Anal. Calcd. for $C_3H_4O_2$: C, 50.0; H, 5.56; neut. equiv., 72; MR_D, 15.51; mol. wt., 72. Found: C, 49.87; H, 5.57; neut. equiv., 72.3; MR_D, 15.67; mol. wt. (cryoscopic in benzene), 74.

Pure I is relatively stable at room temperature. There is no evidence of change in two to three months. However, it reacts rapidly and exothermically at room temperature with a wide variety of organic and inorganic compounds. In many cases polymerization of I is a competing reaction and in general this polymerization is minimized by operating at low temperatures.

The lactone is miscible at room temperature with most organic solvents such as ether, acetone, alcohol, benzene and acetic acid. It is 37% soluble (by volume) in water at 25° but the lactone is slowly hydrolyzed to hydracrylic acid and at least five days are required for complete reaction. With an equal molar quantity of water the hydracrylic acid obtained contains about 20% poly-hydracrylic acids as determined by acid and saponification equivalents.

Polymerization to Poly-ester Acids (II).—A. With Heat.—Three hundred grams (4.16 moles) of I was heated at 130–150° for five hours with stirring. The material gradually became more viscous and the cooled product (300 g.) was a viscous oil which partially solidified. No materials volatile at 100° under vacuum were present.

B. With Ferric Chloride.—A trace of ferric chloride (0.1 g.) was added to 25 g. of I in an open beaker at 25°. Within thirty seconds a violent exothermic reaction occurred and the entire contents were expelled.

A controlled polymerization was carried out by adding 300 g. of I dropwise to a stirred solution of ferric chloride (3 g.) in 125 ml. of benzene. Reflux was maintained by the rate of addition which required thirty minutes. The benzene was decanted from the poly-ester acid (300 g.) which partially solidified on cooling.

C. With Sulfuric Acid.—Addition of I (3 moles, 216 g.) slowly (one hour) to 1 g. of concentrated sulfuric acid at 60–80° with external cooling gave a semi-solid reaction product (210 g.). The product was melted, dissolved in 1000 ml. of hot acetone which in turn was poured into 3000 ml. of cold water. The solid which separated was filtered, washed with water, and dried; wt. 176 g. (82%), m. p. 84–86°.

Anal. Calcd. for $C_{36}H_{48}O_{24}$, IIa: C, 50.00; H, 5.56; neut. equiv., 864; mol. wt., 864; sapn. equiv., 72; iodine no., 29.4. Calcd. for $C_{36}H_{50}O_{25}$, IIb: C, 48.98; H, 5.67; neut. equiv., 882; mol. wt. 882; sapn. equiv., 73.5; iodine no., 0. Calcd. for 63% IIa and 37% IIb: C, 49.61; H, 5.60; neut. equiv., 870; iodine no., 18.5. Found: C, 49.48; H, 5.70; neut. equiv., 870; mol. wt. (ebullioscopic in chloroform), 850; sapn. equiv., 74; iodine no. (by perbenzoic acid oxidation), 18.5.

The agreement of the calculated mixture analysis with that found is significant only to establish a possible composition of poly-ester acids with an average molecular weight of about 870.

Alcoholysis of II, Ethyl Hydracrylate (IV).—A mixture of 100 g. of II (prepared by procedure A, B, or C) and 192 g. anhydrous ethanol containing 1 g. of concentrated sulfuric acid was refluxed for thirty-six hours. The acid catalyst was neutralized with calcium carbonate, most of the excess alcohol distilled at atmospheric pressure, and the residual oil filtered to remove calcium salts. Distillation of the residue at 13 mm. yielded 16.4 g. of forefraction, b. p. 60–81°, and 137 g. (84%) of ethyl hydracrylate, b. p. 81–83°, n^{25}_D 1.4222, d^{20}_4 1.0545.

Anal. Calcd. for $C_5H_{10}O_3$: sapn. equiv., 118. Found: sapn. equiv., 118.2.

Pyrolysis of II, Acrylic Acid (V).—Three hundred grams of II and 3 g. of anhydrous copper acetate (to inhibit polymerization of acrylic acid) were heated to 200° at 80 mm. A fraction of crude acrylic acid (275 g.), b. p. 84–131°, was collected. Redistillation gave 200 g. (67%) of acrylic acid, b. p. 79–80° at 80 mm., m. p. 12–13°. A mixture melting point with an authentic sample of acrylic acid was not depressed.

