oxyhexoses,[3] but when applied to nitrodesoxyinositols no reaction occurred under varying experimental conditions, and the nitrodesoxyinositols could be recovered from the reaction mixture. Consequently, we attempted to desaminate substituted or unsubstituted aminodesoxyinositols to the corresponding hexahydroxycyclohexanes by means of nitrous acid or nitrous anhydride. The reaction products resulting from this treatment still contained 20–30% of the original nitrogen content, reduced Fehling solution in the cold and consisted of a variety of components which could not be separated.

We wish to report some new derivatives of nitrodesoxyinositols which were prepared in the course of these investigations. Nitrodesoxyinositol, I,[1] yielded, on acetylation, two pentaacetates, one of which was identical with that obtained from nitrodesoxyinositol, III.[1] Nitrodesoxyinositol I is thus a mixture of two isomers, as is to be expected from the mode of formation described in the original paper.[1] From nitrodesoxyinositol, II, only one acetate was obtained. Hydrogenation of the pentaacetyl-nitrodesoxyinositols to the corresponding amines could not be accomplished. In acid medium the hydrogenation was incomplete, whereas in neutral medium more than the calculated amount of hydrogen was consumed with simultaneous liberation of acetic acid. In contrast, hydrogenation of free nitrodesoxyinositol, II, yielded the pure amine hydrochloride.

Diacetone-nitrodesoxyinositol II[1] did not react with lead tetraacetate in glacial acetic acid. The position of the free hydroxyl in this compound is thus para to the nitro group.

Experimental

Acetylation of Nitrodesoxyinositol, I.—Ten grams of nitrodesoxyinositol, I, (m. p. 147–148°) was added to a mixture of 50 cc. of acetic anhydride and 2.5 cc. of concentrated sulfuric acid, with cooling. The nitrodesoxyinositol dissolved rapidly and after five minutes crystals appeared. After standing overnight at room temperature the crystals were filtered and washed with acetic anhydride; yield of 3.0 g. (18%) after one recrystallization from dioxane m. p. 258–259°. Admixture of pentaacetyl-nitrodesoxyinositol III[1] produced no depression of the melting point.

Anal. Calcd. for $C_{16}H_{21}O_{12}N$: C, 45.82; H, 5.04; N, 3.33. Found: C, 46.08; H, 4.97; N, 3.20.

The mother liquor was added gradually to two liters of ice-water with stirring. A sirup separated which solidified on standing. This was filtered after five hours and washed with water, 11.6 g. (70%) of product being obtained. Two recrystallizations from dry ethanol yielded 8.5 g. of fine needles melting at 186–188°.

Anal. Calcd. for $C_{16}H_{21}O_{12}N$: C, 45.82; H, 5.04; N, 3.33. Found: C, 46.03; H, 4.97; N, 3.16.

Nitrodesoxyinositol, I, after partial purification according to the method reported previously[1] (m. p. 172–173°), yielded, on acetylation, 56% of the higher melting pentaacetate and 25% of the lower melting one.

Pentaacetyl-nitrodesoxyinositol, II.—On acetylation of nitrodesoxyinositol II the pentaacetate crystallized directly in a 85% yield from the reaction mixture. A small portion of the same material (8%) was obtained from the mother liquor when added to ice-water. After one recrystallization from dioxane the pentaacetyl-nitrodesoxyinositol II melted at 207–209°.

Anal. Calcd. for $C_{16}H_{21}O_{12}N$: C, 45.82; H, 5.04; N, 3.33. Found: C, 46.01; H, 4.98; N, 3.13.

Aminodesoxyinositol (II) Hydrochloride.—An amount of 1.8 g. of nitrodesoxyinositol II was dissolved in 50 cc. of water and hydrogenated in presence of 500 mg. of platinum dioxide. Within three hours 95% of the calculated amount of hydrogen was absorbed. The catalyst was removed by filtration and the solution was neutralized with 1 *N* hydrochloric acid, filtered with some charcoal and concentrated under reduced pressure to 5 cc. On gradual addition of 20 cc. of acetone the amine hydrochloride crystallized with one mole of water in a yield of 64%. After recrystallization from water–acetone it sintered at 255° and melted under decomposition at 265–270° (evacuated capillary tube).

Anal. Calcd. for $C_6H_{14}O_5N\cdot HCl\cdot H_2O$: C, 30.84; H, 6.90; N, 5.99. Found: C, 30.90; H, 6.58; N, 5.72.

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Concerning Anderson's Modifications of the B. E. T. Equation

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In his recent statistical treatment of the sorption of vapors by solids, Dole[1] arrived at his equation 14 which he considered similar to Anderson's equation 6,[2] the two equations giving the same values for the constant N_s (or V_m) but different values for the constant c.

Although Anderson does not give an explicit derivation of his equation, it is clear from his statements that the following relations must exist between the various symbols, where the superscripts *D* and *A* refer to Dole's and Anderson's symbols respectively, *viz.*:

$$k^{D} = (a_2/a_1)^{D} = 1/c^{A}$$

and

$$c^{D} = (a_1/a_L)^{D} = c^{A}k^{A}$$

Substitution of these relations into either of the two equations under discussion shows that they are in fact equivalent.

