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The Structure of Di-*o*-nitrobenzylidene-dulcitol (1,3:4,6-Di-*o*-nitrobenzylidene-dulcitol)

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Tanasescu and Macovski¹ have assigned the structure of a 1,2:5,6-di-*o*-nitrobenzylidene-dulcitol to a substance which they obtained by condensing *o*-nitrobenzaldehyde and dulcitol through the agency of 75% sulfuric acid. They stated that the behavior exhibited by dulcitol in forming this supposed 1,2:5,6-diacetal was a general property of this hexitol and in their communication they assigned 1,2:5,6-diacetal structures to the dimethylene-dulcitol of Weber and Tollens² and the dibenzylidene-dulcitol of Emil Fischer,³ although the original investigators did not designate 1,2:5,6 or any other structure for the diacetals which were described by them. No evidence justifying the assignment of a definitive structure to any of these diacetals appears in the experimental work reported by Tanasescu and Macovski. Recently it has been established that Fischer's dibenzylidene-dulcitol is 1,3:4,6-dibenzylidene-dulcitol⁴ and that the dimethylene-dulcitol of Weber and Tollens is 1,3:4,6-dimethylene-dulcitol.⁵ In the present paper we present conclusive evidence that the di-*o*-nitrobenzylidene-dulcitol of Tanasescu and Macovski possesses an analogous structure and is therefore 1,3:4,6-di-*o*-nitrobenzylidene-dulcitol and not 1,2:5,6-di-*o*-nitrobenzylidene-dulcitol as was assumed by its discoverers.

The di-*o*-nitrobenzylidene-dulcitol which was employed in the investigation was prepared by the method of Tanasescu and Macovski and melted at 261–262° (cor.) in substantial agreement with the melting point of 256–258° (presumably uncor.) reported by them. It formed a dibenzoate which melted at 320–321° (cor.); the melting point recorded for the dibenzoate by them was 310° (presumably uncor.). The diacetal was tested for the presence of contiguous hydroxyl groups by oxidation with lead tetraacetate in glacial acetic acid. It was concluded that they were absent, because of the slight consumption of oxidant (only 0.043 of a molecular equivalent in twenty-two hours); thus hydrolysis of the di-

acetal appears to be necessary before oxidation can proceed. If the compound possessed the structure proposed by Tanasescu and Macovski it would contain a glycol grouping at positions 3 and 4 and it should consume one molecular equivalent of lead tetraacetate upon oxidation. The acetal linkages therefore cannot be at positions 1,2 and 5,6 of the hexitol. Definitive proof of their location at positions 1,3 and 4,6 was obtained when it was found that dibenzoyl-di-*o*-nitrobenzylidene-dulcitol, upon simultaneous hydrolysis and acetylation in a 2% sulfuric acid acetylating mixture, formed the known 2,5-dibenzoyl-1,3,4,6-tetraacetyl-dulcitol. Previous experience has indicated that this reaction proceeds with the substitution of acetyl groups on those hydroxyl groups which are concerned in the acetal formation as evidenced by the formation of 2,5-dibenzoyl-1,3,4,6-tetraacetyl-dulcitol from 2,5-dibenzoyl-1,3:4,6-dibenzylidene-dulcitol⁴ and of 1,6-dibenzoyl-2,3,4,5-tetraacetyl-dulcitol from 1,6-dibenzoyl-2,3,4,5-dibenzylidene-dulcitol.⁶ Acyl migration of benzoyl groups has not been observed in the transformation of a dibenzoylated hexitol diacetal into a dibenzoyltetraacetyl-hexitol by this reagent. The isolation of the same dibenzoyl-tetraacetyl-dulcitol from the dibenzoate of di-*o*-nitrobenzylidene-dulcitol and from 2,5-dibenzoyl-1,3:4,6-dibenzylidene-dulcitol may thus be accepted as strong evidence that the acetal linkages in di-*o*-nitrobenzylidene-dulcitol are at positions 1,3 and 4,6 of the dulcitol moiety.

We express our appreciation to the Atlas Powder Company for furnishing a supply of dulcitol.

Experimental

1,3:4,6-Di-*o*-nitrobenzylidene-dulcitol.—This compound was prepared from dulcitol and *o*-nitrobenzaldehyde by the procedure described by Tanasescu and Macovski.¹ It was recrystallized from 40 parts of acetic acid or dioxane and formed yellow needles which melted at 261–262° (cor.). Tanasescu and Macovski recorded a melting point of 256–258°. The yield of product from 5 g. of dulcitol was 12.0 g. (98%).

Anal. Calcd. for C₂₀H₂₀O₁₀N₂: C, 53.57; H, 4.50; N, 6.25. Found: C, 53.51; H, 4.47; N, 6.17.

(6) Haskins, Hann and Hudson, *ibid.*, **64**, 137, 139 (1942).

(1) Tanasescu and Macovski, *Bull. soc. chim.*, [4] **53**, 1097 (1933).

(2) Weber and Tollens, *Ann.*, **299**, 316 (1898).

(3) Fischer, *Ber.*, **27**, 1534 (1894).

(4) Haskins, Hann and Hudson, *THIS JOURNAL*, **64**, 132 (1942).

(5) Hann, Haskins and Hudson, *ibid.*, **64**, 986 (1942).