Summary

The polymers of β-lactone are poly-ester acids. The polymerization is markedly catalyzed by certain acids, bases and salts. The poly-ester acids are characterized by pyrolysis to acrylic acid and by alcoholysis to hydracrylates.

BRECKSVILLE, OHIO RECEIVED JULY 21, 1947

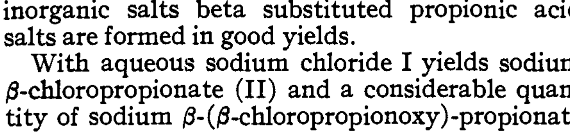
[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

β-Propiolactone. II. Reactions with Salts of Inorganic Acids

BY T. L. GRESHAM, J. E. JANSEN, F. W. SHAVER AND J. T. GREGORY

In the previous paper[1] the rapid polymerization of β-propiolactone (I) as catalyzed by certain inorganic salts was described. In water solutions of inorganic salts beta substituted propionic acid salts are formed in good yields.

With aqueous sodium chloride I yields sodium β-chloropropionate (II) and a considerable quantity of sodium β-(β-chloropropionoxy)-propionate (III) and higher analogs.



$$\underset{\text{I}}{\begin{array}{c}CH_2\,CH_2\\ |\quad\;\; |\\ O—C{=}O\end{array}} + NaCl \longrightarrow ClCH_2CH_2COONa \quad \text{II}$$

$$\begin{array}{c}CH_2CH_2\\ |\quad\;\; |\\ O—C{=}O\end{array} + ClCH_2CH_2COONa \longrightarrow$$

$$ClCH_2CH_2COOCH_2CH_2COONa \quad \text{III}$$

The secondary reaction of I with the primary product is minimized by increasing the molar ratio of salt to I and by the addition of hydrochloric acid. This latter effect may be due to reduction in the concentration of the chloropropionate ion at the lower *p*H.

Reactions of I with lithium, ammonium, calcium, barium or ferric chloride in aqueous solution give salts of β-chloropropionic acid in a manner similar to that with sodium chloride. With sodium bromide and iodide there is less tendency for the secondary reactions to occur. The yields of *beta* substituted propionic acids under similar conditions increase in the order: NaCl < NaBr < NaI. In all of the above reactions some hydrolysis of I occurs.

The reaction of I with aqueous sodium hydrogen sulfide results in excellent yields of sodium β-mercaptopropionate (IV). The secondary reaction occurs only at the mercapto group to give

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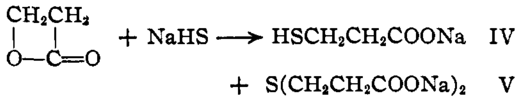
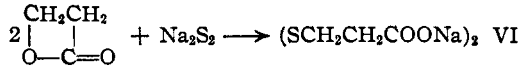
[1] Gresham, Jansen and Shaver, THIS JOURNAL, **70**, 998 (1948).

a small amount of the salt of bis-(2-carboxyethyl) sulfide (V) and is not minimized by the use of an excess of sodium hydrogen sulfide. The addition of I to a solution containing equal molar amounts of sodium chloride and sodium hydrogen sulfide results in almost exclusive reaction with the sodium hydrogen sulfide. With aqueous sodium sulfide the reaction is more complex and hydrolysis occurs to a major extent. In concentrated solutions, however, a mixture of sodium β-mercaptopropionate (IV) and bis-(2-carboxyethyl) sulfide (V) is obtained in poor yield. The ratio of IV to V is about 1:2 even when an excess of sodium sulfide is present, indicating a preference for I to react at the alkyl mercapto group. With aqueous sodium disulfide a high yield of bis-(2-carboxyethyl) disulfide (VI) is obtained.

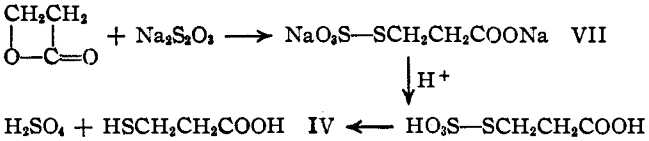


$$\begin{array}{l} CH_2CH_2 \\ |\qquad | \\ O\text{—}C{=}O \end{array} + NaHS \longrightarrow HSCH_2CH_2COONa \quad \text{IV} + S(CH_2CH_2COONa)_2 \quad \text{V}$$



$$2\begin{array}{l} CH_2CH_2 \\ |\qquad | \\ O\text{—}C{=}O \end{array} + Na_2S_2 \longrightarrow (SCH_2CH_2COONa)_2 \quad \text{VI}$$