Beebe and co-workers[3] have published heat of adsorption data for nitrogen and argon on carbon blacks, plotted in their figures 3 to 8. In three out of the four cases where the differential heats fall off sharply at about the monolayer volume, this drop occurs at an adsorption somewhat larger than the B.E.T. monolayer. Since Anderson's equation 6[2] predicts a monolayer volume some 8 to 15% higher than the B. E. T. monolayer, it appears that his modification corrects the B. E. T. equation, in three cases out of four, in the right direction by about the right amount, as judged by the above heat data. Actually it would be more

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[3] R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, This Journal, 69, 95 (1947).

correct to compare heat of adsorption data with adsorption data plotted according to equation 8 of Walker and Zettlemoyer.[4]

Beebe, *et al.*,[3] indicated the Anderson monolayer volume at a smaller value than the B. E. T. monolayer, thus making Anderson's modification appear to be in the wrong direction. It is true that for a given amount adsorbed, the numerical value of V/V_m from Anderson's equation will be smaller than from the B. E. T. equation, but for this very reason, if the point where Anderson's V/V_m is unity is marked off on a scale graduated in terms of B. E. T.'s V/V_m, it must fall at a place where the graduation shows B. E. T.'s V/V_m to be greater than unity.

These facts support Anderson's equation 6. However, in deriving his equation 17,[2] he has used an expression (equations 13 and 15) for the volume adsorbed in the *n*th layer, V_n, which holds only for the simple B. E. T.[5] model. The appropriate expression for Anderson's model instead of his equation 15, is given by

$$V_n = \frac{V_m c j^{n-1} x^n}{1 + (c - j)x}$$

This, when summed for values of n from 1 to ∞, gives an isotherm equation which is identical with the one obtained by a more direct method in a later publication,[6] as it must since the two equations are deduced from identical postulates.

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Furan-2-glyoxal

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During work on the synthesis of polycarbonyl compounds, it became desirable to prepare the hitherto unknown furan-2-glyoxal. Several approaches were considered, and two were investigated. The first required the preparation of 2-acetylfuran, followed by oxidation of the ketone with selenium dioxide[1a] to the glyoxal. The second procedure involved the preparation of 2-diazoacetylfuran from furoyl chloride and diazomethane, followed by interaction with hydrogen chloride to give 2-chloroacetylfuran,[2] treatment with pyridine to yield the pyridinium chloride, transformation to the nitrone with *p*-nitrosodimethylaniline and, finally, acid hydrolysis to the glyoxal hydrate.[3]

Until the recent work of Hartough and Kosak[4] on the catalytic acetylation of furan with acetic anhydride and hydriodic acid, the preparation of adequate amounts of 2-acetylfuran was a rather difficult problem. Previously, it had been synthesized by the hydrolysis of ethyl furoylacetate,[5,6,7] from furan, acetyl chloride[8] or acetic anhydride[9] and stannic chloride, from 2-chloromercurifuran and ketene,[10] and from 2-cyanofuran and methylmagnesium iodide.[11]

In the present work which was originated before the disclosures of Hartough and Kosak,[4] the method of the Russian workers[9] was first studied. Their high yields could not be duplicated, much of the furan being lost by resinification. Attention was directed therefore, to treatment of the readily, available furoyl chloride with dimethylcadmium.[12a,b] This reaction gave 2-acetylfuran in 28% yield and was used routinely until displaced by the simpler catalytic technique. Oxidation of the ketone with selenium dioxide went smoothly, and furan glyoxal was isolated in 47% yield.

The Kröhnke-Börner method proceeded as anticipated and furan glyoxal hydrate was isolated in about 11% over-all yield from furoyl chloride, the most severe losses being encountered in the purification of the pyridinium salt. It is not improbable that the yield could be increased considerably by eliminating rigid purification procedures at each step.

Furan-2-glyoxal is a yellow oil with a piercing aroma, develops a green-blue coloration with a mixture of acetic anhydride and sulfuric acid, dissolves in saturated sodium bisulfite with generation of heat, forms a crystalline hydrate on treatment with water, and gives a mono-semicarbazone on interaction with a molar quantity of semicarbazide.

Experimental

2-Acetylfuran. (a) From Furan and Acetic Anhydride.—The method of Hartough and Kosak[4] was followed but it was found desirable to add the hydriodic acid at −10° instead of 0°. This modification seemed to aid in the control of the subsequent exothermic reaction.

(b) From Furoyl Chloride and Dimethylcadmium.—The Grignard reagent was prepared in a nitrogen atmosphere from 7.4 g. (0.304 mole) of magnesium turnings and 42.5 g. (0.3 mole) of methyl iodide in 200 ml. of anhydrous ether. The dimethylcadmium was made by the addition of 29.4 g. (0.16 mole) of dry cadmium chloride according to the directions of Cason.[12] To the organometallic solution in benzene was added at room tempera-

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