

8. Behavior of fumaric and maleic acid towards fuming hydrobromic acid. Fittig & Dom; Ann. 188, p. 87.
9. Conv. of fumaric acid into malic by means of aqueous sodium hydroxide at 100°. Loydl & Linnemann: Ann. 192.80.
10. Form. of crotonic acid by action of alcoholic potash on monobrombutyric ethyl ester. C. Hehl & E. Lauber; Ber. 7, 560-564.

VIII. α acetyl propionic, β acetyl propionic or levulinic, brom phenylpropionic, phenyl lactic, glycerinic acids.

1. By action of sodium carbonate sol. brom levulinic acid gives β acetyl acrylic acid and β hydroxylevulinic acid:

$$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{Br})\text{CH}_2\text{COOH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}=\text{CHCOOH} + \text{HBr}$$

$$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{Br})\text{CH}_2\text{COOH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_2\text{COOH} + \text{HBr}$$
2. Two homologues of acetopropionic acid. Bischoff & Wislicenus; Ann. 206, 313.
3. A new synthesis of succinic acid with side formation of β acetyl propionic acid. Noldecke & Wislicenus; Ann. 149, 228.
4. A study of levulinic acid. Grote & Tollens; Ber. 11, 2177.
5. Acid and ketone splitting of aceto acetic ester. Wislicenus; Ann. 206, 308.
6. Splitting of aceto succinic ethyl ester. Conrad & Wislicenus; Ann. 188, 218.
7. Synthesis of glycerinic acid by the action of silver oxide on monochlorlactic acid. Frank & Wislicenus; Ann. 206, 338.
8. A study of the action of various reagents on monobromphenylpropionic acid obtained by the action of bromine on hydrocumaric acid. Glaser; Ann. 143, 343.
9. 'Über atrolactensäure und phenylmilchsaure' Fittig & Kast; Ann. 206.27.

IX. Action of various substituting reagents on organic halogen compounds.

1. Chem. dynamics of the reactions between sod. thiosulphate and organic halogen compounds. Slator & Colaborators; J. Ch. Soc. 85, 1286.
 J. Ch. Soc. 87, 481.
 J. Ch. Soc. (Feb 1909) p. 93-103.
2. Reaction between silver nitrate and organic halogen compounds. Hans Euler; Ber. 39, 2726-2734.

8. Behavior of fumaric and maleic acid towards turning hydro-
bromic acid. Tittig & Dorn: Ann. 188, p. 87.
9. Conv. of fumaric acid into maleic by means of aqueous sodium
hydroxide at 100°. Loyd & Linnemann: Ann. 192, 80.
10. Form. of crotonic acid by action of alcoholic potash on
monobromobutyric ethyl ester.
C. Heide & E. Lauber: Ber. 7, 560-564.

VIII. Acetyl propionic, B acetyl propionic or levulinic, from
phenylpropionic, phenyl lactic, glycerinic acids.

1. By action of sodium carbonate sol. from levulinic acid
gives B acetyl acrylic acid and B hydroxylevulinic acid:
 $\text{CH}_3\text{C}(\text{COOH})=\text{CHCOOH} \rightarrow \text{CH}_3\text{C}(\text{COOH})=\text{CHCOOH} + \text{H}_2\text{O}$
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2. Two homologues of acetoacetic acid.
Bischhoff & Wislizenus: Ann. 206, 213.
3. A new synthesis of succinic acid with side formation of
B acetyl propionic acid.
Noelcke & Wislizenus: Ann. 149, 238.
4. A study of levulinic acid.
Grotes & Tollens: Ber. 11, 2177.
5. Acid and ketone splitting of aceto acetic ester.
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hydroacetic acid. Glaeser: Ann. 143, 343.
9. Über strolactemassure and phenylmethylsaur:
Tittig & Kast: Ann. 206, 27.

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2. Reaction between silver nitrate and organic halogen com-
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Hans Euler: Ber. 39, 2728-2734.

3. Reactivity of the halogens in organic compounds.

George Senter; Trans. L. Ch. Soc. 91,460.

Proc. L. Ch. Soc. (1908) 24.89

esp. Part III by same author J. L. Ch. Soc. Dec. 1909 p. 1827.

Reaction of bromoacetic, α -bromopropionic and α -bromobutyric acids and their sodium salts with water and with alkali.

4. Reactivity of alkyl haloids with silver nitrate.

Burke & Donnan; Trans. L. Ch. Soc. 1904p. 555

5. Conc. the speed of the action of alcoholic potash on the halogen derivatives of the fatty hydrocarbons.

Mejer Wildermann; Zeit für phys. Ch. 8,661-676.

6. Action of silver nitrate and other reagents on alkyl bromides.

Lengfeld; Amer. Ch. J. 17,p.54.

7. Prep. of olefines by heating alkyl haloids with oxide of lead at 220°-225°.

G. Wagner; Ber. 11,414.

8. Action of alcoholic potash, potassium acetate and silver acetate resp. on n. propyl bromide and iodide.

Chapman & Smith;

On alkyl haloids: Reichenbach 158, 164
@ Action of pot. ethylate, silver acetate + glacial acetic, pot. acetate, pot. cyanide

10. Relation of opt. active to corresp. dl amylalcohols

Marckwald & Nolda; Ber. (June 1909) p. 1583.

X. Work of P. Walden of 'Walden Inversion'.

Malic

Chlorosuccinic Ber. 28,1293

Ber. 32,1833.

Asparaginic Ber. 29,135

Ber. 32,1855.

Ber. 30,3147.

XI

Work of Purdie and Williamson on 'Walden Inversion'.1. Conv. of dextrolactic into laevolactic by means of the action of silver oxide on α -chloropropionic acid.

Trans. L. Ch. Soc. 1896 p. 838.

XII. Work of Emil Fisher on 'Walden Inversion.'

Lactic

Ber. 40,1051 'Zur Kenntnis der Waldensche Umkehrung.'

Bromopropionic

Ber. 41.889. A study of opt. active valin.

Alanin

Ber. 41.2891 Proof of 'double inversion' in the case of opt. active valin.

Ber. 41,1286. A study of phenylamino acetic acid

Ber. May 1909 p. 1219 No inversion with β

Chlorbutyric.

Ber. Oct. 1909 A test of Guye & Crum Brown's hypothesis.

Propyl isopropyl cyan acetic acid

Ber. Jan. 1910 Action of calcium oxide and of zinc oxide on halogen fatty acids in water sol. at 100°.

3. Reactivity of the halogens in organic compounds.
George Senter; Trans. I. Ch. Soc. 91, 480.
Proc. I. Ch. Soc. (1908) 24, 89
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G. Wagner; Ber. 11, 414.

8. Action of alcoholic potash, potassium acetate and silver
acetate resp. on n. propyl bromide and iodide.
Chapman & Smith;

9. Relation of opt. active to corresp. di. amyloalcohols
Marchwald & Wold; Ber. (June 1909) p. 1583.

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at 100°.

XIII. Work of MacKenzie on 'Walden Inversion.'

- Mandelic J. L. Ch. Soc. ? Anomalous results with potassium hydroxide, silver oxide, etc.
 Phenylchloroacetic J. L. Ch. Soc. ? Harmonizes some of his results by assuming an inversion with ammonia.
 Phenylamino acetic J. L. Ch. Soc. ? No inversion with opt. active β -bromopropionic acid.

XIV. Excellent reviews of work on 'Walden Inversion.'

Annual Report of the Progress of Chemistry for 1907 J. L. Ch. Soc. 1908
 L. H. Cone. Chapter on Stereochemistry. J. Am. Ch. Soc. 1910.
Abstract of J. L. Ch. Soc. ?

XV. An ingenious idea developed from observations on pinene as to how phosphorus pentachloride may cause inversion.
 H. E. Armstrong J. L. Ch. Soc. 69, 1399.

XVI. Asymmetric synthesis.

1. McKenzie & Humphries; J. L. Ch. Soc. July 1909.
 Neither acylation nor subsequent hydrolysis cause inversion.
2. Racemic phenomena during the hydrolysis of optically active menthyl and bornyl esters by alkali.

XVII. 'Zur Stereochemie der Katalyse'.

G. Bredig & Fajans; Ber. 41, 752.

XVIII. Influence of Solvent on the Rotation of Opt. Active Compounds.
 Patterson & Montgomerie; J. L. Ch. Soc. July 1909, p. 128

~~XIX~~
~~XIX~~ Action of various reagents on complex halogen substituted acids
 Decomposition of bromcamphoric acid with sodium carbonate and with boiling water.

1. Kipping & Armstrong; J. L. Ch. Soc. (1896) p. 65.

2. Some hydrocarbons obtained from the homologues of cinnamic acid.
 W. H. Perkin (1877) J. L. Ch. Soc. [2] 660.

3. Some derivatives of propionic, acrylic and glutaric acid.
 Perkin; J. L. Ch. Soc. Trans. 1896 p. 1457.

XX. Conc. the rule for the addition of halogen compounds to unsaturated acids.
 Michael; J. Pr. Ch. [1899] vol. 10 p. 171.

XXI. Action of sodium alcoholate on brom-fatty acid esters.

B

Bischoff: Ber. 32, 1748.
 Ber. 32, 1899.

XIII. Work of MacKenzie on 'Walder Inversion.'
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Decomposition of bromosulphonic acid with sodium carbonate and with
boiling water.

1. Kipping & Armstrong: J. I. Ch. Soc. (1896) p. 65.

2. Some hydrocarbons obtained from the homologues of cinnamic
 acid. W. H. Perkin (1877) J. I. Ch. Soc. 2, 666.

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 Bischoff: Ber. 32, 1748.
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XXII. Studies in Organic Acids.

