

Sodium or sodium-potassium alloy cleaved alkyl and aryl disulfides to the metal mercaptides.

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The Action of Alkalies on the Monobasic Sugar Acids.¹ I. Conversion of Gluconic to Mannonic and of Galactonic to Talonic Acids by the Action of Barium Hydroxide

BY HOWARD T. BONNETT AND FRED W. UPSON

This paper records experiments on the action of barium hydroxide on several monobasic sugar acids. It has been found that epimerization of these acids may be produced by the action of barium hydroxide and that the action of pyridine, quinoline and other tertiary amines is not specific in this process. Thus, *d*-gluconic acid has been converted to *d*-mannonic acid, *d*-mannonic to *d*-gluconic, and *d*-galactonic to *d*-talonic acid. The mannonic and talonic acids have been isolated in the form of their γ -lactones.

The preparation of *d*-mannonic acid by the epimerization of *d*-gluconic acid was discovered by Fischer² and recently Nelson and Cretcher³ have described its preparation from ivory-nut meal.

d-Talonic acid was prepared from *d*-galactonic acid by Fischer,⁴ and Cretcher⁵ has recently published an improved method.

That barium hydroxide is capable of producing epimeric change is of interest in connection with the general problem of the oxidation of sugars in alkaline solution. Thus in the oxidation of glucose by Fehling's solution⁶ and by the Soldaini reagent,⁷ mannonic acid or a derivative has been isolated as one product, and gluconic acid has been obtained in the oxidation of mannose.⁸ In like manner *d*-talonic acid was found as an oxidation product of galactose in the work of Anderson.⁹ Nef⁸ and also Anderson⁹ explained the formation of the isomeric hexonic acid in the oxidation of a given hexose, as the result of a benzilic acid rearrangement of the 1,2-osone, formed by the oxidation of the 1,2-enediol of the hexose. Jensen and Upson¹⁰ suggested that an alternative explanation is to be

(1) An abstract of a part of a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Nebraska.

(2) Fischer, *Ber.*, **23**, 799 (1890).

(3) Nelson and Cretcher, *THIS JOURNAL*, **52**, 403 (1930).

(4) Fischer, *Ber.*, **24**, 3622, 3629 (1891).

(5) Cretcher, *THIS JOURNAL*, **49**, 478 (1927); **54**, 1590 (1932).

(6) Nef, *Ann.*, **357**, 276 (1907).

(7) Jensen and Upson, *THIS JOURNAL*, **47**, 3019 (1925).

(8) Nef, *Ann.*, **357**, 281 (1907).

(9) Anderson, *Am. Chem. J.*, **42**, 402 (1909).

(10) Jensen and Upson, *THIS JOURNAL*, **47**, 3024 (1925).

found in the well-known Lobry de Bruyn-van Ekenstein¹¹ reaction. Through the action of the alkali a given hexose may be converted to its isomeric sugar which then undergoes direct oxidation to the corresponding hexonic acid.

The experiments presented in this paper suggest a third possible mechanism. Since the Fehling's solution reactions are usually carried out at temperatures of 100°, it is entirely possible that the mannonic acid recovered in the oxidation of glucose results, in part at least, from the epimerization of gluconic acid through action of the alkali. The same theory would account for the formation of gluconic acid in the oxidation of mannose and of talonic acid in the oxidation of galactose.

It is not possible with the evidence at hand to decide between the three possible mechanisms. Any one may be, or possibly all three are, involved in the formation of the isomeric hexonic acid in the oxidation of a given hexose.

Experimental

Preparation of γ -*d*-Mannonic Lactone.—282 g. of barium gluconate and 158 g. of barium hydroxide ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) were dissolved in water in a one-liter round-bottomed flask with the aid of heat, and the volume made up to 1 liter. The flask was stoppered and maintained at a temperature of 95–97° for one hundred and fifteen hours. The hot solution was neutralized to litmus with 6 *N* sulfuric acid and the barium sulfate removed by filtration. The resulting solution was concentrated to 600 cc. and allowed to stand for twenty-four hours in a refrigerator. The barium gluconate which separated was filtered out and washed with ice water. The combined filtrate and washings was concentrated to 200 cc. and a second crop of barium gluconate removed in the same way. Thus there was removed 186 g. of barium gluconate or 66% of the original amount used.

