[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

β-Propiolactone. XIII. Reactions with Sodium Nitrite, Sodium Dithionite, Sodium Cyanide, Sodium Thiocyanate, Sodium Succinimide and Aryl Sulfinic Acids and Their Salts[1]

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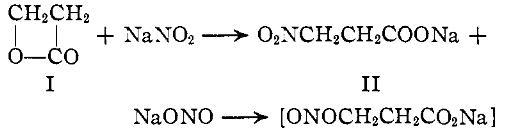
The reactions of β-propiolactone with certain salts are described. Sodium nitrite reacts to form sodium β-nitropropionate. Acidification of the salt product from sodium dithionite gives β,β-sulfonyldipropionic acid. Sodium cyanide reacts to form sodium β-cyanopropionate from which β-cyanopropionic acid can be obtained. In a similar manner β-thiocyanopropionic acid is given with sodium thiocyanopropionate. Sodium β-(arylsulfonyl)-propionates are obtained from the reaction with sodium arylsulfinates. The corresponding acids are obtained in the reaction of β-propiolactone and the arylsulfinic acid. Sodium succinimide and the lactone react to give sodium β-succinimidopropionate.

In previous papers[2] the reactions of β-propiolactone (I) and salts of organic and inorganic acids were described. The present work considers additional reactions of this type.

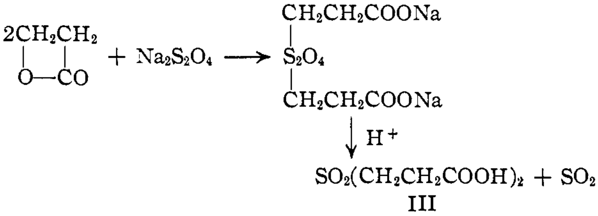
Sodium nitrite and I in water react to give sodium β-nitropropionate (II) from which β-nitropropionic acid was isolated on acidification.[3] This product accounted for about half of I and the remainder was lost by polymerization and hydrolysis to hydracrylic acid.[2a] The formation of β-(carboxyethyl)-nitrite might be expected but none was isolated.



$$\begin{array}{l} CH_2CH_2 \\ |\quad\;\; | \\ O{-}CO \end{array} + NaNO_2 \longrightarrow O_2NCH_2CH_2COONa + NaONO \longrightarrow [ONOCH_2CH_2CO_2Na]$$

I, II

Two moles of I react with sodium dithionite to form a complex salt which evolves sulfur dioxide on acidification and heating to yield β,β-sulfonyldipropionic acid (III).[4]



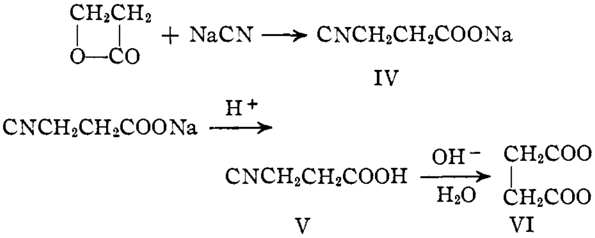
$$2\begin{array}{l} CH_2CH_2 \\ |\quad\;\; | \\ O{-}CO \end{array} + Na_2S_2O_4 \longrightarrow \begin{array}{l} CH_2CH_2COONa \\ | \\ S_2O_4 \\ | \\ CH_2CH_2COONa \end{array} \xrightarrow{H^+} SO_2(CH_2CH_2COOH)_2 + SO_2$$

III

The formation of the sulfonyl linkage illustrates the strong tendency for formation of carbon–sulfur bonds in the reactions of I. It also demonstrates the possibility for the dithionite to react at the sulfur atom. This is similar to the reaction described by Binz,[5] wherein dimethyl sulfone was formed from sodium dithionite and dimethyl sulfate.

The yields of III were limited since it was not possible to use an excess of salt to minimize the reaction of I with the carboxyl ions in the primary products.[2c] Because of the instability of dithionous acid it was impractical to control these secondary reactions by lowering the *p*H of the solution.

