equiv. of benzoyl chloride in the conditions described for I gave 18 mg. (51%) of crystalline XXVII, m.p. 203–204°, and 7 mg. (25%) of XXVIII, m.p. 135–137°.

When the benzoylation was carried out with 1.1 mole-equiv. of benzoyl chloride, keeping the reaction mixture at −20° for 3 days followed by 24 hr. at 0°, no tribenzoate was obtained, and only 16% of impure dibenzoate. The starting material XXIII was recovered to the extent of 81%.

*1,6-Anhydro-2,4-di-O-benzoyl-3-O-p-tolylsulfonyl-β-*D*-glucopyranose* (XXX). A mixture of the cooled solutions of 92 mg. of XXVIII and 143 mg. of *p*-toluenesulfonyl chloride (3 mole-equiv.), each in 1 ml. of anhydrous pyridine, was kept at 0° for 2 hr. and at room temperature overnight. It was then extracted with chloroform and gave 108 mg. of sirup which was dissolved in benzene and chromatographed on silicic acid. A mixture of benzene and ether (19:1) eluted 32 mg. of sirup which, by crystallization from a mixture of acetone, ether, and pentane, gave 15 mg. (11%) of long, slender needles, m.p. 125–127°.

Anal. Calcd. for $C_{27}H_{24}O_9S$: C, 61.82; H, 4.61; S, 6.11. Found: C, 61.68; H, 4.45; S, 6.09.

Mixtures of benzene and ether (9:1, 4:1 and 1:1) eluted 67 mg. of starting material.

*1,6-Anhydro-2,4-di-O-benzoyl-3-O-methyl-β-*D*-glucopyranose* (XXIX) *from* XXVIII. A mixture of 50 mg. of XXVIII, 50 mg. of silver oxide, and 3 ml. of methyl iodide was stirred for 1 day at room temperature under moisture protection. After addition of another 50-mg. portion of silver oxide, the mixture was stirred for 9 hr. longer. It was then filtered through a double layer of Darco G-60 and Celite, and the silver residue was washed exhaustively with hot acetone. After concentration of the filtrate 57 mg. of sirup was obtained. It was recrystallized twice from a mixture of acetone, ether, and pentane to give 29 mg. (56%) of XXIX, thick prisms, m.p. 137–140°, $[\alpha]_D^{24}$ − 30 ± 1° (in chloroform, *c*, 1.50). No depression of the melting point was observed in admixture with a sample of XXIX prepared by benzoylation of XXII as described above.

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BOSTON, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

6,6′-Diglycose Anhydrides[1]

ROY L. WHISTLER AND ARMIN FROWEIN

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5,6-Anhydro-1,2-*O*-isopropylidene-D-glucose reacts in the melted state with either 1,2-*O*-isopropylidene-D-glucose or 1,2:3,4-di-*O*-isopropylidene-D-galactose to produce in good yield the 6,6′-anhydrides. Addition of an alkaline catalyst increases reaction with secondary hydroxyls and consequently also increases the polymerization. Both diglycose anhydrides are obtained amorphous but the 6,6′-di-D-glucose anhydride octaacetate is obtained crystalline.

Sugar derivatives with 5,6-anhydro rings have proved useful in many synthetic reactions. The sugar derivative most extensively investigated is 5,6-anhydro-1,2-*O*-isopropylidene-D-glucofuranose whose reactivity is intensively examined in the work of Ohle.[2] In general, the derivative reacts with compounds containing an active hydrogen, with opening of the oxirane ring between the oxygen and carbon C-6. Consequently, the D-glucose configuration is predominantly retained and substitution occurs on carbon C-6. Addition reactions under anhydrous conditions are base-catalyzed by such reagents as pyridine and sodium ethoxide. Under certain basic conditions ring opening occurs to a small extent between the oxygen and carbon C-5 with derivatization and inversion of carbon C-5. Consequently, there is obtained a small amount of product with the L-idose configuration.

In this work attention was given to the use of 5,6-anhydro-1,2-*O*-isopropylidene-D-glucofuranose to derivatize corn amylose and to react with a second sugar derivative to create a 6,6′-diglycose anhydride. First attempts to react the 5,6-anhydro sugar with corn amylose led to self polymerization of the anhydride and to some degradation of the amylose with little evident substitution of the amylose. Hence, most of the effort was directed toward the reaction of the anhydro sugar with another sugar derivative.

