Acetylation of Alkyl Lactates

METHYL AND ETHYL ALPHA-ACETOXYPROPIONATES

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Methyl acetoxypropionate, the acetyl derivative of methyl lactate, is an important intermediate because it yields methyl acrylate on pyrolysis. The present paper describes simple and efficient methods for acetylating methyl lactate with acetic anhydride, ketene, and acetyl chloride. Methyl lactate was acetylated continuously and in high yields with acetic anhydride and ketene. Large-scale laboratory apparatus suitable for preparing methyl acetoxypropionate continuously at rates as high as 95 pounds per 24-hour day is described.

SEVERAL papers (*4, 12, 13, 26, 27, 34*) have been published recently on the transformation of carbohydrates into methyl acrylate, a synthetic rubber (*1, 2, 5, 8, 10, 18, 28, 29, 30, 35, 39, 41*) and resin (*20*) intermediate, by the following series of operations: (*a*) fermentation (*24*) of carbohydrates → lactic acid (*32*); (b) esterification of lactic acid → methyl lactate (*31, 33, 37*); (*c*) acetylation (*7*) of methyl lactate → methyl α-acetoxypropionate; and (*d*) pyrolysis (*4, 34*) of methyl acetoxypropionate → methyl acrylate + acetic acid. Although considerable information has been made available regarding steps *a*, *b*, and *d*, the acetylation of methyl lactate (step *c*) has received little attention. The present paper describes both batch and continuous methods for acetylating methyl lactate and similar lactic esters in high yields. More attention was devoted to the acetylation of methyl lactate because the methyl ester of acetoxypropionic acid can be transformed satisfactorily by pyrolysis into methyl acrylate, whereas low yields of acrylic esters are obtained when the higher alkyl acetoxypropionates are decomposed (*4, 34*).

Several methods (*3, 4, 6, 7, 13–16, 18, 21, 23, 36*) have been used to prepare the acyl derivatives of the alkyl lactates and similar lactic esters. Methyl and ethyl lactates have been acetylated in high yields with acetyl chloride, acetic anhydride, and ketene (Table I). The use of acetic acid, the low-cost starting material employed in the production of acetic anhydride, acetyl chloride, and ketene to acetylate alkyl lactates apparently has not been described.

Various preparations and physical properties of methyl and ethyl acetoxypropionates are listed in Table I. Patterson and co-workers (*21, 22*) determined the density of methyl acetoxypropionate at temperatures from −7.4° to 141°C. Their density data are described by the equation:

$$d_4^t = \frac{970.5 - t}{873.3}$$

ACETYLATION WITH ACETIC ANHYDRIDE

Rather involved procedures (*6, 34*) have been used previously to acetylate alkyl lactates with acetic anhydride. Usually one of the reagents was added gradually to the other, with cooling and stirring. Sulfuric acid was used as catalyst, and in some instances the mixture was heated or allowed to stand for several hours. The catalyst was then neutralized, and the mixture filtered or decanted and fractionally distilled.

To simplify and improve the acetylation, the reaction between methyl lactate and acetic anhydride was studied. In the absence of a catalyst, little or no acetylation occurred when methyl lactate and acetic anhydride were mixed in equimolar proportions and allowed to stand at room temperature for as long as 5 days. The addition of a small amount of sulfuric acid, however, started a vigorous reaction, which caused the temperature of the reaction mixture to rise to approximately 120° C. In view of the heat generated and the probable hazards involved, one reagent was added slowly to the other in the present work when a large quantity of methyl lactate was acetylated by the batch method. High yields were obtained either by adding the anhydride to methyl lactate or by using the reverse order of addition. The acetylation was carried out also in the absence of a catalyst by distilling the acetic acid as it was formed.

The knowledge gained in the acetic anhydride acetylations may be summarized as follows:

Little or no acetylation occurs at room temperature in the absence of a catalyst.
Mineral acids, such as sulfuric acid, are effective catalysts even in minute quantities.
Once started, the reaction proceeds vigorously, generates much heat, and is complete in a short time.
Because of the heat generated, it is hazardous to acetylate in large batches without suitable facilities.
When small but effective amounts of sulfuric acid are used as catalyst, it is not necessary to neutralize prior to distillation.
The acetylation can be carried out in the absence of a catalyst at elevated temperatures.
The yield of methyl acetoxypropionate is nearly quantitative.

