(50 gallons of feed) showed 83% of the adsorbed hafnium in the sulfuric strip as 50 wt. % hafnium oxide.

After conversion to the tetrachloride, the enriched hafnium made available by the first process cycle was further concentrated in a second similar cycle to 90 wt. % hafnium oxide. The over-all yield for the entire operation averaged 70%. Further concentration of hafnium by adsorption would probably require a zirconium-selective adsorbent.

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NOTES

Carbohydrate Thioacetals. I. Lead Tetraacetate Oxidation of D-Arabinose Derivatives

BY S. B. BAKER

Sugar thioacetals are important intermediates in carbohydrate syntheses and the oxidation of these sulfur-containing derivatives by means of glycol-cleaving oxidants should yield valuable intermediates. However, divalent sulfur atoms readily oxidize to form sulfones.[1] Some work has been done[2,3] on the periodate and lead tetraacetate oxidations of sugar thioacetals. The relative position of a glycol group to a thioacetal group may have some effect on the mode of oxidation and the present paper shows that this apparently occurs with arabinose thioacetal derivatives.

Two derivatives of D-arabinose dibenzyl thioacetal were prepared to determine what effect the position of a glycol had on the mode of oxidation of a thioacetal by lead tetraacetate. The first derivative, 4,5-isopropylidene-D-arabinose dibenzyl thioacetal, on reaction with one molecular equivalent of lead tetraacetate was oxidized in the normal manner, as shown by the isolation of isopropylidene-D-glyceraldehyde in good yield. The second derivative, 2,3-dibenzoyl-D-arabinose dibenzyl thioacetal did not yield formaldehyde on reaction with one molecular equivalent of lead tetraacetate, because the oxidant was apparently consumed in the oxidation of a sulfur atom.[3] On addition of a second equivalent of oxidant, the latter was consumed and approximately one equivalent of formaldehyde was produced as determined by the formation and isolation of formaldimethone.

Thus it seems that oxidation of arabinose thioacetal derivatives containing a glycol group in different positions relative to the thioacetal group can follow two paths and the point of reaction is apparently dependent on these relative spacial positions of the two groups.

Experimental

D-Arabinose Dibenzyl Thioacetal.—D-Arabinose (100 g.) was dissolved in cold concentrated hydrochloric acid (200 cc.). Benzyl mercaptan (200 cc.) was added and the mixture was vigorously agitated. After about 30 min. the mixture, which had become homogeneous with evolution of heat, began to cool and solidify. The hard reaction mixture was broken up, filtered and washed with water (6000 cc.), dilute ammonium hydroxide (400 cc.) and finally with water again. The crude air-dried material was recrystallized from 1-propanol-petroleum ether (3:1). The yield was 215 g. (80%) and melted at 148–149°; $[\alpha]^{22}\text{D}$ +18.3 (*c* 2.6, pyridine). Pacsu[4] reported a melting point of 144° and $[\alpha]^{20}\text{D}$ −18.86 for the L-isomer.

4,5-Isopropylidene-D-Arabinose Dibenzyl Thioacetal.—D-Arabinose dibenzyl thioacetal (70 g.) and anhydrous cupric sulfate (350 g.) were suspended in anhydrous acetone (1750 cc.) in a 5 l. round-bottomed flask. The mixture was vigorously agitated for 7 days on a shaking machine. The reaction mixture was filtered and the partially hydrated copper sulfate washed with chloroform. The filtrates were combined and concentrated to dryness at 50° *in vacuo*. The crystalline residue was dissolved in chloroform (100 cc.), the solution decolorized with charcoal and then filtered. The colorless filtrate was treated with low-boiling petroleum ether until turbid. Crystallization commenced immediately and the mixture was then cooled at −15° overnight for maximum crystallization; yield 70 g. (90%). A portion was twice recrystallized from boiling petroleum ether (65–110°) and dried at 65° *in vacuo*, melted at 100–100.5° and $[\alpha]^{24}\text{D}$ −56.5° (*c* 1.7, chloroform).

Anal. Calcd. for $C_{22}H_{28}S_2O_4$; C, 62.85; H, 6.66; S, 15.2. Found: C, 62.7; H, 6.9; S, 15.2.