When 5,6-anhydro-1,2-*O*-isopropylidene-D-glucofuranose is melted with 1,2-*O*-isopropylidene-D-glucofuranose, there occurs an extensive opening of the oxirane ring and combination of the two sugars with the formation of intermolecular anhydrides. The predominant product is the 1,2:1′,2′-di-*O*-isopropylidene-6,6′-di-D-glucofuranose anhydride which hydrolyzes to 6,6′-di-D-glucose anhydride. This compound is isolated in the amorphous condition but is readily converted to the crystalline octaacetate. Paper chromatographic analysis of the hydrolyzed products from the melt reaction suggests the presence of small amounts of polymer and possibly of 3,6′- and 5,6′-di-D-glucose anhydrides. Predominance of the 6,6′-anhydro linkage is evidence that the primary alcohol groups of the second sugar are more reactive than the secondary hydroxyls. Reaction with secondary hydroxyl

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(2) See the review by S. Peat, *Adv. Carbohydrate Chem.*, 2, 37 (1946).

groups is increased if a basic catalyst such as pyridine or sodium ethoxide is present in the melt. These catalysts also increase polymer formation either of the mixture or of the 5,6-anhydro derivative alone. Even with the pure 5,6-anhydro derivative, polymerization is slow and does not go beyond low molecular weight compounds.

Reaction in the uncatalyzed melt state of the 5,6-anhydro-D-glucose derivative with 1,2:3,4-di-*O*-isopropylidene-D-galactose also produces an inter sugar anhydride as practically the sole product. Aqueous acid hydrolysis gives rise to an amorphous product which is presumably D-glucose-D-galactose 6,6′-anhydride. On treatment of this product in hot 48% hydrobromic acid solution, the anhydride bond is hydrolyzed with liberation of D-glucose and D-galactose.

Proof that a 6,6′-anhydride linkage is present in both the di-D-glucose and the D-glucose-D-galactose compounds is obtained through periodate oxidation of the unsubstituted anhydride. Both dialdose anhydrides consume the expected amount of oxidant and produce the expected amount of formic acid (Table I). Conclusive evidence for the 6,6′-linkage is obtained, however, by borohydride reduction of the 2,2′-diglycolaldehyde anhydride which results as an oxidation end product, and conversion of the β,β'-dihydroxyethyl ethers to their crystalline di-2,4-dinitrobenzoates.

TABLE I

	Moles of Formic Acid	
	Found	Calcd.
Anhydride I	7.6	8
Anhydride II	7.6	8
D-Glucose	4.8	5

EXPERIMENTAL

1,2-O-Isopropylidene-6-O-tosyl-D-glucofuranose. This preparation was a modification of that of Ohle and Dickhäuser.[3] Twenty-two grams (0.1 mole) of 1,2-*O*-isopropylidene-D-glucofuranose[4] was dissolved in 120 ml. of dry pyridine and 100 ml. of dry benzene was added. While this mixture was stirred at 60°, there was added, slowly and dropwise, a solution of 19 g. (0.1 mole) of *p*-toluenesulfonyl chloride in 80 ml. of dry benzene. The mixture was then stirred for 1 hr. and the solvent removed under reduced pressure. The remaining sirup was shaken at 60° with 280 ml. of benzene, cooled to room temperature, and shaken with a mixture of 100 ml. of diethyl ether and water. The upper layer was removed, washed successively with 2*N* sulfuric acid, a 2% solution of sodium hydrogen carbonate, and water. When dried over sodium sulfate, the solution was warmed, filtered and concentrated under reduced pressure at 40° until crystallization occurred. Purification was effected by dissolving the solid in 40 ml. of warm carbon tetrachloride, and crystals were allowed to form in the refrigerator. Yield, 18.7 g. (50.0%); m.p., 106–108°.

