be noted that the compensating complex with methyl β-idoside itself has an over-all levorotational shift (−105°); this would be expected on the basis of the 1B3 conformation (2,3-angle, +90; 3,4-angle, −60°) but not the 2B3 conformation (2,3-angle, +60; 3,4-angle, −90°). It therefore seems likely that the β-idosides are best represented by the continuous series of structures, C1 $\rightleftarrows$ HC3 $\rightleftarrows$ 1B3. The reason for the adoption of this pathway over the alternate possibility, C1 $\rightleftarrows$ HC2 $\rightleftarrows$ 2B3 may lie in the fine structure of the skew and half-chair intermediates. When models of the two skew forms are compared, the OH groups at C_1 and C_2 are found to be nearly eclipsed in 2B3 and there is a closer approach of the OH at C_4 to the ring oxygen than in 1B3. In 1B3 there is, however, a possible slight Δ2 condition. The situation is similar in the half-chair conformations, and in addition in HC2 the oxygens at C_1, C_2 and C_4 are more crowded than in HC3. Despite the slight Δ2 conditions in both HC3 and 1B3 these conformations are apparently the more stable.

Of the possibilities considered here, the closest approach to a single geometrical description of the β-D-idosides is probably the half-chair structure, HC3, with the actual conformation somewhere in the series C1 $\rightleftarrows$ HC3 $\rightleftarrows$ 1B3. The extreme skew structure may be reached under the influence of the 4,6-benzylidene group; in 3-methyl idoside, where only the 1*a*,3*a*-complex is possible, the conformation may move in the direction of the chair structure, C1. With the α-idosides, on the other hand, the single chair conformation 1C accounts for all of the observations. Methyl α-D-idoside in 1C conformation has an equatorial arrangement for the C_1–OCH_3 group; the same is true of methyl β-D-idoside in the conformational series C1 $\rightleftarrows$ HC3 $\rightleftarrows$ 1B3. The somewhat more rapid chlorine oxidation of the β-anomer is therefore a result of the lower stability of the half-chair and skew conformations as opposed to the chair conformation.

Acknowledgment.—The assistance of Clara P. Thiessen in carrying out the chlorine oxidation experiments is gratefully acknowledged.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Acetals and Dithioacetals of 2-*S*-Ethyl-2-thio-D-xylose(lyxose)

BY M. L. WOLFROM AND WALTER VON BEBENBURG[1]

RECEIVED NOVEMBER 21, 1959

The free hydroxyl of carbon two of 3,4,5-tri-*O*-benzoyl-D-xylose diethyl dithioacetal was substituted by an ethylthio group by the action of ethanethiol and dry hydrogen chloride, to initiate a series of acetal and dithioacetal derivatives. The position of the ethylthio substituent was determined to be C2 by desulfurization of the debenzoylated derivative followed by periodate oxidation to produce propionaldehyde, isolated as its dimedone derivative.

In the previous paper of this series,[2] the synthesis of 3,4,5-tri-*O*-benzoyl-D-xylose diethyl dithioacetal (I) was described. The corresponding 3,4,5,6-tetra-*O*-benzoyl-D-glucose diethyl dithioacetal had been reported by Brigl and Mühlschlegel[3] and its unsubstituted hydroxyl on carbon two had been replaced by an ethylthio group.[4] We report herein a series of reactions starting with the substitution of an ethylthio group for the free hydroxyl in 3,4,5-tri-*O*-benzoyl-D-xylose diethyl dithioacetal (I).[2] Substance I was treated with ethanethiol[4,5] and dry hydrogen chloride to replace the hydroxyl on carbon two with an ethylthio group, producing 3,4,5-tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (II). Position C2 was established as the point of ethylthio substitution by reductive desulfurization of the debenzoylated substance VI with Raney nickel followed by periodate oxidation to produce propionaldehyde and formaldehyde, isolated as their dimedone derivatives. As it is not established whether the replacement of hydroxy by ethylthio occurs with or without Walden inversion, the configuration of C2 is unknown in these 2-*S*-ethyl-2-thio derivatives. Treatment of II with mercuric chloride and methanol in the presence of cadmium carbonate[6] produced sirupy 3,4,5-tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-xylose(lyoxse) dimethyl acetal (III) which was debenzoylated to yield sirupy 2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (V) and this upon acetylation produced crystalline 3,4,5-tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose)dimethyl acetal (IV). Sirupy II was debenzoylated to yield sirupy 2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (VI) which produced a crystalline triacetate VII. Removal of the dithioacetal group from VII with mercuric chloride and cadmium carbonate in methanol or in benzyl alcohol yielded the crystalline acetylated dimethyl acetal IV or the crystalline acetylated dibenzyl acetal VIII, respectively. Sirupy 2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (V) was obtained in an analytically pure condition by deacetylation of its crystalline triacetate.