Lead Tetraacetate Oxidation of 4,5-Isopropylidene-D-Arabinose Dibenzyl Thioacetal.—The presumed 4,5-isopropylidene derivative (6.07 g.) was dissolved in thoroughly dried benzene (150 cc.). Twice recrystallized lead tetraacetate (6.4 g., 1 mole) was added rapidly and the mixture was agitated for 30 min. with occasional cooling. The mixture was then allowed to stand for 2 hr. and a 1-ml. aliquot showed that all the lead tetraacetate was consumed. The mixture was filtered through a sintered glass filter and the filter washed well with two portions of anhydrous benzene (25 cc.). The combined filtrates were then distilled through a 30-cm. column to remove the benzene and the residue slowly distilled under reduced pressure. A fraction (1.6 g.) was obtained, boiling at 42–44° (13 mm.), $n^{21}\text{D}$ 1.4559; $[\alpha]^{22}\text{D}$ +68.1 (*c* 0.45, benzene). These constants were in agreement with those found by Baer and Fischer[5] for isopropylidene-L-glyceraldehyde except for the direction of rotation.

A fraction (0.5 g.) was dissolved in saturated 2,4-dinitrophenylhydrazine hydrochloride and the solution after stand-

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[1] W. A. Bonner and R. W. Drisko, THIS JOURNAL, **73**, 3699 (1951).

[2] B. H. Nicolet and L. A. Shinn, *ibid.*, **61**, 1615 (1939).

[3] C. F. Huebner, R. A. Pankratz and K. P. Link, *ibid.*, **72**, 4811 (1950).

[4] Pacsu and Ticharich, *Ber.*, **62**, 3008 (1929).

[5] E. Baer and H. O. L. Fischer, THIS JOURNAL, **61**, 764 (1939).

ing overnight deposited yellow needles. After recrystallization from 50% ethanol the melting point was 147–148°. The reported[5] melting point for the 2,4-dinitrophenylhydrazone of L-glyceraldehyde is 147–148°.

2,3-Dibenzoyl-4,5-Isopropylidene-D-Arabinose Dibenzyl Thioacetal.—4,5-Isopropylidene-D-arabinose dibenzyl thioacetal (86 g.) was dissolved in anhydrous pyridine (200 cc.) and after cooling to −15° benzoyl chloride (60 cc.) was added dropwise with stirring. The mixture was then allowed to stand at room temperature for 48 hours. The reaction mixture was added to ice water with stirring and after about 30 min. the sirupy product crystallized. The solid mass was broken up, filtered and washed with water to remove most of the pyridine. After air drying, the crude product was recrystallized from methanol in the presence of decolorizing charcoal. The material was recrystallized twice more from methanol with very little loss; yield 117 g. (91%), m.p. 103.5–104°; $[\alpha]^{22}\text{D}$ +81.5° (*c* 1.9, chloroform). *Anal.* Calcd. for $C_{36}H_{36}S_2O_6$: C, 68.82; H, 5.73; S, 10.19; benzoyl, 33.4. Found: C, 68.7; H, 5.9; S, 10.1; benzoyl, 33.2.

Monobenzoyl-D-Arabinose Dibenzyl Thioacetal.—2,3-Dibenzoyl-4,5-isopropylidene-D-arabinose dibenzoyl thioacetal (45 g.) was dissolved in ethanol (250 cc.). Dilute (5%) hydrochloric acid (70 cc.) was added and the solution heated on the steam-bath for one hour. The reaction mixture was cooled and neutralized with saturated sodium bicarbonate solution and the mixture concentrated under reduced pressure until viscous. Chloroform was added and the mixture warmed for a few minutes to hasten solution and then filtered. The chloroform solution was dried over anhydrous sodium sulfate, treated with charcoal, and then filtered. The colorless filtrate was concentrated to dryness and the viscous, colorless sirup triturated with hot ether. The sirup crystallized and after filtration and washing with ether it was recrystallized from absolute ethanol containing about 10% petroleum ether; yield was 25 g. (71%), m.p. 112–112.5°; $[\alpha]^{23}\text{D}$ −25.4° (*c* 2.1, chloroform). *Anal.* Calcd. for $C_{26}H_{28}S_2O_5$: S, 13.2. Found: S, 13.2.

A sample (0.5 g.) was heated on the steam-bath for 30 min. with 2% sodium hydroxide solution (40 cc.). The hot solution was filtered rapidly through a preheated funnel and a precipitate separated which was filtered and washed with water until the washings were neutral. After drying the product weighed 0.3 g. (79%), m.p. 147–148°. A mixed melting point determination with authentic D-arabinose dibenzyl thioacetal showed no depression.

2,3-Dibenzoyl-D-arabinose Dibenzyl Thioacetal.—2,3-Dibenzoyl-4,5-isopropylidene-D-arabinose dibenzyl thioacetal (50 g.) was heated on the steam-bath for one hour in 80% acetic acid (500 cc.). The solvent was removed under reduced pressure and the nearly colorless sirup dissolved in ether and the solution washed with saturated bicarbonate and then with water. The ethereal solution was then dried over anhydrous sodium sulfate in the presence of decolorizing charcoal. After filtration the solvent was removed and a perfectly colorless sirup was obtained that would not crystallize after three months. On prolonged standing in an evacuated desiccator over phosphorus pentoxide, the sirup became a colorless glass; yield was 44 g. (93%); $[\alpha]^{26}\text{D}$ +56.5° (*c* 1.7, chloroform). It was insoluble in water and soluble in all the usual organic solvents, including warm petroleum ether.

