the indices of refraction (n^{25}D) of benzoylacetic methyl ester and β-methoxycinnamic methyl ester, respectively, as 1.537 and 1.550. Thus the yield of copper derivative shows a benzoylacetic ester content of 30%, while the index of refraction checks this approximation with benzoylacetic ester content of 35%.

(b). In **Aqueous Methanol.**—Eight grams of phenylpropiolic methyl ester was added to a solution of 6.5 g. of potassium isocyanide in 10 cc. of water and 50 cc. of methanol and allowed to stand at room temperature for four hours and, then, for an additional twenty hours in a bath at -20°. One gram of crystallized potassium salt was filtered and the solution was diluted with 500 cc. of ether, yielding an additional 5.8 g. of potassium salt. The combined potassium salts was suspended in ether and shaken with dilute acid. The dried ether solution yielded 3.5 g. of phenylpropiolic acid. The filtrate from the salt was shaken with dilute acid, changing from deep orange to pale yellow. The dried ether solution was concentrated and left 5 g. of solid, which was extracted repeatedly with petroleum ether, thus leaving 4 g. of pure β-cyanobenzylcyanoacetic ester (IX). The petroleum ether extracts yielded 1 g. of phenyl propiolic acid.

Summary

1. The formation of pyrotartaric dinitrile from potassium isocyanide and allyl cyanide proceeds primarily through rearrangement of allyl cyanide to crotononitrile.

2. The mechanisms hitherto proposed for the syntheses of β-cyano-ketones, -esters and -nitriles from the corresponding α,β-Δ-ketones, -esters and -nitriles, which was assumed to proceed by addition of hydrocyanic acid or through a complex salt with potassium isocyanide to the Δ-carbons of the Δ-compounds has been shown to be impossible.

3. The formation of β-cyano-ketones, -esters and -nitriles from the corresponding α,β-ethylenic compounds proceeds through the formation of enolates, or iminolates, by 1,4-addition of potassium isocyanide to the conjugated groups of the unsaturated compounds, the metal uniting with carbonyl oxygen or cyano nitrogen.

4. When the reaction products from potassium isocyanide and the α,β,Δ-esters are poorly neutralized enolates, in the absence of water, they realize a better intramolecular neutralization by addition to unchanged ester.

5. The action of potassium isocyanide upon fumaric methyl ester proceeds primarily by 1,4-addition; under certain conditions, the enolate adds to unchanged fumaric ester and the addition product condenses to a cyclopentanone derivative. With citraconic methyl ester, the first phase consists in rearrangement to the itaconic ester, which undergoes the 1,4-addition with the isocyanide and is then changed to a cyclic nitrogen derivative.

6. According to the experimental conditions, phenylpropiolic ester unites by 1,4-addition with one and then with a second molecule of isocyanide. The first addition product is an enolate of the structure $C_6H_5C(CN){=}C{=}C(OK)OMe$; a type of enolate involving the enolization of an unsaturated α-CH group of an α,β,Δ-ester.

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[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

The Catalytic Hydrogenation and Esterification of C_4-Saccharinic Acid Lactones and the Hydrogenation of Butyl Erythronate[1]

BY J. W. E. GLATTFELD AND ANNE M. STACK

Various reduction methods have been studied in these Laboratories with the object of finding a practical method for the reduction of the C_4-saccharinic acids to the corresponding aldehydes and alcohols and for the reduction of erythronic lactone to erythrose. Low pressure catalytic reduction of aldonic acids was studied by Glattfeld and Shaver[2] and by Glattfeld and Schimpff.[3] The work reported in this paper is a continuation of these experiments and includes a study of the catalytic hydrogenation, under pressures of 2–136 atmospheres, of 2,3-dihydroxybutyric acid lactone and one of its derivatives, of 1,3-dihydroxybutyric acid lactone, and of the butyl ester of *dl*-erythronic acid. The last named compound was first prepared in these Laboratories by Snoddy.[4] His method of preparation was followed in general but, as a few changes were made, the procedure is given in some detail in the Experimental Part. (Hereinafter the 2,3- and 1,3-dihydroxybutyric

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(1) This article is condensed from a dissertation which will be presented by Anne M. Stack in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

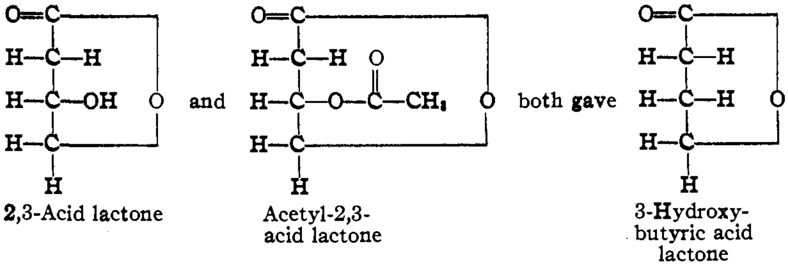
(2) Glattfeld and Shaver, THIS JOURNAL, **49**, 2305 (1927).