The filtrate from the second crop of barium gluconate was heated and the barium ion exactly removed with sulfuric acid. After removal of the barium sulfate, the filtrate was decolorized and concentrated under reduced pressure to a thin sirup from a bath at 60°. Four hundred cc. of normal butyl alcohol and some ethyl alcohol were added to dissolve the sirup. A small amount of material remained undissolved and was filtered out. This mixture was distilled under reduced pressure from a bath maintained at a temperature of 45–50° until it became faintly turbid. It was then diluted with butyl alcohol and warmed slightly to a clear solution. It was allowed to cool to room temperature, and a few milligrams of γ -*d*-mannonic lactone added. The distillation was continued until approximately 60–70% of the butyl alcohol had been removed. During the distillation, the mannonic lactone began to crystallize. The mixture was allowed to stand at room temperature for twenty-four hours. The crystals were filtered, washed with *n*-butyl alcohol and dried. The yield was 30 g. (17%) of crude mannonic lactone, m. p. 147–149°. The lactone was recrystallized from ethyl alcohol and then from acetic acid for final purification; m. p. 151°, $[\alpha]_D^{20} +51.8^\circ$.

The time consumed in carrying out the preparation of γ -*d*-mannonic lactone from gluconic acid may be materially shortened if the temperature is increased. This is shown by the following experiment: 56.3 g. of barium gluconate and 31.5 g. of barium hydroxide were dissolved in hot water and diluted to 200 cc. The mixture was placed in a 200-cc. round-bottomed flask having the stopper securely wired in place, and heated

(11) Lobry de Bruyn and van Ekenstein, *Rec. trav. chim.*, **14**, 201 (1895).

for one hour on an oil-bath at 140°. On removal from the bath and cooling, the mixture was treated as described above; 25.5 g. (45%) of barium gluconate was recovered and 7.3 g. (20%) of γ -*d*-mannonic lactone was obtained.

Conversion of Mannonic to Gluconic Acid.—17.8 g. of *d*-mannonic lactone and 47 g. of barium hydroxide were dissolved in water and diluted to 200 cc. The solution was heated on a water-bath maintained at 95–97° for one hundred hours. Upon removal from the water-bath, the solution was neutralized to litmus with 6 *N* sulfuric acid, and the barium sulfate filtered off. The solution of barium salts was concentrated under reduced pressure to 40 cc., inoculated with barium gluconate, and placed in the refrigerator for several days. The crystals were filtered out, washed with ice cold water, and dried. The barium gluconate thus obtained weighed 3 g., corresponding to 12% of the lactone originally used.

A portion of the barium salt was used to prepare the phenylhydrazide. On recrystallization from water, the phenylhydrazide melted at 200–202°. From another portion of the barium salt, the brucine salt was prepared by the usual method. The brucine salt, dried *in vacuo* over concentrated sulfuric acid, melted at 155–157°, and gave $[\alpha]_D^{20} -18.9^\circ$. Nef¹² gives *d*-gluconic phenylhydrazide, m. p. 200–201°, brucine *d*-gluconate, m. p. 155–157°, $[\alpha]_D^{20} -18.76^\circ$.

The barium ion was exactly removed from the solution of the soluble barium salt with sulfuric acid, and the barium sulfate filtered out. The filtrate was distilled, using butyl alcohol according to the method given previously under the preparation of *d*-mannonic lactone, and thus 10.8 g. (61%) of γ -*d*-mannonic lactone was recovered.