Anal. Calcd. for $C_{33}H_{32}S_2O_6$: C, 67.35; H, 5.44; S, 10.9; benzoyl, 35.7. Found: C, 67.2; H, 5.6; S, 10.9; benzoyl, 35.3.

A sample (0.5 g.) of 2,3-dibenzoyl-D-arabinose dibenzyl thioacetal was dissolved in anhydrous acetone (350 cc.) containing anhydrous cupric sulfate (15 g.) in suspension. The mixture was agitated for 5 days at room temperature, then filtered and the filter washed with dry acetone. The solvent was removed from the filtrate and the gummy residue triturated with a little methanol. Immediate crystallization occurred. The product was recrystallized from methanol. A mixed melting point determination with authentic 2,3-dibenzoyl-4,5-isopropylidene-D-arabinose dibenzyl thioacetal showed no depression.

Lead Tetraacetate Oxidation of 2,3-Dibenzoyl-D-Arabinose Dibenzyl Thioacetal.—Oxidation of a sample (0.2536 g.) of the above compound with 90 ml. of 0.048 *M* lead tetraacetate in glacial acetic acid, made up to 100 ml. with the same solvent showed that 0.09, 1.6, 1.9, 2.4, 2.9, 3.2, 4.4, 4.6 and 4.9 molecular equivalents of the oxidant were consumed in $^1/_{12}$, $^1/_4$, $^3/_4$, 2, 3.5, 5.5, 24, 28.5 and 48 hours, respectively. The analytical results thus indicated that oxidation of the divalent sulfur atoms occurred.

In another experiment a sample of the above compound was oxidized in glacial acetic acid with one molecular equivalent of lead tetraacetate. The oxidant was consumed but formaldehyde could not be detected. Two molecular equivalents of lead tetraacetate were consumed with the formation of a high yield (93%) of formaldimethone. The authenticity of the latter compound was determined by a mixed melting point of 188–190°. The reported m.p. is 189–190°.

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S-(*n*-Butyl)-homocysteine (Butionine)

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Ethionine is known to act as an antagonist to the utilization of methionine[1,2]; to some extent, it can be utilized by the living cell instead of the latter amino acid.[2,3] It seemed, therefore, interesting to study a higher homolog of ethionine, such as S-(*n*-butyl)-homocysteine (Butionine). This substance, however, proved to cause no response on the part of *Escherichia coli.*[2]

β-Butylthio-ethanol.—Butyl bromide (12 ml.) was added at 0° to a solution of 15.6 g. of β-thioethanol and 13 g. of potassium hydroxide in 65 ml. of alcohol. The mixture was refluxed for three hours and, after addition of water, extracted with ether; b.p. 118° (28 mm.); yield 17.5 g. (65%). This method is preferable to that of Whitner and Reid[4] who prepared the compound from ethylene chlorohydrin and butyl mercaptan (b.p. 92–93° (3 mm.)).

Anal. Calcd. for $C_6H_{14}OS$: S, 23.9. Found: S, 23.7.

β-Butylthioethyl Chloride.—At 0° with agitation, 17.5 g. of β-butylthioethanol was added to 10.5 ml. of phosphorus trichloride. After two hours, at room temperature, the upper layer was treated with ice-water and extracted with ether; b.p. 96° (26 mm.); yield 10.5 g. (54%) (literature,[4] b.p. 68° (6 mm.)).

Anal. Calcd. for $C_6H_{13}ClS$: Cl, 23.0. Found: Cl, 23.1, 23.2.

Diethyl (β-Butylthioethyl)-phthalimidomalonate.—An intimate mixture of 10.5 g. of β-butylthioethyl chloride and 25.6 g. of diethyl sodiophthalimidomalonate[5] was heated at 160° for six hours and then at 200° for 15 minutes. The mass was triturated with hot water and the oily reaction product extracted with ether; b.p. 265–270° (13 mm.); yield 12.6 g.

Anal. Calcd. for $C_{21}H_{27}NO_6S$: C, 60.0; H, 6.4; N, 3.3 S, 7.6. Found: C, 60.3; H, 6.6; N, 3.7; S, 7.6.

S-(*n*-Butyl)-homocysteine.—To the foregoing product in 12 ml. of alcohol, 33.6 ml. of 5 *N* sodium hydroxide was added. With evolution of heat, a salt crystallized out. The mass was heated on the water-bath for two hours, di-

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