(3) Glattfeld and Schimpff, *ibid.*, **57**, 2204 (1935).

(4) J. A. Snoddy, S.M. Dissertation, University of Chicago, 1934.

acid lactones will be called, respectively, the 2,3- and 1,3-acid lactones, and the *dl*-butylerythronate, the butyl ester.)

Attempts to reduce the 2,3-acid lactone at low pressures (2–3 atmospheres), with small amounts of catalyst were at first unsuccessful. When the rate of shaking was tripled[3] and the amount of catalyst greatly increased, a 21% reduction of the 2,3-acid lactone and a 67% reduction of the 1,3-acid lactone (products not isolated) were effected. At high pressures (119–133 atmospheres), 37–65% reductions of the 2,3-acid lactone and a 54% reduction of the acetyl-2,3-acid lactone were obtained: the main product was 3-hydroxybutyric acid lactone,

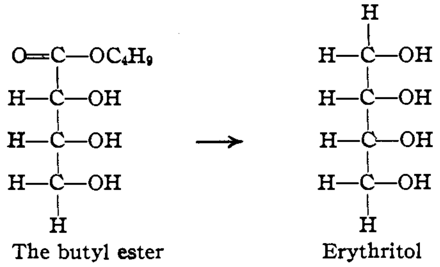


2,3-Acid lactone

Acetyl-2,3-acid lactone

3-Hydroxybutyric acid lactone

The 1,3-acid lactone and the 2,3-acid amide yielded no definite results. A few experiments on the high pressure reduction of erythronic lactone and of erythronamide gave no definite results. The butyl ester was then prepared and reduced to erythritol in good yield under both low and high pressures.



The butyl ester

Erythritol

Further work on catalytic hydrogenation in this field is in progress.

Experimental Part

Apparatus.—The apparatus used for pressures up to three atmospheres was that made by the Burgess–Parr Company of Moline, Illinois. In the work at higher pressures, two different bombs made in the Chemistry Department shop were used. One of these (Bomb A), was essentially the bomb described by Peters and Stanger.[5] We used a glass container with a pin-hole opening inside this bomb. The other bomb (Bomb B) was similar to the one made by the American Instrument Company and diagramed by Tongue.[6] The inside of this bomb was first tinned and then silvered.. For valuable help in connection with the construction and testing of these bombs, we wish to thank Dr. F. N. Peters, Jr., and Mr. J. Pokorny of the Quaker Oats Company, Dr. C. W. Lenth of the Miner Laboratories, and the Crane Company of Chicago.

Materials.—(1) The 1,3- and 2,3-acid lactones were prepared according to the procedures developed in these Laboratories and published in previous articles.[7] The crude lactones were twice fractionated and then had the boiling ranges, 110–112° at 2–4 mm., and 148–150° at 2–4 mm., respectively. They were faintly yellow mobile liquids. (2) The acetyl-2,3-acid lactone has been prepared[8] in 52.7% yield by the addition of the 2,3-acid lactone to a cooled (0°) mixture of acetic anhydride and freshly fused zinc chloride. Our product was prepared by the interaction of the sodium salt of the 2,3-acid with acetyl chloride (see below). (3) The *dl*-erythronic lactone was prepared according to the method of Braun.[9] It was a perfectly white crystalline material, m. p. 91–92°. (4) Platinic oxide monohydrate (in the quantities recommended by Schimpff[8]) and palladium oxide were prepared by the procedure of Adams, Voorhees and Shriner.[10] (5) The copper–chromium oxide catalyst was prepared according to Adkins and Connor.[11] (6) The copper–barium–chromium oxide catalyst (37 KAF), was prepared by the method of Connor, Folkers and Adkins.[12] (7) The "Raney" (Ni) catalyst was kindly supplied by the Quaker Oats Company. It had been prepared by the procedure of Covert and Adkins.[13]

Preparation of Acetyl-2,3-acid Lactone.—The sodium salt of the 2,3-acid was prepared by the titration of a heated 10% aqueous solution of the 2,3-acid lactone with a 0.5 *N* solution of sodium hydroxide. The resulting solution was concentrated to dryness at reduced pressure and the sodium salt obtained in the form of a light brown gum. Six equivalents of acetyl chloride was added to each of a 77 and 79-g. batch of sodium salt. The mixtures were refluxed in a water-bath at 50–60° for four hours and at 60–85° for two hours, at the end of which time all of the sodium salt had disappeared. The solutions were combined, the sodium chloride was separated by filtration and washed with glacial acetic acid and the combined mother liquor and washings concentrated to dryness at reduced pressure at 60°. The residue was fractionated in two batches since it had previously been noted that long continued heating results in some decomposition. A large fraction distilled over at 119–121°, 4 mm. At 121° some

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(5) Peters and Stanger, *Ind. Eng. Chem.*, **20**, 74 (1928).

(6) H. F. Tongue, "The Design and Construction of High Pressure Chemical Plant," Chapman and Hall, Ltd., London, 1934, p. 289.

