water. After each addition the mixture was shaken vigorously for two minutes and cooled under the water tap so that the reaction temperature was kept at about 70°. When all the permanganate had been introduced, the excess was reduced with about 100 cc. of alcohol and the manganese dioxide filtered off and washed with water. The filtrate and washings were combined and evaporated down to 400 cc., then acidified with concentrated hydrochloric acid. The 1.5 g. of benzoic acid which separated was removed by filtration. When the addition of hydrochloric acid failed to precipitate any more benzoic acid the solution was extracted several times with ether. On evaporation of the ether, 20.4 g. of a light yellow liquid remained. This crude benzoylformic acid contained 2 to 3 cc. of water which made it quite insoluble in carbon disulfide. The water was removed by distilling with 7 cc. of toluene. An alternative procedure for removing the water was to dry the ether solution with calcium chloride. The residual acid, 18 g. (0.120 mole) or 69% yield, was dissolved in 30 cc. of carbon disulfide and the solution cooled with ice and salt. About 10 g. of crystals came down in the first crop and 5–6 g. in subsequent crops. Recrystallization gave 14.5 g. (0.096 mole) or 55% yield, of benzoylformic acid which melted at 59–61°.

Oxidation of Styrene of about 50% Purity.—A 26.5-g. fraction, b. p. 141–142°, obtained from drip oil, contained 13.3 g. (0.128 mole) of styrene. The quantities of other reagents were based on the styrene content; hence, 55.5 g. (0.351 mole) of potassium permanganate was used. The experimental details were the same as those outlined previously, but this time no benzoic acid separated after

(2) Brown, Ind. Eng. Chem., **20**, 1178 (1928).

(3) Org. Syntheses, **8**, 84 (1928).

(4) Grateful acknowledgment is made to the Dow Chemical Company for a generous supply of styrene.

(5) An abundant supply of drip oil was generously furnished by Mr. G. J. Hart, Norshore Gas Co., Waukegan, Ill.