aqueous solution remaining from the hydrolysis was not treated with hydrogen peroxide in this case. A saturated solution of lead acetate was added to it until no further precipitate resulted. A part of this lead salt was suspended in water and treated with dilute hydrochloric acid. The mixture was filtered, and the filtrate was extracted several times (10) with small (15-cc.) portions of ether. On removal of the ether a few crystals remained. These melted at 105°, and a mixture of them with malonic acid (m. p. 132°) melted at 120°. This evidence also indicates that vinylacrylic acid is reduced in the 1,4-positions to form Δ^2-pentenic acid, $CH_3{-}CH{=}CH{-}CH_2{-}COOH$; 2.23 g. of the lead salt of malonic acid was obtained from 2.5 grams of the pentenic acid, which is 29% of the theoretical amount. The yield was low, probably because malonic acid decomposed when the solution of the hydrolysis products of the ozonide was warmed to ensure complete removal of the aldehydes.

Several attempts were made to reduce vinylacrylic acid electrolytically in a solution which was 0.5 molar in hydrogen ion. These conditions approximate those used by Pomilio[3] for the reduction of unsaturated acids. In the case of vinylacrylic acid, however, no reduction occurred. An attempt was also made to reduce the sodium salt of vinylacrylic acid. To obtain this, the calculated amount of pure sodium hydroxide was added to a solution of vinylacrylic acid in 95% ethyl alcohol. No reduction occurred under these conditions, but when enough hydrochloric acid was added to the solution to make it approximately neutral to litmus, hydrogen was absorbed. By adding acid and alkali alternately and observing whether or not hydrogen was absorbed, it was found that the most rapid reduction occurred when the solution was neutral or faintly acid.

Summary

Vinylacrylic acid was reduced electrolytically. It was shown that hydrogen is first added in the 1,4-positions to give Δ^2-pentenic acid, $CH_3{-}CH{=}CH{-}CH_2{-}COOH$. This is in agreement with the reduction of vinylacrylic acid by means of sodium amalgam, but is in contrast with the catalytic hydrogenation of vinylacrylic acid, whereby hydrogen is added in the 3,4-positions.

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Action of Triphenylmethyl Chloride on α-Methyl-*l*-fucoside[1]

BY R. C. HOCKETT[2] AND C. S. HUDSON

By the direct action of triphenylmethyl chloride upon various carbohydrates containing both primary and secondary alcohol groups, Helferich and his colleagues[3] have obtained many sugar derivatives whose primary groups alone are etherified, and have thus amply demonstrated that triphenylmethyl chloride may exercise a preferential action toward primary in the presence of secondary hydroxyl groups. Although the pioneers in this field have offered no general rule that such a selection must invariably occur, a tacit assumption seems to have arisen among other workers that the reaction is so completely specific as to be available for analytical determination of the number of primary hydroxyl groups in any complex molecule of uncertain structure.[4]

This procedure seemed justified *a priori* by such observations as those of Valentin,[5] who found that a number of polyhydroxy alcohols of known constitution absorb the predicted number of triphenylmethyl residues, only the primary alcohol groups being reactive.

The present authors[6] recently observed the reaction of triphenylmethyl chloride with a number of methyl pentosides whose content of primary hydroxyl was uncertain as contingent upon the final assignment of ring structures and therefore considered it necessary to obtain further evidence as to whether a reaction may occur in the presence of secondary hydroxyls only.

α-Methyl-*l*-fucoside, a typical sugar derivative which crystallizes well and which contains four secondary groups but no primary ones, was chosen as a test substance.

This compound readily forms a substitution derivative when treated at room temperature with a dry pyridine solution of triphenylmethyl chloride under the conditions described by Helferich.[3a] The product has been isolated both as a crystalline mono-ethyl alcoholate and as an anhydrous powder. Its analyses indicate that it is a monotrityl-α-methyl-*l*-fucoside. The prop-

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(1) This paper was delivered before the Organic Division of the American Chemical Society at Washington, D. C., in March, 1933. Publication is authorized by the Surgeon General, U. S. Public Health Service.

(2) National Research Fellow during a part of this work.

(3) (a) *Ann.*, **440**, 1 (1924); (b) **447**, 19, 27 (1926); (c) *Ber.*, **58**, 872 (1925).

(4) (a) Josephson, *Ann.*, **472**, 230 (1929); *Ber.*, **62**, 313 (1929); (b) Pacsu, THIS JOURNAL, **53**, 3099 (1931).

(5) F. Valentin, *Coll. Czechoslov. Chem. Comm.*, **3**, 499 (1931).