6,6′-Di-D-glucose anhydride (anhydride I). Two grams (10 mmoles) of 5,6-anhydro-1,2-*O*-isopropylidene-D-glucofuranose prepared from 1,2-*O*-isopropylidene-6-tosyl-D-glucofuranose by the method of Ohle and Vargha[5] and 3 g. (13.6 mmoles) of 1,2-*O*-isopropylidene-D-glucofuranose were mixed thoroughly in a test tube and heated to 160° for 3.5 hr. in an oil bath. The cooled mixture was dissolved in 50 ml. of a 50% acetic acid solution, the solution was heated on a steam bath for 2 hr. and concentrated under reduced pressure to a sirup. This was taken up in 40 ml. of water and chromatographed on a carbon column[6] using 0.2% aqueous ethanol to remove free D-glucose and aqueous 10% ethanol to remove the anhydride. Sequential fractions of eluate were examined by paper chromatography and fractions of relatively pure anhydride combined, concentrated under reduced pressure to a sirup, dissolved in a little methanol, and dried upon 4 g. of powdered cellulose. This was placed at the top of a cellulose column which was then irrigated with ethyl acetate–pyridine–water (10:4:3 v/v). Sequential fractions of eluate were tested with silver nitrate reagent.[7] A component with a paper chromatographic flow rate equivalent to that of hydroxymethylfurfural was eluted first, followed by the anhydride. Those fractions which seemed to contain anhydride were combined and concentrated at 60° under reduced pressure to a sirup. This sirup was dissolved in methanol, treated with a small amount of carbon and again concentrated to a sirup which was dried at 50° and 0.1 mm. pressure over phosphorus pentoxide; yield, 32%. Mol. wt. found by the Barger-Rast method[8] was 360; calcd., 342; $[\alpha]^{25}_{D}$ +81° (*c*, 1.15 in water).

D-Glucose-D-galactose 6,6′-anhydride (anhydride II). Two grams (10 mmoles) of 5,6-anhydro-1,2-*O*-isopropylidene-D-glucofuranose and 3.9 g. (15 mmoles) of 1,2:3,4-di-*O*-isopropylidene-D-galactose[9–11] were heated 4 hr. at 165°, hydrolyzed in 50% aqueous acetic acid, and chromatographically purified as described above; yield, 0.92 g. (27%). The final clear sirup, on drying at reduced pressure over phosphorus pentoxide, showed a Barger-Rast mol. wt. of 365; calcd., 342; $[\alpha]^{25}_{D}$ +72° (*c*, 1.1 in water).

On repeating the preparation it was found that the purification could be simplified. The sirup concentrate from the carbon column containing hydroxymethylfurfural as the only impurity was dissolved in methanol, filtered through a small amount of carbon, and the anhydride precipitated by addition of diethyl ether. After washing with diethyl ether, the product was dried in a vacuum desiccator.

6,6′-Di-D-glucose anhydride octaacetate. To a mixture of 100 mg. of sodium acetate and 2 ml. of acetic anhydride at 155° was added, portionwise, 100 mg. of the sugar anhydride. After complete dissolution the mixture was cooled, 5 g. of ice was added, and the mixture was stirred until crystallization occurred. Then 15 ml. of water was added and after 30 min. the crystals were filtered. Yield, 280 mg. (70%); m.p., 166°. After dissolution in 3 ml. of ethanol, carbon treatment and crystallization, the melting point and rotation were: m.p., 171°; $[\alpha]^{25}_{D}$ +61° (*c*, 1 in chloroform). Barger-Rast mol. wt., 660; calcd., 678.

Anal. Calcd. for $C_{28}H_{38}O_{19}$: C, 49.56; H, 5.64; acetyl, 50.74. Found: C, 49.42; H, 5.63; acetyl, 50.39.

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Periodate oxidation. For oxidation, 100 mg. of sugar was dissolved in 50 ml. of water, 50 ml. of 0.3*M* solution of sodium periodate added, and the mixture kept at 25° in the dark. Formic acid was liberated with 0.05*N* sodium hydroxide solution added in 5-ml. aliquots. Maximum amounts were formed in 3 days.

To test for formaldehyde, 10 ml. of the final oxidation mixture was distilled at 60° under reduced pressure to collect 7 ml. of distillate in a receiver at 0°. One milliliter of fuchsin sulfurous acid was added and after 10 min. 1 ml. of concd. hydrochloric acid was added. While D-glucose gave a positive blue color, both anhydrides gave a negative test.

