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.

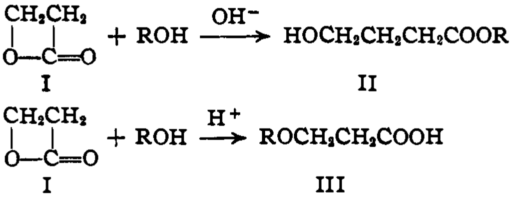
BRECKSVILLE, OHIO RECEIVED JULY 21, 1947

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

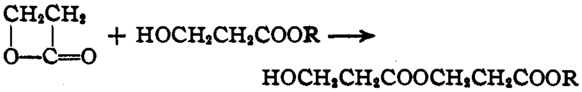
β-Propiolactone. V. Reaction with Alcohols

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]



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,



IV

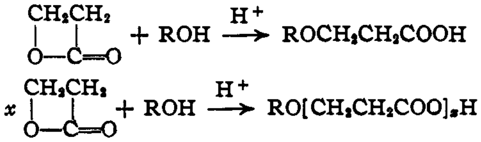
$$2HOCH_2CH_2COOR \longrightarrow HOCH_2CH_2COOCH_2CH_2COOR + ROH$$

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



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

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

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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).

TABLE I

BASE CATALYZED REACTIONS OF β-PROPIOLACTONE WITH ALCOHOLS

Alcohol	Hydracrylate yield, %	B. p. °C.	B. p. Mm.	n^{20}_D	d^{20}_4	Mol. refraction Calcd.	Mol. refraction Found	Sapn. equiv. Calcd.	Sapn. equiv. Found	Polymeric residue, yield, %
Methyl	85.1[a]	71	13	1.4225	1.1153	23.85	23.73	104	104.5	10
Ethyl	80.1[b]	75	8	1.4222	1.0545	28.47	28.45	118	117.2	13
n-Propyl	65.5	98	19	1.4251	1.0217	33.09	33.04	132	132	28
n-Butyl	77.2	114	20	1.4284	0.9989	37.71	37.63	146	147.7	9[c]
n-Octyl	64.5	104	4	1.4392	0.9484	56.18	56.05	202	202	7[c]

[a] 76% yield at 25°. [b] 69% yield with 4 g. trimethylbenzylammonium hydroxide. [c] Some pyrolysis of the residues occurred due to the higher flask temperatures at the end of the distillation.

with terminal alkoxy groups are formed. The composition of the mixture obtained is dependent on the reaction conditions employed, the most important factors of which are the acid catalyst concentration, the temperature, time and the molar excess of alcohol. The primary reaction of I gives β-alkoxypropionic acids. A competing reaction is polymerization. Secondary reactions of esterification and alcoholysis account for the other products.

The rate of the acid catalyzed reaction is intermediate between that of the non-catalyzed and base catalyzed. As is shown in Table II, the amount of hydracrylate formed by the secondary reaction increases with time with a corresponding decrease of polymer and none of it is formed in incomplete reactions. Also, more esterification occurs with increased time while the combined yields of alkoxy acid and ester remain constant.

The polymerization, alcoholysis and esterification are favored with increasing catalyst concentration and temperature. However, with high acid concentration only insoluble higher molecular weight polymers result. These, therefore, are alcoholized very slowly.[1a] Decrease in the excess alcohol favors the polymerization.

Both the primary and secondary reactions are slower with the higher primary alcohols. Secondary and tertiary alcohol reactions are still slower and little if any secondary reactions occur.

The polymeric residues from these acid catalyzed reactions contain poly-ester acids with end alkoxy groups. It was possible to isolate methyl β-(β-methoxypropionoxy)-propionate from the methyl alcohol residues in fair amounts. Neutralization equivalents show, however, that most of the residue consists of poly-ester acids.

Experimental

Base Catalyzed Reactions.—One mole of β-propiolactone was added dropwise with stirring to a solution of 2 g. of sodium hydroxide in six moles of the alcohol. The reactions were highly exothermic and a Dry Ice–acetone-bath was employed to maintain the temperature at 0° with a fifteen-minute addition time. The catalyst was neutralized with an equivalent of concentrated hydrochloric acid, the solution filtered from salt, and the alcohol and the product were distilled at reduced pressure. Yields and other data are listed in Table I.