(6) Hockett and Hudson, THIS JOURNAL, **53**, 4456 (1931).

erties are enumerated in the experimental part.[7]

We must conclude therefore that a distinction is to be drawn between a preferential action and a specific action in the case of the introduction of trityl radicals into carbohydrates. The former we know to exist; the latter, as we have now shown beyond doubt, does not exist. Consequently, great caution must be used in any attempt to apply this reagent for analytical purposes or the determination of structure.[8]

Bredereck[9] has recently attempted to use the same reagent to determine the ring structure of the ribose nucleosides, uridine and cytidine. His conclusions, resting upon the absence of reaction between triphenylmethyl chloride and a methylriboside mixture, seem to us of doubtful validity since his glycosides were sirups. It is extremely difficult to remove all traces of water from a sirup, and we have observed that small amounts of moisture will inhibit this reaction. Moreover, since all the other obtainable methyl pentosides have been shown to react under the proper conditions, it would be remarkable if the methylribosides should fail to do so. Such a situation could only be explained on some such grounds as those of steric hindrance and the admission of such influences as active in determining whether or not a reaction is to occur, could only tend further to invalidate the use of this reaction in the study of carbohydrate structure.

Experimental Part

Monotrityl-α-methyl-*l*-fucoside.—Thirteen grams of α-methyl-*l*-fucoside ($[\alpha]^{20}_{D}$ −195.3°) was dissolved in 100 cc. of dry pyridine which had been distilled from potassium hydroxide and kept over barium oxide (b. p. 118°). Thirty grams of Eastman's triphenylmethyl chloride which had been kept over calcium chloride, was added. After five days at room temperature, the solution was warmed under reflux on a boiling water-bath for one hour. Moisture was at all times excluded by calcium chloride tubes. After cooling, water was added to the solution drop-by-drop to the point of turbidity. By morning, the solution had become a solid mass of slender needles. They were filtered and washed with water–pyridine mixtures with an increasing proportion of water until finally pure water was used; yield, 25 g.

The substance was recrystallized from absolute alcohol, from which it separated as clear six-sided prisms of the mono-alcoholate. On filtering, the crystals were washed with absolute alcohol and dried in a vacuum desiccator over calcium chloride. Under these conditions, efflorescence gradually set in. After many recrystallizations, measurements of the specific rotation were made, using large crystals which were watched to see that no efflorescence occurred during drying.

The constant rotation obtained was $[\alpha]^{20}_{D}$ −51.4° (0.5906 g. in 25 cc. of $CHCl_3$; 2-dm. tube; $\alpha = -7.02°$ saccharimeter). The melting point was 123–126° (corr.).

A sample of the alcoholate was ground, weighed and transformed into the anhydrous substance by drying to constant weight at 75° in a vacuum.

Anal. Subs., 2.6735 g.; after drying, 2.4057 g.; loss, 0.2678 g. Calcd. for monotrityl-α-methyl-*l*-fucoside-monoethyl alcoholate: C_2H_5OH, 9.87. Found: C_2H_5OH 10.01.

The anhydrous monotrityl-α-methyl-*l*-fucoside gave a constant specific rotation of $[\alpha]^{20}_{D}$ −59.5° (0.5437 g. in 25 cc. $CHCl_3$ soln.; 2-dm.; $\alpha = -7.48°$ saccharimeter) and melted at 126–128° (corr.).

Anal. Calcd. for $C_{25}H_{25}O_4(OCH_3)$: OCH_3, 7.37. Found: (Clark's modification of Schwappach–Vieböck semi-micro titration[10]) OCH_3, 7.3, 7.2. Calcd. for $(C_6H_5)_3$-$C(C_7H_{13}O_5)$: trityl, 57.85. Found: (Valentin method, Ref. 5, p. 501) trityl, 57.76, 57.93.

No combustion data are included owing to the fact that a sudden decomposition of the sample occurred during the preparatory drying at 80°. Crystalline triphenylcarbinol and α-methylfucoside were recovered from the decomposition mixture. This occurrence may indicate a relatively low stability on the part of this trityl compound.

Our thanks are due to Dr. F. H. Goldman of this Laboratory for the methoxyl analyses.

Summary

α-Methyl-*l*-fucoside, a sugar derivative containing only secondary hydroxyl groups, reacts readily with triphenylmethyl chloride to form a monotrityl ether which crystallizes with one molecule of ethyl alcohol. This reaction disproves the hypothesis that triphenylmethyl chloride is completely specific in action toward primary hydroxyl groups, although a preferential action is known to take place in many individual cases.

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[7] A preliminary report of this substance was made before the Fourth Organic Symposium at New Haven, Conn., Dec., 1931, in a paper "Some Novel Substances of the Sugar Group," presented by C. S. Hudson.

[8] *Cf.* Oldham and Rutherford, THIS JOURNAL, **54**, 366 (1932).

[9] Bredereck, *Ber.*, **65**, 1830 (1932); *cf.* Levene and Tipson, *J. Biol. Chem.*, **101**, 531 (1933).

[10] Clark, *J. Assoc. Off. Agr. Chem.*, **15**, 136 (1932).