β-Mercaptopropionic acid is the product formed from I and sodium thiosulfate. An intermediate thiosulfate (VII) and the corresponding acid are both stable in the solution at 25° but the acid is hydrolyzed by boiling. A by-product of this reaction is bis-(2-carboxyethyl) disulfide (VI) formed by the oxidation of IV with the small amount of sodium thiosulfate present when the solution is acidified.



$$\begin{array}{l} CH_2CH_2 \\ |\qquad | \\ O\text{—}C{=}O \end{array} + Na_2S_2O_3 \longrightarrow NaO_3S\text{—}SCH_2CH_2COONa \quad \text{VII} \xrightarrow{H^+} HO_3S\text{—}SCH_2CH_2COOH \longrightarrow H_2SO_4 + HSCH_2CH_2COOH \quad \text{IV}$$

Experimental

β-Choropropionic Acid (II).—One mole (72 g.) of I was added (five minutes) to a solution of one mole (58.5 g.) of sodium chloride in 400 ml. of water. The reaction was stirred and held at 25° with external cooling for one hour after which there was no detectable temperature rise. After three hours, the clear solution was acidified with concentrated hydrochloric acid. The product, part of which separated as a heavy oil layer, was separated by continuous extraction with ether. The residue from evaporation of the ether extract was distilled at reduced pressure to give 37.2 g. (34%) of β-chloropropionic acid, b. p. 69–75° (1 mm.); m. p. 36–39°; m. p. 41–42° (after one recrystallization from ether–petroleum ether).

Anal. Calcd. for $C_3H_5O_2Cl$: C, 33.19; H, 4.61; Cl, 32.7; neut. equiv., 108.57. Found: C, 33.16; H, 4.57 Cl, 32.6; neut. equiv., 108.7.

The residue (35.7 g.) from the above distillation was a viscous slightly colored oil consisting of a mixture of β-(β-chloropropionoxy)-propionic acid III and higher analogs.

Anal. Calcd. for $C_6H_9O_4Cl$ (III): Cl, 19.66; neut. equiv., 180.5; for $C_9H_{13}O_6Cl$: Cl, 14.06; neut. equiv., 252.2. Found: Cl, 14.8; neut. equiv., 229.

When the above experiment was carried out with one mole of I and three moles of salt in 400 ml. of water the yield of III was 73.7% and the residue weighed 17 g.

With one mole of I, 1.4 moles of salt and 1.1 moles of concentrated hydrochloric acid in 338 ml. of water a yield of 91.2% of β-chloropropionic acid was obtained. The residue weighed 2 g.

β-Bromopropionic Acid.—This experiment was carried out similar to the preparation of II but substituting one mole (103 g.) of sodium bromide. After cooling and acidification the product was extracted in a continuous manner with a mixture of one part of ether and fifteen parts of hexane and finally with ether alone. The combined residues from the extracts were distilled at reduced pressure to give 88.5 g. (58%) of β-bromopropionic acid, b. p. 88° (0.5 mm.); m. p. 58–60°. After recrystallization from hexane the acid melted at 61–62°.

Anal. Calcd. for $C_3H_5O_2Br$: C, 23.55; H, 3.29; Br, 52.23; neut. equiv., 152.9. Found: C, 23.69; H, 3.43; Br, 52.17; neut. equiv., 153.8.

The residue (15 g.) was a slightly colored viscous oil.

Anal. Calcd. for $C_6H_9O_4Br$: Br, 35.55; neut. equiv., 255. Calcd. for $C_9H_{13}O_6Br$: Br, 26.85; neut. equiv., 297. Found: Br, 28.1; neut. equiv., 252.

β-Iodopropionic Acid.—An experiment similar to that for the preparation of II but substituting one mole (150 g.) of sodium iodide was held at 0° after acidification. The crystals of β-iodopropionic acid which separated were filtered, washed with cold water and dried at 25°; m. p. 75–82°; yield, 123 g. (61.5%); m. p. 82–83° (after recrystallization from chloroform–hexane).

Anal. Calcd. for $C_3H_5O_2I$: C, 18.01; H, 2.52; I, 63.5; neut. equiv., 200. Found: C, 18.10; H, 2.59; I, 63.4; neut. equiv., 201.