Methyl β-(Hydroxypropionoxy)-propionate (IV).—The oily residues from base catalyzed reactions with methanol were insoluble in aqueous caustic. Distillation of 34 g. gave a fraction of IV (30 g.), b. p. 85–86° (0.3 mm.); n^{20}_D 1.4429; d^{20}_4 1.1902.

Anal. Calcd. for $C_7H_{12}O_5$: sapn. equiv., 88; *MR*D, 39.36. Found: sapn. equiv., 89; *MR*D, 39.21.

Acid Catalyzed and Non-catalyzed Reactions.—One mole of β-propiolactone was added dropwise over a twenty minute period to six moles of the alcohol. A three-neck ground-glass jointed flask fitted with a glass stirrer, thermometer, dropping funnel and a reflux condenser was used and the desired reaction temperature maintained by immersing the flask in a constant temperature bath. Stirring was continued throughout the experiment. With the acid catalyzed experiments the sulfuric acid was added at the start and neutralized at the end by the addition of two grams of calcium carbonate per gram of acid used and the solution filtered from calcium salts before distillation. The excess alcohol was distilled rapidly at reduced pressure keeping the flask temperature below 30° and the residue was fractionally distilled through a 1" × 24" packed column. The experimental data are listed in Table II and the physical and analytical data for the products in Table III.

TABLE II

ACID CATALYZED AND NON-CATALYZED REACTIONS OF β-PROPIOLACTONE WITH ALCOHOLS[a]

Alcohol	H_2SO_4,[e] g.	Temp., °C.	Time, hr.	Alkoxy acid yield, %	Alkoxy ester yield, %	Hydracrylate yield, %	Recovered lactone, %	Polymeric residue yield, %
Methyl	0	0	72	0	0	0	70	12
Methyl	0	46	16	42	2	0	12	17
Methyl	0	65	16	73	4	0	0	16
Methyl	1	0	6	8	0	0	..	81[b]
Methyl	1	0	72	8	25	23	0	36
Methyl	1	46	3	15	23	24	0	34[c]
Methyl	1	46	6	11	28	29	0	21
Methyl	1	46	16	0	34	40	0	13
Methyl	0.12	65	2	24	45	11	0	19[c]
Methyl	0.5	65	2	11	37	26	0	11
Methyl	1.0	65	2	0	34	43	0	23
Methyl	2.0	65	2	0	25	50	0	27[c]
Methyl	4.0	65	2	0	0	0	0	100
Ethyl	0	65	16	73	2	0	0	15
Ethyl	1	46	6	7	47	0	0	50[c]
Ethyl	1	80	2	0	54	25	0	23[c]
n-Propyl	0	65	16	73	4	0	4	14
n-Propyl	1	46	6	20	25	0	..	47[b]
n-Propyl	1	80	2	0	53	0	..	46[b]
n-Butyl	0	65	16	65	6	0	5	22
n-Butyl	1	46	6	0	28	0	39[d]	35[c]
n-Butyl	1	80	2	0	25	0	25[d]	56[c]
i-Propyl	0	65	16	45	0	0	36	16
i-Propyl	1	80	2	27	11	0	..	65[c]

[a] All reactions carried out with 5 moles of β-propiolactone. [b] Includes recovered lactone. [c] The combined yields and residues total more than 100% due to an undetermined amount of ester and alkoxy groups combined in the polymers. [d] Unreacted lactone distilled with the butanol and was determined by titration. [e] Grams of acid per mole of the lactone.

TABLE III

ALKOXY ACIDS AND THEIR ESTERS[a]

Compound	B. p. °C.	B. p. Mm.	n^{25}_D	d^{25}_4	Mol. refraction Calcd.	Mol. refraction Found	Neut. equiv. Calcd.	Neut. equiv. Found
$CH_3OCH_2CH_2COOH$	102	13	1.4160	1.0982	23.85	23.76	104	106
$C_2H_5OCH_2CH_2COOH$	108	10	1.4178	1.0450	28.47	28.44	118	118
n-$C_3H_7OCH_2CH_2COOH$	76	1	1.4204	1.0043	33.09	33.29	132	133
i-$C_3H_7OCH_2CH_2COOH$	70	1	1.4222	1.0032	33.09	33.43	132	131
n-$C_4H_9OCH_2CH_2COOH$	72	0.1	1.4240	0.9876	37.71	37.73	146	146
$CH_3OCH_2CH_2COOCH_3$	63	40	1.3993	1.0052	28.59	28.40	118[b]	119[b]
$C_2H_5OCH_2CH_2COOC_2H_5$	60	13	1.4041	0.9461	37.82	37.77	146[b]	145[b]
n-$C_3H_7OCH_2CH_2COOC_3H_7$-n	87	13	1.4139	0.9369	47.06	46.40	174[b]	170[b]
i-$C_3H_7OCH_2CH_2COOC_3H_7$-i	67	13	1.4059	0.9150	47.06	46.71	174[b]	170[b]
n-$C_4H_9OCH_2CH_2COO.C_4H_9$-$n$	97	6	1.4190	0.9109	56.30	56.00	202[b]	198[b]

