salts similar to the color obtained from α,α-dipyridyl. It was shown to be *o*-phenanthroline by oxidation with alkaline permanganate, forming a dicarboxylic acid crystallizing in needles. On heating, the dicarboxylic acid lost carbon dioxide and gave α,α-dipyridyl, as shown by its melting point (68°) and agreement with the known substance in odor, crystalline form and reaction with ferrous sulfate. The dicarboxylic acid was isolated by filtering off the manganese dioxide, making just acid with sulfuric acid, then alkaline with ammonia and evaporating to dryness. The residue was extracted with hot absolute alcohol. The acid left after evaporation of the alcohol crystallized from water in needles.

Summary

1. The double Skraup reaction can be satisfactorily applied to the *m*- and *p*-phenylenediamines with proper observance of water concentration, temperature and time of heating. The separation and purification of the respective phenanthrolines are described.

2. Oxidation of the phenanthrolines to their dicarboxylic acids by permanganate is best conducted at low temperatures with the addition of alkali.

3. β,β-Dipyridyl is satisfactorily prepared by heating its dicarboxylic acid in glycerine. α,β-Dipyridyl is prepared from its dicarboxylic acid by first eliminating one carboxyl at 200–210° and the other at 280–290°.

4. The double Skraup reaction when applied to *o*-phenylenediamine could not be made to yield *o*-phenanthroline but resulted only in a variable and small yield of a yellow crystalline substance, $C_{12}H_8N_2O$.

5. *o*-Phenanthroline was prepared from *o*-aminoquinoline. Its identity was established by oxidation to the dicarboxylic acid, which gave α,α-dipyridyl on heating.

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THE PREPARATION OF GAMMA-*d*-MANNONIC LACTONE

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RECEIVED AUGUST 19, 1929 PUBLISHED JANUARY 8, 1930

Mannosaccharic lactone is a substance possessed of quite extraordinary properties.[1] The investigation of this lactone has been under way in this Laboratory for some time and has been especially time-consuming because of the difficulty of the preparation of the lactone in good yield. Fischer[2] reports only 2% on the basis of the weight of ivory nut meal hydrolyzed and oxidized and 7.5% from the oxidation of mannose.

The yield from the oxidation of pure mannonic lactone, however, is 30–35% according to Fischer[2] and even higher by the recently published method of Kiliani.[3]

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[1] *Cf.* Butler and Cretcher, THIS JOURNAL, **51**, 2167 (1929), for literature references.

[2] Fischer, *Ber.*, **24**, 539 (1891).

[3] Kiliani, *ibid.*, **54**, 456 (1921).

It would thus appear that a simple method for the preparation of the latter substance is desirable.

Mannonic lactone was obtained in poor yield by Fischer and Hirschberger[4] by oxidation of mannose with bromine. The product of the oxidation was a sirup which would not crystallize even after standing for months. He states that for the preparation of the crystalline lactone it is necessary to convert to the phenylhydrazide, from which the desired product can be obtained on hydrolysis with aqueous barium hydroxide. The use of phenylhydrazine renders this method too expensive and inconvenient.

By application of the method of oxidation of sugars by bromine in the presence of buffering salts recently described by Hudson and Isbell,[5] we have been able to prepare γ-mannonic lactone from mannose in good yield. The lactone crystallizes on evaporation of the aqueous solution obtained after removal of excess bromine and hydrobromic acid. The method has also been successfully applied to the mannose-containing solution obtained on hydrolysis of ivory nut meal. It was not necessary to isolate the sugar before oxidation.

Experimental Part

Preparation from Mannose.—Eighteen grams of *d*-mannose was oxidized in the manner described by Hudson and Isbell[5] for the oxidation of glucose to gluconic acid. Their directions were followed in every particular except that after removal of hydrobromic acid, the solution was not boiled with calcium carbonate to convert the sugar acid to a salt, but was evaporated under reduced pressure to a thick sirup. Mannonic lactone usually crystallized during the process of evaporation; if not, crystallization took place immediately on scratching the walls of the flask. Fifteen cc. of absolute alcohol was added to facilitate removal from the flask. After filtering and air drying the product weighed 15.5 g. and melted at 148–151°. On recrystallization from 95% alcohol 11.2 g. (63%) of γ-mannonic lactone melting at 151° was obtained.

