Summary

The literature dealing with the preparation and the separation of the xylenes is contradictory and misleading.

It has been found that fractional distillation, selective sulfonation, crystallization of the sulfonic derivatives and selective hydrolysis of xylene-sulfonic acid all tend to bring about a partial separation of the 3 xylenes present in coal-tar xylene, but that none of these processes alone is entirely suitable for the isolation of the *ortho* and *para* derivatives. A satisfactory procedure is described in which the above processes are combined.

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FLUORO-ACETYL DERIVATIVES OF SUGARS. I

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Introduction

Moissan[1] prepared several organic fluorine derivatives by the action of dry silver fluoride on iodine and chlorine derivatives of organic compounds. A modification of Moissan's method was applied by shaking dry silver fluoride with an ether solution of bromo-acetyl glucose, but no fluorine derivative could be obtained. Fischer and Armstrong[2] used liquid hydrochloric and hydrobromic acids for obtaining the crystalline chloro- and bromo-acetyl derivatives of several sugars, the time of action being 15–20 hours at room temperature. This procedure suggested the use of water-free hydrofluoric acid. After several unsuccessful attempts in which sirupy reaction products were obtained, it was found that if the time or reaction were shortened to $^1/_2$ hour, crystalline fluoro-acetyl derivatives could be obtained. The yield was small but the compounds were stable, which facilitated the investigation.

A subsequent paper will deal with the application of the process to other sugars and the description of the properties of the new class of compounds.

Experimental Part

General Method of Preparation.—Ruff and Plato[3] have given detailed directions for preparing and handling water-free hydrofluoric acid. The hydrofluoric acid used in this investigation was distilled in a small platinum still. The retort contained about 80 g. of dry potassium hydrogen fluoride,

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[1] Moissan, *Compt. rend.*, **110**, 951 (1890); *Ann. chim.*, [6] **19**, 270 (1890); *J. pharm. chim.*, [5] **23**, 329 (1891).

[2] Fischer and Armstrong, *Ber.*, **34**, 2885 (1901).

[3] Ruff and Plato, *ibid.*, **37**, 675 (1904).

KF.HF, and the receiver 10 g. of the powdered acetyl sugar. The platinum condenser was provided with a glass jacket for cooling with ice water and was connected with the platinum receiver by a lead stopper and a calcium chloride tube of copper.[3] Molten sulfur was used for sealing the joints and the receiver was cooled in an ice- and salt-bath. The distillation was finished in about $^1/_2$ hour and the tared receiver was quickly closed with a platinum stopper and weighed, the yield of hydrofluoric acid being in general about 20 g. The cold liquid in the receiver was now poured[4] into a separatory funnel containing water, ice and chloroform. The mixture was well shaken and the cold portion of chloroform used for rinsing out the receiver was added. The chloroform was drawn off into another separatory funnel containing ice water, and again shaken. This process was again repeated. The chloroform solution after, being dried with anhydrous sodium sulfate, yielded on evaporation in a current of air on the steam-bath a sirup, which soon solidified when stirred with petroleum ether.

Fluoro-tetra-acetyl Glucose.—The slightly yellow sirup obtained from evaporation of the chloroform soon solidified when stirred with petroleum ether. The crystalline mass was dissolved in a small amount of hot 95% alcohol and filtered; as the solution cooled, beautiful crystals separated. Only a few crystallizations were necessary in order to obtain the pure substance, m. p. 108°, as ascertained by the melting point and specific rotation. The yield was 4 g. from 10 g. of β-penta-acetyl glucose. The substance is stable, no decomposition being noticeable in several months when kept without special precaution; it is colorless and odorless and has a very slightly bitter taste. It is very sparingly soluble in petroleum ether, a little more soluble in alcohol and readily soluble in chloroform. After a third recrystallization from 95% alcohol 0.7613 g. made up to 25 cc. with chloroform produced a rotation in a 2dcm. tube of 5.486 circular degrees to the right; hence $[\alpha]^{20}_{D} = +90.08°$.

Analyses. Subs., 0.2525: CO_2, 0.4424; H_2O, 0.1268. Subs., 0.5738: CaF_2, 0.0609. Subs., 0.5000, 0.500: 98.48 cc. of 0.25 N H_2SO_4; 317.0 cc., 316.5 cc. of 0.1 N NaOH. Subs., 2.1040, 3.6836, 4.7405: C_6H_6, 100; Δf, 0.301°, 0.518°, 0.663°. Calc. for $C_{14}H_{19}O_9F$: C, 47.98; H, 5.47; F, 5.43; 71.3 cc. of 0.1 N NaOH for AcOH + HF; mol. wt., 350. Found: C, 47.78; H, 5.62; F, 5.16; 70.9 and 70.8 cc. of 0.1 N NaOH; mol. wt., 349, 355, 357.