(7) (a) Glattfeld and Sander, THIS JOURNAL, **43**, 2675 (1921); (b) Glattfeld, Leavell, Spieth and Hutton, *ibid.*, **53**, 3164 (1931).

(8) C. E. Ford, S.M. Dissertation, University of Chicago, 1932

(9) Braun, THIS JOURNAL, **51**, 235 (1929).

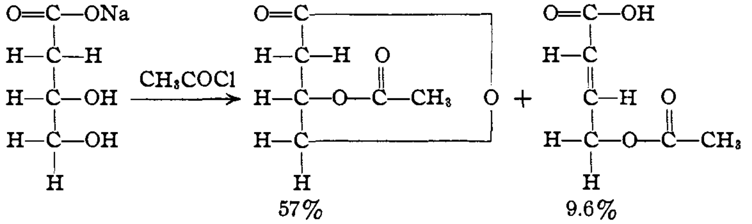
(10) Adams, Voorhees and Shriner, "Organic Syntheses," Vol. VIII, John Wiley and Sons, Inc., New York City, 1928, p. 92.

(11) Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

(12) Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

(13) Covert and Adkins, *ibid.*, **54**, 4116 (1932).

fuming was noted; at 133° crystals appeared in the condenser: a mixture of solid and oil distilled at 133–140°, 4.5 mm. The 119–121° fraction was redistilled to give 90 g. of boiling range 119–121°, 4 mm., a 57% yield of acetyl-2,3-acid lactone. The solid was separated by filtration from the high boiling oil which came over with it, and dried on a porous plate to give 19.5 g. of crude material. This was recrystallized from a small amount of hot ethyl acetate and dried to give 15.3 g. of white crystalline material, melting range 99–102°. It was distilled under reduced pressure for further purification: the distilled solid had the same melting range. This compound, obtained in 9.6% yield, may be the *trans*-3-acetyl crotonic acid, melting point 97–98°, reported by Rambeau.[14]



Anal. Calcd. for $C_6H_8O_4$: C, 49.99; H, 5.60. Found: (liquid, 119–121°, 4 mm.) C, 49.85, 49.98; H, 5.56, 5.53; (solid, m. p. 99–102°) C, 49.92, 50.22; H, 6.27, 5.74.

Neutralization equivalent. Calcd. for $C_6H_8O_4$, 72. Found: liquid, 74.2 and 74.6 (0.2184, 0.2333 g. required 29.44 and 31.28 cc. 0.1 *N* alkali); solid, 72.1 and 72.0 (0.1841, 0.2059 g. required 25.55 and 28.60 cc. 0.1 *N* alkali).

Results of Reduction Experiments.—The results obtained and the conditions used in some representative experiments are recorded in the tables. A few experiments will be discussed in detail to illustrate the experimental procedures used.

Reduction of Lactones

High Pressure Reduction of 2,3-Acid Lactone (Expt. No. 5 in Table I).—Fifty grams of 2,3-acid lactone was put into the glass container of Bomb A and 6.2 g. of copper-barium-chromium oxide catalyst (37 KAF) added. The air was displaced and the bomb placed on two electric heaters mounted in a shell which rocked at the rate of 42 cycles per minute. The material was put under pressure of 88 atmospheres of hydrogen and heating started. After one hour the temperature had reached 167° and the pressure 129 atmospheres, and, after another half hour, 182° and 125 atmospheres. The temperature remained at 182° for three and seven-tenth hours and the pressure continued to drop as hydrogen was used. Heating was then discontinued but the bomb was allowed to rock under pressure for two more hours. At the end of this time the bomb had cooled to 74° and the pressure, 77 atmospheres, could be released without loss of material. The liquid was filtered and fractionated at reduced pressure. The first fractionation yielded 24 g. of material of boiling range 76–78° at 5 mm. This was refractionated at atmospheric pressure and yielded 21.4 g. of material of boiling range 199–202°, 50.8% calculated as 3-hydroxybutyric acid lactone.

The liquid was identified as 3-hydroxybutyric acid lactone by its neutralization equivalent and by oxidation to succinic acid.

Anal. Subs., 0.2038, 0.2613 g.: 0.1 *N* alkali 23.65, 30.39 cc. Neutralization equivalent calcd. for $C_4H_6O_2$, 86.0. Found: 86.2, 86.0.

Conversion to Succinic Acid.—Ten grams of chromic anhydride was made up to 70 cc. with water and 6 cc. of concentrated sulfuric acid. Five grams of the liquid was mixed with 54.3 cc. of this solution, which volume contained 7.75 g. of chromic anhydride, the amount necessary for this oxidation. The mixture was refluxed for one and one-half hours until the original yellow color had changed to green, extracted four times with ether using 150 cc. for each extraction, and the ether extract concentrated at reduced pressure at 60°. The white residue, dried over sulfuric acid, weighed 3.0 g. After two recrystallizations from water 0.6 g. of white crystalline material, melting range 182–184°, 8.7% calculated as succinic acid, was obtained. No attempt was made to rework the mother liquor.

