uniformly more bitter than those of α-glucose.[9] The isomeric substances mannitol, sorbitol and dulcitol have approximately the same degree of sweetness while the two anhydrides mannide and isomannide are also of about the same degree of bitterness.

Summary

1. The removal of water from a sugar alcohol with the formation of the anhydride as a rule destroys the sweet taste of the former.

2. Erythritan, the first anhydride of erythritol, possesses a bitter taste in high concentrations but a sweet taste in threshold quantities.

3. Polygalitol, the 1,5-anhydride of mannitol, possesses a sweet taste in high concentration and an astringency in high dilution.

4. No relationship between the number of carbon atoms or hydroxyl groups in the molecule or the molecular weight or spatial configuration and sweet taste has been observed in this class of compounds.

BALTIMORE, MD. RECEIVED JUNE 9, 1936

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[9] Brigl and Scheyer, *Z. physiol. Chem.*, **160**, 214 (1926); *C. A.*, **21**, 418 (1927).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Some Derivatives of 1,3-Diketohydrindene

BY W. H. HUNTER AND E. C. YACKEL[1]

Degradation of 2-acyl-1,3-diketohydrindenes by hydrolysis cannot be carried out successfully, and although these substances are converted by oxidation into a monocarboxylic acid and phthalic acid, the reaction does not always proceed smoothly. In connection with studies on the nitration of acyl diketohydrindenes we have found that bromination in acetic acid offers a superior method of degradation, the triketone being cleaved into 2,2-dibromo-1,3-diketohydrindene and a monocarboxylic acid. For example, 2-benzoyl-1,3-diketohydrindene yields dibromodiketohydrindene and benzoic acid. It is noteworthy that this cleavage, otherwise quite similar to the haloform reaction,[2] takes place in the absence of alkalies.

By means of this reaction it has been found that the nitration of 2-benzoyl-1,3-diketohydrindene yields 2-*m*-nitrobenzoyl-1,3-diketohydrindene, since bromination of the product yields dibromodiketohydrindene and *m*-nitrobenzoic acid.

Although the products obtained are too unstable to withstand the hydrolyzing action of the nitrating mixture, it is noteworthy that the O-acetate of 2-carbethoxy-1,3-diketohydrindene may be obtained by the action of acetyl chloride on either the sodium or the silver salt of the diketo ester, while the O-benzoate may be obtained only from benzoyl chloride and the silver salt.[3] The use of the sodium salt in the latter instance gives rise to an as yet unidentified substance, which is not the isomeric C-benzoate.

Experimental

Cleavage of 2-Benzoyl-1,3-diketohydrindene.—A solution of the triketone[4] (3 g.) and bromine (6 g.) in acetic acid (60 ml.) is warmed on a water-bath for two hours. After the bromine color has disappeared the mixture is cooled and diluted. The crystalline product separating melts at 178–179° and is 2,2-dibromo-1,3-diketohydrindene.[5]

Anal. Calcd. for $C_9H_4O_2Br_2$: Br, 52.7. Found: Br, 52.3, 52.7.

Evaporation of the mother liquor yields benzoic acid, purified by sublimation and identified by nitration.

Nitration of 2-Benzoyl-1,3-diketohydrindene.—The triketone (5 g.) is dissolved in sulfuric acid (40 ml.) at −5°, and treated at this temperature with a mixture of fuming nitric acid (1.5 g.) in sulfuric acid. After thirty minutes the solution is poured onto ice. The solid is washed with water and with much hot alcohol and crystallized from chloroform. The product forms microscopic needles that melt with decomposition at 228–229°; yield 70%.

Anal. Calcd. for $C_{16}H_9O_5N$: N, 4.74. Found: N, 4.73, 4.65.

On bromination in acetic acid, the nitrotriketone yields dibromodiketohydrindene and *m*-nitrobenzoic acid, identified by mixed melting points.

Acetylation of Ethyl 1,3-Diketohydrindene-2-carboxylate.—The sodium salt of the diketo ester[6] may be purified by crystallization from water with the aid of charcoal, and

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[1] The work presented in this paper is taken from a thesis by E. C. Yackel presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Master of Science, October, 1929.—C. F. KOELSCH.

[2] *Cf.* Fuson, *Chem. Rev.*, **15**, 299 (1934).

[3] Hantzsch and Gajewski, *Ann.*, **392**, 306 (1912).

[4] Schwerin, *Ber.*, **27**, 106 (1894).

[5] Kronfeld, *ibid.*, **17**, 720 (1884).

[6] Wislicenus, *ibid.*, **20**, 594 (1887).

freed of water of hydration by drying at 170° for three hours. The silver salt, obtained by treatment of the sodium salt in aqueous solution with silver nitrate, separates directly without water of crystallization.

