

Anal. Calcd. for $C_8H_{17}ClN_4$: C, 47.1; H, 7.94; N, 27.6. Found: C, 46.7; H, 8.30; N, 27.4.

Nitrate Salts from 1,3-6,8-Diendomethylene-1,3,6,8-tetraazacyclodecane. A. With Six Equivalents of Acid.—A solution of 90 ml. of 70% nitric acid (1.5 moles) in 150 ml. of absolute ethanol was added with vigorous stirring to a solution of 42 g. (0.25 mole) of the base in 400 ml. of ethanol. As the addition proceeded a thick yellow slurry came down. When the temperature was allowed to rise to 17° the slurry dissolved and a fine white powder precipitated. After complete addition the system was shaken for 15 min., then filtered and the solid washed with ether and vacuum-dried, 80 g., m.p. 140–141°. Essentially the same yield (m.p. 143.8°) was obtained when anhydrous reagents were used. This salt is unstable and decomposes, especially in presence of moisture, with evolution of formaldehyde. When heated to 95° for 1 hr. on a watchglass it was converted to 94% of the theoretical yield of 1,2-diaminoethane dinitrate. A satisfactory analysis of the compound could not be obtained. The formula most closely approaches that of methylene-bis-imidazolidine tetranitrate.

Anal. Calcd. for $C_8H_{20}N_8O_{12}$: C, 20.5; H, 4.93; HNO_3 , 61.7. Found: C, 19.8; H, 5.12; HNO_3 , 60.7.

B. With Two Equivalents of Nitric Acid.—A solution of 16 ml. (0.25 mole) of 70% nitric acid in 100 ml. of dioxane was added at 0° with vigorous stirring to 21 g. (0.125 mole) of I in 110 ml. of dioxane. A fine white solid precipitated as the acid solution was added. This was filtered, washed with acetone and with ether and dried at 10° (0.1 mm.) for 15 min., m.p. 15–19°. Calcd. for $C_8H_{18}N_6O_6$: HNO_3 , 42.8. Found (Treadwell, ferrous sulfate): HNO_3 , 44.0. When this compound (which decomposed slowly to a tar even over phosphorus pentoxide) was treated with nitric acid in ethanol it formed a mixture of 1,2-diaminoethane dinitrate and the salt obtained by procedure A.

1,3-Dinitro-1,3-diazacyclopentane. A. From the Hydrochloride.—A mixture of 1 ml. (0.02 mole) of 98% nitric acid and 2.5 g. (0.02 mole) of 95% acetic anhydride was prepared at –35°. To this solution at –35° during 10 min. was added 1 g. (0.005 mole) of diendomethylenetetraazacyclodecane monohydrochloride. After gradual warming to 0° during 7 hr. the system was poured into 25 g. of ice. The precipitated oil had solidified after one day and was filtered, 1.0 g. (60% on 1:2 basis), m.p. 124–127°. This crude product was heated with 10 ml. of 70% nitric acid for 4 min., then 25 ml. of water was added and the system cooled, 0.60 g., m.p. 134–134.8°.

Anal. Calcd. for $C_5H_6N_4O_4$: C, 22.2; H, 3.73; N, 34.6. Found: C, 22.5; H, 3.80; N, 34.3.

B. From the Tetranitrate.—A solution of 0.42 g. (0.0054 mole) of acetyl chloride, 0.48 ml. (0.0108 mole) of 98% nitric acid, 78.4 g. (0.73 mole) of acetic anhydride and 30 ml. (0.53 mole) of acetic acid was prepared at 2°. To this stirred system was added 22.6 g. (0.054 mole) of freshly prepared and finely ground tetranitrate salt during a 13-minute period at 4°. The thick slurry was allowed to warm to 25° during 30 min. and then was stirred for 15 hr. The system was then filtered to remove 9.2 g., m.p. 128–130° after washing with acetic acid. The filtrate and washings were poured into 150 g. of ice. The solid which separated was filtered off and water-washed, 4.8 g., m.p. 126–128°, m.m.p. with first crop not depressed. The total dry product, 14 g. (73% on 1:2 basis) was crystallized from 350 ml. of 95% ethanol, m.p. 130°. A mixture melting point with the product of procedure A was not lowered.