Anal. Subs., 0.2275, 0.2488 g.: 0.1 *N* alkali 38.08, 41.64 cc. Neutralization equivalent calcd. for $C_4H_6O_4$, 59. Found: 59.7, 59.8.

High Pressure Reduction of Acetyl-2,3-acid Lactone (Expt. No. 8 in Table I).—Fifty grams of acetyl-2,3-acid lactone was put into the glass container of Bomb A and 0.4 g. of platinic oxide monohydrate added. The air was displaced, the material was put under pressure of 97 atmospheres of hydrogen, rocked at the rate of 42 cycles per minute, and heating begun. In one hour the temperature had reached 158° and the pressure 129 atmospheres. The temperature remained between 161 and 142° for the next 20.1 hours at the end of which time the pressure had dropped to 82 atmospheres. Heating was stopped but rocking continued. The pressure was released 4.4 hours later when the temperature of the bomb was 31°. The glass container had leaked at the stopper and the bomb now contained only 37.6 g. of filtered material. The liquid, fractionated at reduced pressure, yielded 24.9 g. of material, boiling range 20–68°, 5 mm. On redistillation at atmospheric pressure, 12.2 g. of material, boiling range 195–203°, was obtained. This is a yield of 54.3% calculated as 3-hydroxybutyric acid lactone on the basis of 37.6 g. of original material.

Anal. Subs., 0.2014 g.: 0.1 *N* alkali 23.33 cc. Neutralization equivalent calcd. for $C_4H_6O_2$, 86.0. Found: 86.3.

Alkalinity Developed by $PtO_2 \cdot H_2O$.—Certain results, obtained in the analysis of samples from low pressure reduction experiments, indicated that the acid was being neutralized very slowly during the reduction. That the catalyst was responsible for this was shown by the experiment outlined below.

A 2-g. sample of the catalyst was added to 50 cc. of water and the mixture shaken under pressure of 2.8 atmospheres

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(14) Rambeau, *Bull. soc. chim.*, [5] 1, 1317 (1934).

Table I

High Pressure Reduction[a] of the 2,3-Acid Lactone, the Acetyl-2,3-acid Lactone and the 1,3-Acid Lactone

Expt.	Lactone	Amt., g.	Vol. aq. soln., cc.	Catalyst	Cat., g.	Max. press., atm.	Range of max. temp., °C.	Time of hyd. over range of max. temp., hrs.	Total time of hyd., hrs.	% yield of 3-hydroxybutyric acid lactone, Isolated	Corr.[b]
1	2,3-Acid	20	95	$PtO_2 \cdot H_2O$	0.2	126	158–167	5.9	7.9	23.7	46.9
2	2,3-Acid	20	60	$PtO_2 \cdot H_2O$	.2	133	182–189	5.9	10.8	31.4	65.4
3	2,3-Acid	49	25	Cu–Cr oxide	6.0	119	150–159	1.8	6.1	26.6	39.2
4	2,3-Acid	50	..[c]	PdO	0.4	127	171–182	4.5	8.9	37.2	
5	2,3-Acid	50	..	Cu–Ba–Cr oxide (37 KAF)	6.2	129	182	3.7	7.2	50.8	
6	2,3-Acid	50	..	Cu–Cr oxide	6.0	57	211–242	3.1	11.9	19.0	
7	2,3-Acid	50	..	"Raney"	13.0 (moist)	129	169–173	8.1	11.0	48.7	54.3
8	Acetyl-2,3-acid	50	..	$PtO_2 \cdot H_2O$	0.4	129	142–161	20.1	25.5	54.3	
			Solv. vol., cc.								
9	1,3-Acid	20	25, 95% alc.	$PtO_2 \cdot H_2O$	0.4	112	146–176	16.6	22.7	..	
10	1,3-Acid	20	20 water	$PtO_2 \cdot H_2O$	.4	128	156–168	26.1	27.2	..	
11	1,3-Acid	20	20 water	"Raney"	8.0 (moist)	115	145–161	19.0	22.2	..	
12	1,3-Acid	20	20 water	Cu–Ba–Cr oxide (37 KAF)	3.0	136	154–181	25.8	26.8	..	

[a] The rate of rocking was 42 cycles per minute. [b] 3-Hydroxybutyric acid lactone distils with steam. The distillate was saved and titrated for acidity. Consideration of this factor gave a corrected yield. [c] No solvent was used in Experiments 4–8.

of hydrogen for three-tenths hour. A 1-cc. sample now required 2.49 cc. of 0.01 *N* acid for neutralization. The 49 cc. of solution was again shaken under pressure of 2.8 atmospheres of hydrogen for four-tenths hour. A 1-cc. sample now required 2.60 cc. of 0.01 *N* acid, showing practically no increase in alkalinity during the second period of hydrogenation. A further 2 g. of catalyst was added to the 48 cc. of solution which remained. The mixture was again shaken under pressure of 2.8 atmospheres of hydrogen for one-half hour. A 1-cc. sample now required 5.28 cc. of 0.01 *N* acid, indicating that the second 2 g. of catalyst had generated an alkalinity equivalent to 2.68 cc. of 0.01 *N* acid. From a consideration of these data and others, it was concluded that an average alkalinity equivalent to 2.55 cc. of 0.01 *N* acid was generated by the introduction of 2 g. of the catalyst used in the reduction of the 2,3-acid lactone. The corresponding correction factor on the particular lot of catalyst used in the reduction of the 1,3-acid lactone was found to be 3.26 cc.