The reaction between the sodium salt (10 g.) and acetyl chloride (50 ml.) is completed by boiling the mixture for one hour. The sodium chloride is filtered off, the acetyl chloride is evaporated, and the residue (3.4 g.) is crystallized from ether. Similar treatment of the silver salt yields the same compound (mixed melting point) which forms yellow needles that melt at 77–78°.

Anal. Calcd. for $C_{14}H_{12}O_5$: C, 64.6; H, 4.6. Found: C, 64.7; H, 4.8.

Ethyl 3-acetoxyindone-2-carboxylate is readily hydrolyzed, even on exposure to atmospheric moisture, to 1,3-diketohydrindene.

Benzoylation of Ethyl 1,3-Diketohydrindene-2-carboxylate.—The reaction of the silver salt of the diketo ester with benzoyl chloride in benzene is completed by warming for one hour, and the product is crystallized from benzene and ether. In agreement with the description of Hantzsch and Gajewski,[3] the benzoate forms yellow crystals that melt at 146–148°.

The sodium salt of the diketo ester does not react with benzoyl chloride in boiling benzene. However, if the sodium salt (54 g.) is stirred with benzoyl chloride (60 g.) at 80° for five hours, a reaction takes place. Separated from the sodium chloride with ether and crystallized from benzene, the organic product forms large yellow prisms that melt at 140–141°.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.3; H, 4.1. Found: C, 69.4; H, 4.4.

The substance depresses the melting point of the benzoate. Treated with sodium ethoxide in alcohol it gives a red solution which becomes yellow on acidification. Benzoic acid may be sublimed from the tarry residue obtained by evaporating this solution.

Summary

Bromination is suggested as a method for cleaving 2-acyl derivatives of 1,3-diketohydrindene. Some reactions of 2-benzoyl diketohydrindene and of ethyl 1,3-diketohydrindene-2-carboxylate are described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Deuterium Exchange Equilibria in Solution and the Quinhydrone Electrode[1]

BY SAMUEL KORMAN AND VICTOR K. LA MER

Introduction

For the elucidation of the isotopic influence of deuterium upon various phenomena in heavy water (deuterium oxide), it is important to know with some degree of precision the magnitude of the equilibrium constants of the exchange processes set up between the protons and deutons in the solvent and solute molecules. For example, the interpretation of acid and base catalysis in D_2O–H_2O mixtures requires a knowledge of the distribution of deuterium and protium between the various substrate, catalyst (*e. g.*, H_3O^+ and D_3O^+) and solvent molecules.[2]

The measurement of the e. m. f. of galvanic cells involving D_2O furnishes a precise means of determining these exchange constants. To exclude the experimental complications and the theoretical uncertainties inherent in galvanic cells with liquid junction potentials, we have restricted our investigation to cells without transference. The experimental difficulties attendant upon the use of the deuterium gas electrode with small quantities of solution make an appropriate substitute highly desirable.

We have found that the quinhydrone electrode[3] establishes equilibrium quickly and is particularly well adapted for the micro technique necessary for heavy water studies. To this end, the following cells were investigated

(I) Pt, $Q\cdot QH_2$/HCl (0.01 M) in H_2O/AgCl, Ag

(II) Pt, $\{Q\cdot QH_2 + Q\cdot QD_2\}$/HCl-DCl (0.01 M) in H_2O-D_2O/AgCl, Ag

(III) Pt, $Q\cdot QH_2/\{HA(m_1) + NaA(m_2) + NaCl(m_3)\}$ in H_2O/AgCl, Ag

(IV) Pt, $Q\cdot QD_2/\{DA(m_1) + NaA(m_2) + NaCl(m_3)\}$ in D_2O/AgCl, Ag

where $Q\cdot QH_2$ and $Q\cdot QD_2$ represent light and heavy quinhydrone, and HA and DA are the light and heavy varieties of a weak acid.

For (I) and (II) the cell reactions may be written

$$\text{(A)}\quad 2HCl\ (0.01\ M) + Q(H_2O) + 2Ag(s) = 2AgCl(s) + QH_2(H_2O);\ E_H$$

$$\text{(B)}\quad 2DCl\ (0.01\ M) + Q(D_2O) + 2Ag(s) = 2AgCl(s) + QD_2(D_2O);\ E_D$$

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[1] From a thesis submitted by Samuel Korman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

[2] Hamill and La Mer, *J. Chem. Phys.*, **4**, 294 (1936); **4**, 395 (1936); Urey and Teal, *Rev. Modern Phys.*, **7**, 34 (1935). For a discussion of the importance of exchange reactions see pp. 52, 59, 60.

[3] La Mer and Korman, THIS JOURNAL, **57**, 1510 (1935).