Kekule: Ann. Suppl. 1,129-138.
Ann. Suppl. 2,85.

XXIII. Studies of Unsaturated Acids.

halogen Fittig and Colaborators.
Decomposition of ~~the~~ substitution products of the lower fatty acids
with water *and alkali.*

1. Studies in unsaturated acids.
Fittig: Ann. 200.21.
2. Fittig & Thomsen: Ann. 200.75.
3. Properties of methylacrylic acid.
Fittig & Engelhorn: Ann. 200.65.
4. 'Hydrosorbinsaure und sorbinsaure'.
Fittig, Stahl, Landsberg, and Engelhorn: Ann. 200.42.
5. 'Brenzterebinsaure'.
Bredt & Fittig: Ann. 200.58.
6. Conc. the addition products of cinnamic acid.
Fittig & Binder: Ann. 195,132.
7. Phenylaminopropionic acid.
Fittig & Posen: Ann. 195,143.
8. Phenyllactimid.
Posen: Ann. 200.97.
9. Addition of hydrogen bromide to 'brenzterebinsaure'.
Fittig & Geisler: Ann. 208,44.
10. Teracrylic acid and heptolactone.
Fittig & Kraft: Ann. 208.86.
11. The crotonic acids resulting from citraconic and mesaconic acids.
Fittig & Prehn: Ann. 188,142.
12. Also Ann. 188.87 Fittig & Horn
Ann. 143,343 Glaser
Ann. 206.27 Fittig & Kast
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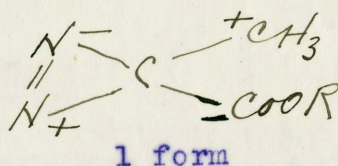
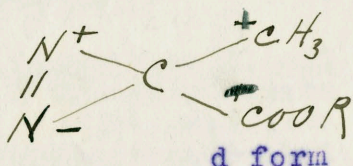
XXII. Studies in Organic Acids.
 Kekulé: Ann. Suppl. 1, 129-138.
 Ann. Suppl. 2, 85.

XXIII. Studies of Unsaturated Acids.
 Wittig and Collaborators.
 Decomposition of the substitution products of the lower fatty acids
 with water.

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REPORT OF WORK ON THE WALDEN INVERSION.

This investigation was undertaken at the suggestion and under the guidance of Professor J. U. Nef with the purpose of obtaining independent experimental evidence in favor of his idea that the four valences of the carbon atom are not mutually equivalent but only in pairs. Accordingly we should be able to prepare two space-isomeric ~~and~~ diazo propionic esters:



The first of these must give with water or haloid acid d lactic or d halogen propionic acid whereas the second is necessarily converted with evolution of nitrogen into the corresponding antipodes. It is of course at once apparent that if the two valences of the carbon bound to nitrogen in diazopropionic ester were equivalent, both d and l alanin must give on treatment with nitrous acid or nitrosyl halides respectively equal amounts of the d and l derivatives (i.e. racemates)--which is however not the case; consequently the two diazopropionic esters which are the intermediate products in the various reactions are not identical but isomers of space- in other words, the two valences of carbon joined to nitrogen in these compounds are not equivalent. The preparation of the ~~the~~ diazo fatty acid esters is no easy matter and besides it was necessary first to become thoroughly familiar with the properties of the optically active acids of the C₃ series.

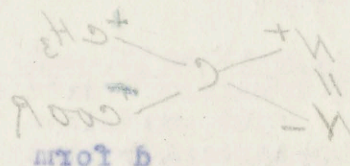
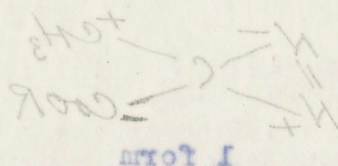
Optically active alanin was prepared according to Fisher's method³ by resolution of benzoyl alanin by means of brucin in aqueous solution. Benzoyl l alanin made in this way melted 147 - 149 degrees. The free base (l alanin) was made from the benzoyl derivative according to the directions of Fisher and Raske⁴ by hydrolysis with dilute hydrochloric acid (1-1 by vol) at 100 degrees and subsequent treatment of the amino acid hydrochloride with lead oxide. 12.93 g of pure l alanin was converted into dextrorotatory brompropionic acid by means of nitric oxide and bromine in acid solution according to the latest directions of Fisher and Raske⁵ who used sulphurous acid in place of mercury to remove excess of bromine. 13.6 g of pure d brompropionic were obtained boiling constantly 109 - 110 degrees (22 - 25 mm.). Pure dl brompropionic acid (Kahlbaum product) was found to boil constantly 105 - 106 degrees (16 mm.). 1.5727 g of the above active preparation dissolved in 22.7777 g of water at 29.5 degrees rotated + 2.97 degrees in a 2 dcm tube; $p = 1.020$; $[\alpha]_D^{29.5} = +24.36$ degrees. The rotation given by Warburg⁶ for purest l brompropionic acid obtained by fractional crystallization (20 times) of the chinchonin salt was- 26.7 degrees.

$$\frac{24.36}{26.7} = 91.24 \%$$

- ① Nef: Jour. Amer. Chem. Soc. [1908], Vol. 30, p. 645
- ② Curtis and students: J. P. Ch. 38, 401; Ber. 18, 1294
- ③ E. Fisher: Ber. 32 II, 2454. J. P. Ch. 38, 4564; Ber. 18, 1298
- ④ E. Fisher & Raske: Ber. 32 II, 2454; J. P. Ch. 38, 4554; Ber. 19, 850
- ⑤ E. Fisher & Warburg: Ann. 340, 171
- ⑥ Warburg: Ann. 340, 168

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$$\frac{24.36}{25.7} = 91.24\%$$

[Handwritten notes and signatures at the bottom of the page, including names like 'J. U. Nef' and 'J. Fisher']

The above preparation of d propionic acid contains, therefore, 4.38% of the optical antipode as against 8% usually obtained by Fischer.

Inasmuch as nearly all of the experiments where an inversion was observed had been carried out in water solution, we set out to determine whether or not the same inversion could be obtained in non-aqueous solution. In order to establish first of all the influence of the solvent and to avoid also the presence of any possible trace of free base, Dr. Neff suggested making a careful study of the action of silver acetate on d propionic acid in absolute ether solution.

Acetate (I mol) on d propionic acid (1 mol) in abs. ether
The action, carried out here at ordinary temperature with 10 g of the acid, was slow to start but after short period of induction gave considerable heat evolution and rapid separation of silver propionate. Silver propionate had to all appearances separated out quantitatively in 20-30 minutes but flask was allowed to stand at room temperature for 24 hours in order to be sure of complete reaction. Examination of the silver residue according to Mieser's directions proved that it consisted almost entirely of silver propionate and contained only the slightest trace of metallic silver.

From the standpoint of metalopates, we should expect to obtain in the ethereal filtrate α acetyl propionic acid.

Action I

d propionic acid
which would have the structure as given if no inversion accompanies the change. Such an acid according to Bischoff does not exist but would lose carbon dioxide spontaneously, just as acetoacetic acid does, and would yield acetyl ester (CH₃COOCH₂CH₂COOCH₃) which would then be subsequently hydrolyzed to give acetic acid.

It, however, α acetyl propionic acid is capable of existence, just as much as β acetyl propionic acid (lactulinic) prepared and studied by Tollens and others, we should obtain by hydrolysis of the active form the corresponding lactic acid since it has been shown repeatedly that no inversion of optical activity occurs in the process of hydrolysis.

Still another action is possible here - silver acetate may pull off hydrogen propionate giving silver propionate and setting free acetic acid.

Action II

It is impossible to get any acrylic acid from 2 brom acid under any conditions yet known.

If the reaction proceeds rapidly the unsaturated intermediate product (carboxyethylidene) would rearrange at once to the more stable acrylic acid (carboxyethylene). This interpretation is in harmony with the idea of Nef that the hydrogen and halogen always come off from the same carbon atom and is entirely analogous to the change of ethylidene into ethylene. That hydrogen and bromine may split off from different carbon atoms to give acrylic acid directly, in accordance with the ideas presented by Fittig, is not excluded.

By carefully distilling of the ether from a waterbath using Glynsky and subsequently heating finally to 100 degrees at 20mm. pressure only a very small amount (0.4 g.) of free acetic acid was obtained from 10 g. of brompropionic. The fact that an appreciable quantity of free acetic acid is obtained shows, however, that Action I is not the sole reaction in this case; still, it is not to be overlooked that a small amount of acetic acid may be formed by splitting of the acylated product through heating.

If Action I takes place almost exclusively, we should get by hydrolysis pure lactic (α hydroxypropionic) acid. Any acrylic acid as such or be converted into hydracrylic acid. After filtering off the ether and washing well with cold dry ether 0.4g gum remained sticking to the silver bromide which was subsequently extracted with absolute alcohol. This material gave in absolute alcohol solution $[\alpha]_D^{20} = +9.5^\circ$. After complete hydrolysis of the main portion, 6.25 g. oil soluble in ether, and distillation of the water at reduced pressure, there was obtained, instead of the ordinary syrupy lactic acid, 4.3 g. of gum which dissolved in water but had very little mobility. A portion of the hydrolyzed gum (0.7g) gave after acylation 0.83 g. acylated material, which in absolute alcohol solution gave $[\alpha]_D^{20} = +20.57$ degrees. The lack of mobility of the hydrolyzed gum found further confirmation in the fact that when it was titrated with $\frac{1}{10}$ potassium hydroxide, only 50% of the gum behaved as a free acid even after standing 46 hours in cold water solution.