In the reaction of sodium cyanide and I it was necessary to use concentrated solutions to minimize the hydrolysis of the cyanide.[6] The product was sodium β-cyanopropionate (IV) from which the free acid (V) could be isolated by controlled acidification. Alkaline hydrolysis of IV gave good yields of sodium succinate from which the hexahydrate of the sodium salt, the calcium salt, or the free acid could be isolated readily.



$$\begin{array}{l} CH_2CH_2 \\ |\quad\;\; | \\ O{-}CO \end{array} + NaCN \longrightarrow CNCH_2CH_2COONa$$

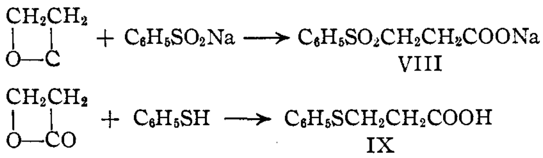
IV

$$CNCH_2CH_2COONa \xrightarrow{H^+} CNCH_2CH_2COOH \xrightarrow[H_2O]{OH^-} \begin{array}{l} CH_2COO \\ | \\ CH_2COO \end{array}$$

V, VI

Addition of I to an aqueous solution of sodium or potassium thiocyanate gave the corresponding salt of β-thiocyanopropionic acid (VII).[2b] The thiocyanopropionic acid was hydrolyzed to β-carbamylmercaptopropionic acid as described by Fredga[7] who had prepared VII from the salts of β-chloropropionic acid and sodium thiocyanate.

Sodium benzenesulfinate and I in water gave β-(phenylsulfonyl)-propionic acid (VIII) as the only isolable product. Some of I was lost in the usual side reactions.[2a] That the product was a sulfone rather than a sulfinite ester was shown by an independent synthesis involving the formation and subsequent oxidation of the corresponding sulfide (IX).[8]



$$\begin{array}{l} CH_2CH_2 \\ |\quad\;\; | \\ O{-}C \end{array} + C_6H_5SO_2Na \longrightarrow C_6H_5SO_2CH_2CH_2COONa$$

VIII

$$\begin{array}{l} CH_2CH_2 \\ |\quad\;\; | \\ O{-}CO \end{array} + C_6H_5SH \longrightarrow C_6H_5SCH_2CH_2COOH$$

IX

Difficulties were encountered in the isolation of the acid of VIII due to the similar solubilities of it and the unreacted sulfinic acid. Heating the

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[1] Presented in part at the XIIth International Congress of Pure and Applied Chemistry, New York City, September 10–13, 1951.

[2] (a) T. L. Gresham, J. E. Jansen, F. W. Shaver and J. T. Gregory THIS JOURNAL, **70**, 999 (1948); (b) T. L. Gresham, U. S. Patents 2,449,987–89–93 (Sept. 28, 1948); (c) T. L. Gresham, J. E. Jansen and F. W. Shaver, THIS JOURNAL, **70**, 1003 (1948); (d) T. L. Gresham and J. E. Jansen, U. S. Patent 2,449,990 (Sept. 28, 1948).

[3] Since this work was completed, U. S. Patent 2,449,987, Sept. 28, 1948, the reaction was also reported by H. B. Hass, H. Feuer and S. M. Pier, THIS JOURNAL, **73**, 1858 (1951).

[4] M. R. Frederick, U. S. Patent 2,485,271 (October 18, 1949).

[5] A. Binz, *Ber.*, **37**, 3549 (1904).

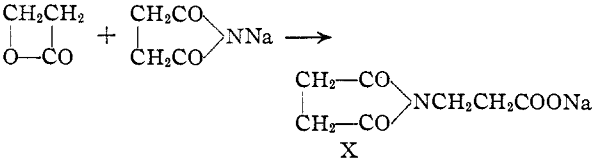
[6] T. L. Gresham, U. S. Patent 2,449,988 (Sept. 28, 1948).

[7] A. Fredga, *J. prakt. Chem.*, **123**, 110 (1928).