When methyl lactate is acetylated with acetic anhydride, long heating periods would be expected to cause a reaction between methyl acetoxypropionate and acetic acid, with the formation of methyl acetate and acetoxypropionic acid. For example, Burns, Jones, and Ritchie (*4*) heated a mixture of butyl lactate and acetic anhydride at 100° C. for 50 hours and obtained 61 and 27% yields, respectively, of butyl acetate and butyl acetoxypropionate. Fortunately, this side reaction occurs slowly and is not troublesome when the acetylation is carried out in a reasonable time.

The several batch preparations of methyl acetoxypropionate (Table II) were highly satisfactory and simpler than those previously described. In some instances methyl lactate and acetic anhydride were merely mixed and distilled under atmospheric pressure. Diphenyl ether was used in some of the experiments to expel all the methyl acetoxypropionate toward the end of the distillation. In certain of the earlier experiments it was possible to distill acetic acid rapidly from the reaction mixture in the absence of added catalyst. When redistilled methyl or ethyl lactate was used in some of the later experiments, however, several hours were required to distill the acetic acid formed in the acetyla-

TABLE I. PREVIOUS PREPARATIONS AND PHYSICAL PROPERTIES OF METHYL AND ETHYL α-ACETOXYPROPIONATE

Lactic Acid Derivative or Methanol	Acylating Agent	Catalyst	Temp., °C.	Time, Hr.	Acetyl Derivative: Yield, % of theoretical	Acetyl Derivative: Distillation Temp., °C.	Acetyl Derivative: Distillation Pressure, mm.	Acetyl Derivative: Density (°C.)	Acetyl Derivative: Refractive index (°C.)	Citation
Methyl lactate	Acetyl chloride, excess	....	Reflux	..	..	171–2 68–70	Atm. 13	1.0885 (19.8)	....	(21)
Methyl *l*-lactate	Acetyl chloride	....	....	..	..	68	13	1.0866 (20.4)	....	(22)
Methanol (2.5 ml.)	Acetoxypropionyl chloride (3.5 g.)	Pyridine (2.2 g.)	15	5	66	63–5	10	....	....	(14)
Methyl lactate	Acetic anhydride	H_2SO_4	....	..	About 90	171.5–72 76–7	760 12	1.088 ($^{20}_{4}$)	1.4111 (20)	(4)
Methyl lactate	Acetic anhydride	H_2SO_4	....	..	92	68–73	14	....	....	(7)
Methyl lactate (312 g.)	Acetic anhydride (337 g.)	H_2SO_4 (0.3 ml.)	Under 60	4	93.5	85	31.5	....	....	(34)
Methyl lactate (6 moles)	Ketene	H_2SO_4 (2 drops)	....	22	96.4	68–73	14	....	....	(7)
Ethyl *d*-lactate	Acetyl chloride	....	....	..	..	76–8	15	1.0513 ($^{14}_{4}$)	....	(25)
Ethyl lactate	Acetyl chloride	....	Reflux	..	..	176–7	733	1.0458 (17)	....	(40)
Ethyl *d*-lactate	Acetyl chloride	....	....	..	80	170–2	760	1.050 (18)	....	(15)
Ethyl *d*-lactate	Acetyl chloride	....	....	..	..	73–4	11	....	1.4096 (19)	(18)
Ethyl lactate	Acetic anhydride	H_2SO_4	....	..	87–91	177–8	Atm.	....	....	(4)
Ethyl lactate	Acetic anhydride	H_2SO_4	....	..	91	73–6	11	....	....	(7)
Ethyl lactate	Ketene	H_2SO_4	....	..	98	73–6	11	....	....	(7)
Ethyl toluene sulfonoxypropionate	Sodium acetate	....	....	..	80	71–2	10	1.0442 ($^{18}_{4}$)	1.4096 (19)	(18)
Ethyl lactate	Acetyl chloride	....	Water bath	4	84	181–2	Atm.	1.044 ($^{25}_{4}$)	1.4065 (25)	(16)

tion. Perhaps catalytic impurities were responsible for the rapid acetylations observed in the earlier experiments. Lactic acid apparently can catalyze the acetylation (Table II). Figure 1 shows the effect of pressure on the boiling point of methyl α-acetoxypropionate.