In contrast to the anomalous behavior noted above, I wish to submit the following observations: By prolonged heating with water to 120 degrees, ordinary dl lactic (Kahlbaum C. P. product), lactyl lactic (the so called lactic anhydride obtained by heating dl lactic acid for 3 hours at 120 -140 degrees) as well as polylactyl lactic (the so called oily lactid described in the literature obtained by heating dl lactic for 3 hrs. at 180 degrees), all regenerate lactic acid in the form of a mobile oil which titrates over 90% in the cold. Pure monomolecular lactid which is a beautiful crystalline body melting at 125 degrees and is deliquescent, gives ultimately by prolonged heating with water, according to Wislicenus, dl lactic acid. In short, all attempts to prepare from dl lactic by heat or by hydrolysis of any of its simple anhydrides, a stiff gum comparable with that obtained by the action of acetate of silver on α brompropionic acid were of no avail.

The remainder of the water solution, heated in a boiling water bath for 18 hrs. with zinc carbonate, gave after filtration, evaporation etc. a very large crop of crystals which had practically the same solubility in water as zinc lactate. The crystalline form

(1) Ann. 298
(2) Fittig, Ann. 200, 87.

(13) E. Klemenko: Ber. 23, 325-4890
(14) Pelouze:
(15)
(16) Wislicenus: Ann. 167, 303.

If the reaction proceeds rapidly the unsaturated intermediate product (carboxystyrene) would rearrange at once to the more stable acrylic acid (carboxystyrene). This interpretation in harmony with the idea of Net that the hydrogen and halogen atoms come off from the same carbon atom and is entirely analogous to the change of ethylene into ethylene. That hydrogen and bromine may split off from different carbon atoms to give acrylic acid directly in accordance with the ideas presented by Wittig is not excluded.

By carefully distilling of the ether from a waterbath using Glyoxy and subsequently heating finally to 100 degrees at 10 mm. pressure only a very small amount (0.4 g.) of free acetic acid was obtained from 10 g. of bromopropionic. The fact that an appreciable quantity of free acetic acid is obtained shows, however, that Action is not the sole reaction in this case; still, it is not to be overlooked that a small amount of acetic acid may be formed by splitting of the acylated product through heating.

If Action I takes place almost exclusively, we should get by hydrolysis pure lactic (α -hydroxypropionic) acid. Any acrylic acid at prolonged heating with water at 120 degrees would either remain as such or be converted into hydroacrylic acid. After filtering off the ether and washing well with cold dry ether 0.4 g. gum remained sticking to the silver bromide which was subsequently extracted with absolute alcohol. This material gave in absolute alcohol solution 0.25 g. After complete hydrolysis of the main portion, 6.25 g. oil soluble in ether, and distillation of the water at reduced pressure there was obtained, instead of the ordinary syrupy lactic acid, 4.3 g. of gum which dissolved in water but had very little mobility. A portion of the hydrolyzed gum (0.7) gave after acylation 0.83 g. acylated material, which in absolute alcohol solution gave 20.57 degrees. The lack of mobility of the hydrolyzed gum found further confirmation in the fact that when it was titrated with potassium hydroxide, only 50% of the gum behaved as a free acid even after standing 48 hours in cold water solution.

In contrast to the anomalous behavior noted above, I wish to submit the following observations: By prolonged heating with water to 120 degrees, ordinary lactic (Kahlbaum C. P. product), lactic lactic (the so called lactic bromide obtained by heating lactic acid for 3 hours at 120-140 degrees) as well as polylactic lactic (the so called oil lactic described in the literature obtained by heating lactic for 3 hrs. at 180 degrees), all regenerate lactic acid in the form of a mobile oil which titrates over 90% in the cold. Pure monomolecular lactic which is a beautiful crystalline body melting at 125 degrees and is deliquescent, gives ultimately by prolonged heating with water, according to Wallach, di lactic acid. In short, all attempts to prepare from di lactic by heating hydrolysis of any of its simple anhydrides, a stiff gum comparable with that obtained by the action of acetate of silver on α -bromopropionic acid were of no avail.

The remainder of the water solution, heated in a boiling water bath for 18 hrs. with zinc carbonate, gave after filtration, evaporation etc. a very large crop of crystals which had practically the same solubility in water as zinc lactate. The crystalline form

was not examined under the microscope. A determination of the water of hydration of sample from Crop I gave 18.19% whereas Zn. dl lactate. $3 \text{ H}_2\text{O}$ demands 18.18%. Because of this excellent agreement it was considered unnecessary at that time to make careful determinations of zinc in the various crops. Later work on the action of silver oxide on α brompropionic acid very probably gives complete information as to zinc content of these zinc salts. As first crop, 3.63 g. of crystalline zinc salts were obtained having all the appearance of zinc lactate.

1.0193 g. of the hydrated salt from Crop I dissolved by warming in 23.7834 g. of water gave after cooling to room temperature (27°) in 2 dcm. tube an average rotation of $+0.07^\circ$; $p=1.020$; $[\alpha]_D^{27} = +0.835^\circ$. 1.0870 g. of the anhydrous zinc salt dissolved by warming in 32.4896 g. of water gave in a 4 dcm. tube at 28° the following very small rotations, $+0.08$, $+0.05$, $+0.06$, with instrument in perfect adjustment $[\alpha]_D^{28}$ for anhyd. salt $+0.455^\circ$. Some racemization may occur in drying salt. If the crystalline zinc salt is really zinc lactate, we have in Crop I. $\frac{0.835}{7.7} = 10.85\%$ of Zn. l lactate, mixed with 89.15% of Zn. dl lactate. (17)

how do you know
and salt present?
Percent of active material =

The mother liquor from Crop I gave, however, a very much larger rotation in the positive direction. 31.36 g. of solution gave in a 4 dcm. tube an average rotation of $+0.84^\circ$; $p=1.029$; $[\alpha]_D^{28} = +3.37^\circ$.
Percent of active material = $\frac{3.37}{7.4} = 45.54$.

The total mother liquor from Crop I of crystalline zinc salts was then evaporated to a very small volume (8.7 g. of solution). By allowing to stand for several days, filtering and washing with 50% alcohol according to Purdie's directions, a second crop of 0.8355 g. hydrated zinc salts was obtained. Although this crop undoubtedly contained a very large amount of active zinc salt, it gave 18.41% of water of hydration. Zn. dl lactate, $3 \text{ H}_2\text{O}$ demands 18.18% of crystal-water, while Zn d or l lactate $2 \text{ H}_2\text{O}$ requires only 12.76%. (19)

Assuming as others have done that lactic acid is formed here and is the only product present, the rotations given above indicate that as a result of the action in absolute ether of silver acetate on d brompropionic acid and subsequent hydrolysis with water at 120° there was formed 22.08% of l lactic acid and 77.92% of the dl form. Hence an inversion must have occurred to the extent of 61.04% while 38.96% of the d form is present in the racemic zinc salts. That silver acetate has a powerful racemising effect has also been observed by Marckwald. (20) It is of some interest to note further that the anhydrous potassium salt of the total acid product obtained in this experiment, gave a mean positive rotation of 3.78° whereas the mean rotation of the total hydrated zinc salts was only 1.70° which corresponds to 2.08° for the anhydrous zinc salt.

An experiment carried out with 1.56 g. d brompropionic acid (1 mol.) and 1.71 g. silver acetate (1 mol.) in water solution as a check gave an altogether similar result- much less racemization accompanied the change. The filtrate from the silver bromide was hydrolyzed as in the previous experiment and then heated at 100° for 4 hrs. with zinc carbonate. 44.11 g. of the solution containing the soluble zinc salts gave in a 4 dcm. tube at 28° a mean rotation of $+0.46^\circ$; $[\alpha]_D^{28} = +3.33^\circ$. This experiment gave therefore

28.39% d lactic
71.61% l lactic

$\frac{3.33}{7.7} = 43.22\%$ Zn l lactate
56.78% Zn dl lactate.

These percentages of active material are calculated from the constants reported by Pelletier and adapted by E. J. Fisher. Jungfleisch finds values considerably different from these.

(18) Purdie
(19) Purdie
(20) Marckwald's results; see Purdie, 1909, p. 1583.

was not examined under the microscope. A determination of the water of hydration of sample from Group I gave 18.1% whereas Zn. di lactate 3 H₂O demands 18.18%. Because of this excellent agreement it was considered unnecessary at that time to make careful determinations of zinc in the various crops. Later work on the action of silver oxide on bromopropionic acid very probably gives complete information as to zinc content of these zinc salts. As first crop, 3.63 g. of crystalline zinc salts were obtained having all the appearance of zinc lactate.

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The mother liquor from Group I gave, however, a very much larger rotation in the positive direction. 31.36 g. of solution gave in a 4 dm. tube an average rotation of +0.84; $\rho = 1.029$; $[\alpha]_D^{27} = +3.37$. of active material = $\frac{3.37}{1.029} = 3.27$.

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28.39% d lactic
71.61% l lactic

The percentage of active zinc salt present here is undoubtedly slightly higher than the value given since some loss of lactic must occur by volatilization in distilling off the water at reduced pressure. The solvent therefore causes a profound difference in the amount of racemation accompanying the change; but, judging from the sign of the rotation and other properties, ^{it} does not alter the character of the reaction products. Hence although water alone causes inversion, as Walden has shown, ^{this} inversion, which is assumed to take place with various bases and salts in water solution, must be attributed either to the specific action of the metal, as would seem from the fact that we have purposely avoided any trace of freebase in the experiment with silver acetate. It may be attributed even here, however, to the presence of silver ^{oxide} or hydroxide ^{resp.} since silver acetate is continually dissociating in the presence of light, water, etc., into silver oxide or silver hydroxide resp. and acetic acid just as copper acetate, when it acts, for example, as an oxidizing agent on the sugars ⁽²²⁾, dissociates readily in the presence of water giving cupric hydroxide and acetic acid.