These facts and the further fact that water, shaken up with a sample of the catalyst, gave no test for nitrates before reduction, yet gave a test for ammonia after reduction, indicated that the alkalinity developed was due to the formation of ammonia by the reduction of oxides of nitrogen occluded by the catalyst.

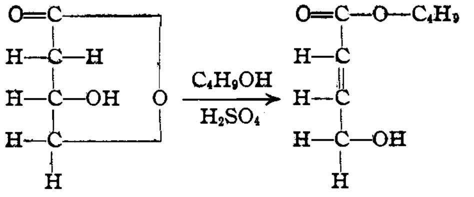
Low Pressure Reduction of 2,3-Acid Lactone.—A 5.06 g. sample of 2,3-acid lactone was dissolved in water, made up to a volume of 100 cc., 2 g. of platinum catalyst added and the solution hydrogenated in the Burgess–Parr apparatus under 2.9 atmospheres of hydrogen for two and six-tenths hours with shaking at the rate of 360 cycles per minute. A 1-cc. sample required 47.11 cc. of 0.01 *N* alkali for neutralization. (This includes the correction introduced because of alkalinity generated by the catalyst.) A 1-cc. sample of the original solution was neutralized by 49.63 cc. of 0.01 *N* alkali. A 5.1% reduction had therefore occurred. Periodic addition of a total of 16 g. of catalyst over a period of 12.4 hours effected a reduction of only 21.4%.

Low Pressure Reduction of 1,3-Acid Lactone.—A 5.06-g. sample of 1,3-acid lactone was dissolved in water and made up to a 50-cc. volume. The procedure was identical with that of the preceding experiment. A 67.3% reduction was effected after the addition of 12 g. of platinum catalyst, in portions, over a period of 36.9 hours.

Attempts to Prepare Esters of C_4-Saccharinic Acids

The direct reduction of the 2,3- and 1,3-acid lactones to the corresponding alcohols not having proved feasible, it was decided to attempt to reduce esters of the acids in the hope that these might be more susceptible to the type of reduction sought. In spite of many trials none of the desired esters could be prepared. The results of some of the experiments, however, may be worthy of record.

Butyl 3-Hydroxyisocrotonate from 2,3-Acid Lactone.—Fifty-one grams of 2,3-acid lactone was dissolved in 112 cc. of absolute butanol, 1.4 cc. of concentrated sulfuric acid added, and the solution refluxed for ten hours. It was concentrated to dryness at reduced pressure, finally at 50°, to give an 88.7-g. residue. Five grams of calcium carbonate and 50 cc. of water were added to the residue and the mixture was concentrated to dryness at reduced pressure finally at 68°. The residue was extracted and the salts were washed thoroughly with ether. The ether



2,3-Acid lactone

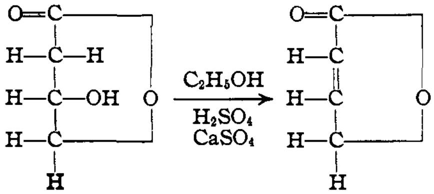
Butyl-3-hydroxy-isocrotonate

extract was dried over anhydrous sodium sulfate and concentrated at atmospheric pressure to give 72 g. of crude residue which, on fractionation, gave 40.2 g. of water-insoluble liquid, boiling range 179–183° (3 mm.), a 50.9% yield calculated as butyl 3-hydroxyisocrotonate. In another experiment in which 102 g. of lactone was treated according to the same procedure, a 75.5-g. sample, 47.8% yield, boiling range 174–181° (2 mm.) was obtained.

Anal. Subs. 0.2701, 0.3089 g.: 0.1 *N* alkali 17.07, 19.64 cc. Neutralization equivalent calcd. for $C_8H_{14}O_3$, 158.1. Found: 158.2, 157.3.

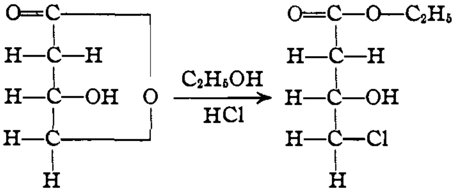
3-Hydroxyisocrotonic Lactone from 2,3-Acid Lactone.—Two hundred and five grams of 2,3-acid lactone was dissolved in 1040 cc. of absolute ethanol, four drops of concentrated sulfuric acid and 100 g. of anhydrous calcium sulfate added, and the mixture refluxed for seventy-five and seven-tenths hours. The solution was filtered and the alcohol was distilled off at reduced pressure to give a 235 g. residue which was dissolved in water. The solution was neutralized with sodium bicarbonate and the water distilled off at reduced pressure, finally at 60°. The residue was dissolved in ether and the ether solution dried over anhydrous sodium sulfate. The ether was distilled off at atmospheric pressure and the residue fractionated to give 99.6 g. of material, boiling point 76–77° (3.5 mm.), m. p. 5°, a 59% yield calculated as 3-hydroxyisocrotonic lactone. The titration results varied due probably to some structural change which the lactone undergoes in hot solution.[7b]

Under the conditions of this experiment, the lactone was simply dehydrated.