Acknowledgment.—The counsel and assistance of Doctors F. Shafizadeh and A. Thompson are gratefully acknowledged.

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[1] Postdoctoral Fellow under Grant No. CY-3232 from the Department of Health, Education and Welfare, Public Health Service, National Institutes of Health, Bethesda 14, Md. (R. F. Proj. 759B).

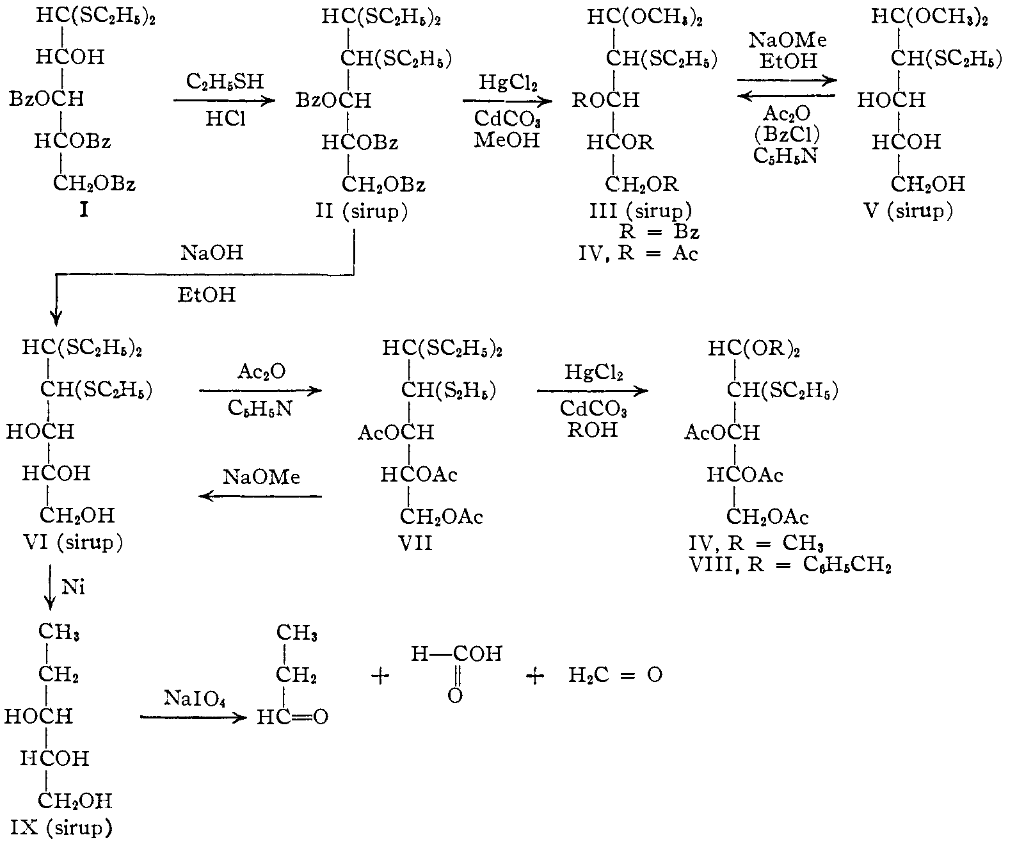
[2] M. L. Wolfrom and W. v. Bebenburg, THIS JOURNAL, **81**, 5705 (1959).