Action of potassium acetate in absolute alcohol sol.

In order to disprove Walden's idea ⁽²¹⁾ that the inversion takes place only with silver hydroxide, water and analagous weak bases and never with bases or salts derived from the metals, (e. g. sodium, potassium, etc.), whose action on water gives rise to the strong bases, the following experiment was carried out: 2.52 g. of d brom-propionic acid (1 mol.) ~~was~~ treated with 1.6 g. of potassium acetate in absolute alcohol solution (25cc). The mixture was allowed to stand at room temperature for 25 days in which time only a small amount of potassium bromide had separated out. It was then rinsed into larger flask with 50 c.c. more absolute alcohol and heated in oil bath at 95°-97° under reflux condenser for 3½ hrs. Distilled off alcohol at reduced pressure and extracted the salt residue thoroughly with 100 c.c. dry ether (heating under reflux). The salt residue (2.0 grams) titrated rapidly with ^{N/10} silver nitrate solution, using potassium chromate as indicator, showed the presence of 1.659 g. potassium bromide (85.5% theory). 2.04 g of material were obtained after distilling off ethereal extract finally at reduced pressure. This gum gave $[\alpha]_D^{20} = +20.56^\circ$ in absolute ^{alcohol} solution and was difficultly soluble in water. After complete hydrolysis with water 0.92 g. of stiff gum ~~was~~ recovered, which was converted into zinc salt by boiling for 4 hrs. with an excess of zinc carbonate. By concentrating to a very small volume (3.43 g. of solution) etc., washing finally with 50% alcohol, 0.7575 g. of air-dried zinc salts were obtained. This material lost after drying 100°-115° 0.1781 g. of water (23.5%). All of this anhydrous Zn. salt dissolved in 29.4718 g. of water gave in 4 dcm. tube at 24° a mean rotation of $+0.23^\circ$. $[\alpha]_D^{24} = +2.95^\circ$. The mother liquor from the first crop of zinc salts was evaporated on the boiling water bath to get rid of alcohol. Dissolved then in hot water and ~~filtering~~ ^{after} obtaining a solution of total weight 31.13 g. In 4 dcm. tube at 26° a mean rotation of $+0.16^\circ$ was observed $[\alpha]_D^{26} = +1.86^\circ$. The geometrical mean of the two rotations observed is 2.37° (calc'd for the anhyd. salt) which corresponds to 27.15 % Zn. l lactate, 72.85% Zn dl lactate, or 63.58% l lactate, and 36.42% d lactic. Just as in the previous experiment with silver acetate in absolute ether, a very considerable amount of racemation apparently takes place. We have however ^{just} as conclusive evidence that an inversion occurs with potassium salts as Walden and Fisher have brought forth to prove that it takes place with silver salts.

(2) Walden: Ber.

(23) Walden: Ber.

(22) W. J. H. Am.

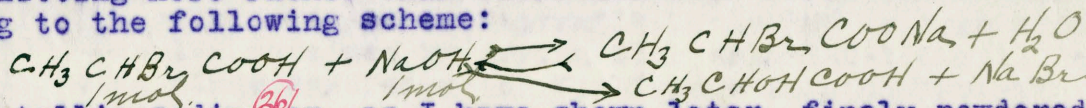
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Reaction of very dilute solution of d bromopropionic acid.
1.5727 g. d bromopropionic ($[\alpha]_D^{29.5} = +24.36^\circ$) dissolved in 88 c.c. of water ^{water} was treated with 0.42 g. (1 mol.) sodium hydroxide (97.1%) dissolved in 312 c.c. of water. This mixture was allowed to stand 22 days to ^{ensure} allow the reaction to become complete. A sweet ethereal odor was observed on opening and the solution gave a decided acid reaction towards litmus. The water was then distilled off at reduced pressure (25-30 mm.) and salt residue thus obtained was thoroughly extracted with 100 c.c. of dry ether. The turbid ether extract gave, by addition of water to the oil obtained after distilling off ether on the water bath, a globule of oil insoluble in water. The total oil thus obtained (0.55 g.) was converted into zinc salt by boiling for 3 hrs. with excess of zinc carbonate. The total zinc salts gave, when dissolved in 32.72 grams of water, in a 4 dcm. tube at 24° a mean rotation of $+0.24^\circ$. $[\alpha]_D^{24} = +2.66^\circ$. $\frac{2.66}{\frac{0.55}{32.72}} = 30.47\%$ molar

Titration of the salt residue rapidly with $\frac{N}{10}$ silver nitrate, using pot. chromate as indicator as in previous experiment, showed 58.5% sodium bromide and 41.50% unchanged sodium brompropionate. The remainder of the water solution of the salt residue, concentrated by distillation at reduced pressure, gave in a 4 dcm. tube at 27° a mean rotation of $+0.25^{\circ}$. $[\alpha]_D^{27} =$ From this data we might also calculate the amount and percentage of unchanged sodium brompropionate. This experiment shows that sodium brompropionate is fairly stable towards cold water and very dilute alkali, which is contrary to the statement given in Beilstein. The velocity of this reaction has been studied by Senter and compared with that of silver nitrate on α brompropionic acid. A repetition of the above experiment, using very dilute potassium or sodium hydroxide in absolute alcohol solution, must show whether the inversion obtained here is due to the action of water on sodium brompropionate to give sodium bromide and free lactic acid or to the action of a trace of sodium hydroxide on free brompropionic acid. The latter action is much more likely since sodium brompropionate is being constantly dissociated in water solution to give sodium hydroxide and the corresponding free acid. Since very dilute sodium hydroxide has much stronger basic reaction than pure water, we should expect the alkali to cause the splitting here rather than water and thus force the action according to the following scheme:



Metallic sodium or, as I have shown later, finely powdered sodium hydroxide when brought in contact with an equivalent amount of α -bromopropionic acid in absolute ether, ~~form~~ give readily and quantitatively the sodium salt of the halogen fatty acid. There is little doubt, therefore, that when the stronger bases act on α -bromopropionic acid, a fairly stable metallic salt is first formed as intermediate product which slowly splits by means of water, alkali, acid, heat, etc. When the bromo acid is treated with more concentrated aqueous solutions of sodium or potassium hydroxide we should naturally expect to obtain (especially by boiling) sodium bromide and lactic acid or sodium lactate resp. in a perfectly normal manner. With silver hydroxide, water, etc. no such salt is formed, the action must take place as result of splitting the free acid.

The previous work just reported, was done at the Kent Chemical Laboratory in the summer of 1908 and, if we assume, as everyone else has assumed, that lactic acid is the ultimate product formed and interpret the amount of racemation from this point of view, as I have done, it may be considered a complete and important contribution to our knowledge of the "Walden Inversion".

(24)

(26) Bischoff Walden: Ber. 26, 263.

25 Lenter: { Trans. C. Ch. Soc. 9, 460
Proc. C. Ch. Soc. 11, 908
4, 5, C. Ch. Soc. Rec. 1909, p. 1827

27 July. Ann. 200, 87.

Action of very dilute sodium hydroxide (0.1%) in water solution on bromopropionic acid.

1.5327 g. of bromopropionic acid was treated with 0.42 g. (1 mol.) sodium hydroxide (97.1%) dissolved in 312 c.c. of water. This mixture was allowed to stand 22 days to allow the reaction to become complete. A sweet etherial odor was observed on opening and the solution gave a decided acid reaction towards litmus. The water was then distilled off at reduced pressure (25-30 mm.) and salt residue thus obtained was thoroughly extracted with 100 c.c. of dry ether. The turbid ether extract gave by addition of water to the oil obtained after distilling off ether on the water bath a globule of oil insoluble in water. The total oil thus obtained (0.55 g.) was converted into zinc salt by boiling for 3 hrs. with excess of zinc carbonate. The total zinc salts gave, when dissolved in 32.72 grams of water in a 4 dm. tube at 24° a mean rotation of $+0.25^\circ$.

Titration of the salt residue rapidly with silver nitrate using pot. chromate as indicator as in previous experiment showed 58.5% sodium bromide and 41.50 unchanged sodium bromopropionate. The remainder of the water solution of the salt residue concentrated by distillation at reduced pressure gave in a 4 dm. tube at 27° a mean rotation of $+0.25^\circ$. From this data we might also calculate the amount and percentage of unchanged sodium bromopropionate in the fairly stable towards cold water and very dilute alkali, which is contrary to the statement given in Belletain. The velocity of this reaction has been studied by Jenter and compared with that of silver nitrate on bromopropionic acid. A repetition of the above experiment, using very dilute potassium or sodium hydroxide in absolute alcohol solution, must show whether the inversion obtained here is due to the action of water on sodium bromopropionate to give sodium bromide and free lactic acid or to the action of a trace of sodium hydroxide on free bromopropionic acid. The latter action is much more likely since sodium bromopropionate is being constantly dissociated in water solution to give sodium hydroxide and the corresponding free acid. Since very dilute sodium hydroxide has much stronger basic reaction than pure water we should expect the alkali to cause the splitting here rather than water and thus force the action according to the following scheme:

Metallic sodium or, as I have shown later, finely powdered sodium hydroxide when brought in contact with an equivalent amount of bromopropionic acid in absolute ether form give readily and quantitatively the sodium salt of the halogen fatty acid. There is little doubt, therefore, that when the stronger bases act on bromopropionic acid a fairly stable metallic salt is first formed as intermediate product which slowly splits by means of water, alkali, acid, heat, etc. When the brom. acid is treated with more concentrated aqueous solutions of sodium or potassium hydroxide we should naturally expect to obtain especially by boiling sodium bromide and lactic acid or sodium lactate resp. in a perfectly normal manner. With silver hydroxide, water, etc. no such salt is formed, the action must take place as result of splitting the free acid.