[8] (a) T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, W. L. Beears and M. G. Prendergast, THIS JOURNAL, **71**, 661 (1949); (b) T. L. Gresham and F. W. Shaver, U. S. Patent 2,449,992 (Sept. 28, 1948).

reaction mixtures, however, converted the sulfinic acid to the relatively insoluble thiosulfonate and the very soluble sulfonic acid allowing partial separation of the desired product. Reactions of I and sodium benzene-, *p*-toluene-, *p*-chlorobenzene- and 2,5-dichlorobenzenesulfinates gave the sulfonylpropionic acids in 17 to 58% yields. These acids also were obtained but in lower yields from the reactions of I and the corresponding arylsulfinic acids.

Aqueous sodium succinimide and I react to give sodium *β*-succinimidopropionate (X) from which *β*-succinimidopropionic acid can be isolated after acidification.



X

Experimental[9]

β-Nitropropionic Acid (II).—Two moles (144 g.) of *β*-propiolactone was added during one hour to a solution of two moles (138 g.) of sodium nitrite in 800 ml. of water. The reaction mixture was stirred and held at 15–25° with external cooling. After an additional hour the clear solution was cooled to 0°, acidified slowly with concd. hydrochloric acid and extracted with 600 ml. of ether in a continuous manner. Chloroform (150 ml.) was added to the reddish colored extract and after treatment with decolorizing charcoal the solution was evaporated to 250 ml. under reduced pressure. On cooling in an ice-bath, crystals of *β*-nitropropionic acid[10] separated; yield 112 g. (47%), m.p. 60–66°.[11] After two recrystallizations from chloroform the melting point was 67.5–68.5°.

Anal. Calcd. for $C_3H_5NO_4$: C, 30.25; H, 4.20; N, 11.76; neut. equiv., 119. Found: C, 30.16; H, 4.36; N, 11.67; neut. equiv., 118.

β,β′-Sulfonyldipropionic Acid (III).—*β*-Propiolactone (2 moles, 144 g.) was dissolved in 75 ml. of acetone and added (1 hour) to a well stirred suspension of 193 g. (1 mole) of 90% sodium dithionite in 400 ml. of water. The temperature was held at 18–25° with external cooling and after an additional hour the solution was acidified with concd. hydrochloric acid and heated to boiling for 30 min. with evolution of sulfur dioxide. On cooling a copious white precipitate of *β*,*β*′-sulfonyldipropionic acid separated which was recrystallized from hot water, filtered and dried; wt. 91 g. (43.5%); m.p. 210–213°. Recrystallization from acetic acid gave a product melting at 215–217°. The melting point of a mixture with an authentic sample prepared by oxidizing *β*,*β*′-thiodipropionic acid[2a] as described by Loven[12] (m.p. 219–221°) was 215–219°.

Sodium β-Cyanopropionate (IV).—One mole (72 g.) of *β*-propiolactone was added (15 min.) to a solution of 49 g. (1 mole) of sodium cyanide in 67 ml. of water and 67 ml. of ethanol with good stirring. The temperature was maintained at 50° throughout the addition and external cooling was required. After an additional ten minutes the solution was diluted with 100 ml. of ethanol and cooled to 0° while stirring vigorously. The sodium *β*-cyanopropionate monohydrate which separated was filtered at once, washed with two 100-ml. portions of cold ethanol and dried; m.p. 91–93°; wt. 94 g. (68%); m.p. 92–93° (after recrystallization from aqueous ethanol).

Anal. Calcd. for $C_4H_4NO_2Na \cdot H_2O$: C, 34.53; H, 4.31; N, 10.07; Na, 16.55. Found: C, 34.54; H, 4.46; N, 10.06; Na, 16.62.

β-Cyanopropionic Acid (V).—A reaction mixture similar to that obtained above instead of being diluted with ethanol was cooled to 0° and slowly acidified with cold concd. hydrochloric acid while stirring vigorously. The cold solution was extracted with three 100-ml. portions of cold ether. The ether extracts were dried over anhyd. magnesium sulfate, treated with decolorizing charcoal, all at 0°, and the ether evaporated under reduced pressure. The residue of crude *β*-cyanopropionic acid[13] weighed 72 g. (73%); m.p. 49–51° after recrystallization from chloroform.