[3] P. Brigl and H. Mühlschlegel, *Ber.*, **63**, 1551 (1930).

[4] P. Brigl, H. Mühlschlegel and R. Schinle, *ibid.*, **64**, 2921 (1931).

[5] M. L. Wolfrom and A. Thompson, THIS JOURNAL, **56**, 1804 (1934).

[6] M. L. Wolfrom, L. J. Tanghe, R. W. George and S. W. Waisbrot, *ibid.*, **60**, 132 (1938).



Experimental

3,4,5-Tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) Diethyl Dithioacetal (VII).—A solution of 20 g. (0.035 mol.) of 3,4,5-tri-*O*-benzoyl-D-xylose diethyl dithioacetal[2] (I) in 200 ml. of chloroform and 30 ml. of ethanethiol was nearly saturated with dry hydrogen chloride at 0°. After standing at room temperature for 24 hr. the chloroform and ethanethiol were evaporated under reduced pressure. The residue was dissolved in 200 ml. of water, washed with sodium bicarbonate solution and water, dried with anhydrous magnesium sulfate and the ether evaporated. The remaining sirup did not crystallize during six months. Silicate chromatography[7] failed to bring it to crystallization. This sirupy, 3,4,5-tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (II, 30 g.) was dissolved in 200 ml. of absolute ethanol containing 250 mg. of sodium ethoxide and kept at room temperature for 48 hr. The solution was concentrated under reduced pressure and the concentrate was washed with 1500 ml. of water and 500 ml. of petroleum ether (b.p. 30–60°). The aqueous layer was filtered through a short column of aluminum oxide, concentrated under reduced pressure and extracted with three 200-ml. portions of ether. The combined extracts were dried with anhydrous magnesium sulfate and evaporated to a pale yellow sirup, 2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (VI); yield 11 g.

The above sirup (VI, 11 g.) was dissolved in 150 ml. of pyridine, cooled to 0° and 17 g. of acetic anhydride was slowly added. After standing for 40 hr. at room temperature, the solution was poured into 300 ml. of water and extracted with three 150-ml. portions of ether and the combined extracts were dried with anhydrous magnesium sulfate. 3,4,5-Tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (VII) crystallized upon slow evaporation of the ether. Pure material was obtained upon recrystallization from ether–petroleum ether; yield 15 g., m.p. 61–62°, $[\alpha]^{25}_{D}$ +58.5° (*c* 2.6, acetone).

Anal. Calcd. for $C_{17}H_{30}O_6S_3$: C, 47.91; H, 7.09; S, 22.55. Found: C, 48.28; H, 7.09; S, 22.56.

Pure 2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (VI) was also obtained as a sirup on deacetylation of the acetate VII (2 g.) by the procedure described above for its preparation from the benzoate II; yield 0.9 g.

Reductive Desulfurization and Periodate Oxidation of 2-*S*-Ethyl-2-thio-D-xylose(lyxose) Diethyl Dithioacetal (VI).—2-*S*-Ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (VI, 0.9 g.), prepared from crystalline VII, was dissolved in 100 ml. of ethanol and refluxed with 40 g. of Raney nickel for 24 hr. with stirring. The solution was filtered and the residue was extracted with absolute ethanol in a Soxhlet apparatus for 20 hr. The combined filtrate and extract was evaporated under reduced pressure to a sirup (IX). The sirup was dissolved in ethanol, diluted with ether, filtered to remove inorganic material and again evaporated to a sirup; yield 150 mg. This colorless sirup was dissolved in 25 ml. of water and to this was added a solution of 500 mg. of sodium metaperiodate in 100 ml. of water. The volatile products were flushed into a flask containing 50 ml. of a saturated aqueous solution of dimedone (5,5-dimethyl-1,3-cyclohexanedione) by passing in a slow current of air for 20 hr. The precipitate which formed was filtered; yield 50 mg. of colorless plates, m.p. 145–150°. Pure material was obtained upon recrystallization from methanol; m.p. 150–155° unchanged upon admixture with authentic propionaldehyde dimedone derivative; X-ray powder diffraction data[8]: 8.70 vw, 7.73 s(3), 7.04 w, 6.39 m, 5.95 s(1), 5.35 w, 4.73 vw, 4.44 s(2), 3.80 vw, 3.66 vw, 3.54 vw; identical with that of an authentic sample.