The previous work just reported, was done at the Kent Chemical Laboratory in the summer of 1908 and, if we assume, as everyone else has assumed, that lactic acid is the ultimate product formed and interpret the amount of racemization from this point of view as I have done, it may be considered a complete and important contribution to our knowledge of the "Walden Inversion".

Is lactic acid the only substitution product formed by the action of silver oxide in water solution on α brompropionic acid and, if so, are any intermediate products formed when an inversion occurs?

?
!!
vague
The acid gum, obtained by hydrolysis when d brompropionic was treated with silver acetate in absolute ether, possessed very little mobility and titrated only 50% as a free acid - it gave, however, a difficultly soluble crystalline zinc salt having all the appearance and properties of zinc lactate. Further experiments were made, therefore, during the summer and fall just past to prove that this hydrolyzed gum was either totally different from lactic acid or was an intermediate condensation product of lactone character which would give lactic only by hydrolysis with strong alkali. This phase of the work is nearing completion but in view of the fact that it must be interrupted for several months, it was deemed advisable to submit here a complete report of the results already obtained although final data is unfortunately not at hand. Careful examination of the acid gum, obtained by hydrolysis, shows properties entirely foreign to those of ordinary lactic acid. Can simple boiling with zinc carbonate convert this material into the zinc salt of lactic acid where prolonged boiling with water or even with sodium carbonate has undoubtedly failed to give lactic acid or sodium lactate resp? We must have something more upon which to base our statement that an absolute turning about of the configuration of a compound takes place as the result of a simple change than the fact that the zinc salt of lactic happens to rotate opposite to the free acid, and happens to give figures for water of hydration, percentage of zinc and solubility in water very similar to those observed for zinc salt of our crude hydrolyzed acid gum.

It is... doubtful
if any
lactic is
actually formed!
would be ridiculous to publish
Further experiments will be carried out along the following lines: The acid material (obtained by the action of silver oxide on dl brompropionic acid in water sol., recovered from the brucin, zinc and phenyl hydrazine salts as well as from the product obtained by heating the crude gum with 33% sodium hydroxide for 8 hrs., will be heated in water solution to 120° for six hours to determine whether the same stiff gum soluble in water, titrating only 50% as free acid is recovered. Results obtained by drying zinc salt 140-160° will be carefully noted since, according to Wislicenus, zinc dl lactate, after drying at 100°, can be heated to 200° without decomposition. Molecular weight determinations by the freezing and boiling point methods will be tried with the crude gum obtained from the actions in water and absolute ether solution resp. to determine from the crude acid product whether a condensation product is present. Further attempts will also be made to prepare pure lactic ethyl ester. Very little remains to be done to have complete information on this whole subject; the work already done indicates very strongly that a huge blunder has been made - if it turns out, however, that the zinc salt obtained is really zinc lactate, as has been assumed on all sides, we have at any rate isolated here the intermediate product which is responsible for the inversion taking place when mild bases are used to replace the halogen in halogen fatty acids. ?
!!

(?)
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Another point of difference, not previously mentioned, was that the crude (acylated?) product, obtained from the action of silver acetate on d brompropionic acid in absolute ether, was, before hydrolysis, almost completely insoluble in water. Acetyl lactic (properly α acetyl propionic acid), as I have found, dissolves readily in water, both crystallized lactic and the body previously described as polylactyl lactic, although insoluble in water, give by hydroly-

Lactic acid the only anhydride product formed by the action of silver oxide in water solution on bromopropionic acid and, if so, are any intermediate products formed when an inversion occurs?

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sis with water mobile syrupy lactic acid.

6 Acylation of dl lactic acid with acetic anhydride.

The crude acylated gum (33.0 g.), obtained by treating dl lactic (25.5g.) with acetic anhydride, dissolves readily in water; and all but one very small fraction obtained by fractional distillation dissolve with the greatest ease in water—even that fraction dissolves in an equal volume of water by shaking for two-three minutes. The main reaction product is undoubtedly acetyl lactic although it does not boil constantly. Even fractionating several times, no constant boiling material could be obtained. But by allowing the higher boiling fraction, 4.76 g., 155-175° mainly 162-168° (18mm.), to stand for several hours in water solution, distilling off water at reduced pressure and again fractionating at reduced pressure, it gives 4.68 g. Boiling constantly 140-148° mainly 140-145° (18mm.) for acetyl lactic. 6.7 g. of lower boiling fraction [146-160° mainly 149-151° (23mm.)], treated similarly with water etc., gave 5.84 g. boiling constantly 142-143° (22mm.). 4.0 g. of another fraction boiling at 138-158° (19mm.), treated similarly with water etc., gave 3.55 g. boiling nicely without decomposition at 138-145° (21mm.) mainly 142-144°. All of these fractions were easily soluble in water. I have observed also that acetyl lactic can be shaken out with dilute soda from ether solution and recovered without appreciable decomposition. To make pure acetyl lactic, free from traces of acetic and lactic acid, this method may be of considerable use. 5.84 g. of acetyl lactic [rectified with water as above and boiling 142-143° (22mm.)], by treatment with soda, neutralizing the soda solution with a slight excess of standard dilute hydrochloric acid, distillation of water at reduced pressure, extraction with dry ether, etc., gave 4.48 g. unchanged acetyl lactic, of syrupy consistency similar to lactic acid, boiling constantly 138° (18mm.). My preparation has therefore all the properties of acetyl lactic, as prepared by Anschütz and Bertrand from dl lactic acid and acetyl chloride, who found that it melted at 57-60°, boiled at 127° (11mm.) and was readily soluble in water. The boiling point seems to agree however, more nearly with that observed by Julius Rath ⁽³⁰⁾ who gives it as 134° (15mm.).

Just how the water causes such a transformation, as noted above, is hard to explain since very little acid material is swept over in the volatile distillate when the water added is distilled off at reduced pressure—this negates the idea that acetyl lactic acetate is formed as the first product. That acetyl lactic may form a higher boiling condensation product, just as lactic does, which readily gives in the presence of water free acetyl lactic is quite plausible. It is not out of the question also that, in the presence of acetic anhydride which acts as a strong dehydrating agent, lactyl lactic is formed from dl lactic at a lower temperature (80-100°) than is required to transform dl lactic when alone (120-140°)—the lactyl lactic, thus formed, would then be ultimately transformed into polylactyl lactic (insoluble in water). That such an intermediate formation of lactyl lactic does not take place in the presence of acetic anhydride is excluded by the fact that the crude acylated gum dissolves readily in water and gives by decomposition with water practically nothing but pure acetyl lactic. There was also obtained a very small amount of oil (4.1 g.) boiling above 180° (20mm.) and 13.5 g. non-volatile thick gum, partly insoluble in water, as a result of fractionating the 33.0 g. crude acylated gum. The fraction, boiling above 180°, is the one which requires several minutes shaking to become soluble in water. Both of these high boiling fractions, which might be attributed to the second action, could

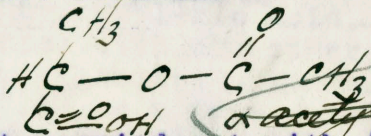
(29) Anschütz & Bertrand: Ber. 34, 3971. (30) Julius Rath: Centralblatt, 1908, I, p. 717.

The crude acylated gum (33.0 g.) obtained by treating di-
 lactic (25.5g.) with acetic anhydride dissolves readily in water, and
 all but one very small fraction obtained by fractional distillation
 dissolves with the greatest ease in water-even that fraction dis-
 solves in an equal volume of water by shaking for two-three minutes.
 The main reaction product is undoubtedly acetyl lactic although it
 does not boil constantly. Even refractionating several times no
 constant boiling material could be obtained. But by allowing the
 higher boiling fraction 4.76 g. (155-175 mainly 162-168 (18mm.))
 to stand for several hours in water solution, distilling off water
 at reduced pressure and again refractionating at reduced pressure,
 it gives 4.68 g. boiling constantly 140-148 mainly 140-145 (18mm.))
 for acetyl lactic. 6.7 g. of lower boiling fraction (146-160
 mainly 149-151 (23mm.)) treated similarly with water etc., gave
 5.84 g. boiling constantly 142-143 (23mm.)) 4.0 g. of another
 fraction boiling at 138-158 (19mm.)) treated similarly with water
 etc. gave 3.55 g. boiling nicely without decomposition at 138-145
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 out with dilute soda from ether solution and recovered without
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 consistency similar to lactic acid boiling constantly 138 (18mm.)).
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 presence of acetic anhydride which acts as a strong dehydrating
 agent, lactic acid is formed from di lactic at a lower temperature
 (80-100) than is required to transform di lactic when alone (120-
 140)- the lactic acid thus formed would then be ultimately
 transformed into poly lactic lactic insoluble in water. That such
 an intermediate formation of lactic acid does not take place in
 the presence of acetic anhydride is excluded by the fact that the
 crude acylated gum dissolves readily in water and gives by decom-
 position with water practically nothing but pure acetyl lactic.
 There was obtained a very amount of oil (4.1 g.) boiling above 180
 (20mm.)) and (3.5 g.) non-volatile thick gum, partly insoluble in
 water, as a result of fractionating the 33.0 g. crude acylated gum.
 The fraction boiling above 180 is the one which requires several
 minutes shaking to become soluble in water. Both of these high boil-
 ing fractions, which might be attributed to the second action, could