2,3-Acid lactone 3-Hydroxyisocrotonic lactone

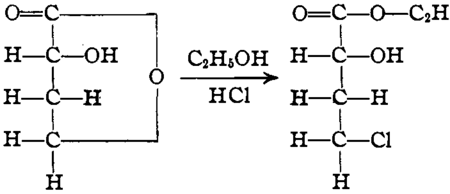
Ethyl 2-Hydroxy-3-chlorobutyrate[15] from 2,3-Acid Lactone.—Ten grams of 2,3-acid lactone was dissolved in 100 cc. of absolute ethanol, the solution was cooled in an ice-bath, and dry hydrogen chloride was passed in to saturation (one and one-half hours). After twelve hours in the ice box, the alcohol was removed by vacuum distillation and the 14 g. of residue was extracted with ether. The ether solution was dried over anhydrous sodium sulfate, the ether distilled off, the residue fractionated, and 7.0 g. of material of boiling range 92–95° (4 mm.), a 42.9% yield calculated as ethyl 2-hydroxy-3-chlorobutyrate, was obtained. Experiments were performed in which the volume of the alcohol varied from five to fifty times that of the lactone: the chief product was always ethyl 2-hydroxy-3-chlorobutyrate.



2,3-Acid lactone Ethyl 2-hydroxy-3-chlorobutyrate

Anal. Subs., 0.2972, 0.3422, 0.2623 g.: 0.1 *N* alkali 35.40, 40.79 cc.; 0.1 *N* silver nitrate 15.43 cc. Calcd. for $C_4H_{11}O_3Cl$: neutralization equivalent, 83.2; Cl, 21.31. Found: neutralization equivalent 84.0, 83.9; Cl, 20.86.

Ethyl 1-Hydroxy-3-chlorobutyrate from 1,3-Acid Lactone.—Fifty-one grams of 1,3-acid lactone was dissolved in 500 cc. of absolute ethanol, the solution was cooled in an ice-bath, and dry hydrogen chloride passed in to saturation (eight and three-tenths hours). The alcohol was distilled from the solution at reduced pressure and 71.6 g. of residue obtained. Water was added and the hydrochloric acid neutralized with sodium bicarbonate. The neutral mixture (two layers) was concentrated to dryness with a water pump finally at a bath temperature of 50°. The residue was extracted with absolute ethanol, the sodium chloride separated by suction filtration, and the filtrate concentrated to dryness with a water pump, finally at 50°, to give a 63.6-g. residue. The residue was shaken with 100 cc. of water, the layers separated, the 43 g. of water-insoluble material dissolved in 220 cc. of ether, and the solution dried over anhydrous sodium sulfate. Removal of the ether and fractionation of the 38.6 g. of residue gave 28.2 g. of material, boiling range 84–87°, 1.5 mm. Refractionation gave 27 g. of material, 92–95°, 1.5 mm., a 32.5% yield calculated as ethyl 1-hydroxy-3-chlorobutyrate.



1,3-Acid lactone Ethyl 1-hydroxy-3-chlorobutyrate

Anal. Subs., 0.2908, 0.2913, 0.2756, 0.2850 g.: 0.1 *N* alkali 34.22, 34.40 cc.; 0.1 *N* silver nitrate 16.04, 16.64 cc. Calcd. for $C_4H_{11}O_3Cl$: neutralization equivalent, 83.2; Cl, 21.31. Found: neutralization equivalent, 85.0, 84.7; Cl, 20.64, 20.70.

Reduction of Butyl Erythronate

Preparation of Butyl Erythronate.—This compound was made by a modification of Snoddy's adaptation of a special method of preparation of the esters of aldonic acids.[16] The necessary calcium erythronate was prepared in 87% yield by the treatment of a water solution of erythronic lactone with calcium carbonate at 90° followed by concentration of the filtered solution at reduced pressure and addition of absolute ethanol to precipitate the salt.

Eighty grams of calcium erythronate, dried to constant weight in an air oven at 95°, was mixed with 288 cc. of absolute butanol in a three-necked tube fitted with a mercury-seal stirrer and inlet and outlet tubes for hydrogen chloride. As dry hydrogen chloride was passed into the suspension, the salt dissolved. In forty-five minutes the

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(15) G. Braun, THIS JOURNAL, **52**, 3167 (1930).

