of the methyl desoxysorboside by sodium periodate.

The structure of the 5-desoxy-2-ketohexose was established by oxidizing the phenyl-5-desoxy-L-sorbosotriazole with one mole of either lead tetraacetate or sodium periodate. When the latter reagent was employed, the osotriazole was cleaved smoothly into two fragments which were identified as 2-phenyl-4-formylosotriazole and β-hydroxypropionaldehyde. The former was obtained as the solid crystalline aldehyde and the latter was characterized through the dimedone "anhydride."

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Reductive Acetolysis of Nitrate Esters

BY D. O. HOFFMAN,[1] R. S. BOWER[1] AND M. L. WOLFROM

The denitration of cellulose nitrate with ammonium and the alkali metal hydrosulfides[2,3] has been an established commercial process. Rassow and Dörr[3] were able to denitrate cellulose nitrate with aluminum, activated by mercuric chloride, in various solvents but were unable to separate the cellulosic product from the aluminum compounds formed. These investigators also denitrated cellulose nitrate with Devarda's alloy[4] in strongly alkaline solution, a medium which is known to produce profound chemical alterations in cellulose nitrate. The nitrate ester in several D-glucose derivatives has been reductively hydrolyzed to the parent alcohol by means of iron dust[5] (or zinc and iron dust[6]) and glacial acetic acid. All of these methods pose difficult isolation problems when applied to nitrates of water-soluble carbohydrates because of the large amounts of inorganic salts in the reaction mixtures. Kuhn[7] has reported an excellent method for the catalytic hydrogenolysis of nitrate esters to the parent alcohol, employing a supported palladium catalyst under pressure.

We wish to report herein a method by which a nitrate ester may be simultaneously denitrated and acetylated. A solution of the nitrate ester in acetic anhydride is reduced with zinc dust and a suitable promoter to a solution free of nitrate, as demonstrated by the very sensitive color test with diphenylamine and sulfuric acid. The most satisfactory promoter found was anhydrous hydrogen chloride. Dry pyridine gave a nitrate-free reaction mixture but the yield of acetate was lower.

The crystalline nitrate esters of methyl α-D-glucopyranoside, levoglucosan (1,6-anhydro-D-glucopyranose), erythritol (the *meso*-tetritol) and D-mannitol were converted in good yield to their acetates with the hydrogen chloride promoter (Table I). The same result but with a markedly lower yield, was obtained using pyridine and is illustrated with D-mannitol hexanitrate in the data of Table I.

TABLE I

SIMULTANEOUS DENITRATION AND ACETYLATION OF NITRATE ESTERS OF SUGAR DERIVATIVES AND OF POLYHYDRIC ALCOHOLS

		Acetate derivative					
		Yield, %		Found		Accepted	
Substance	Promoter for denitration	Crude	Re-crystd.[a]	M. p., °C.	$[\alpha]^{20-25}D$, c 4–6, $CHCl_3$	M. p., °C.	$[\alpha]D$, $CHCl_3$
Methyl α-D-glucopyranoside tetranitrate	HCl	93	62	100–102	+130°	100–101	+131°
Levoglucosan trinitrate	HCl	83	59	108–109	− 47[b]	110	− 45.5[b]
Erythritol tetranitrate	HCl	81	65	87–88	*meso*	89	*meso*
D-Mannitol hexanitrate	HCl	75	69	120–121	+ 25.5	120	+ 26
D-Mannitol hexanitrate	Pyridine	34	29	118–119	+ 25	120	+ 26

[a] From 95% ethanol. [b] Solvent 95% ethanol. Found in chloroform, $[\alpha]^{25}D$ −59° (c 4).

A sample of high-viscosity cellulose nitrate of 13% nitrogen content was subjected to the

TABLE II

VISCOSITY CHARACTERISTICS OF PRODUCTS FROM THE SIMULTANEOUS DENITRATION AND ACETYLATION OF CELLULOSE NITRATE

	Acetone solution, 25°		
Substance	Time of outflow, sec.[a]	Sp. gr.	c, g./100 ml. soln.
Cellulose nitrate (13% N)	446.5	0.792	0.709
Denitration product, hydrogen chloride promoter	81.0	.797	.788
Denitration product, pyridine promoter	65.3	.797	.709
Acetone	62.3	.788	

[a] Ostwald type viscometer.

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[1] Research Associate of The Ohio State University Research Foundation (Project 212).

[2] H. de Chardonnet, German Patent 56,655 (1890).

[3] B. Rassow and E. Dörr, *J. prakt. Chem.*, **216**, 113 (1924).

[4] *Cf.* A. Devarda, *Z. anal. Chem.*, **33**, 113 (1894).

[5] J. W. H. Oldham, *J. Chem. Soc.*, **127**, 2840 (1925).

[6] J. Dewar and G. Fort, *ibid.*, 492, 496 (1944); J. Dewar, G. Fort and N. McArthur, *ibid.*, 499 (1944).

[7] L. P. Kuhn, THIS JOURNAL, **68**, 1761 (1946).

above-described denitration procedure and the product was isolated as an acetate in the form of an amorphous powder. The yield of water-insoluble product employing the hydrogen chloride promoter was practically quantitative whereas that from the pyridine procedure was low (*ca.* 60%). Both products were highly degraded, as the viscosity data of Table II indicate. Nevertheless the procedure employing hydrogen chloride may prove useful in investigations wherein subsequent hydrolysis of the denitrated product is envisioned.