Preparation from Ivory Nut Meal.—Six hundred grams of 20-mesh ivory nut meal was added to 6000 cc. of boiling 1% sodium hydroxide solution. The flame was removed before adding the meal. The mixture was allowed to stand with occasional stirring for thirty minutes and then filtered and washed with water until the washings were neutral and practically colorless.[6] The product was dried at 80°. The yield was 420 g.

One hundred grams of the purified meal was added in small portions and with constant stirring to 100 g. of cold 75% sulfuric acid and allowed to stand overnight. Eleven hundred cc. of water was added and the mixture boiled for three hours.[7] The hot solution was neutralized with barium carbonate, treated with decolorizing carbon and filtered. The filtrate was again treated with carbon and became practically colorless. Titration with iodine indicated the presence of about 90 g. (0.5 mole) of reducing hexose. The solution was diluted to 3750 cc. and cooled. Two hundred and eighty-

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[4] Fischer and Hirschberger, *Ber.*, **22**, 3218 (1889).

[5] Hudson and Isbell, THIS JOURNAL, **51**, 2225 (1929).

[6] Horton, *J. Ind. Eng. Chem.*, **13**, 1040 (1921).

[7] Hudson and Sawyer, THIS JOURNAL, **39**, 471 (1917).

five grams of barium benzoate was added and the mixture stirred until nearly all of the benzoate was dissolved. Thirty-one cc. of bromine was added and the flask shaken until all the bromine was in solution. The flask was set aside in a dark place for twenty-four hours. The precipitated benzoic acid was removed by filtration, the excess bromine by a stream of air and the barium by sulfuric acid. After filtration the solution was heated and treated with 140 g. of lead carbonate in aqueous suspension. After cooling and filtering the remaining bromide was removed with silver carbonate and the excess lead and silver precipitated with hydrogen sulfide. The insoluble sulfides were removed, the filtrate was heated with decolorizing carbon and evaporated under reduced pressure to 400 cc. The benzoic acid which had separated from solution was filtered off and that in solution was extracted with chloroform. Evaporation *in vacuo* was continued until the lactone suddenly precipitated in a solid crystalline mass. Enough 95% alcohol was added to dissolve all the lactone (hot). On cooling, the product crystallized. After filtering and drying it melted at 138–141°.

It was recrystallized from alcohol. Thirty-six grams of γ-mannonic lactone melting at 151° was obtained; $[\alpha]_D^{25}$ +51.3°. The physical constants of this substance as determined by Nef[8] are: m. p. 151° and $[\alpha]_D^{20}$ +51.8°. On concentration of the combined mother liquors an additional 4 g. of pure lactone was recovered.

Summary

The method of oxidation of aldehyde sugars recently described by Hudson and Isbell applied to mannose has made possible the preparation of γ-*d*-mannonic lactone in improved yield.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

FURTHER OBSERVATIONS ON THE INTERFERENCE OF NITRO GROUPS ON THE ZEREWITINOFF METHOD FOR THE QUANTITATIVE ESTIMATION OF ACTIVE HYDROGEN

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RECEIVED AUGUST 19, 1929 PUBLISHED JANUARY 8, 1930

Introduction

Where there is no hydrogen there can be no active hydrogen.

Recently, Gilman and Fothergill[1] showed that nitro, nitroso and azo groups interfered with the Zerewitinoff method for the quantitative estimation of active hydrogen. Long years ago attention was directed by Hibbert and Sudborough[2] to abnormal results given by some nitro substituted compounds. They obtained slightly more than the calculated volume of gas (based on the one hydroxyl group) when *o*-nitrophenol was treated at room temperature with an amyl ether solution of methylmagnesium iodide. The volume of gas increased when the mixture was allowed to stand for an additional eight hours at room temperature.

[8] Nef, *Ann.*, **403**, 316 (1914).

[1] Gilman and Fothergill, THIS JOURNAL, **49**, 2815 (1927); **50**, 867 (1928).

[2] Hibbert and Sudborough, *J. Chem. Soc.*, **85**, 933 (1904).