[a] Data for hydracrylates in Table I. [b] Saponification equivalents.

Methyl β-(β-Methoxypropionoxy)-propionate.—Combined distillation residues (77 g.) from acid catalyzed experiments with methanol were distilled through a short column. Only one fraction could be collected before pyrolysis set in. This fraction was methyl β-(β-methoxypropionoxy)-propionate; b. p. 86° (1.5 mm.), wt. 29.4 g., $n^{25}D$ 1.4260.

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.51; H, 7.37; mol. wt., 190; sapn. equiv., 95. Found: C, 50.58; H, 7.37; mol. wt. (ebullioscopic in benzene), 187; sapn. equiv., 94.

Summary

The base catalyzed reaction of β-propiolactone with alcohol is rapid and results in hydracrylates. Without added catalysts, alkoxy acids are slowly formed. The acid catalyzed reaction gives alkoxy acids by direct reaction and hydracrylates by alcoholysis of poly-ester acids formed in the competing polymerization of the lactone. The effects of time, temperature and catalyst concentration on the proportions of products in the mixture are demonstrated.

BRECKSVILLE, OHIO RECEIVED JULY 21, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Evidence of an Induction Period in the Alkylation of Isobutane by 2-Butene

BY T. D. STEWART AND WILLIAM H. CALKINS

The reaction between isobutane and 2-butene at 0° in the presence of 96% sulfuric acid is not extremely rapid. This may be shown by passing 2-butene gas at a constant rate into a stirred mixture of sulfuric acid and isobutane. In our experiments the isobutane was initially at atmospheric pressure; the isobutane consumption was measured by observing the input of isobutane required to maintain a constant pressure in the reactor. Figure 1 shows the observations made during a typical experiment.

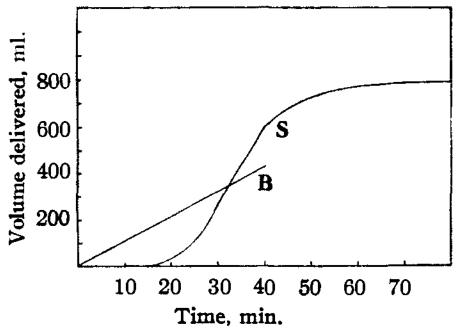

Fig. 1.—Rate of consumption of isobutane (S) gas produced by the addition of 2-butene (B) gas at a constant rate, in sulfuric acid.

At first little or no isobutane is consumed. After about twenty minutes, during which about 200 ml. of 2-butene has been introduced, the consumption of isobutane approaches a constant rate. When the 2-butene supply is shut off the consumption of isobutane continues for over an hour. These periods will be referred to as the induction period, the steady state period and the terminal reaction period, respectively. When the steady state is established the rate of consumption of isobutane is two to three times that of 2-butene. The best yields of alkylate accompanied the higher ratios. An approximate calculation shows that if the alkylation reaction involves a ratio of unity and if the condensed isoöctanes dissolve the expected amount of isobutane, a ratio of about three should be observed. Any ratio less than that involves polymerization or other consumption of 2-butene apart from alkylation.

The reaction studied is a complex one leading to a variety of products.[1a,b,c] Under the conditions

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[1] (a) S. H. McAllister, J. Anderson, S. A. Ballard and W. E. Ross, *J. Org. Chem.*, **6**, 647 (1941), list two main fractions of trimethylpentanes and some 2,3-dimethylbutane from the reaction catalyzed by sulfuric acid. (b) L. Schmerling, THIS JOURNAL, **68**, 275 (1946), lists nineteen products from the reaction catalyzed by aluminum chloride. (c) M. H. Gorin, C. S. Kuhn and C. B. Miles, *Ind. Eng. Chem.*, **38**, 795 (1946), list six fractions from the reaction catalyzed by hydrogen fluoride.