(9).

also be accounted for by the amount of lactyl lactic ^{originally} present in the lactic ^{acid used} as a result of standing. If acetic anhydride replaces the alcohol hydroxyl (OH) group in lactic acid, we should expect acylated lactic to have formula:



An experiment carried out with (1 mol.) dl brompropionic acid (10.0g) and (1½ mols.) silver acetate (17.72g.) in absolute ether ^{how much?} gave after distilling off ethereal filtrate with Glynsky 6.55 g. crude gum and 0.4g. acetic acid. This 6.55g., treated with 13c.c. of cold water and shaken for 10-15 minutes, gave 3.6g. stiff gum ^{insoluble} in water, 2.85g. soluble. The insoluble gum, shaken out ^{from sol?} with soda from ether solution, gave 3.25g. stiff acid gum. The soluble gum, as proved by a later experiment, gave by distillation at reduced pressure with much decomposition only about 0.6g. of material boiling 140-152° (19mm.) for acetyl lactic: the main portion boiled ^{from} 152-190° (19mm.) mainly 170-180°. Having established that the main reaction product in this experiment was not acylated lactic acid, as we should expect by simple metalepsis, and that apparently very little free acetic acid was formed, nothing further was done with this material. It is a question, however, whether or not considerably more acetic acid was actually present than this experiment showed where, after distilling off the dry ether carefully from a water-bath using Glynsky, the acid material was heated for a long time at the temperature of the boiling water bath (20mm.) to drive over the acetic. The following experiment will serve as an illustration: 25.5g. dl lactic, treated in the usual manner with acetic anhydride, gave by distillation as above at 100° (20mm.) 36.05g. crude acylated gum. 32.5g. of this material, heated further over metal bath 140-160°, gave 2.81g. of acetic acid and acetic anhydride of B.pt 64-72° (18-20mm.) - odor and mobility of acetic acid. Thus it is seen that very considerable amount of acetic acid always remains sticking to the crude acylated gum which can only be removed by heating higher 140-150° (20mm.) or by sweeping over ^{with} water in case the acylated gum does not split readily with water, as is the case with acetyl lactic. ³¹

Action of ^{dl} silver oxide on dl brompropionic acid in abs. ether.

In order to study more carefully the nature of the acid gum obtained by hydrolysis, it was deemed advisable ~~for simplicity~~ to carry out the experiment in absolute ether not as above with silver acetate but with oxide of silver ^{and dl brompropionic acid (10g.)}.

After a short period of induction, as in the previous experiment with silver acetate, 7.68g. silver oxide (½ mol.) pulls off hydrogen bromide from 10.13 dl brompropionic acid (1 mol.) dissolved in dry ether giving considerable heat evolution and to all appearances a complete separation of silver bromide inside of one hour. Examination of the silver residue, obtained by filtration, showed no metallic silver which indicated that no appreciable amount of oxidation had taken place. 5.6g. of gum were obtained from the ethereal filtrate. This gum, by standing for a short time, became altogether non-mobile and, to all appearances, was the same as that obtained by the action of silver acetate on dl brompropionic as well as dl brompropionic in absolute ether. This gum (200c.c. ether) was shaken out with soda (100c.c. 5% soda solution) from ether.

(31)

(9)
also be accounted for by the amount of lactic acid present in the
lactic as a result of standing. If acetic anhydride replaces the
alcohol hydroxyl (OH) group in lactic acid, we should expect acy-
lated lactic to have formula:

An experiment carried out with (1 mol.) di bromopropionic acid
(10.0g) and (1/2 mole) silver acetate (17.72g) in absolute ether
gave after distilling off etheral filtrate with Glymk 6.55 g.
crude gum and 0.4g. acetic acid. This 6.55g. treated with 130.c.
of cold water and shaken for 10-15 minutes, gave 3.6g. stiff gum in-
soluble in water, 2.85g. soluble. The insoluble gum, shaken out
with soda from ether solution, gave 3.25g. stiff acid gum. The sol-
uble gum, as proved by a later experiment, gave by distillation re-
duced pressure with much decomposition only about 0.6g. of material
boiling 14-152 (19mm.) (for acetyl lactic: the main portion boiled
152-190 (19mm.) mainly 170-180. Having established that the main
reaction product in this experiment was not acylated lactic acid,
as we should expect by simple metal salts, and that apparently very
little free acetic acid was formed, nothing further was done with
this material. It is a question, however, whether or not consid-
erably more acetic acid was actually present than this experiment
showed where, after distilling off the dry ether carefully from a
water-bath using Glymk, the acid material was heated for a long
time at the temperature of the boiling water bath (20mm.) to drive
over the acetic. The following experiment will serve as an illus-
tration: 25.5g. di lactic treated in the usual manner with acetic
anhydride gave by distillation as above at 100(20mm.) 36.05g. crude
acylated gum. 32.5g. of this material heated further over metal
bath 140-160 gave 2.81g. of acetic acid and acetic anhydride of B.pt
64-72 (18-20mm.) -odor and mobility of acetic acid. Thus it is seen
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by the action of silver acetate on di bromopropionic as well as di
bromopropionic in absolute ether. This gum (200c.c. ether) was shaken
out with soda (100c.c. soda solution) from ether

solution (200 c.c. ether). The slightly alkaline soda solution was heated at 100° for 5½ hrs; then treated with slight excess of standard dilute hydrochloric acid, distilled off water at reduced pressure, extracted with dry ether etc. - there was obtained thus 4.25 g. of a gum which had only very slight mobility and which titrated only 47.0% as a free acid. 13.1 g. of lactyl lactic, treated in a similar way with soda and heated in alkaline solutions at 100° for six hours etc., gave 2.55 g. of fairly mobile gum which titrated 78.5% as a free acid. 10.35 g. crude lactyl lactic, prepared by heating dl lactic 120°-140° for 3 hrs., dissolved readily in 30.5 c.c. of acetic anhydride. When this mixture was heated 7½ hrs. 80°-90°, it gave, after distilling off acetic acid and excess of acetic anhydride at 25 mm. (heating finally to 100° for ½ hr.), 13.0 g. crude acylated product. By treatment with 13 c.c. cold water, this material gave 7.05 g. gum insoluble in water and 4.85 g. soluble in water (free from acetic). 4.9 g. of the insoluble gum gave, after complete hydrolysis with water, 4.95 g. mobile oil which titrated 89.1% as a free acid and 94.5% after standing in water solution for 64 hrs.

Action of silver oxide in water solution on dl brompropionic acid.

Another experiment with (½ mol.) silver oxide (7.68) and (1 mol.) dl brompropionic (10.2 g.) in 100 c.c. water gave, after short period of induction (10-15 minutes), rapid separation of silver bromide together with considerable heat evolution which was ^{checked} by means of ice-water-complete reaction inside of one hour. No metallic silver was found on examination of the silver residue with 40% potassium cyanide solution. By distilling off the aqueous filtrate at reduced pressure, a fairly mobile acid gum (4.95 g.) was obtained which was completely soluble in water. This gum was shaken out with 100 c.c. 5% soda solution from ether (200 c.c.); the soda solution was then heated at 100° for 5½ hrs. By treating with very slight excess of standard dilute hydrochloric acid, distilling off water at reduced pressure, extraction with dry ether, etc., 3.65 g. of a fairly stiff gum was obtained which titrated only 55.0% as a free acid. The remainder of the water solution, as well as that left from the experiment with silver oxide in absolute ether solution, was converted into zinc salts by boiling with excess of zinc carbonate and gave difficultly soluble, crystalline, zinc salts which have properties similar in every respect to those of zinc lactate. Analysis of two crops obtained from the experiment with silver oxide in water solution gave

	Crop 1.	Crop 2.	Calc'd value
% Water of hydration	17.85	18.13	18.16 (Zn. dl lactate + 3H ₂ O)
% Zn. in anhyd. salt	26.96	26.39	26.89 (Zn. dl lactate)

3.0 g. of gum gave thus by treatment with zinc carbonate etc. 3.69 g. (air-dry) first crop, 0.7423 g. (air-dry) second crop, and only 0.30 g. remained. Both crops, as analyzed, contained a trace of basic zinc salt insoluble even in hot water and hence the above results are a shade high for percentage of zinc. 2.38 g. of anhydrous zinc salt (of crop I), left from analysis, required 200 c.c. of cold water for complete solution by shaking violently at frequent intervals during three hours. It is to be noted that the percentage of zinc is low rather

solution (2000 c.c. ether). The slightly alkaline soda solution was heated at 100° for 3½ hrs; then treated with slight excess of standard dilute hydrochloric acid, distilled off water at reduced pressure, extracted with dry ether etc. - there was obtained thus 4.25 g. of a gum which had only very slight mobility and which titrated only 47.0% as a free acid. 3.1 g. of lactic lactic, treated in a similar way with soda and heated in alkaline solutions at 100° for six hours etc. gave 2.55 g. of fairly mobile gum which titrated 78.5% as a free acid. 10.35 g. of crude lactic lactic, prepared by heating dl lactic 120-140° for 3 hrs., dissolved readily in 30.5 c.c. of acetic anhydride. When this mixture was heated 7½ hrs. 80-90° it gave, after distilling off acetic acid and excess of acetic anhydride at 25 mm. (heating finally to 100° for ½ hr.), 13.0 g. crude acetylated product. By treatment with 13 c.c. cold water, this material gave 7.05 g. gum insoluble in water and 4.85 g. soluble in water (free from acetic). 4.9 g. of the insoluble gum gave, after complete hydrolysis with water, 4.95 g. mobile oil which titrated 89.1% as a free acid and 94.5% after standing in water solution for 64 hrs.