Experimental

Simultaneous Denitration and Acetylation of Nitrate Polyesters Using Zinc, Acetic Anhydride and Hydrogen Chloride.—A solution of 2 g. of the crystalline nitrate ester (*cf.* Table I) in 25 ml. of acetic anhydride was cooled by immersion in a bath containing 8 liters of water at 10–15°. This solution was treated under mechanical stirring with zinc dust (added in small portions to the total extent of 6–7 g.) and a stream of anhydrous hydrogen chloride was led into the mixture at such a rate as to maintain the temperature of the reaction mixture at 30–35°. The stream of hydrogen chloride was discontinued when a negative test for the nitrate group was obtained with the diphenylamine reagent (no blue coloration with a 0.2% solution of diphenylamine in 90% sulfuric acid). This required approximately one hour. Stirring was then maintained for fifteen minutes whereupon the mixture was poured slowly with stirring onto *ca.* 500 g. of ice and water. After one hour the mixture was extracted with chloroform and the extract washed with a saturated aqueous solution of sodium bicarbonate until neutral to moist litmus paper, dried and concentrated to a crystalline residue under reduced pressure. Recrystallization was effected from 95% ethanol. The yields and constants found are shown in Table I.

Dry cellulose nitrate (2 g., 13% N) was treated in the manner described above. Denitration was slower and a total of 8 g. of zinc dust was required over a five hour period. The precipitate obtained on pouring the reaction mixture onto the ice and water was dissolved in 25 ml. of acetone and reprecipitated by pouring into 600 ml. of water. The light brown, amorphous powder was removed by filtration; yield practically quantitative. The viscosity of the product is shown in Table II.

Simultaneous Denitration and Acetylation of Nitrate Polyesters using Zinc, Acetic Anhydride and Pyridine.—A solution of 5.0 g. of D-mannitol hexanitrate in 50 ml. of dry pyridine and acetic anhydride (1:7 by volume) was treated under stirring with zinc dust added in small portions while maintaining the temperature of the reaction mixture at 40–45°. A negative diphenylamine nitrate test (*cf.* above) was obtained after the addition of 10 g. of zinc over a period of ninety minutes. The reaction mixture was then poured slowly and with stirring onto 800 g. of ice and water. After one hour, the solution was extracted with chloroform and the extract washed with a saturated aqueous solution of sodium bicarbonate until neutral to moist litmus paper, dried and concentrated to a black sirup. The sirup was extracted with acetone, the extract concentrated to dryness and crystallized (decolorizing charcoal) from 95% ethanol. The yield and constants found are shown in Table I.

Dry cellulose nitrate (5 g., 13% N) was dissolved in 200 ml. of the pyridine and acetic anhydride mixture and treated in the manner described above. Denitration required the addition of 18 g. of zinc over a period of two hours. The product was isolated and purified as described above for the denitration of cellulose nitrate with the hydrogen chloride promoter. The product was a light yellow, amorphous powder; yield 58%. The viscosity of the product is shown in Table II.

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Summary

1. Nitrate esters (of polyhydric alcohols and of sugar derivatives) are simultaneously denitrated and acetylated by acetic anhydride and zinc in the presence of either hydrogen chloride or pyridine.

2. Cellulose nitrate is also denitrated and acetylated but is very considerably degraded in the process.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND COMPANY]

Hydrogenation of Vitamin Bc (Pteroylglutamic Acid)[1] and Related Pterines

BY B. L. O'DELL, J. M. VANDENBELT, E. S. BLOOM AND J. J. PFIFFNER

Soon after crystalline vitamin Bc was isolated by Pfiffner, *et al.*,[2] the presence of a pyrimidopyrazine ring in its molecular structure was suspected[3] and studies were undertaken to compare the response of vitamin Bc and pterines of known structure to catalytic reduction. The substituted pteridines shown in the formulas were investigated.

Kuhn and Ströbele[4] have shown that riboflavin can be reduced in dilute alkali through a series of colored intermediates to the dihydro compound, leucoflavin, which in turn can be readily dehydrogenated by shaking with oxygen. By vigorous catalytic hydrogenation of flavines, Karrer, *et al.*[5]

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[1] By synthesis Angier, *et al.* [*Science*, **103**, 667 (1946)] have proved the structure of the liver *L. casei* factor to be N-[4-{[(2-amino-4-hydroxy-6-pteridyl)-methyl]-amino}-benzoyl]-glutamic acid and have named the compound pteroylglutamic acid. In our laboratories a comparison of vitamin Bc with the synthetic compound generously supplied by the Lederle Laboratories has shown them to be identical.

[2] Pfiffner, Binkley, Bloom, Bird, Emmett, Hogan and O'Dell, *Science*, **97**, 404 (1943).

[3] Bloom, Vandenbelt, Binkley, O'Dell and Pfiffner, *Science*, **100**, 295 (1944).

[4] Kuhn and Ströbele, *Ber.*, **70**, 753 (1937).

[5] Karrer and Ostwald, *Rec. trav. chim.*, **57**, 500 (1938).