The molecular weight, determined ebullioscopically in benzene, averaged 155; calcd. 162. The solubility in 100 ml. of aqueous solution was found to be 0.1 g. at 20°, 0.3 g. at 44°, 0.6 g. at 60°, 1.5 g. at 80° and 4.7 g. at 100°. After boiling the compound for 60 hr. in 1% sulfuric acid 17% was decomposed to 1,2-dinitraminoethane. Dinitrodiazacyclopentane forms a eutectic, m.p. 70.5°, with 14% of trinitrotoluene. The substance is comparable with tetryl in explosive properties, since its figure of insensitiveness is 0.78 that of picric acid, while its power (Trauzl) is 1.36 that of picric acid. It decomposes without ignition at 205° but ignites at once when it is dropped on a surface at 350°. In hot 50% sulfuric acid the substance decomposes rapidly to give a quantitative yield of gas (1:2 basis) which is 94% nitrous oxide and 6% nitrogen.

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A Note on the Synthesis of Glycosides¹

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During investigations into the correlation of the structure of glycosides² attempts were made to develop simplified procedures for the synthesis of certain methyl glycosides. In a previous communication the use of insoluble acid catalysts such as cation exchange resins for the preparation of methyl glycosides was described.³ This paper is concerned with two other procedures that were investigated.

Treatment of acetyl glycosyl halides with methanolic magnesium methoxide leads directly to the formation of the corresponding glycoside. The reaction proceeds rapidly since it is carried out in a homogeneous system.⁴ Deacetylation proceeds at the same time. If the methyl glycoside does not separate from the reaction mixture it can be separated from magnesium bromide by reacetylation. This method was used for the synthesis of methyl β -D-glucopyranoside and methyl β -lactoside.⁵

The preparation of methyl glycosides by the Fischer method^{6,7} can be simplified in certain cases by adding an inert solvent such as ethylene dichloride⁸ to cause the methyl glycoside to crystallize directly from the reaction mixture. This avoids neutralization and concentration according to the customary procedure.^{6,7} Methyl α -D-mannopyranoside and methyl β -L-arabopyranoside were made by this method.

Experimental

A. 1. Methyl 2,3,4,6-Tetra-O-acetyl- β -D-glucopyranoside.—To a solution of 2,3,4,6-tetra-O-acetyl α -D-glucosyl bromide (crude reaction product prepared in the usual way⁹ or by the simplified method^{10,11} from 20 g. of D-glucose pentaacetate in absolute methanol (200 ml.)) was added a methanolic solution of magnesium methoxide prepared by dissolving 1.0 g. of magnesium filings in absolute methanol (100 ml.).

After standing overnight the reaction mixture was evaporated to dryness *in vacuo*. In order to eliminate the magnesium bromide the residue was dissolved in acetic anhydride (100 ml.), fused sodium acetate (5.0 g.) was added and the mixture was refluxed for 10–20 minutes. The cooled reaction mixture was then poured with stirring into water (1000 ml.). When the excess acetic anhydride had decomposed the aqueous mixture was extracted twice with chloroform, the chloroform extract was washed with water, dried ($CaCl_2$) and concentrated to a small volume *in vacuo*. Petroleum ether (b.p. 30–60°) was added until turbidity was reached and the product allowed to crystallize (yield 7.2

(1) Paper No. 3294, Scientific Journal Series, Minnesota Agricultural Experiment Station, University of Minnesota, St. Paul, Minn. From a thesis presented to the graduate faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy by John W. Van Cleve, 1951.

(2) F. Smith and J. W. Van Cleve, *THIS JOURNAL*, **75**, 3091 (1955).

(3) J. E. Cadotte, F. Smith and D. Spriestersbach, *ibid.*, **74**, 1501 (1952).

(4) Cf. W. Koenigs and E. Knorr, *Ber.*, **34**, 957 (1901).

(5) Cf. F. Smith and J. W. Van Cleve, *THIS JOURNAL*, **74**, 1912 (1952).

(6) E. Fischer, *Ber.*, **26**, 2400 (1893); **28**, 1145 (1895).

(7) E. Bourquelot, *Ann. chim.*, **3**, 298 (1915).

(8) Cf. R. O. Clinton and S. C. Laskowski, *THIS JOURNAL*, **70**, 3135 (1948).