Methyl lactate was acetylated continuously in the earlier experiments (Table III) by passing (*19*) a mixture of methyl lactate and acetic anhydride (approximately equimolar proportions) through a heated glass coil (capacity 17 ml.) into a continuous still (apparatus *A*). The over-all height of the distillation column was approximately 183 cm., and the diameter was 22 mm. The material to be distilled was passed into the electrically heated column at a point approximately two-fifths of the total distance from the bottom. The upper three fifths of the column was packed with small Berl porcelain saddles; the lower two fifths had indentations of the Vigreux type. The lower portion of the column and the 100-ml. still pot (from which methyl acetoxypropionate was withdrawn continuously) were kept near the boiling point (172° C.) of methyl acetoxypropionate. The temperature of the upper section of the column and still head was controlled in such a manner that acetic acid distilled.

Larger equipment (apparatus *B*, Table III), similar to that described above, was used in some of the continuous acetylations with acetic anhydride. The distillation column was 2 inches in diameter and packed over a length of 6 feet with small Berl saddles. An equimolar mixture of acetic anhydride and methyl lactate (ethyl lactate in experiment 1, Table III) was passed through the preheater (electrically heated glass coil having a capacity of 17 ml.) and into the center of the distillation column. In experiments 4 and 5 methyl lactate, acetic anhydride, and a small quantity of sulfuric acid were mixed (with stirring) and passed by gravity over calcium carbonate chips into a one-liter graduate. The liquid in the graduate (principally methyl acetoxypropionate and acetic acid) was then passed at a constant rate (*19*) through the preheater and into the center of the distillation column. Methyl acetoxypropionate was withdrawn continuously from a small flask at the bottom of the column, and acetic acid was distilled from the top. When ethyl lactate was acetylated, slightly different temperatures were used in the column because of the higher boiling point (177–179° C.) of ethyl acetoxypropionate.

In experiments 7 to 10 acetylation was affected with stirring in a three-neck flask, and the resulting mixture was distilled through apparatus *B* (Table III). These experiments were carried out with 2 or 3 drops of concentrated sulfuric acid per 7 moles of methyl lactate, and the sulfuric acid was not neutralized prior distillation.

Although the feed rate and temperatures were not kept completely constant, the results of the continuous experiments showed

TABLE II. ACETYLATION OF METHYL AND ETHYL LACTATE WITH ACETIC ANHYDRIDE (BATCH METHODS)

Expt. No.	Methyl Lactate, Moles	Acetic Anhydride, Moles	Catalyst	Phenyl Ether, Ml.	Hours to Distill Acetic Acid	Acetyl Derivative: Yield % of theoretical	Acetyl Derivative: Distillation Temp., °C.	Acetyl Derivative: Distillation Pressure, mm.	Refractive index at 20° C.	Remarks
1	1.5	1.66	H_2SO_4, 1 drop	50	..	96	168–73[a]	Atm.	1.4091	Allowed to stand 45 min. before distn.
2	1.5	1.66	H_2SO_4, 1 drop	50[b]	..	96.4	76	20	..	Anhydride containing H_2SO_4 added gradually to ester; temp. rose to 96° C.
3	8	8.4	H_2SO_4, 0.5 ml.	None	..	95	63–4	10	..	Methyl lactate added slowly to reaction mixt.; kept at about 60°
4	1	1	Acetyl chloride, 1 ml.	50[b]	..	94	...	Atm.	..	Temperature rose to 102° in 2.5 min. when acetyl chloride was added
5	1	1	None	75	9	92.5	85	27–28	1.4090	Acetic acid distd. slowly as formed
6	1	1	None	75[b]	10	94.5	85	27–28	1.4090	Acetic acid distd. slowly as formed
7	2[c]	2	None	None	8.5	93.5	91	28	1.4092	Acetic acid distd. slowly as formed
8	1	1.1	None	None	6	93.0	172	Atm.	1.4095	Forerun added to residue and redistd.; acetic acid distd. slowly as formed
9	2[c]	2	H_2SO_4, 3 drops	15[d]	..	94.0	101	45	1.4090	.....
10	5	5	H_2SO_4, 5 drops	None	..	96.0	79	23	1.4095	.....
11	1	1	None	50	4.5	89.0	80	24	1.4094	Acetic acid distd. slowly as formed
12	1	1	None	None	3	88.0	84	31	1.4090	Acetic acid distd. slowly as formed
13	2	2	80% lactic acid 5g.	75	3	87.0	78	20	1.4095	.....

