sulfides from unbranched dienes and dimercaptans are solids showing definite crystallinity in their X-ray patterns. Attempts at end group determination by oxidation gave increased molecular weights as measured by intrinsic viscosity but conclusive evidence of thiol end groups was not obtained.

URBANA, ILLINOIS RECEIVED OCTOBER 14, 1947

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

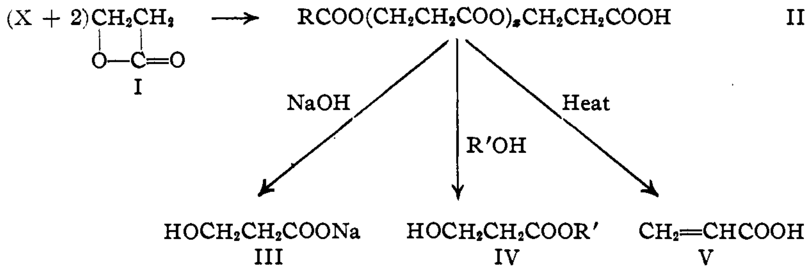
β-Propiolactone. I. Polymerization Reactions

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

β-Propiolactone (I) was first prepared[1] from the silver salt of β-iodopropionic acid. Only a few reactions such as its hydrolysis with acids and bases were described. Apparently no further investigations of this interesting β-lactone have been made.

The availability of I, by the practical synthesis from ketene and formaldehyde discovered by Küng,[2] has made possible an extensive study of its many reactions. This has revealed that β-propiolactone is a highly reactive and synthetically useful chemical.

Pure I polymerizes slowly when heated, and several hours at 150° are required for complete reaction. This polymerization is markedly catalyzed by acids, bases or salts. The most effective catalysts, such as ferric chloride, stannic chloride, sulfuric acid and sodium hydroxide, are moderately soluble in the lactone. Such catalyzed reactions are extremely vigorous and explosive in nature and are highly exothermic. Less effective catalysts are sodium chloride, calcium hydroxide, anhydrous hydrogen chloride and acetic acid. Solutions of polymerization catalysts in I at 0° are relatively stable. The polymerization reaction may be controlled by adding I slowly to a solution of the catalyst in an inert solvent. It is of interest to note that polymerization does not occur with sulfuric acid in ether solution even at the reflux temperature.



R represents $CH_2{=}CH{-}$(IIa) or $HOCH_2CH_2{-}$(IIb)

The polymers of I, prepared with or without added catalysts, are similar and are poly-ester acids (II). They vary from colorless viscous oils to white solids depending on the degree of polymerization and their alkali metal salts are soluble in water. Precipitation of the higher molecular weight fractions by dilution of hot acetone solutions with water yields solid polymers melting about 86°, with an average molecular weight in the range of 800–1000 as determined ebullioscopically in chloroform. Titration with base indicates a similar molecular weight range and thus shows that the polymers contain one carboxyl group per molecule. The other end group is either vinyl or a β-hydroxyethyl. The analysis for carbon and hydrogen and iodine number indicate that there are more vinyl than β-hydroxyethyl groups present in the mixture. These analyses are characteristic of a certain polymer since less unsaturation but similar molecular weights are sometimes obtained without known variants in the preparation. This could be due to variations in traces of moisture.

In boiling aqueous caustic, the polymers are saponified to salts of hydracrylic acid (III) and saponification equivalents are in close agreement with those expected for the basic unit of 72. Prolonged treatment of the polymers with alcohols when catalyzed by acids results in almost complete conversion to hydracrylate esters (IV). Basic catalysts are unsatisfactory for this alcoholysis due to the sensitivity of the hydracrylate esters to alkali. Pyrolysis[3] of the poly-ester acids to acrylic acid (V) is rapid and complete at 150°.

Other reactions of β-propiolactone to be reported in later papers include reactions with salts of inorganic acids, salts of dithiocarbamic acids, salts of carboxylic acids, alcohols, phenols and thiophenols, amines, organic and inorganic acid chlorides, metal organic compounds, inorganic acids and compounds with labile hydrogen or active methylene groups. Further work is now being undertaken to determine the mechanisms of these reactions.

Experimental

β-Propiolactone (I).—Physical constants: b. p. 51° at 10 mm., 150° at 750 mm., (with extensive decomposition); m. p. −33.4°; d^{20}_4 1.1460; n^{20}_D 1.4131; dipole moment 3.8 ± 0.1 *D*.

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(1) Johannson, Lund University Annual, New Series, Div. 2, Vol. 12, No. 8 (1915).

(2) Küng, U. S. Patent 2,356,459 (1941).

(3) Küng, U. S. Patent 2,361,036 (1944).

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^{26}_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

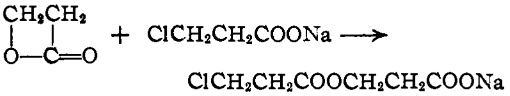
[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

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

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

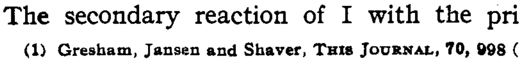
In the previous paper[1] the rapid polymerization of β-propiolactone (I) as catalyzed by certain inorganic salts was described. In water solutions of inorganic salts beta substituted propionic acid salts are formed in good yields.

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



$$\underset{\text{O—C=O}}{\text{CH}_2\text{CH}_2} + \text{NaCl} \longrightarrow \text{ClCH}_2\text{CH}_2\text{COONa} \quad \text{II}$$

I



$$\underset{\text{O—C=O}}{\text{CH}_2\text{CH}_2} + \text{ClCH}_2\text{CH}_2\text{COONa} \longrightarrow \text{ClCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{COONa} \quad \text{III}$$

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).