The Preparation of γ -*d*-Talonc Lactone.—98 g. of *d*-galactonic lactone monohydrate and 158 g. of barium hydroxide were dissolved in hot water, diluted to 500 cc. and placed in a 500-cc. round-bottomed flask. The flask was stoppered, and the mixture heated on a water-bath maintained at 95–97° for one hundred and fifty hours. Upon removal from the water-bath, the hot solution was neutralized to litmus with 6 *N* sulfuric acid, diluted to 3 liters, heated to boiling, and a hot solution of 105 g. of cadmium sulfate added slowly. The mixture was treated with activated charcoal and filtered while hot. The solution of the cadmium salt was concentrated under reduced pressure to 500 cc. and allowed to stand for several hours. The cadmium galactonate was filtered off, and the mixture further concentrated to 100 cc. and allowed to stand. A second small fraction of cadmium galactonate was obtained. The filtrate from the second crop of cadmium galactonate was treated with hydrogen sulfide, and the cadmium sulfide filtered out. The sulfate ion remaining in the solution was exactly removed as barium sulfate with barium hydroxide. The filtrate was concentrated *in vacuo* from a bath at 45–50° until it had reached the consistency of a thin sirup; 250 cc. of *n*-butyl alcohol was added, the mixture heated to a temperature of approximately 40°, and sufficient ethyl alcohol added to dissolve the sirup. A small amount of insoluble material was filtered out. The alcoholic mixture was concentrated under reduced pressure in a bath at a temperature of 45–50°, to a volume of 75 cc. and allowed to stand. The gummy crystals were filtered off and recrystallized from absolute ethyl alcohol. The crystals melted at 132–134° and possessed a specific rotation of -34.5° (0.4208 g. in 19.0407 g. of water gave $\alpha = -1.49^\circ$). The weight of purified crystals was 11.4 g. (13%). These constants agree with those given by Cretcher⁶ for γ -*d*-talonc lactone.

Further studies of the action of alkalies on sugar acids are in progress.

Summary

1. It has been shown that epimerization may be produced by the action of barium hydroxide. Gluconic acid has been converted to mannonic

acid, mannonic acid to gluconic acid and galactonic acid to talonic acid, in yields comparable with those obtained by the use of pyridine and quinoline.

2. The process described furnishes perhaps the most convenient method for obtaining mannonic and talonic lactones.

3. A possible mechanism has been suggested for the formation of isomeric hexonic acids in the alkaline oxidation of hexoses.

LINCOLN, NEBRASKA

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The Polymerization of Some Unsaturated Hydrocarbons. The Catalytic Action of Aluminum Chloride¹

BY W. H. HUNTER AND R. V. YOHE

The action of aluminum chloride on unsaturated hydrocarbons has not been studied very extensively. However, as a result of a study of the action of this reagent with ethylene, Stanley² concluded that any explanation of the reaction must take into account the formation of an aluminum chloride-hydrocarbon complex which he has shown to lead to the formation of olefinic compounds. An earlier study with ethylene, propylene, isobutylene, *n*-octene and diamylene led Szayna³ to somewhat similar conclusions. Aside from these investigations, the action of aluminum chloride on unsaturated hydrocarbons has received very little attention. Since aluminum chloride forms complexes so readily with hydrocarbons and certain other substances, it was decided to study the action of some of these complexes as polymerizing agents. The unsaturated hydrocarbons used in this study were acetylene, ethylene and isobutylene.

Preparation and Purification of Materials

Acetylene.—Tank acetylene was purified by passing it through saturated bisulfite solution, concentrated sulfuric acid, concentrated alkali, granular calcium chloride and anhydron.

Ethylene.—Anesthesia ethylene was used without further purification.

Isobutylene.—Isobutylene was prepared by the dehydration of tertiary butyl alcohol with aluminum oxide at 400°, and also by treating tertiary butyl chloride with alcoholic potassium hydroxide. The isobutylene was washed with water, then passed over soda lime, solid sodium hydroxide, calcium chloride and anhydron, and was finally condensed in small cylinders.

Aluminum Chloride.—Mallinckrodt anhydrous resublimed c. p. aluminum chloride was used without further purification except in the cases when it was sublimed into adsorption chambers.

(1) The work described in this paper constituted part of a thesis submitted to the graduate Faculty of the University of Minnesota by R. V. Yohe, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931. This paper was prepared by the junior author after the death of Dr. Hunter.—L. I. SMITH. (Original manuscript received June 27, 1932.)

(2) Stanley, *J. Am. Concrete Inst.*, **49**, 349-541 (1930).

(3) Szayna, *Przemysl Chem.*, **12**, 637-47 (1928).