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Calc'd value Crop 2. Crop 1.

% Zn. in anhyd. salt	% Water of hydration		
26.96	17.85	18.13	18.16 (Zn. dl lactate)
26.96	26.39	26.89	26.89 (Zn. dl lactate)

3.0 g. of gum gave thus by treatment with zinc carbonate etc. 3.65 g. first crop, 0.7423 g. as second crop, and only 0.30 g. remained. Both crops, as analyzed, contained a trace of basic zinc salt in-soluble even in hot water and hence the above results are a shade high for percentage of zinc. 2.38 g. of anhydrous zinc salt (of crop 1) left from analysis required 200 c.c. of cold water for complete solution by shaking violently at frequent intervals during three hours. It is to be noted that the percentage of zinc is low rather

high which indicates very strongly that acrylic acid, dilactic acid (as well as other similar condensation products) are not present. When the zinc salts are dried, however, at 150° in place of 100° it may turn out that the percentage of zinc will run far above that demanded for zinc lactate. After the zinc was precipitated in boiling solution with hydrogen sulphide, 1.6 g. of fairly mobile acid gum were obtained which on treatment with an equal volume of phenyl hydrazine and absolute alcohol crystallized completely in fifteen minutes. This is very strong evidence that the acid product is homogeneous. After filtering off, washing well with ether and drying on clay plate 2.02 g. of crude phenyl hydrazine compound were obtained melting at 105° - 115° . When 5c.c. dl lactic (88.1%) or the product (obtained after heating dl lactic in water solution at 120° for six hours and subsequently distilling off water at reduced pressure), is treated in a similar manner with an equal volume of phenyl hydrazine and absolute alcohol, there was a very considerable formation of crude phenyl hydrazine ^{salt} compound in fifteen minutes. After filtering, washing well with ether and drying on clay plate, the crude salt weighed 9.12 g. and melted at 100° - 114° with gas evolution. An attempt to recrystallize the crude salt from hot acetic ethyl ester failed in as much as considerable loss of material took place. The experiment showed that only about one quarter of the material is thus recovered and the melting point is not improved. Simple washing with ether gives, however, a product in almost quantitative yield which has only a very slight yellow color. The phenyl hydrazine derivative may therefore be of considerable use for identification of pure lactic acid- to separate lactic acid from a mixture, however, the phenyl hydrazine derivative will undoubtedly be of no more use than it is for the separation of other similar oxy acids derived from the sugars, as Nef has repeatedly found. (32)

In order to make a more complete study of the action of silver oxide on brompropionic acid, two more experiments were carried out under exactly the same conditions, one in water solution, and the other in absolute ether. 10.2 g. dl brompropionic acid (1 mol.) treated with 7.73 g. silver oxide ($\frac{1}{2}$ mol) in 100 c.c. absolute ether gave 5.2 g. crude acid gum which becomes absolutely non-mobile when cold. 4.85 g. of this material, shaken for ten minutes with 9.7 c.c. of water, gave 3.65 g. gum insoluble in water and only 0.95 g. that ^{was} soluble. And what is more, the soluble gum here titrated only 38.5% as a free acid. The 3.6 g. insoluble gum, hydrolyzed twice with five parts of water at 110° - 120° , gave an acid solution which when cold, titrated 97.0% as a free acid. After distilling off the remainder of the water solution at reduced pressure (25 mm.), 3.2 g. of stiff gum were obtained which titrated only 53.3% as a free acid. 0.85 g. of this material, heated in water solution with zinc carbonate, gave a difficultly soluble crystalline zinc salt having all the properties of zinc lactate. 5c.c. dl lactic (88.1% Kahlbaum product) titrated 80.2% as a free acid; when another 5c.c. was dissolved in 50 c.c. of water, ^{gave} after distilling off water at reduced pressure, ^{gave} 5.1 g. of mobile syrup which titrated 81.5% as a free acid. when 11.5c.c. dl lactic (88.1% Kahlbaum product) is heated for four hrs. 90° - 100° (20mm.), some ^{lactic} anhydride formation takes place but it takes place only very slowly and to a very slight extent.

In another experiment 11.65 g. dl lactic (88.1% Kahl.prod.) was heated for 6 hrs. with 50 c.c. water in an oil bath kept at 110° - 120° . The solution, thus obtained, when cold titrated 98.6% as a free acid. The remainder of the solution gave, after again distilling off

after distilling off water at reduced pressure, 10.0 g mobile oil (was obtained) which titrated 95.7% as a free acid.

(32) Nef: Article to be published soon in Liebigs Annalen.

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cation of pure lactic acid - to separate lactic acid from a mixture,
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six hours and subsequently distilling off water at reduced pressure,
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grams were obtained which on treatment with an equal volume of phenyl
ing solution with hydrogen sulphide, 1.6 g. of fairly mobile acid
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In order to make a more complete study of the action of silver oxide on bromopropionic acid, two more experiments were carried out under exactly the same conditions, one in water solution, and the other in absolute ether. 10.2 g. of bromopropionic acid (1 mol.) treated with 7.73 g. silver oxide ($\frac{1}{2}$ mol) in 100 c.c. absolute ether gave 5.2 g. crude acid gum which becomes absolutely non-mobile when cold. 4.85 g. of this material, shaken for ten min. with 9.7 c.c. of water, gave 3.65 g. gum insoluble in water and only 0.95 g. that is soluble. And what is more, the soluble gum here titrated twice 38.5% as a free acid. The 3.6 g. insoluble gum, hydrolyzed twice with five parts of water at 110-120°, gave an acid solution which when cold, titrated 97.0% as a free acid. After distilling off the remainder of the water solution at reduced pressure (25 mm.), 3.2 g. of stiff gum were obtained which titrated only 53.3% as a free acid. 0.85 g. of this material heated in water solution with zinc carbonate, gave a difficultly soluble crystalline zinc salt having all the properties of zinc lactate. 50 c.c. of lactate (88.1% Karlbaum product) titrated 80.2% as a free acid; when another 50 c.c. was dissolved in 50 c.c. of water and after distilling off water at reduced pressure gave 5.1 g. of mobile syrup which titrated 81.5% as a free acid. 11.50 c.c. of lactate (88.1% Karlbaum product), heated for four hrs. 90-100° (20 mm.) some little anhydride formation takes place but it takes place only very slowly and to a very slight extent. In another experiment 11.65 g. of lactate (88.1% Karlbaum prod.) was heated for 6 hrs. with 50 c.c. water in an oil bath kept at 110-120°. The solution, thus obtained when cold titrated 98.6% as a free acid. The remainder of the solution gave, after again distilling off

water at reduced pressure, 9.45 g. mobile oil. By heating with 3 pts. of acetic anhydride 80°-100° for 7 hrs. and distilling off acetic acid and excess of acetic anhydride at reduced pressure (20mm.) heating finally to 100 for $\frac{1}{2}$ hr., 12.9 g. mobile acylated oil were obtained. This crude oil dissolves completely by shaking for five minutes with 25c.c. cold water. By sweeping over ~~the~~ water and remaining acetic acid at reduced pressure, 12.45 g. of acylated gum were left. This gave by fractional distillation: @ 6.83 g. of B. pt. 133°-137° (18mm.) mainly 134°-6° acetyl lactic, @ 4.0 g. boiling 137°-180° (18mm.) mainly 140°-160°, @ 0.4 g. (pract. nothing) higher boiling was left in distilling flask. This experiment with dl lactic shows that a decided gain (31.75%) in wt. takes place when heated with acetic anhydride which indicates ~~that~~ a normal acylation has taken place. The acylated product is completely soluble in water, and gives practically nothing but acetyl lactic and condensed acetyl lactic. If the acylated gum had been allowed to stand several hours in water solution, considerable more free acetyl lactic boiling 134°-136° (18mm.) would undoubtedly have been obtained.

To revert now to the experiment with silver oxide in absolute ether solution. After sampling out ~~how much~~ for the experiment with zinc carbonate, the remainder of the water solution, distilled off at reduced pressure, gave 2.3 g. of very stiff gum almost non-mobile (which according to the previous titration contained only about 50% of free acid). This material was heated for 7 hrs. 80°-90° with 3 pts of acetic anhydride and gave after distillation of acetic acid and excess of acetic anhydride at reduced pressure, 2.65 g. of mobile gum. This gave, by shaking for ten minutes with two parts of cold water, 1.35 g. gum insoluble in water and 1.15 g. soluble. The oil, soluble in water, again acylated, gave 1.27 g. crude acylated gum which on shaking with two parts of water for ten minutes gave 0.9g. insoluble and left thus finally only 0.37 g. material soluble in water. The material (2.25 g. $\frac{1}{2}$ total), insoluble in water, was hydrolyzed twice with water in oil bath kept at 110°-120° and was then heated in water solution with 10.0 g. brucin. The results of examination of the brucin salts will be best considered a little later.

Action of silver oxide on dl brompropionic acid in water solution (Expt. 2).