[a] Most of the product distilled at 172–3° C.
[b] Phenyl ether was added just prior to distillation.
[c] Ethyl lactate was acetylated.
[d] Phenyl ether was added prior to redistillation of mixture of forerun and residue.

that methyl and ethyl lactate can be acetylated continuously and high yields with acetic anhydride. The high-boiling product obtained from the lower end of the continuous distillation column usually contained more than 95% of the acetyl derivative (determined by distillation and refractive index data). The methyl acetoxypropionate produced in this manner was almost colorless and suitable for pyrolysis. Methyl acetoxypropionate was made in the larger unit (apparatus *B*) at rates as high as approximately 95 pounds per 24-hour day.

constituent of the products formed in experiments 3 and 5 was methyl acetoxypropionate, these products would not require purification prior to pyrolysis.

The use of ketene to acetylate methyl lactate as one step in the manufacture of methyl acrylate seems to have several advantages. Ketene can be made (*9*) by the pyrolysis of acetic acid, the principal by-product obtained when methyl acetoxypropionate is converted into methyl acrylate. Unlike the procedures using acetyl chloride and acetic anhydride, no by-product is formed

TABLE III. CONTINUOUS ACETYLATION OF ALKYL LACTATES WITH ACETIC ANHYDRIDE

Expt. No.	Equimolar Mixt. Methyl Lactate + Acetic Anhydride, Kg.	Catalyst	Apparatus	Feed Rate, Ml./Hr.	Contact Time in Preheater, Min.	Temperature, ° C. Preheater	Still pot	Upper heated jacket	Lower heated jacket	Still head (acetic acid vapor)	n_D^{20} High-Boiling Products[a]
1	0.44[b]	None	*A*	100[c]	10	111	171–6	116–20	174–7	119–24	1.4085
2	0.412	None	*A*	100[c]	10	132–41	165–70	114–17	168–75	119–21	1.4080
3	0.618	None	*A*	120[c]	8.5	118	168–76	113	156–69	118–20	1.4070
4	...	H_2SO_4	*B*	120	8.5	124–30	170–4	116	165–75	114–16	1.4078
				475	2.1	153	173	119	172	117	1.4088
5	...	H_2SO_4	*B*	700	1.5	120	173	119	184	117	1.4090
				1160	0.9	127	170	127	185	117	1.4080
				360	2.8	154	170	120	181	118	1.4090
6	...	None	*B*	460	2.2	154	165	116	184	118	1.4080
7	6.7	H_2SO_4	*B*	1550	1.7[d]	140	171–6	117	169–81	115–16	1.4093
8	15.8	H_2SO_4	*B*	1975	1.3[d]	128–30	171–4	127	171–3	116–17	1.4088
9	8.1	H_2SO_4	*B*	2080	1.3[d]	130	174	126	175	116–18	1.4088
10	51.2	H_2SO_4	*B*	2550	1.0[d]	130	173–7	116–20	168–81	116–18	1.4088[e]

[a] Refractive index of pure methyl acetoxypropionate at 20° was 1.4095.
[b] Equimolar mixture of ethyl lactate and acetic anhydride was used.
[c] Grams per hour. [d] Volume of preheater was 45 ml. [e] Average.