The periodate reaction mixture was treated with 50 ml. of saturated aqueous dimedone solution. The precipitate which formed was filtered; yield 50 mg., m.p. 187–190° unchanged upon admixture with an authentic sample of formaldehyde dimedone derivative.

3,4,5-Tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) Dibenzyl Acetal (VIII).—To a suspension of 40 g. of cadmium carbonate in a solution of 10 g. of 3,4,5-tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (VII) in 100 ml. of dry benzyl alcohol, heated to 80° with stirring,

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(7) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

(8) Interplanar spacing, Å., CuKα radiation. Intensity of lines, estimated visually: s, strong; m, medium; w, weak, v., very; parenthetic numerals, three most intense lines, 1 the most intense.

was added a warm solution of 40 g. of mercuric chloride in 100 ml. of dry benzyl alcohol. The heating and stirring were continued for 4.5 hr. The mixture was then cooled to room temperature, filtered, washed with aqueous potassium iodide solution and water, dried with anhydrous magnesium sulfate and evaporated to a sirup at 1 mm. pressure. The residue was extracted several times with petroleum ether (b.p. 30–60°). When the extract was concentrated to 100 ml., the material crystallized as fine needles, and was recrystallized from ethanol–water; yield 6.5 g., m.p. 61–63° depressed to 54–60° when mixed with starting material of m.p. 61–62°, $[\alpha]^{25}D$ +25° (*c* 1.5, acetone).

Anal. Calcd. for $C_{27}H_{34}O_8S$: C, 62.54; H, 6.60; S, 6.18. Found: C, 62.56; H, 6.28; S, 6.02.

3,4,5-Tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) Dimethyl Acetal (IV).—Sirupy 3,4,5-tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (II, 20 g.) was demercaptalated by the procedure described above for the preparation of 3,4,5-tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) dibenzyl acetal using methanol instead of benzyl alcohol to produce sirupy 3,4,5-tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (III); yield 16 g. This sirup (III, 16 g.) was dissolved in 50 ml. of ethanol containing 50 mg. of sodium methoxide. After standing for 48 hr. in the refrigerator, the ethanol was evaporated under reduced pressure, the residue was extracted with ether, the extracts filtered and again evaporated to a sirup. The sirup was dissolved in water and washed with petroleum ether (b.p. 30–60°). The petroleum ether was washed several times with water. The combined aqueous solutions were evaporated under reduced pressure to a sirup; yield 6 g. A portion of the sirup (1 g.) was distilled at 0.05 mm. and 100° bath temperature. The distilled, sirupy 2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (V, 250 mg., see below) was dissolved in 3 ml. of dry pyridine and treated with 450 mg. of acetic anhydride. After standing for 48 hr. it was mixed with 10 ml. of cold water, extracted with ether, dried with anhydrous sodium sulfate and evaporated to a sirup which crystallized (IV) upon addition of petroleum ether (b.p. 30–60°); yield 200 mg., m.p. 58–59°, $[\alpha]^{20}D$ +43° (*c* 2, chloroform).

Anal. Calcd. for $C_{15}H_{26}O_8S$: C, 49.16; H, 7.15; S, 8.75. Found: C, 49.43; H, 7.19; S, 8.71.

In subsequent preparations the crystalline material was obtained by acetylation of undistilled V.

3,4,5-Tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (IV) can also be obtained (68% yield) from 3,4,5-tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) diethyl dithioacetal (VII) by substituting methanol for benzyl alcohol in the procedure described above for preparing the corresponding dibenzyl acetal VIII.