Failure of Lead Tetraacetate to Oxidize 1,3:4,6-Di-*o*-nitrobenzylidene-dulcitol.—To a solution of 0.1605 g. of the di-*o*-nitrobenzylidene-dulcitol in 80 cc. of glacial acetic acid, 12 cc. of 0.09108 *N* lead tetraacetate-glacial acetic acid solution (3.05 molecular equivalents) was added and the volume was adjusted to 100 cc. with glacial acetic acid. Analysis of 5-cc. aliquots at the expiration of fifteen minutes, one hour, and twenty-two hours, at 20°, showed that 0.016, 0.016 and 0.043 molecular equivalents of oxidant had been consumed; this slight reducing action was presumably due to a slow hydrolysis of the diacetal. A 1,2:5,6-di-*o*-nitrobenzylidene-dulcitol should reduce one molecular equivalent of lead tetraacetate; the failure of the substance to reduce lead tetraacetate indicated that it does not contain a glycol grouping, and therefore cannot possess the 1,2:5,6-diacetal structure proposed by Tanasescu and Macovski.

2,5-Dibenzoyl-1,3:4,6-di-*o*-nitrobenzylidene-dulcitol.—A solution of 1.0 g. of the di-*o*-nitrobenzylidene-dulcitol in 20 cc. of pyridine was cooled in an ice-bath and after the addition of 5.0 g. of benzoyl chloride, the reaction mixture was allowed to stand at room temperature (25°) for seventy-two hours. The dibenzoate, which precipitated in quantitative yield from the mixture upon the addition of water, was recrystallized from 15 parts of pyridine; it formed yellow prisms which were devoid of optical activity in pyridine solution and melted at 320–321° (cor.) on an electrically heated microscope stage. Tanasescu and Macovski recorded a melting point of 310° for the compound.

Anal. Calcd. for C₃₄H₂₈O₁₂N₂: C, 62.19; H, 4.30. Found: C, 62.16; H, 4.19.

2,5-Diacetyl-1,3:4,6-di-*o*-nitrobenzylidene-dulcitol.—The diacetate was obtained in quantitative yield by the acetylation of the di-*o*-nitrobenzylidene-dulcitol in pyridine solution with acetic anhydride. The substance was practically insoluble in boiling alcohol or chloroform, but could be recrystallized from 200 parts of acetic anhydride; it formed small needles which melted at 320–321° (cor.) on an electrically heated microscope stage.

Anal. Calcd. for C₂₄H₂₄O₁₂N₂: C, 54.13; H, 4.54; CH₃CO, 16.2. Found: C, 54.00; H, 4.66; CH₃CO, 16.0.

2,5-Ditosyl-1,3:4,6-di-*o*-nitrobenzylidene-dulcitol.—A solution of 1.0 g. of the di-*o*-nitrobenzylidene-dulcitol and 1.5 g. of *p*-toluenesulfonyl chloride in 25 cc. of pyridine was refluxed for two hours; the 1.0 g. of precipitate which formed on cooling the solution was separated by filtration and recrystallized from 50 parts of acetic anhydride to constant physical properties. The ditosylate formed light

yellow needles which decomposed at 221–222° (cor.) and were optically inactive in pyridine.

Anal. Calcd. for C₃₄H₃₂O₁₄S₂N₂: C, 53.96; H, 4.26; S, 8.47. Found: C, 54.15; H, 4.31; S, 8.32.

2,5-Dibenzoyl-1,3,4,6-tetraacetyl-dulcitol from 2,5-Dibenzoyl-1,3:4,6-di-*o*-nitrobenzylidene-dulcitol.—A suspension of 2.0 g. of the dibenzoyl-di-*o*-nitrobenzylidene-dulcitol in 50 cc. of an acid acetylating solution, prepared by adding 1 cc. of concentrated sulfuric acid dropwise to an ice-cold mixture of 35 cc. of acetic anhydride and 15 cc. of acetic acid, was agitated until the suspended solid dissolved completely (two and one-half hours) and the solution was allowed to stand at 20° overnight. The mixture was then poured into 300 cc. of ice-cold water and the crystalline precipitate (1.0 g., 59%) which formed was separated by filtration and recrystallized twice from 25 parts of alcohol. It then showed a melting point of 157–158° (cor.), and a mixed melting point with authentic 2,5-dibenzoyl-1,3,4,6-tetraacetyl-dulcitol¹ showed no depression. The conversion of the dibenzoate of the di-*o*-nitrobenzylidene-dulcitol of Tanasescu and Macovski to 2,5-dibenzoyl-1,3,4,6-tetraacetyl-dulcitol is a definitive proof that the acetal linkages in the former compound are at positions 1,3 and 4,6 of the dulcitol molecule and not at the 1,2 and 5,6 positions as assumed by these investigators.

Anal. Calcd. for C₂₈H₃₀O₁₂: C, 60.21; H, 5.41. Found: C, 60.32; H, 5.49.

Summary

The di-*o*-nitrobenzylidene-dulcitol described by Tanasescu and Macovski is not oxidized by lead tetraacetate in glacial acetic acid and therefore cannot possess the structure of 1,2:5,6-di-*o*-nitrobenzylidene-dulcitol arbitrarily assigned to it by its discoverers. Its crystalline dibenzoate is converted to the known 2,5-dibenzoyl-1,3,4,6-tetraacetyl-dulcitol by treatment with an acid acetylating mixture, a fact which proves that the acetal linkages are at positions 1,3 and 4,6 of the dulcitol molecule. The compound of Tanasescu and Macovski is therefore 1,3:4,6-di-*o*-nitrobenzylidene-dulcitol and its structure is analogous to that of the diacetals which dulcitol forms with benzaldehyde and formaldehyde.

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