ACETYLATION WITH KETENE

Claborn and Smith (*7*) showed that ketene can be used to convert methyl lactate into methyl acetoxypropionate in high yields, but sulfuric acid was employed as a catalyst, and the acetylation was not carried on continuously. It was found in the present work that a catalyst is not necessary, and that the acetylation can be carried on continuously.

Ketene was generated by the thermal decomposition of acetone in equipment of the type described by Williams and Hurd (*38*). Continuous acetylation was effected by passing methyl lactate and ketene countercurrently through a column 0.5 inch in diameter and packed over a length of 30 inches with small porcelain Berl saddles. Heat generated by the acetylation increased the temperature of the column to approximately 50° C.

TABLE IV. CONTINUOUS ACETYLATION OF METHYL LACTATE WITH KETENE

Expt. No.	Methyl Lactate, Grams	Feed Rate, Drops/Min.	Catalyst	n_D^{20} of Crude Product	Compn. of Product, % by Vol. Acetone	Methyl lactate	Methyl acetoxypropionate
3	130	20	None	1.4100	14	2	84[a]
4	127	30	H_2SO_4	..	11	42	47[b]
5	..	20	None	1.4061	0	10	90
6	..	40	None	1.4100	6	52	42
7	..	50	None	1.4120	3	67	37

[a] Based on unrecovered methyl lactate, this yield was 93% of theoretical.
[b] Based on unrecovered methyl lactate, this yield was 94% of theoretical.

The results of the ketene experiments (Table IV) show that this method gives high yields of the acetyl derivative, the conversion per pass depending largely upon the rate of addition of methyl lactate. The ketene generator was operated as constantly as possible, and it was assumed that ketene was produced at approximately the same rate (0.3 mole per hour) in all the experiments. The presence of acetone in the crude acetylation product indicated that some of this ketone in the ketene generator was carried over with the ketene and methane. Since the chief

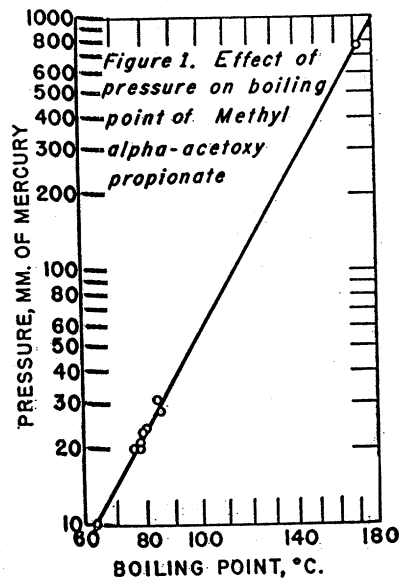

Figure 1. Effect of pressure on boiling point of Methyl alpha-acetoxy propionate

when the acetylation is affected with ketene. Because of the absence of a principal by-product, such as acetic acid, the methyl acetoxypropionate made with ketene is more suitable for direct pyrolysis than the crude acetylation mixture made with acetic anhydride. When it is not practicable to have a ketene plant near the pyrolysis units, however, it might be necessary to transport acetic anhydride to the methyl acrylate plant and return the acetic acid to the ketene plant for reconversion into acetic anhydride.

ACETYLATION WITH OTHER REAGENTS

Methyl lactate was acetylated with redistilled acetyl chloride for comparison and to determine whether a high yield of methyl acetoxypropionate could be obtained by a simple procedure. Acetyl chloride (86.4 grams or 1.1 mole) was added from a separatory funnel during approximately 5 minutes to 104 grams (1 mole) of methyl lactate contained in a three-neck flask. The

temperature of the material in the flask, which was provided with a reflux condenser and mechanical stirrer, rose to 58° C. during the addition. The yield of methyl α-acetoxypropionate, most of which distilled at 78° C. under 21 mm. of mercury pressure, was 132.5 grams or 90.7% of the theoretical. The refractive index of the product was 1.4089 at 20° C. Apparently, previous preparations of methyl acetoxypropionate with acetyl chloride have been more complicated and have given lower yields.

