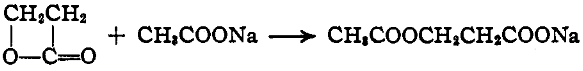
[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

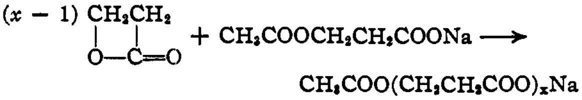
# β-Propiolactone. IV[1,2] Reactions with Salts of Carboxylic Acids

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

Salts of β-acetoxypropionic acid II and poly-ester acids (III) are formed in the reaction of β-propiolactone (I) with aqueous sodium acetate. The strong tendency for the reaction of I with the primary products is minimized by increasing the mole excess of sodium acetate.



I II



III

β-Acetoxypropionic acid (IV) is completely pyrolyzed to acetic acid and acrylic acid by distillation at atmospheric pressure.

$$\underset{\text{IV}}{CH_3COOCH_2CH_2COOH} \longrightarrow CH_3COOH + CH_2{=}CHCOOH$$

Attempts to prepare esters of IV by direct esterification result in alcoholysis and esterification to hydracrylates and acetates.

The poly-ester acids V are colorless oils and they differ from polymers obtained from I by heat or with catalysts[3] only in the end acetoxy group. Alcoholysis with methanol, using acid catalysis, results in a mixture of methyl acetate and methyl hydracrylate in amounts as expected from the average molecular weight, assuming one acetoxy group per molecule.

$$\underset{\text{V}}{CH_3COO(CH_2CH_2COO)_xH} + CH_3OH \longrightarrow CH_3COOCH_3 + xHOCH_2CH_2COOCH_3 + H_2O$$

With several moles of I and one mole of sodium acetate the products are exclusively salts of poly-ester acids (III). Low temperatures are required to avoid hydrolysis of I. Since the yield of polymer is higher than that expected from the molecular weight if each polymer molecule contains an acetoxy group, some polyhydracrylic acid is present due to hydrolysis of the polymers or polymerization of I.

Products similar to those with sodium acetate are formed with salts of other carboxylic acids. The poly-ester acids from sodium caprate (VI) and disodium phthalate (VII) were viscous oils.

$$CH_3(CH_2)_8COO(CH_2CH_2COO)_{2.5}H$$

VI

$$C_6H_4[(COO(CH_2CH_2COO)_{1.5}H]_2$$

VII

Direct esterification of these products resulted in alcoholysis to esters of the parent acids and esters of hydracrylic acid.

## Experimental

**β-Acetoxypropionic Acid (IV).**—One mole (72 g.) of I was added (fifteen minutes) to a stirred solution of 82 g. (1 mole) of sodium acetate in 300 ml. of water at 20° with cooling. After stirring for one hour the colorless solution was cooled to 0°, acidified with concentrated hydrochloric acid and the product extracted with ether. The ether extract was dried over anhydrous sodium sulfate, evaporated under reduced pressure and the residue fractionally distilled at reduced pressure. After removal of some acetic acid, 42.5 g. (32%) of β-acetoxypropionic acid was collected; b. p. 83–84° (0.4 mm.); $n^{25}_D$ 1.4311; $d^{25}_4$ 1.1963.

*Anal.* Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.06; neut. equiv., 132; sapn. equiv., 66; $MR_D$ 28.48. Found: C, 45.32; H, 6.16; neut. equiv., 132; sapn. equiv., 68; $MR_D$, 28.56.

The residue (46 g.) from the above distillation was a viscous colorless oil and consisted of a mixture of poly-ester acids. These poly-ester acids are soluble in acetone, chloroform and aqueous sodium hydroxide from which they are reprecipitated on acidification.

*Anal.* Calcd. for $C_{11}H_{16}O_8$ (V, $x = 3$): neut. equiv., 276; sapn. equiv., 69. Found: neut. equiv., 268; sapn. equiv., 67.

When the above reaction was repeated, except that two moles of sodium acetate were used, 75 g. (57%) of β-acetoxypropionic acid and 22 g. of residue were obtained. Similarly, with four moles of sodium acetate, 97 g. (73%) of β-acetoxypropionic acid and 9.5 g. of residue resulted.

**Ethyl β-Acetoxypropionate.**—β-Acetoxypropionic acid (23 g.) was treated with thionyl chloride (40 g.) for five hours at 25°. The excess thionyl chloride was removed at reduced pressure and absolute ethanol (16 g.) was added to the crude acid chloride residue. After standing for two hours, the mixture was diluted with ether, washed with aqueous sodium carbonate and water and dried over anhydrous sodium sulfate. Distillation of the residue at reduced pressure, after evaporation of the ether, gave ethyl β-acetoxypropionate; b. p. 33.5–35° (0.3 mm.); $n^{20}_D$ 1.4163.