β-Mercaptopropionic Acid (IV) (From Sodium Hydrogen Sulfide).—Seventy-two grams (1 mole) of I was added while stirring (15 min.) to a solution of 1.06 moles (59 g.) of sodium hydrogen sulfide, freshly prepared from sodium hydroxide and hydrogen sulfide, in 160 ml. of water. A reaction temperature of 5° was maintained. After an additional hour the solution was acidified with concentrated hydrochloric acid and the product isolated by continuous extraction with ether. Distillation of the ether extract residue at reduced pressure gave 85.6 g. (80.7%) of β-mercaptopropionic acid; b. p. 114–115.5° at 13 mm.; d^{20}_4 1.2188; n^{20}_D 1.4921.

Anal. Calcd. for $C_3H_6O_2S$: C, 34.0; H, 5.66; S, 30.19; neut. equiv., 106. Found: C, 34.0; H, 5.84; S, 30.21; neut. equiv. (neutral red), 105.4.

The residue (13.4 g.) from the above distillation was dissolved in acetone, the solution decolorized with Nuchar and evaporated. The solid residue was recrystallized from hot water yielding 8 g. (9.0%) of bis-(2-carboxyethyl) sulfide; m. p. 128–130°.

Anal. Calcd. for $C_6H_{10}O_4S$: C, 40.45; H, 5.65; S, 17.97; neut. equiv., 89. Found: C, 40.50; H, 5.67; S, 18.04; neut. equiv., 88.8.

A similar experiment but using two moles of sodium hydrogen sulfide gave 89 g. (84%) of β-mercaptopropionic acid and 6.6 g. (7.4%) of bis-(2-carboxyethyl) sulfide.

A third experiment wherein the water was replaced with 500 ml. of anhydrous ethanol gave a reaction mixture containing a heavy precipitate of the mono-sodium salt of β-mercaptopropionic acid. The suspension was acidified with 128 ml. of concentrated hydrochloric acid, filtered from sodium chloride, and concentrated by distillation at atmospheric pressure. Fractional distillation of the residue at 20 mm. gave a forerun (25 g., b. p. 23–76°) the water insoluble portion of which was returned to the distillation flask. Completion of the rectification gave two fractions. The first fraction, 47.7 g. (35.6%), b. p. 79–79.5° (20 mm.), was redistilled to give pure ethyl β-mercaptopropionate, b. p. 79–79.5° (20 mm.); n^{20}_D 1.4561; d^{20}_4 1.0550.

Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.78; H, 7.52; S, 23.87; sapn. equiv., 134.1; MR_D, 34.53. Found: C, 44.79; H, 7.58; S, 23.91; sapn. equiv., 136; MR_D 34.63.

The second fraction, b. p. 122–123.5° (20 mm.), wt.

158.8 g. (55.5%) was β-mercaptopropionic acid, $n^{20}\text{D}$ 1.4902; d^{20}_4 1.2169.

Anal. Calcd. for $C_3H_6O_2S$: neut. equiv., 106. Found: neut. equiv., 108.5 (neutral red).

β-Mercaptopropionic Acid (IV) (From Sodium Sulfide).—One mole (72 g.) of I was added slowly (thirty minutes) to a stirred solution of 1.2 moles (288.5 g. nonahydrate) of sodium sulfide in 200 ml. of water with control of the temperature at 15°. Part of the sodium sulfide was undissolved at the start. After several hours the clear solution was acidified with concentrated hydrochloric acid and the product isolated by ether extraction. Distillation of the ether extract residue at reduced pressure gave 11 g. (10%) of β-mercaptopropionic acid, b. p. 100° (7 mm.); $n^{20}\text{D}$ 1.4921.

Anal. Calcd. for $C_3H_6O_2S$: neut. equiv., 106. Found: neut. equiv., 108 (neutral red).

The solid residue from the above distillation was recrystallized twice from ether–petroleum ether to give 16.2 g. (18.2%) of bis-(2-carboxyethyl) sulfide, m. p. 128–130°. The melting point of a mixture with an authentic sample was not depressed.

An experiment carried out as above but with no control of the temperature resulted in its rise to 99°. The product was a mixture consisting of 9 g. (8%) of β-mercaptopropionic acid and 20.5 g. (22%) of bis-(2-carboxyethyl) sulfide.

Another experiment at 0° and at greater dilution, 1000 ml. of water, resulted in no ether extractable product.

bis-(2-Carboxyethyl) Disulfide (VI) (From Sodium Disulfide).—A solution of 0.5 mole (43.5 g.) sodium disulfide was prepared from 61 g. (1.1 mole) of sodium hydrogen sulfide and 16 g. (0.5 mole) of sulfur in 400 ml. of water by warming the suspension at 50° while stirring. To the orange-red solution was added slowly (thirty minutes) 72 g. (1 mole) of I at 0°. After an additional hour the clear yellow solution was acidified with concentrated hydrochloric acid, diluted with water and the copious white precipitate filtered, washed with water and recrystallized from 1000 ml. of hot water. The yield of impure bis-(2-carboxyethyl) disulfide was 98.5 g. (94%), m. p. 135–149°. The mixture melting point with an authentic sample (m. p. 153–155°) was 148–153°.