Anal. Calcd. for $C_4H_5NO_2$: neut. equiv., 99. Found: neut. equiv., 98.2.

Succinic Acid (VI).—A reaction mixture containing sodium *β*-cyanopropionate (IV), prepared as above, was added to a solution of 40 g. of sodium hydroxide in 300 ml. of water. The solution was boiled for 1.5 hours allowing the alcohol–water binary to escape. After cooling to 75°, 200 ml. of alcohol was added and the solution cooled to 0°. The crystalline precipitate of sodium succinate hexahydrate which separated was filtered, washed with two 100-ml. portions of ethanol and dried; wt. 210 g. (78%).[14]

Anal. Calcd. for $C_4H_4O_4Na_2 \cdot 6H_2O$: equiv. wt., 138. Found: equiv. wt., 135.

Succinic acid was isolated from the solution of sodium succinate prepared as above by adding 14.4 g. (0.25 mole) of ammonium chloride, to buffer the solution, and 122 g. (1.1 moles) of calcium chloride in 350 ml. of water. This mixture was digested for 30 minutes at 90°. The precipitate of calcium succinate was filtered, washed with two 100-ml. portions of hot water and acidified with 340 g. (0.85 mole) of 25% sulfuric acid. The acid solution was decolorized by digesting for 15 minutes with charcoal, and filtered from calcium sulfate and charcoal. The solids were washed with three 100-ml. portions of hot water and the combined filtrate and washes were evaporated to give 95.6 g. (81%) of succinic acid, m.p. 183–184° after one recrystallization from water. The melting point of a mixture with an authentic sample was not depressed.

β-Thiocyanopropionic Acid (VII).—One mole (72 g.) of *β*-propiolactone was added (1 hr.) to a solution of 89 g. (1.1 moles) of sodium thiocyanate in 75 ml. of water. The reaction mixture was stirred and maintained at 21–28° with external cooling. After the addition was completed the clear solution was acidified with concd. hydrochloric acid and diluted with 50 ml. of water. This solution was extracted with three 10-ml. portions of chloroform. Vacuum evaporation of the combined chloroform extracts and cooling in a refrigerator overnight yielded 106 g. (81%) of *β*-thiocyanopropionic acid, m.p. 9.0–9.5°.[7]

Anal. Calcd. for $C_4H_5NO_2S$: N, 10.69; neut. equiv., 131. Found: N, 10.58; neut. equiv., 134.

When 13 g. (0.1 mole) of VII and 50 ml. of 4 *N* hydrochloric acid were heated for six hours at 50° and then allowed to evaporate at 40° overnight, 12 g. (80%) of *β*-carbamylmercaptopropionic acid was obtained; m.p. 149–150° (after two recrystallizations from water).[7]

Anal. Calcd. for $C_4H_7NO_3S$: N, 9.39. Found: N, 9.14.

β-(*o*-Tolylsulfonyl)-propionic Acid (a) From Sodium *p*-Toluenesulfinate.—*β*-Propiolactone (10.8 g., 0.15 mole) was added to a stirred solution of 26.7 g. (0.15 mole) of sodium *p*-toluenesulfinate in 200 ml. of water at 25°. The temperature reached a maximum of 31° within 40 minutes and after an additional two hours the solution was acidified with concd. hydrochloric acid. On cooling a light yellow oil separated and then solidified. This solid was separated by filtration and digested in refluxing water (50 ml.) for seven hours. The solution was made basic by adding 8 g. of sodium hydroxide, filtered from 0.5 g. of di-*p*-tolyl disulfide (m.p. 35–37°) and acidified with concentrated hydrochloric acid. The crude (*p*-tolylsulfonyl)-propionic acid[15] was filtered and dried; wt. 20 g. (58.2%); m.p. 109–110.5° after two recrystallizations from water.

Anal. Calcd. for $C_{10}H_{12}O_4S$: C, 52.62; H, 5.29; S, 14.05; neut. equiv., 228.3. Found: C, 52.64; H, 5.30; S, 13.96; neut. equiv., 229.9.