(16) Hlasiwetz and Habermann, *Ann.*, **155**, 127 (1870); Herzfeld, *ibid.*, **244**, 294 (1888); Kohn, *Monatsh.*, **16**, 333 (1895).

temperature of the cloudy solution was 61°. At the end of two hours a heavy precipitate was present but the stream of hydrogen chloride was allowed to run during another forty minutes. The mixture of sirup and precipitate was transferred from the tube to a beaker by means of dry ether and stored in a desiccator over calcium chloride. When the fine white precipitate had settled the ether was decanted, fresh ether added and the solid again allowed to settle out in the desiccator. This process, which was repeated a third time, removed the butanol and some of the hydrogen chloride. The white solid $[(C_3H_7O_3COOC_4H_9)_2 \cdot CaCl_2]$ was very hygroscopic. It was separated quickly from the ether by suction filtration, washed several times with dry ether, and stored over calcium chloride in a desiccator which was evacuated continuously until all of the ether was removed. Dry air was then drawn through the desiccator until all of the hydrogen chloride had been removed. At this point the salt was added to a similar lot obtained in a previous run from 53 g. of calcium erythronate. The weight of the material from the combined runs was 179 g., a 73.3% yield based on erythronic lactone.

The dried solid was dissolved in a very small amount of water and treated with a little silver oxide to remove residual hydrogen chloride. The procedure from this point on was that of Hlasiwetz and Habermann. A slight excess of sodium sulfate in water solution was added and the calcium sulfate separated by suction filtration. The filtrate was concentrated to dryness at reduced pressure with the bath finally at 50°. The residue was extracted with ether and the ether solution concentrated at reduced pressure until it appeared cloudy. It was then cooled, the solid separated by suction filtration and washed with a little dry ether. The washings and mother liquor were further concentrated and cooled to give more solid. The solid, after drying in a vacuum desiccator over calcium chloride, weighed 102 g. and melted at 62–64°, a 53.9% yield based on erythronic lactone.

Anal. Subs., 0.2962, 0.3156 g.: 0.1 N alkali 15.50, 16.42 cc. Neutralization equivalent calcd. for $C_8H_{16}O_5$, 192.1. Found: 191.1, 192.2. A fairly satisfactory analysis for C and H has been reported already by Snoddy.

Butyl erythronate is a glistening white odorless compound, is decidedly "greasy" to the touch, and is very soluble in alcohol, acetone and water. It may be crystallized from ether.

High Pressure Reduction (Expt. No. 1, Table II).—Thirty grams of butyl erythronate was dissolved in 156 cc. of 95% ethanol (solution volume, 179 cc.). A 2-cc. sample was removed for analysis and the remainder of the solution was put into Bomb B. Five grams of platinum oxide catalyst was added, the air was displaced, and the material put under pressure of 97 atmospheres of hydrogen and rocked at the rate of 42 cycles per minute. After 25.6 hours the bomb was opened and a 2-cc. sample removed for analysis. A 53.25 cc. volume of 0.1 N sodium hydroxide was added to the sample and the solution was refluxed for 0.75 hour to ensure complete hydrolysis of the ester. Titration with 0.1 N hydrochloric acid showed that the sample had neutralized 11.29 cc. of 0.1 N alkali. Since a 2-cc. sample of solution before reduction required 18.44 cc. of 0.1 N alkali, a 38.8% reduction had been accomplished. Three grams of catalyst was added to the remaining solution which was put under pressure of 95 atmospheres of hydrogen and the above procedure carried out again. This process was continued until a complete reduction of the ester was effected. This required a period of 114.1 hours and the addition, in portions, of 20 g. of catalyst. Erythritol was isolated in 60.1% yield.

Low Pressure Reduction (Expt. No. 2, Table II).—Thirty grams of butyl erythronate was dissolved in 151 cc. of 95% ethanol. A 2-cc. sample was removed, the remaining solution was put into a pressure bottle, 1 g. of platinum oxide catalyst added, the bottle evacuated, and the material put under pressure of 2–3 atmospheres of hydrogen. The procedure for removal of sample, analysis, addition of more catalyst, etc., was identical with that used in the high pressure experiment. Complete reduction of the ester was effected in 329.5 hours by the addition, in portions, of 14.7 g. of catalyst. Erythritol was isolated in 68.5% yield.

TABLE II

REDUCTION OF BUTYL ERYTHRONATE

Sample, 2 cc.	$PtO_2 \cdot H_2O$, g.	Time of hyd., hrs.	0.1 N NaOH, cc.	Ester, %	Reduction, %	Erythritol isolated, %
Expt. 1[a]: 30 g. of butyl erythronate in 156 cc. 95% alc.						
Orig.	..	...	18.44	100.0	0.0	
A	5	25.6	11.29	61.2	38.8	
B	3	21.9	7.54	40.9	59.1	
C	3	13.9	4.61	25.0	75.0	
D	5	25.2	1.44	7.8	92.2	
E	4	27.5	0.00	0.0	100.0	
Summary	20	114.1				60.1
Expt. 2[b]: 30 g. of butyl erythronate in 151 cc. 95% alc.						
Orig.	..	...	18.19	100.0	0.0	
A	1	2.9	17.96	98.7	1.3	
B	1	18.5	16.42	90.3	9.7	
C	1	27.5	14.74	81.0	19.0	
D[c]	0.5	21.1	13.71	75.4	24.6	
E	.5	2.8	13.14	72.2	27.8	
F	.5	20.0	12.14	66.7	33.3	
G	2.0	23.5	8.86	48.7	51.3	
H	2.0	24.3	5.68	31.2	68.8	
I	2.0	40.7	2.13	11.7	88.3	
J	3.0	18.1	1.30	7.1	92.9	
K	0.6	20.3	0.73	4.0	96.0	
L	..[d]	67.5	.54	3.0	97.0	
M	0.6	42.3	.00	0.0	100.0	
Summary	14.7	329.5				68.5