β-Mercaptopropionic Acid (IV) (From Sodium Thiosulfate).—I (144 g., 2 moles) was added slowly (two hours) to a stirred solution of 496 g. (2 moles) sodium thiosulfate pentahydrate in 400 ml. water at 30°. After acidification with 330 ml. concentrated hydrochloric acid an ether extraction yielded no product. However, after heating the water layer for three hours at 100° a white precipitate of bis-(2-carboxyethyl) disulfide separated. This was filtered and recrystallized from hot water, m. p. 153–155°; wt. 29 g. (13.8%).

Anal. Calcd. for $C_6H_{10}O_4S_2$: C, 34.25; H, 4.79; S, 30.42. Found: C, 34.28; H, 4.77; S, 30.46.

The above filtrate was continuously extracted with ether and the residue, after evaporation of the ether, was distilled at reduced pressure. β-Mercaptopropionic acid, 148.5 g. (70%) was collected, b. p. 94° (5 mm.); $n^{20}\text{D}$ 1.4921; d^{20}_4 1.2188.

Anal. Calcd. for $C_3H_6O_2S$: neut. equiv., 106. Found: neut. equiv., 105.4 (neutral red).

The residue (12 g.) from the distillation yielded 11 g. (5%) of crude bis-(2-carboxyethyl) disulfide after recrystallization from hot water, m. p. 131–144°.

bis-2-(Carboxyethyl) Disulfide (VI) (By Oxidation).—A solution containing 95.4 g. (0.9 mole) β-mercaptopropionic acid, 25 g. (0.1 mole) sodium thiosulfate pentahydrate in 360 ml. of water was acidified with 16.5 ml. of concentrated hydrochloric acid. The solution was held at 100° for one hour during which time the small sulfur deposit disappeared and hydrogen sulfide was evolved. An equal volume of hot water was added and after cooling, the precipitate of bis-(2-carboxyethyl) disulfide was filtered and recrystallized from 600 ml. of hot water; wt. 80 g. (84.5%); m. p. 150–152.5°. A mixture melting point with an authentic sample was not depressed.

Summary

Reactions of β-propiolactone with aqueous solutions of alkali halides, sodium hydrogen sulfide, sodium sulfide, sodium disulfide and sodium thiosulfate are described. The primary products are salts of *beta* substituted propionic acids. In certain cases salts of poly-ester acids are formed as secondary reaction products.

BRECKSVILLE, OHIO RECEIVED JULY 21, 1947

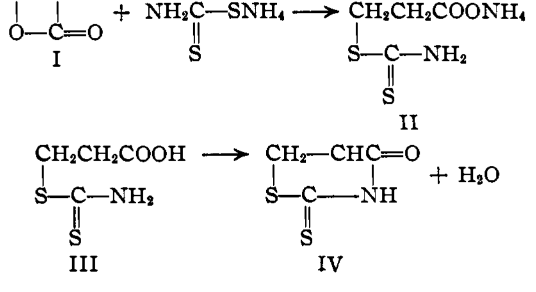
[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

β-Propiolactone. III. Reactions with Dithiocarbamic Acids, their Salts and Thiourea

BY T. L. GRESHAM, J. E. JANSEN AND F. W. SHAVER

The previous work[1] showed that salts of *beta*-substituted propionic acid were formed from β-propiolactone (I) and salts of inorganic acids. Similar products are formed from salts of dithiocarbamic acids and there is no tendency for secondary reactions to occur.

With ammonium dithiocarbamate, an excellent yield of ammonium β-dithiocarbamyl propionate (II) is obtained and the corresponding acid is readily cyclized to 2-thiono-4-keto-1,3-thiazane (IV). Similarly salts of N-alkyl and N,N-dialkyl dithiocarbamic acids form salts of *beta*-substituted propionic acids. Ring closure occurs only with the mono alkyl substituted acids.



β-Dithiocarbamylpropionic acids III are also formed from I and the free dithiocarbamic acids in water solution. The yields are equally high.

With thiourea, I forms β-isothioureido propionic

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(1) Gresham, Jansen, Shaver and Gregory, THIS JOURNAL, **70**, 999 (1948).