(b) From *p*-Toluenesulfinic Acid.—*β*-Propiolactone (0.8 g., 0.15 mole) was added to a stirred mixture of 23.4 g. (0.15 mole) of toluenesulfinic acid in 100 ml. of water. The solution was refluxed for seven hours. After cooling to

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[9] All melting points reported herein are uncorrected.

[10] I. M. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1943, p. 238.

[11] Compare Hass, Feuer and Pier, ref. 3.

[12] J. M. Loven, *Ber.*, **29**, 1136 (1896).

[13] D. J. G. Ives and K. Sames, *J. Chem. Soc.*, 513 (1943).

[14] O. Doepping, *Ann.*, **47**, 253 (1843).

[15] F. Arndt, *Ber.*, **58B**, 1612 (1925).

room temperature the crystalline product which formed was filtered, washed with water and dried; wt. 15 g. The solid was treated with boiling water and 6 g. of the thiosulfonate separated as an oil. Crystals of β-(*p*-tolylsulfonyl)-propionic acid separated on cooling the aqueous solution; wt. 9 g. (26%), m.p. 106–107°. The melting point of a mixture with acid prepared above was not depressed.

A number of β-(arylsulfonyl)-propionic acids were prepared using the same procedures as are described for β-(*p*-tolylsulfonyl)-propionic acid.

β-(Phenylsulfonyl)-propionic Acid (VIII). From Sodium Benzenesulfinate.—Wt. 3.7 g. (17.5%); m.p. 119–120°.[16]

Anal. Calcd. for $C_9H_{10}O_4S$: C, 50.49; H, 4.67; S, 14.94; neut. equiv., 214. Found: C, 50.55; H, 4.72; S, 14.89; neut. equiv., 215.

Sodium benzenesulfinate and sodium β-chloropropionate in water gave, on warming, followed by acidification, a 28% yield of β-(phenylsulfonyl)-propionic acid; m.p. 121–123°. The melting point of a mixture with the above sample was not depressed.

β-(*p*-Chlorophenylsulfonyl)-propionic Acid (a) From Sodium Chlorobenzenesulfinate.—Wt. 13 g. (3.5%), m.p. 142–143°.

Anal. Calcd. for $C_9H_9ClO_4S$: C, 43.47; H, 3.65; S, 12.89; Cl, 14.26; neut. equiv., 248.7. Found: C, 43.51; H, 3.68; S, 12.87; Cl, 14.35; neut. equiv., 250.4.

(b) From *p*-Chlorobenzenesulfinic Acid.—Wt. 6.5 g. (17.4%), m.p. 138–140°. The melting point of a mixture with the above sample was not depressed.

β-(2,5-Dichlorophenylsulfonyl)-propionic Acid (a) From Sodium 2,5-Dichlorobenzenesulfinate.—Wt. 12.2 g. (29%), m.p. 149–150°.

Anal. Calcd. for $C_9H_8Cl_2O_4S$: C, 38.18; H, 2.85; S, 11.32; Cl, 25.05; neut. equiv., 283.1. Found: C, 38.27; H, 3.15; S, 11.43; Cl, 25.03; neut. equiv., 288.6.

(b) From 2,5-Dichlorobenzenesulfinic Acid.—Wt. 9 g. (21.2%), m.p. 149–151°. The melting point of a mixture with the above sample was not depressed.

(c) From β-(2,5-Dichlorothiophenoxy)-propionic Acid.—β-(2,5-Dichlorothiophenoxy)-propionic acid (IX) was prepared from β-propiolactone and 2,5-dichlorothiophenol[8] and oxidized with aqueous potassium permanganate.[16] The resulting β-(2,5-dichlorophenylsulfonyl)-propionic acid melted at 150–151° after recrystallization from water. Melting points of mixtures with the above samples were not depressed.