2-*S*-Ethyl-2-thio-D-xylose(lyxose) Dimethyl Acetal (V).—3,4,5-Tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose(lyxose) dimethyl acetal (crystalline IV, 5 g.) was dissolved in 50 ml. of absolute ethanol containing 150 mg. of sodium methoxide and allowed to stand at room temperature for 24 hr. The sodium ion was removed by stirring with an excess of cation exchange resin (Amberlite IR-120)[9] and the solution was evaporated under reduced pressure to a sirup. The sirup was extracted with ether, the extract evaporated to a sirup and distilled at 0.05 mm. and a bath temperature of 100°; yield 1.1 g. (V), $[\alpha]^{20}D$ +38° (*c* 1, chloroform).

Anal. Calcd. for $C_9H_{20}O_5S$: C, 44.94; H, 8.39; S, 13.34. Found: C, 45.25; H, 8.40; S, 13.36.

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[9] A product of the Rohm and Haas Co., Philadelphia, Pa.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Controlled Thermal Decomposition of Cellulose Nitrate. VII. Carbonyl Compounds[1,2]

BY M. L. WOLFROM AND G. P. ARSENAULT

RECEIVED OCTOBER 15, 1959

An investigation of the carbonyl compounds formed from the ignition of cellulose nitrate was made. Isolated as the 2,4-dinitrophenylhydrazine derivatives were acetone, acetaldehyde, formaldehyde, methylglyoxal, glyoxal, mesoxaldehyde and hydroxypyruvaldehyde. A gas chromatographic study of the cellulose nitrate (cast from ethyl acetate) ignition products demonstrated the presence therein of acetaldehyde, acetone, acrolein, ethyl acetate, hydrogen cyanide and a new, unidentified substance which is not a carbonyl compound. Ethanol is not a product of ignition of cellulose nitrate. The origin of the compounds isolated is discussed.

The controlled thermal decomposition of cellulose nitrate has been under investigation in this Laboratory.[2–5] Thus, the liquid mixture of cellulose nitrate ignition products has been reported to contain carbonyl compounds, among which formaldehyde, glyoxal and two oxidation stages of glycerose (glyceraldehyde) or dihydroxyacetone (without carbon fragmentation) were isolated.[4] The latter two compounds were present in small amounts only and, at all pressures investigated, the total carbonyl content of the liquid mixture of cellulose nitrate ignition products was larger than the sum of the amounts of carbonyl which could be ascribed to the presence of formaldehyde and glyoxal in the liquid mixture.[6] In the work herein reported, a more thorough investigation was made of the carbonyl compounds present in the liquid mixture of ignition products.

Cellulose nitrate containing 12.6% N was ignited[4] at 75 mm. pressure. A large fraction (74%) of the total carbonyl content of the aqueous solution (product I, Fig. 1) of the resulting liquid mixture of ignition products was accounted for by the presence therein of formaldehyde and glyoxal (Table I). Product I was frozen and sublimed three times at low temperature, under freeze-drying conditions. The sublimates were numbered in the order in which they were obtained (products II–IV, Fig. 1) and the residue of the repeatedly sublimed product I was dissolved in water (product V, Fig.

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[1] This work was supported by the United States Army Ordnance Department under contracts (DA-33-019-ord-727, -1476 and -2042; supervising agency, The Ballistic Research Laboratories, Aberdeen Proving Ground, Md.) with The Ohio State University Research Foundation (Projects 496, 591 and 679).

[2] Previous communication: M. L. Wolfrom, K. S. Ennor and A. Chaney, THIS JOURNAL, **81**, 3469 (1959).

[3] M. L. Wolfrom, J. H. Frazer, L. P. Kuhn, E. E. Dickey, S. M. Olin, D. O. Hoffman, R. S. Bower, A. Chaney, Eloise Carpenter and P. McWain, *ibid.*, **77**, 6573 (1955).

[4] M. L. Wolfrom, J. H. Frazer, L. P. Kuhn, E. E. Dickey, S. M. Olin, R. S. Bower, G. G. Maher, J. D. Murdock, A. Chaney and Eloise Carpenter, *ibid.*, **78**, 4595 (1956).

[5] M. L. Wolfrom, A. Chaney and P. McWain, *ibid.*, **80**, 946 (1958).

[6] Reference 4, Fig. 5.