Since the acetylation with acetyl chloride can be carried out rapidly and by a simple method, possibly this reaction can be operated continuously. Continuous distillation or countercurrent washing with alkaline reagents might be used to remove hydrogen chloride from the product.

Because of the low cost of acetic acid and the fact that it is obtained as a by-product in the pyrolysis of methyl acetoxypropionate, it would be highly advantageous to have a satisfactory method for acetylating methyl lactate with acetic acid. Attempts made in this laboratory to effect the acetylation with acetic acid have been successful in that methyl acetoxypropionate was produced, but the yields of the acetyl derivative were much lower than those obtainable with acetic anhydride, acetyl chloride, and ketene. One of the principal by-products was methyl acetate, which presumably was formed by acidolysis of methyl lactate. The preparation of methyl acetoxypropionate without the use of acetic anhydride, acetyl chloride, or ketene is being studied. These researches have already shown that methyl acetoxypropionate can be made satisfactorily by acetylating lactic acid with acetic acid, followed by treatment of the α-acetoxypropionic acid with either methanol or methyl acetate.

SEPARATION OF ACETIC ANHYDRIDE AND METHYL ACETOXYPROPIONATE

When methyl lactate is acetylated with an excess of acetic anhydride, the reaction mixture contains some acetic anhydride, which must be separated to obtain methyl acetoxypropionate of good quality. It was observed in the present work that the removal by distillation of small amounts of acetic anhydride (boiling point 138° C.) from methyl acetoxypropionate (boiling point 172°) is difficult. When a synthetic mixture of methyl acetoxypropionate (95%) and acetic anhydride (5%) was distilled through a Weston column 15 inches long, most of the acetic anhydride (mixed with methyl acetoxypropionate) was collected at 158–170° C.

Distillation of a similar mixture (produced by the acetylation of methyl lactate with acetic anhydride) through an 18-inch column packed with small stainless steel rings or helices (*11*) failed to separate the acetic anhydride satisfactorily. Although it has been demonstrated in this laboratory that methyl acrylate can be prepared by pyrolyzing mixtures of metyl acetoxypropionate, acetic acid, and acetic anhydride (i.e., the crude acetylation mixture), it was considered desirable to have a satisfactory and effective method of separating acetic anhydride from methyl acetoxypropionate to facilitate the preparation of pure methyl acetoxypropionate.

TABLE V. ACETIC ANHYDRIDE AZEOTROPES

Acetic Anhydride (B.P. 138° C.) with:	Boiling Point, ° C. Second component	Boiling Point, ° C. Constant boiling mixt.	Condensate, % by Vol. in: Lower layer	Condensate, % by Vol. in: Upper layer
Methylcyclohexane	101	98–9	17	83
Ethylcyclohexane	131	118–19	38	62

Several liquids were distilled with acetic anhydride with the expectation that some of the mixtures would distill azeotropically. Toluene, ethylene chloride, and iso-octane were separated from acetic anhydride by distillation. Xylene and acetic anhydride appeared to distill azeotropically, but the distillate did not separate into two layers. Cyclohexane is not completely miscible with acetic anhydride, but a constant boiling mixture was not observed when this hydrocarbon was distilled with an equal volume of acetic anhydride. Methylcyclohexane, ethylcyclohexane, and a heptane fraction from petroleum distilled azeotropically with acetic anhydride, and the distillates separated into two layers. The heptane–acetic anhydride azeotrope contained only a small quantity of acetic anhydride. Probably *n*-octane, *n*-nonane, or *n*-decane would be more satisfactory than heptane for distilling acetic anhydride azeotropically. Further data regarding the methylcyclohexane- and ethylcyclohexane–acetic anhydride azeotropes are given in Table V. Both methylcyclohexane and ethylcyclohexane have been used in this laboratory to separate small amounts of acetic anhydride from methyl acetoxypropionate.

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