(9) F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," U. S. Govt. Printing Office, Washington, D. C., 1942, p. 500; cf. B. Helferich and E. Günther, *Ber.*, **64**, 1279 (1931).

(10) M. Barczai-Martos and F. Korozsy, *Nature*, **165**, 369 (1950).

(11) P. G. Schlenker and F. Smith, *THIS JOURNAL*, **76**, 3224 (1954).

g.). Recrystallization from methanol gave methyl 2,3,4,6-tetra-*O*-acetyl β -D-glucopyranoside, m.p. and mixed m.p. 104–105°, $[\alpha]^{20}_D -22.2^\circ$ in ethanol (*c* 2.7); literature values: m.p. 104–105^{4,12} and $[\alpha]^{20}_D -24.6^\circ$ (ethanol),¹³ -27.2° (ethanol).⁴

Deacetylation of the methyl tetra-*O*-acetyl β -D-glucopyranoside by the Zemplén method¹⁴ using catalytic amounts of sodium methoxide gave methyl β -D-glucopyranoside, m.p. and mixed m.p. 115–116°, $[\alpha]^{20}_D -30.3^\circ$ in water (*c* 2.0) (after recrystallization from methanol-ether); literature values: m.p. 110°,¹⁵ 105°¹⁶ and $[\alpha]^{15}_D -32^\circ$ (H₂O),¹⁵ -34.2° (H₂O).¹⁶

2. Methyl β -Lactoside.—Application of the above procedure to acetobromo lactose yielded the corresponding methyl β -lactoside, m.p. 205°, $[\alpha]^{20}_D +1^\circ$ in water (*c* 5.0). Inasmuch as the pure methyl β -lactoside showed $[\alpha]^{20}_D +5.6^\circ$ in water³ it is believed that the compound above contained some of the α -anomer.

B. 1. Methyl α -D-Mannopyranoside.—To crystalline D-mannose (18.0 g.) was added 3% hydrogen chloride in methanol (15 ml.) and ethylene dichloride (30 ml.). The mixture was refluxed on the water-bath for 4 hours. During the course of the reaction a two-phase liquid system was formed, the lower layer of which soon turned to a solid crystalline mass. After being allowed to cool, the reaction mixture was filtered and washed with a little ice-cold methanol followed by ether. The crystalline methyl α -D-mannopyranoside (yield 9.7 g.) had m.p. and mixed m.p. 191–192°, $[\alpha]^{20}_D +79.0^\circ$ in water (*c* 1.0) (after recrystallization from 80% ethanol); literature values: m.p. 191–192°,¹⁷ $[\alpha]^{20}_D +79^\circ$ (H₂O),¹⁷ $+79.2^\circ$ (H₂O).¹⁸

2. Methyl β -L-Arabinopyranoside.—A mixture of 3% methanolic hydrogen chloride (70 ml.), ethylene dichloride (100 ml.) and L-arabinose (70 g.) was refluxed for 3 hours and allowed to stand overnight. The methyl β -L-arabinopyranoside (yield 23.5 g.) was filtered off and washed with ethyl acetate and recrystallized from absolute ethanol, m.p. and mixed m.p. 166–168°, $[\alpha]^{19}_D +235^\circ$ in water (*c* 1.7); literature values: m.p. 169°¹⁹ and 169–171°.²⁰

Repeated recrystallization did not change the specific rotation which does not agree with the literature value ($[\alpha]^{20}_D +245.5^\circ$ in water).¹⁹ As a further check on its purity a sample of the material ($[\alpha]_D +235^\circ$) was oxidized with periodic acid according to the procedure of Hudson and Jackson.²¹ The D'-methoxydiglycolic aldehyde obtained had $[\alpha]^{20}_D +123^\circ$ (H₂O); Hudson and Jackson²¹ reported $[\alpha]^{20}_D +124^\circ$ (H₂O) for this substance.

(12) J. Moll van Charante, *Rec. trav. chim.*, **21**, 42 (1902).

(13) C. S. Hudson and J. K. Dale, *This Journal*, **37**, 1264 (1915).

(14) G. Zemplén, *Ber.*, **59**, 1258 (1926); G. Zemplén and E. Pacsu, *ibid.*, **62**, 1613 (1929).

(15) T. S. Patterson and J. Robertson, *J. Chem. Soc.*, 300 (1929).