*Anal.* Calcd. for $C_7H_{12}O_4$: C, 52.50; H, 7.50; sapn. equiv., 80. Found: C, 52.36; H, 7.54; sapn. equiv., 83.

**Pyrolysis of β-Acetoxypropionic Acid (IV).**—β-Acetoxypropionic acid (122 g.) was rapidly distilled through a short open column at atmospheric pressure. Distillation started at a flask temperature of 190° and 118 g. of colorless distillate was collected, b. p. 130–150°. One gram of anhydrous copper acetate was added to the distillate, to inhibit polymerization of acrylic acid, and it was fractionally distilled. The first fraction was acetic acid; b. p. 118°; $n^{20}_D$ 1.3790.

*Anal.* Calcd. for $C_2H_4O_2$: neut. equiv., 60. Found: neut. equiv., 63.

The second fraction was acrylic acid; b. p. 135–140°; m. p. 6°; after redistillation, m. p. 12–13°; mixture melting point with an authentic sample, 12–13°.

**Alcoholysis of V.**—A solution of the poly-ester acid residues (115 g., neut. equiv., 268) and 1 g. of sulfuric acid in 320 g. of methanol was refluxed for sixteen hours. The catalyst was neutralized with 3 g. of calcium carbonate; the solution filtered from calcium salts and fractionally distilled using a 30-plate Oldershaw column and a reflux ratio of 20:1. The first fraction was methyl alcohol–methyl

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

(2) Gresham, Jansen and Shaver, *ibid.*, 70, 1001 (1948).

(3) Gresham, Jansen and Shaver, *ibid.*, 70, 998 (1948).

acetate binary; b. p. 53–53.8°; $n^{20}_{D}$ 1.3531; wt. 28 g. (81.3%, 22.7 g. methyl acetate). After removal of the excess methanol, the residue was distilled through a 10 × 2 cm. packed column at reduced pressure and gave 81 g. of methyl hydracrylate; b. p., 70–71° (13 mm.); $n^{20}_{D}$ 1.4213; $d^{20}_{4}$ 1.1205.

*Anal.* Calcd. for $C_4H_8O_3$: sapn. equiv., 104. Found: sapn. equiv., 104.5.

The residue, due to incomplete alcoholysis, weighed 38 g.

**β-(β-Acetoxypolypropionoxy)-propionic Acids (V).**—One mole (72 g.) of I was added (thirty minutes) to a stirred solution of 0.2 mole (16.4 g.) of sodium acetate in 100 ml. of water at 15° while cooling. After four hours, heat was no longer evolved and the clear solution was acidified with 25 g. of concentrated hydrochloric acid. The oil layer was separated, washed with water and dried to constant weight at 40° and 0.5 mm.; wt. 62 g. (76%).

*Anal.* Calcd. for $C_{11}H_{16}O_8$ (V, $x = 3$): neut. equiv., 276. Found: neut. equiv., 280.

A similar experiment but adding 2 moles (144 g.) of I resulted in a mixture of solid and oil after acidification of the reaction mixture. This was dissolved in chloroform, the solution washed with water and the chloroform distilled, partly at atmospheric pressure and finally at reduced pressure (40° (1 mm.)) until there was no further weight loss (four hours). The resulting oil slowly crystallized to a waxy solid; wt. 140.5 g. (90%); m. p. 30–40°.

*Anal.* Calcd. for $C_{20}H_{28}O_{14}$ (V, $x = 6$): neut. equiv., 492. Found: neut. equiv., 506.

**Acknowledgment.**—The authors wish to thank Marie Prendergast for assistance in the experimental work.

## Summary

The reaction of β-propiolactone with aqueous sodium acetate gives a mixture of salts of β-acetoxypropionic acid, β-(β-acetoxypropionoxy)-propionic acid and higher analogs. The effect on the mixture of varying mole ratios of reactants is described and the poly-ester acids are characterized by pyrolysis and alcoholysis. Similar reactions occur with other carboxylic acid salts.

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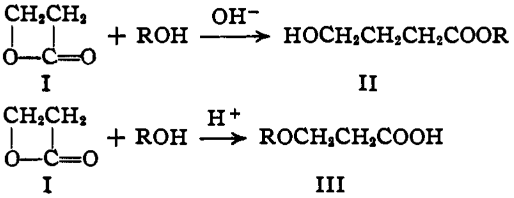
[Contribution from The B. F. Goodrich Research Center]

# β-Propiolactone. V. Reaction with Alcohols

By T. L. Gresham, J. E. Jansen, F. W. Shaver, J. T. Gregory and W. L. Beears

With alcohols, β-propiolactone (I) forms two products, depending on the catalysis. With base catalysis the ring opens at the oxygen–carbonyl carbon bond forming hydracrylate esters II. Without added catalysts or with acid catalysis *beta*-alkoxy acids III are formed as a result of ring opening at the oxygen–methylene carbon bond. This latter ring opening is similar to that observed in the previously described salt reactions.[1]