[a] Rate of shaking, 42 cycles per minute; pressure 82–97 atm. [b] Rate of shaking, 360 cycles per minute; pressure 2–3 atm. [c] Crystals of erythritol on sides of pressure bottle. [d] Aerated, 3.3 hours.

Isolation of Erythritol.—The details of the isolation of erythritol from the reported high pressure run will be given. The solution, analysis of which indicated complete reduction of the ester, was separated from the catalyst by suction filtration. The catalyst was washed with water and the combined washings and mother liquor were subjected to distillation to dryness at reduced pressure to give 19.1 g. of residue. The residue was dissolved in a small amount of water, the solution heated with charcoal to 100°, the charcoal removed and the solution again subjected to distillation to dryness at reduced pressure to give 18.7 g. of residue. Several recrystallizations from 95% alcohol gave successively 8.0 g. of crystals, m. p. 119–121.5°; 2.5 g., m. p. 118–121°; and 0.2 g., m. p. 118–120.5°; a total yield of 10.7 g. The total volume of solution in the reported high pressure experiment was 179 cc., but since 12 cc. of this solution had been used for analyses, the maximum possible yield was 17.8 g. Erythritol was therefore isolated in 60.1% yield.

Summary

1. The method of catalytic hydrogenation at high pressures has been applied to two C_4-saccharinic acid lactones and to erythronic lactone.
2. Both the 2,3-dihydroxybutyric acid lactone and its 2-acetylated derivative have been reduced in good yield to 3-hydroxybutyric acid lactone.
3. The 2,3-dihydroxybutyric acid lactone and the 1,3-dihydroxybutyric acid lactone showed, respectively, by analyses, 21 and 67% reduction at low pressures when large amounts of platinum oxide catalyst were used.
4. Butyl erythronate was prepared according to a modification of Snoddy's adaptation of the method of Hlasiwetz and Habermann. It was reduced to erythritol in good yield at both high and low pressures.
5. The butyl ester of 3-hydroxyisocrotonic acid and the ethyl ester of 1-hydroxy-3-chlorobutyric acid have been prepared.
6. The esters mentioned in 4 and 5 above are new to the literature.
7. Reduction of samples of the catalyst ($PtO_2 \cdot H_2O$) resulted in the production of a slight amount of alkali. This fact should not be ignored in hydrogenations of acids, esters, etc.

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NOTES

The Action of the Sulfonyl Group

BY F. ARNDT

In a recent paper[1] Kohler and Potter, after giving reference to a previous work of Arndt and Martius,[2] and after describing the behavior of a series of sulfonyl ketones, conclude as follows: "The view that sulfonyl groups cannot promote enolization is manifestly no longer tenable." This view, however, has not been expressed by the writer and his co-workers, who have even given detailed experimental evidence to the contrary. Thus, malonic ester does not enolize, whereas tosylmalonic ester enolizes appreciably; malonitrile does not tautomerize, but tosylmalonitrile tautomerizes considerably; acetaldehyde and tosylacetaldehyde do not enolize whereas formyl methionide, where the aldehyde group is combined with *two* sulfonyl groups in the β-position, enolizes to a great extent. On the other hand, Kohler and Potter acknowledge that "it is doubtless true that the sulfonyl group is far less effective than the carbonyl group in promoting enolization." This great difference in *degree* has been attributed by Arndt and Martius to a difference in the *nature* of the action of the sulfonyl and carbonyl groups, respectively. The action of the sulfonyl group is purely acidifying, thereby diminishing the factor which is opposed to enolization, *i. e.*, the "prototropic expenditure of work," whereas carbonyl and other groups containing multiple bonds increase, to a great extent, the active factor which promotes enolization, *i. e.*, the "electromeric effect of the molecule," by forming with the enolic double bond a conjugated system. The view that the sulfonyl group does not act in *this* manner, because it does not contain double bonds, is in no way contradicted by the experimental results of Kohler and Potter. The behavior of the group $COC_6H_2(CH_3)_3$ alone and in combination with one or two sulfonyl groups is, in fact,

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(1) E. P. Kohler and H. A. Potter, THIS JOURNAL, **58**, 2166 (1936).

(2) F. Arndt and C. Martius, *Ann.*, **499**, 228 (1932).