(16) C. N. Riiber, *Ber.*, **57**, 1797 (1924).

(17) M. Bergmann and H. Schotte, *ibid.*, **54**, 1569 (1921).

(18) E. Fischer and L. Beensch, *ibid.*, **29**, 2928 (1896).

(19) C. S. Hudson, *This Journal*, **47**, 267 (1925).

(20) E. Fischer, *Ber.*, **26**, 2407 (1893).

(21) E. L. Jackson and C. S. Hudson, *This Journal*, **59**, 994 (1937).

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The Condensation of D-Arabinose with Nitromethane in Aqueous Solution

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The condensation of nitromethane¹ and nitroethanol² with aldose sugars, as a step in the preparation of higher-carbon aldoses and ketoses, has been carried out previously in dry, alcoholic media. In most successful examples of the reaction, the solu-

bility relationships between the reactants and the alcoholic solvent were such that the alkali-sensitive sugars dissolved and the resulting salts of the nitrodeoxyalditols precipitated as the condensation reaction progressed. While many of the aldose sugars condense satisfactorily with nitromethane in alkaline alcoholic media, others such as D-glucose react to only a minor extent.³

With a view to increasing the scope and utility of the nitroparaffin-sugar condensation, the reaction now is being studied in aqueous solution. The condensation of D-arabinose with nitromethane in aqueous alkali has been found to proceed rapidly and to an extent comparable with that observed in alcoholic media.

It seems likely that the use of aqueous reaction conditions will appreciably extend the applicability of the nitromethane and related syntheses in the sugar field. Further experiments are contemplated to generalize the above results.

Experimental

Solutions containing D-arabinose in 2 equivalents of 2 *M* nitromethane in 2 *N* aqueous sodium hydroxide were allowed to stand at room temperature for varying lengths of time and the resulting *aci*-nitroalcohols then were decomposed by adding the solutions to warm (50°), aqueous sulfuric acid.¹ Following deionization and concentration, D-mannose was precipitated from the resulting solutions as the phenylhydrazone. The relationship between the duration of the condensation reaction and the yield of D-mannose phenylhydrazone was as follows: 5 min., 15.4%; 15 min., 20.6%; 25 min., 21.6%; 1 hr., 18.4%; 2 hr., 17.8%. When the amount of the alkaline nitromethane solution was varied, a condensation reaction time of 15 minutes resulted in the following yields of D-mannose phenylhydrazone: 1 equiv., 16.9%; 2 equiv., 20.6%; 3 equiv., 17.6%.

D-Mannose phenylhydrazone was characterized by conversion to the known anhydro-*O*-tetraacetate,⁴ m.p. 123–124°, $[\alpha]^{25}_D 12^\circ$ in pyridine (*c* 3).

(3) See J. C. Sowden, *Advances in Carbohydrate Chem.*, **6**, 291 (1951).

(4) M. L. Wolfrom and M. G. Blair, *This Journal*, **68**, 2110 (1946).

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Tetraacetates of D-Glucose and D-Galactose

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Helferich and Klein³ first prepared 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose by removal of the trityl (triphenylmethyl) group from 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl- β -D-glucopyranose. The compound has proven to be very useful as an intermediate in the synthesis of disaccharides in the Königs-Knorr type reaction.³ We wish to describe herein a new synthesis for 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose and the corresponding D-galactose derivative. This synthesis is made possible by the discovery⁴ that mercuric acetate is an excellent reagent for replacing halogen in acetylated glycopyranosyl halides. The immediate precursors of the tetraace-

(1) Corn Industries Research Foundation Associate (A. T.) and Fellow (M. I.).

(2) B. Helferich and W. Klein, *Ann.*, **450**, 219 (1926).

(3) W. L. Evans, D. D. Reynolds and E. A. Talley, *Advances in Carbohydrate Chem.*, **6**, 27 (1951).

(4) R. Lindberg, *Acta Chem. Scand.*, **3**, 1355 (1949); L. Asp and R. Lindberg, *ibid.*, **5**, 665 (1951); **6**, 911 (1952).

(1) J. C. Sowden and H. O. L. Fischer, *This Journal*, **69**, 1048, 1963 (1947).

(2) J. C. Sowden, *ibid.*, **72**, 3325 (1950).