Periodate oxidation also produced as one end product an ether which could be characterized. To accomplish this, anhydrides I and II were separately oxidized in 685-mg. quantities with 5.1 g. of sodium meta-periodate in 50 ml. of water. After 5 hr. at 25°, 5 ml. of 2*N* sodium hydroxide solution was added, followed by an excess of sodium borohydride. Reduction was allowed to occur at 25° for 2 hr. and at 45° for 2 hr. The solution was made acid with 2*N* sulfuric acid and neutralized with sodium hydroxide solution. Water was removed by distillation under reduced pressure and the dry residue was extracted several times with absolute tetrahydrofuran. The combined extracts were dried over anhydrous sodium sulfate and concentrated to 10 ml. To this was added 1.4 g. of 2,4-dinitrobenzoyl chloride and 1 ml. of dry pyridine and the mixture was heated 30 min. at 70°. After filtration and distillation to dryness under reduced pressure, the residue was dissolved in warm benzene. This solution was washed first with 2*N* sodium hydroxide solution and then with water and was dried over anhydrous sodium sulfate. The diester crystallized on addition of ether. After recrystallization from a mixture of five parts of heptane and one part of dioxane the melting point was 154°, undepressed on admixture with the authentic sample prepared below. The compounds were also identical in infrared and x-ray patterns.

The authentic sample of β,β'-dihydroxyethyl ether di-2,4-dinitrobenzoate was prepared from a commercial sample of β,β'-dihydroxyethyl ether as described above. Rast mol. wt., 510; calcd., 494.

Anal. Calcd. for $C_{18}H_{14}N_4O_3$: C, 43.73; H, 2.85; N, 11.33. Found: C, 43.82; H, 2.94; N, 11.03.

Hydrolysis of anhydrides I and II. Approximately 5 mg. of anhydride was mixed with 1 ml. of 48% hydrobromic acid and the solutions were heated in a sealed tube for 15 min. at 100°. The contents were diluted with 10 ml. of water and 2 ml. of ethanol. An excess of silver carbonate was added, the mixture filtered and the filtrate treated with hydrogen sulfide. After admixture with carbon, the solution was filtered and concentrated under reduced pressure to a sirup which was taken up in 1 ml. of water. This solution was analyzed by paper chromatography using Whatman No. 1 paper, ethyl acetate–pyridine–water (10:4:3 v/v) as the irrigant and silver nitrate solution as the spray reagent. Anhydride I gave only one hydrolysis component, which had a flow rate equivalent to that of D-glucose. Anhydride II gave evidence of two components in what by visual comparison appeared to be equal amounts, one with the flow rate of D-glucose and one with the flow rate of D-galactose.

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, IMPERIAL OIL LIMITED]

Organic Sulfur Compounds. IV.[1a] Some Addition and Co-oxidation Reactions of 4-Chlorobenzenethiol with Dicyclopentadiene and Aldrin

ALEXIS A. OSWALD[1b] AND FERNAND NOEL

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4-Chlorobenzenethiol readily adds to *exo*- and *endo*-dicyclopentadienes and Aldrin (VIII) by a radical mechanism to yield the *exo* and *endo* isomers of 4-chlorophenylmercaptodihydrodicyclopentadiene (IV and V) and 2-*p*-chlorophenylmercapto-*endo*-5,6,7,8,9,9-hexachloro-*exo*-*endo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (IX). When 4-chlorobenzenethiol solutions were air oxidized with any of the above diolefins, unstable hydroperoxide intermediates (XIII, XVI, XVIII) were obtained. The hydroperoxide intermediate of the thiol-Aldrin co-oxidation, 2-*p*-chlorophenylmercapto-3-hydroperoxy-*endo*-5,6,7,8,9,9-hexachloro-*exo*-*endo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (XVIII) was isolated as a colorless, crystalline substance. In solution, it rearranged to the corresponding 2-*p*-chlorophenylsulfinyl-3-hydroxy derivative (XIX). It is suggested that similar co-oxidation and not addition reactions of thiols and dicyclopentadiene are responsible for gum formation in some cracked gasolines.

The results of investigations of radical type mercaptan-olefin addition and co-oxidation reactions[1a,2] suggested that similar reactions of diolefins and mercaptans may occur. The examination of diolefin-mercaptan addition and co-oxidation was of interest from the viewpoint of gum formation in cracked gasolines. Early studies, summarized by Ellis[3] and Gruse[4] concluded that diolefins cause

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