β-Succinimidopropionic Acid (X).—One mole (72 g.) of β-propiolactone was added during one hour to a solution of one mole (99 g.) of succinimide and one mole (40 g.) of sodium hydroxide in 250 ml. of water. The reaction mixture was stirred and held at 25° with external cooling. After an additional 15 minutes the solution was neutralized with concd. hydrochloric acid and concentrated by vacuum evaporation to 200 ml. Addition of 50 ml. of concd. hydrochloric acid and cooling to 5° gave a crystalline precipitate of β-succinimidopropionic acid which was separated by filtration. The filtrate was concentrated, treated with 75 ml. of ethanol and filtered from salt. Cooling the filtrate gave more product. The combined crude β-succinimidopropionic acid, m.p. 119–123°, weighed 105 g. (61%); m.p. 129–130°[17] after three recrystallizations from ethanol.[18]

Anal. Calcd. for $C_7H_9NO_4$: C, 49.12; H, 5.26; N, 8.19; mol. wt., 171. Found: C, 49.25; H, 5.38; N, 8.1; mol. wt., 174.

Acknowledgment.—The authors wish to take this opportunity to acknowledge with thanks the analytical data furnished by W. P. Tyler, J. R. Kubik, D. W. Beesing, A. K. Kuder and D. M. Kurtz.

BRECKSVILLE, OHIO RECEIVED AUGUST 24, 1951

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[16] E. Schjanberg, *Ber.*, **76B**, 287 (1933).

[17] O. A. Moe and D. T. Warner, THIS JOURNAL, **71**, 1251 (1949).

[18] We are indebted to T. H. Shelley for this experiment.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, GENERAL MILLS, INC.]

Investigation of the Reserve Carbohydrates of Leguminous Seeds. II. Derivatives[1]

BY OWEN A. MOE, SIDNEY E. MILLER AND MARJORIE IWEN BUCKLEY

The preparation of the 2-cyanoethyl ethers of galactomannan and glucomannan polysaccharides is disclosed. The hydrolysis of the resultant ethers is discussed, and the gelation phenomena of the resultant products are reported. The carboxymethyl ether of polysaccharide from guar has been prepared and the properties have been noted.

A previous communication[2] discussed some preliminary studies relevant to the periodate oxidation of reserve carbohydrates from leguminous seeds. The preliminary results were interpreted as indicating the presence of 1,4-linkages in these polymeric galactomannans with the possibility of branching at the C_6-position. Since that time, extensive work involving methylation studies and X-ray diffraction studies has elucidated the structure of these carbohydrates. The results have shown that in the polymeric galactomannans from guar[3-7] and carob bean[8,9] the mannose units form the main chain and are linked in a 1,4-fashion, whereas the galactose units are present as branches (one unit) at the C_6-position. Extensive methylation data[7] may elucidate still finer points of structure. The present publication relates to the preparation and some properties of diverse derivatives of these polysaccharides.

The 2-cyanoethyl ethers of these polysaccharides were prepared by the reaction between the polymeric carbohydrates and acrylonitrile in the presence of an alkaline catalyst. The degree of substitution of the resulting 2-cyanoethyl ethers could be readily controlled by variations in the quantity of acrylonitrile employed. When one mole of acrylonitrile was used per anhydropyranose unit, the resulting 2-cyanoethyl ethers had values of 0.4–0.5 for the degree of substitution, and these values increased to 1.6–1.8 when six moles of acrylonitrile per sugar unit were used. These results were obtained when the reactions were carried out at room temperature for a two-four hour period. The progress of the cyanoethylation reaction could be observed visually since the derivatives separated from the reaction mixtures as nearly white products.

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[1] Paper No. 120, Journal Series, General Mills, Inc., Research Dept.

[2] O. A. Moe, S. E. Miller and M. H. Iwen, THIS JOURNAL, **69**, 2621 (1947).

[3] J. F. Carson and W. D. Maclay, *ibid.*, **70**, 2220 (1948).

[4] J. Swanson, *ibid.*, **71**, 1510 (1949).

[5] K. J. Palmer and M. Ballantyne, *ibid.*, **72**, 736 (1950).

[6] Z. F. Ahmed and R. L. Whistler, *ibid.*, **72**, 2524 (1950).

[7] C. M. Rafique and F. Smith, *ibid.*, **72**, 4634 (1950).

[8] F. Smith, *ibid.*, **70**, 3249 (1948).

[9] E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1278 (1948).