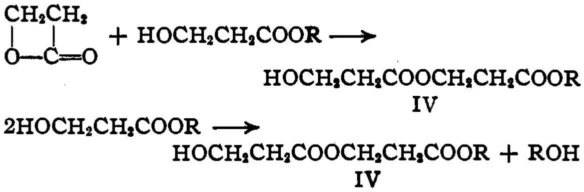
$$\begin{array}{l}\mathrm{CH_2CH_2}\\ |\quad\;\;|\\ \mathrm{O{-}C{=}O}\end{array} + \mathrm{ROH} \xrightarrow{\mathrm{OH^-}} \mathrm{HOCH_2CH_2CH_2COOR}$$

I II

$$\begin{array}{l}\mathrm{CH_2CH_2}\\ |\quad\;\;|\\ \mathrm{O{-}C{=}O}\end{array} + \mathrm{ROH} \xrightarrow{\mathrm{H^+}} \mathrm{ROCH_2CH_2COOH}$$

I III

The base catalyzed reaction gives high yields of hydracrylates. It is extremely rapid with primary alcohols and must be run at low temperatures and in the presence of an excess of alcohol to avoid polymerization. Strong bases, such as sodium hydroxide, sodium alkoxide or trimethylbenzylammonium hydroxide are satisfactory catalysts. The polymers differ from the poly-ester acids previously described[1] in that they are esters of polyhydracrylic acid. Their formation may be due to the reaction of I with the hydracrylate or by the alcoholysis of the hydracrylates with themselves. With secondary alcohols it is more difficult to avoid the polymerization of I,



$$\begin{array}{l}\mathrm{CH_2CH_2}\\ |\quad\;\;|\\ \mathrm{O{-}C{=}O}\end{array} + \mathrm{HOCH_2CH_2COOR} \longrightarrow \mathrm{HOCH_2CH_2COOCH_2CH_2COOR}$$

IV

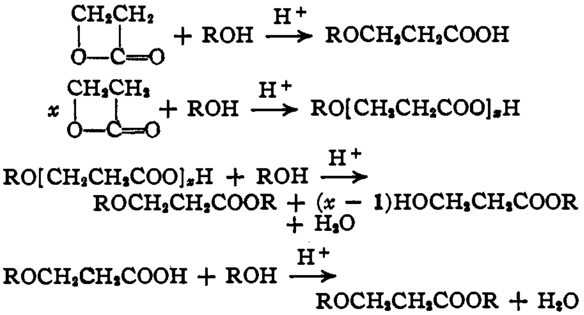
$$\mathrm{2HOCH_2CH_2COOR} \longrightarrow \mathrm{HOCH_2CH_2COOCH_2CH_2COOR} + \mathrm{ROH}$$

IV

probably due to a slower rate of the primary reaction.

The non-catalyzed reaction of I with alcohols[2] is extremely slow and β-alkoxypropionic acids and polymers are the only products. Some esterification of the alkoxy acids occurs, especially with the lower alcohols at higher temperatures. With secondary and tertiary alcohols these non-catalysed reactions are indeed slow, more of I polymerizes and no esters of the alkoxy acids are isolated.

The acid catalyzed reaction of I with alcohols is complex. β-Alkoxypropionic acids and their esters, hydracrylic acid esters and poly-ester acids



$$\begin{array}{l}\mathrm{CH_2CH_2}\\ |\quad\;\;|\\ \mathrm{O{-}C{=}O}\end{array} + \mathrm{ROH} \xrightarrow{\mathrm{H^+}} \mathrm{ROCH_2CH_2COOH}$$

$$x\begin{array}{l}\mathrm{CH_2CH_2}\\ |\quad\;\;|\\ \mathrm{O{-}C{=}O}\end{array} + \mathrm{ROH} \xrightarrow{\mathrm{H^+}} \mathrm{RO[CH_2CH_2COO]}_x\mathrm{H}$$

$$\mathrm{RO[CH_2CH_2COO]}_x\mathrm{H} + \mathrm{ROH} \xrightarrow{\mathrm{H^+}} \mathrm{ROCH_2CH_2COOR} + (x-1)\mathrm{HOCH_2CH_2COOR} + \mathrm{H_2O}$$

$$\mathrm{ROCH_2CH_2COOH} + \mathrm{ROH} \xrightarrow{\mathrm{H^+}} \mathrm{ROCH_2CH_2COOR} + \mathrm{H_2O}$$

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[1] (a) Gregory, Gresham, Jansen and Shaver, This Journal, **70**, 999 (1948); (b) Gresham, Jansen and Shaver, *ibid.*, **70**, 1001 (1948); (c) Gresham, Jansen and Shaver, *ibid.*, **70**, 1003 (1948).

[2] Küng, U. S. Patent 2,352,641 (1944).