158.8 g. (55.5%) was β-mercaptopropionic acid, $n^{20}D$ 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.); $n^{20}D$ 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.); $n^{20}D$ 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.

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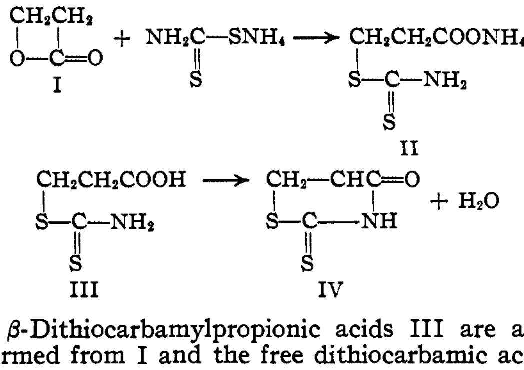
[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

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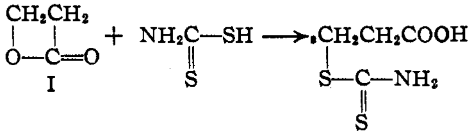
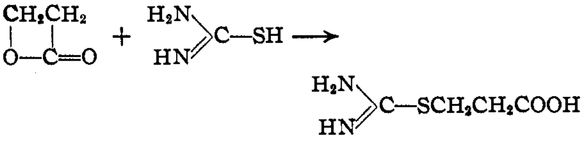
[1] Gresham, Jansen, Shaver and Gregory, THIS JOURNAL, 70, 999 (1948).



I III

acid (V). In polar solvents such as water, the reaction is rapid and nearly quantitative but it does not occur at all in non-polar solvents such as ether.



V

Experimental

β-Dithiocarbamylpropionic Acid (III).—One mole (72 g.) of β-propiolactone was added dropwise (twenty minutes) to a solution of 110 g. (1 mole) of ammonium dithiocarbamate[2] in 300 ml. of water at 20° with stirring. The clear solution was acidified with concentrated hydrochloric acid and after two hours the copious white precipitate was filtered, washed with water and dried; m. p. 124–126°; yield, 152 g. (92%). After recrystallization from ether–petroleum ether the product was collected as small prisms, m. p. 125–126°.

Anal. Calcd. for $C_4H_7O_2NS_2$: C, 29.10; H, 4.24; N, 8.50; S, 38.80; neut. equiv., 165. Found: C, 29.17; H, 4.25; N, 8.59; S, 38.85; neut. equiv., 168.

A solution of dithiocarbamic acid was prepared by carefully acidifying a solution of ammonium dithiocarbamate (110 g., 1 mole in 500 ml. of water) with 100 g. concentrated hydrochloric acid at 0°. One mole (72 g.) of β-propiolactone was added dropwise (thirty minutes) to this solution while stirring. The temperature was maintained at 0° throughout and after three hours the copious white precipitate which had separated was filtered, washed thoroughly with water, and dried; yield, 152 g. (92%); m. p. 124–126°. A mixture melting point with the above sample of β-dithiocarbamylpropionic acid was not depressed.

Reactions with other dithiocarbamates were carried out in a manner similar to the above. Solutions of sodium N-ethyl dithiocarbamate were prepared from ethylamine, carbon disulfide and sodium hydroxide in the usual manner. Solutions of sodium N,N-dimethyl and N,N-diethyl dithiocarbamate were prepared by dissolving the salts in water.

β-(N-Ethyl Dithiocarbamyl)-propionic Acid.—The product separated as fine needles on recrystallization from ether–hexane; m. p. 97–98°; yield, 35 g.[3] (20%).

Anal. Calcd. for $C_6H_{11}O_2NS_2$: C, 37.30; H, 5.74; N, 7.26; S, 33.18; neut. equiv., 193. Found: C, 37.36; H, 5.73; N, 7.25; S, 33.25; neut. equiv., 194.

β-(N,N-Dimethyldithiocarbamyl)-Propionic Acid.—The product separated as prisms from ether–petroleum ether; m. p. 142–143°; yield, 187 g. (97%).

Anal. Calcd. for $C_6H_{11}O_2NS_2$: C, 37.30; H, 5.74; N, 7.26; S, 33.18; neut. equiv., 193. Found: C, 37.24; H, 5.67; N, 7.11; S, 33.25; neut. equiv., 194.

β-(N,N-Diethyldithiocarbamyl)-Propionic Acid.—Yield after recrystallization from ether–petroleum ether, 175 g. (80%); m. p. 97–98°.

Anal. Calcd. for $C_8H_{15}O_2NS_2$: C, 43.44; H, 6.79; N, 6.34; S, 29.00; neut. equiv., 221. Found: C, 43.48; H, 6.78; N, 6.38; S, 29.08; neut. equiv., 222.

2-Thiono-4-keto-1,3-thiazane[4] (IV).—A suspension of 47 g. of III in 100 ml. of acetic anhydride containing 0.1 g. of concentrated sulfuric acid, was stirred and warmed to 50°. The resulting deep yellow solution was poured into ice and water and the solid which separated was filtered, dried, and recrystallized from benzene; m. p. 119–120°; yield, 42 g. (92%).

Anal. Calcd. for $C_4H_5ONS_2$: C, 32.61; H, 3.42; N, 9.52; S, 43.56. Found: C, 32.91; H, 3.52; N, 9.66; S, 43.82.

2-Thiono-3-ethyl-4-keto-1,3-thiazane.—Using a procedure similar to that for IV above this product was obtained as yellow plates, m. p. 65–66°; yield, 78%.

Anal. Calcd. for $C_6H_9ONS_2$: C, 41.15; H, 5.14; N, 8.00; S, 36.60; mol. wt., 175. Found: C, 41.27; H, 5.15; N, 8.04; S, 36.67; mol. wt., 175 (ebullioscopic in benzene).

β-Isothioureidopropionic Acid (V).[5]—One mole (72 g.) of β-propiolactone was added all at once to a solution of 76 g. of thiourea in 300 cc. of water while stirring. The temperature rose about 30° and the product started to separate in a few minutes. After standing for two hours at 10°, the solid hydrate was filtered and recrystallized from hot water. After drying at 100°, anhydrous crystals were obtained; yield, 132 g. (90%); m. p. 178–179°. The mixture melting point with a sample, prepared as directed by Andreasch, was not depressed.

Anal. Calcd. for $C_4H_8O_2N_2S$: N, 18.90. Found: N, 18.72.

Acknowledgment.—The authors express their thanks to Marie Prendergast and R. W. Dundon for their part in the experimental work.

Summary

Reactions of β-propiolactone with dithiocarbamic acids, their salts, and with thiourea are described. In certain cases the products were cyclized to substituted 1,3-thiazanes.

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[2] Mathes, U. S. Patent 2,117,619 (1938), Example 2.

[3] The yield was low due to the poor yield of dithiocarbamate.

[4] Holmberg, *Ber.*, **47**, 159 (1914).

[5] Andreasch, *Monatsh.*, **6**, 832 (1885).