Fluoro-hepta-acetyl Cellulose.—The resulting colorless sirup soon crystallized on stirring with petroleum ether. The yield from 10 g. of β-octa-acetyl cellose was 4 g. of this impure dry product. This was recrystallized several times from 95% alcohol, the yield of pure substance being about 2 g.; m. p., 187°. After a second recrystallization 0.9954 g. made up to 25 cc. in chloroform produced a rotation in a 2dcm. tube of 2.391 circular degrees to the right; hence $[\alpha]^{20}_{D} = +30.03°$. It is a stable substance. It is colorless, odorless, has a slightly bitter taste and, except in chloroform, is not very soluble in the ordinary solvents.

Analyses. Subs., 0.2050: CO_2, 0.3669; H_2O, 0.1032. Subs., 0.5000: CaF_2, 0.0249. Subs., 0.5000: 98.64 cc. of 0.25 N H_2SO_4; 211.5 cc. of 0.1 N NaOH. Subs., 0.6755, 0.6926: C_6H_6, 100; Δf, 0.053°, 0.060°. Calc. for $C_{26}H_{35}O_{17}F$: C, 48.88; H, 5.53; F, 2.97; 62.67 cc. of 0.1 N NaOH for AcOH + HF; mol. wt., 638. Found: C, 48.81; H, 5.63; F, 2.62; 62.7 cc. of 0.1 N NaOH; mol. wt., 637, 608.

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[4] The hands of the operator were protected by rubber gloves.

Fluoro-tri-acetyl Xylose.—The resulting colorless sirup yielded sticky crystals on stirring with petroleum ether. The substance crystallizes very well and beautiful large crystals can be obtained, but its great solubility in all solvents which were found suitable for recrystallization prevented a quick purification. Dissolving it in a small amount of 95% alcohol and allowing the filtered solution to evaporate in a vacuum desiccator over sodium hydroxide proved to be the best procedure. The crystals were separated from the small quantity of mother liquor by suction on a hardened filter and were washed with small quantities of 50% alcohol. The crystals were then crushed in a crystallizing dish with a small pestle and washed by decantation with petroleum ether. Several recrystallizations were necessary before a substance of constant melting point (87°) and specific rotation was obtained. The yield from 10 g. of β-tetra-acetyl xylose was about 3 g. of pure substance. The specific rotation of the pure substance was taken as $[\alpha]^{20}_{D} = +67.24°$. Fluoro-tri-acetyl xylose is a stable substance. It is colorless, odorless, has a very slightly bitter taste, and is soluble in the usual solvents, even appreciably soluble in petroleum ether.

Analyses. Subs., 0.2035: CO_2, 0.3536; H_2O, 0.1017. Subs., 0.5000: CaF_2, 0.0659. Subs., 0.5000: 98.64 cc. of 0.25 N H_2SO_4; 319.3 cc. of 0.1 N NaOH. Subs., 2.5686, 3.8615, 6.1874; C_6H_6, 100; Δf, 0.450°, 0.660°, 1.017°. Calc. for $C_{11}H_{15}O_7F$: C, 47.46; H, 5.44; F, 6.83; 71.91 cc. of 0.1 N NaOH for AcOH + HF; mol. wt., 278. Found: C, 47.39; H, 5.59; F, 6.45; 72.7 cc. of 0.1 N NaOH; mol. wt., 285, 291, 303.

Methods of Analysis.—For combustion the substance was mixed with powdered cupric oxide in a copper boat, and the combustion tube contained lead chromate.

It was necessary that the fluorine determination be performed with care in order to obtain satisfactory results. The substance was mixed thoroughly with dry powdered sodium carbonate and the mixture covered with a layer of pure carbonate. The temperature and period of heating were not greater than strictly necessary. After having been carefully heated the fused mass was dissolved in a small quantity of hot water and the solution was quantitatively filtered into a glass-stoppered Erlenmeyer flask. The solution was acidified with acetic acid and a few drops of approximately 10% calcium chloride solution were added. The resulting precipitate after settling overnight was filtered on a closely packed and weighed Gooch filter and washed with small portions of dil. acetic acid.

The estimation of acetyl and fluorine combined is performed by boiling 0.5000 g. of the finely powdered substance with ±98.48 cc. of 0.25 N sulfuric acid under a reflux condenser for 3 hours (the hydrolysis being complete in 3 hours or less) with the addition of a few drops of 10% calcium chloride solution, and subsequent titration with 0.1 N sodium hydroxide solution using phenolphthalein as indicator.

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Summary

A procedure for the preparation of the fluoro-acetyl derivatives of glucose, cellose and xylose is described as representative of a new class of sugar derivatives. Fluoro-tetra-acetyl glucose, fluoro-hepta-acetyl cellose and fluoro-tri-acetyl xylose are described, analyses are given and also the methods of analysis.

WASHINGTON, D. C.