tane-3,6-dione. A single preparation gave a value of 3000 compared with 396 for a monomolecular product. It is surprising that the fact has been overlooked that reaction with hydrazine cannot, in the absence of molecular weight determinations, be considered as proof or confirmatory evidence for the 1,4-diketone grouping since Fernholz[6] points out that a pyridazine from a 3,6-dione is possible stereochemically only if one of the double bonds is outside of the heterocycle. Moreover, Marker and Wittle[7] have objected to a deduction of others[8] based on "pyridazine" formation on the grounds that the pyridazine in question was probably a linear polymer.

The reaction with hydrazine of the diketone, m. p. 233–235°, from chlorogenin was carried out in the usual way.[2,6] Methyl alcohol was added to a boiling solution of the product in benzene and on cooling a pale yellow oil separated which solidified on rubbing with more methyl alcohol. Solution in benzene and precipitation with methyl alcohol was repeated three times. The product, which was amorphous, was dried at 130° and 3 mm. pressure. It turned a deep yellow at 240°, light brown at 270° and was a dark brown powder at 300°.

Anal. Calcd. for $C_{27}H_{40}O_2N_2$: N, 6.59. Found: N, 7.05, 6.89. When 0.1661 g. was dissolved in 1.889 g. of benzene, the freezing point was depressed 0.16°. Calcd. mol. wt., 425; found, 2770.

The mother liquors from the above preparation were concentrated, dissolved in benzene and precipitated by methyl alcohol. This product showed the same behavior on heating and was found to contain 6.82% nitrogen. When 0.0534 g. was dissolved in 1.247 g. of benzene, the freezing point was depressed 0.11°, indicating a molecular weight of 1981.

In another preparation a product with different properties was obtained although the conditions were to all outward appearances the same. This product was crystalline but showed the same behavior on heating as the previous products.

Anal. Calcd. for $C_{27}H_{40}O_2N_2$: C, 76.38; H, 9.49; N, 6.59. Found: C, 73.73, 73.80; H, 9.62, 9.22; N, 6.49, 6.84.

This crystalline product had only limited solubility in benzene and the solubility appeared to decrease with repeated crystallizations. This solubility behavior is different from that of all previously recorded products, which appear to be characterized by ready solubility in benzene.

In order to get sufficient material into solution for a molecular weight determination, it was necessary to warm the solution but there was no evidence that the material separated before freezing of the benzene took place. A depression of 0.15° was obtained when 0.0950 g. was dissolved in 2.290 g. of benzene, indicating a molecular weight of 1410. A micro Rast determination in camphor by Mr. L. H. Goodson gave a value of 894 for the molecular weight but decomposition of the compound was evident from the brown color of the solution.

A sample of cholestanedione-3,6, m. p. 169–171°, prepared by the method of Dane and Wang,[9] after reaction with hydrazine and purification from benzene and methyl alcohol, gave an amorphous product which darkened at 190° and melted to a red-brown liquid at 210–220°. Windaus[6] reported obtaining a crystalline product which sintered at 188°.

Anal. Calcd. for $C_{27}H_{44}N_2$: N, 7.06. Found: N, 6.72.

When 0.1235 g. was dissolved in 1.750 g. of benzene the freezing point was depressed 0.12°, indicating a molecular weight of 2999.

When 0.1040 g. of the diketone from chlorogenin was dissolved in 1.845 g. of benzene the freezing point depression was 0.69°, giving a molecular weight of 417 compared with a calculated value of 428.

(7) Marker and Wittle, THIS JOURNAL, **61**, 855 (1939).

(8) Odell and Marrian, *J. Biol. Chem.*, **125**, 333 (1938).

(9) Dane and Wang, *Z. physiol. Chem.*, **245**, 86 (1937).

CONVERSE MEMORIAL LABORATORY
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Purification of *p*-Acetaminobenzenesulfonyl Chloride

BY L. H. PENCE AND H. C. WINTER

A convenient method for the purification of large quantities of *p*-acetaminobenzenesulfonyl chloride will be of interest to the many investigators engaged in the synthesis of sulfanilamide and related compounds.

The crude acid chloride obtained by the procedure described by Smiles and Stewart[1] in "Organic Syntheses" frequently may be employed in subsequent reactions without further purification; but they state that it must be used immediately after preparation, since it decomposes rapidly on standing. Once the sulfonyl chloride is purified, however, it may be kept indefinitely. According to their procedure recrystallization of the 90 g. of crude product from benzene yielded 70 g. of pure *p*-acetaminobenzenesulfonyl chloride melting at 149°. However, because of the slight solubility of the sulfonyl chloride in this solvent (2% hot and 0.5% cold), recrystallization from benzene has been reported[1] to be impractical for purifying more than a small amount at a time.

The following modification of the above procedure has been used in our laboratory and found to be much better adapted for the purification of large quantities of the compound from the standpoints of both time and convenience.

(1) Smiles and Stewart, *Org. Syntheses*, **5**, 3 (1925).

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.

BIOCHEMICAL RESEARCH FOUNDATION
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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. Although 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.

(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).

TABLE I

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

Isomer used, g.	Reflux time, min.	Recryst. fractions	G.	$[\alpha]_D$	α-Isomer,[a] %
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).