10.0g dl brompropionic acid treated with 7.57 6. silver oxide in 200c.c. water and allowed to stand for twenty hours, gave a solution of total volume 345 c.c. This solution titrated (1/14 of sol. used for titration) only 75% as a free acid. After distilling water at reduced pressure, and extraction with ether ~~this material~~ gave 5.4 g. mobile gum which titrated (1/10 of ether sol. used for titration). 16% ^{as a free acid} ↑ The anhydride or lactone formed here does not seem to open readily in cold water and hence the amount of free acid was presumably not increased much by standing 20 hrs. in cold water over that formed as direct reaction product. By distilling off ether finally at reduced pressure, 4.6 g. mobile gum (of mobility just like that of lactic) were obtained. 4.25 g. of this material were heated for 6 $\frac{1}{2}$ hrs. with 10 pts. of water under reflux condenser ~~in oil bath~~ kept at 110°-120°. After distilling off water at reduced pressure, heating finally 80°-90° for $\frac{1}{2}$ hr., 3.88 g. of gum were obtained which possessed very little mobility. This material titrated only 55% as a free acid. By distilling off the remainder of the solution at reduced pressure, 3.3g stiff gum were recovered which became much more mo-

water at reduced pressure, 9.45 g. mobile oil. By heating with 3 pts. of acetic anhydride 80-100° for 7 hrs. and distilling off acetic acid and excess of acetic anhydride at reduced pressure (20mm.) heating finally to 100° for 1 hr. 12.9 g. mobile acetylated oil were obtained. This crude oil dissolves completely by shaking for five minutes with 250 c.c. cold water. By sweeping over water and remaining acetic acid at reduced pressure, 12.45 g. of acetylated gum were left. This gave by fractional distillation: 6.83 g. of B. pt. 133-137° (18mm.) mainly 134-6-acetyl lactate 4.0 g. boiling 137-180° (18mm.) mainly 140-180° 0.4 g. (prec. nothing) higher boiling was left in distilling flask. This experiment with dl lactate shows that a decided gain (31.75%) in wt. takes place when heated with acetic anhydride which indicates a normal acylation has taken place. The acetylated product is completely soluble in water, and gives practically nothing but acetyl lactate and condensed acetyl lactate. If the acetylated gum had been allowed to stand several hours in water solution, considerable more free acetyl lactate boiling 134-138° (18mm.) would undoubtedly have been obtained.

To revert now to the experiment with silver oxide in absolute ether solution. After sampling out how much for the experiment with zinc carbonate, the remainder of the water solution, distilled off at reduced pressure, gave 2.3 g. of very stiff gum almost non-mobile (which according to the previous titration contained only about 50% of free acid). This material was heated for 7 hrs. 80-90° with 3 pts of acetic anhydride and gave after distillation of acetic acid and excess of acetic anhydride at reduced pressure, 2.65 g. of mobile gum. This gave by shaking for ten minutes with two parts of cold water, 1.35 g. gum insoluble in water and 1.15 g. soluble. The oil, soluble in water, again acetylated, gave 1.27 g. crude acetylated gum which on shaking with two parts of water for ten minutes gave 0.9 g. insoluble and left thus finally only 0.37 g. material soluble in water. The material (2.25 g.) total insoluble in water was hydrolyzed twice with water in oil bath kept 110-120° and was then heated in water solution with 10.0 g. brucin. The results of examination of the brucin salts will be best considered a little later.

Action of silver oxide on dl prompropionic acid in water so-

lution (Expt. 2).

10.0 g. dl prompropionic acid treated with 7.57 g. silver oxide in 200 c.c. water and allowed to stand for twenty hours, gave a solution of total volume 245 c.c. This solution titrated (1/14 of sol. used for titration) only 75% as a free acid. After distilling water at reduced pressure, and extraction with ether gave 5.4 g. mobile gum which titrated (1/10 of ether sol. used for titration). The anhydride or lactone formed here does not seem to open readily in cold water and hence the amount of free acid was presumably not increased much by standing 20 hrs. in cold water over that formed as direct reaction product. By distilling off ether finally at reduced pressure, 4.6 g. mobile gum (of mobility just like that of lactate) were obtained. 4.25 g. of this material were heated for 6 hrs. with 10 pts. of water under reflux condenser and oil bath kept at 110-120°. After distilling off water at reduced pressure, heating finally 80-90° for 3.88 g. of gum were obtained which possessed very little mobility. This material titrated only 55% as a free acid. By distilling off the remainder of the solution at reduced pressure, 3.3 g. stiff gum were recovered which became much more

bile on standing several days. This material was then heated with 3 pts. of acetic anhydride 80-90° 7 hrs., and gave, after distilling off acetic acid and excess of acetic anhydride at reduced pressure (20mm.) [heating finally at 100° $\frac{1}{2}$ hr.], 4.00 g. mobile gum smelling strongly of acetic anhydride. On shaking this gum for ten minutes with 2 pts. of water, it gave 2.95 g. gum insoluble and 0.95g. soluble in water. The 0.95g. soluble in water, again treated with acetic anhydride as before, gave, after distillation at reduced pressure (heating to 100°), 1.05g. residue which, by shaking with 2 pts. of water for ten minutes, gave 0.82g. insoluble in water, leaving thus finally only 0.23g. material soluble in water. The 2.95g. insoluble gum gave by hydrolysis and subsequent distillation of water at reduced pressure 2.73g. stiff gum; $\frac{5}{6}$ of the solution (cont. 3.1 g. acid) obtained by hydrolysis of the ^{total} insoluble gums, were heated with 13.6 g. brucin. Before discussing the results obtained with brucin, it will be of interest to consider several other experiments. If the hydrolyzed acid product obtained by the action of silver oxide on dl brompropionic acid in water or absolute ether solution were a mobile oil, titrated over 90% as a free acid and gave on treatment with acetic anhydride, in place of a gum insoluble in water, an acylated gum having all the properties of acylated lactic, we could easily formulate both of these actions in terms of lactic, lactyl lactic, and condensed or polylactyl lactic (insoluble in water). Although it gives to all appearances the same zinc salt and phenyl hydrazine compound as lactic, the ~~hydrolyzed~~ ^{by hydrolysis} acid obtained here has properties totally different from the mobile syrupy lactic acid.

Ag carbonate + dl brompropionic acid in water solution

In order to repeat exactly the experiment of Fisher and Walden, ⁽³³⁾ 5.1g. dl brompropionic acid (1 mol.) were treated in 52c.c. water with 4.6g. dry silver carbonate ($\frac{1}{2}$ mol.) Fisher and Walden used an excess of silver carbonate over that required to remove all the halogen and therefore were compelled to decompose subsequently the silver salts obtained. Lively effervescence of carbon dioxide and rapid separation of silver bromide took place—action was apparently complete in one hour. The mixture was allowed to stand, however, 29 hrs. to be sure of complete reaction. No metallic silver was found in the silver residue. The filtrate, heated for seven hours 110°-120° under reflux condenser, gave, after distilling off water at reduced pressure (20mm.) [heating finally 80°-90° $\frac{1}{2}$ hr.], gave 2.05 g. stiff gum which titrated only 59.9% as a free acid. After distilling off water at reduced pressure (20mm.) [heating finally 80°-90° $\frac{1}{2}$ hr.], gave 1.58 g. stiff gum from which nothing crystallized out on standing for two months. (Absence of dilactic). On treatment with an equal volume of phenyl hydrazine and absolute alcohol, only 1.19 g. phenyl hydrazine compound were obtained (well washed with ether and dried on clay plate) of m. pt. 95°-102° with gas evolution. Silver carbonate in water solution therefore gives exactly the same result as silver oxide.

Ag acetate + dl brompropionic acid in water solution.

5.27 g. dl brompropionic acid, dissolved in 53c.c. of water, were treated with 5.8 g. dry silver acetate (1 mol.). Separation of yellow silver bromide was apparent after 10-15 minutes

(33) P. Walden:
E. Fisher:

life on standing several days. This material was then heated with 3 pt. of acetic anhydride 80-90° 7 hrs., and gave, after distilling off acetic acid and excess of acetic anhydride at reduced pressure (20mm.), heating finally at 100° 3 hr., 4.00 g. mobile gum smelling strongly of acetic anhydride. On shaking this gum for ten minutes with 2 pts. of water, it gave 2.95 g. gum insoluble and 0.95g. soluble in water. The 0.95g. soluble in water, again treated with acetic anhydride as before, gave, after distillation at reduced pressure (heating to 100°), 1.05g. residue which, by shaking with 2 pts. of water for ten minutes, gave 0.82g. insoluble in water, leaving thus finally only 0.23g. material soluble in water. The 2.95g. insoluble gum gave by hydrolysis and subsequent distillation of water at reduced pressure 2.73 stiff gum. 5/8 of the solution (cont. 3.1 g. acid) obtained by hydrolysis of the insoluble gum, were heated with 13.6 g. bromine. Before discussing the results obtained with bromine, it will be of interest to consider several other experiments. If the hydrolyzed acid product obtained by the action of silver oxide on di bromopropionic acid in water or absolute ether solution were anhydride oil, titrated over 90% as a free acid and gave on treatment with acetic anhydride in place of a gum insoluble in water an acylated gum having all the properties of acylated lactic, we could easily formulate both of these actions in terms of lactic, lactic, lactic, and condensed or poly(lactic) lactic (insoluble in water). Although it gives to all appearances the same acid salt and phenyl hydrazone compound as lactic, the hydrolyzed acid obtained here has properties totally different from the mobile styryl lactic acid.

In order to repeat exactly the experiment of Fisher and Walden, 5.1g. di bromopropionic acid (1 mol.) were treated in 52c.c. water with 4.6g. dry silver carbonate (2 mol.). Fisher and Walden used an excess of silver carbonate over that required to remove all the halogen and therefore were compelled to decompose subsequently the silver salts obtained. Lively effervescence of carbon dioxide and rapid separation of silver bromide took place action was apparently complete in one hour. The mixture was allowed to stand, however, 29 hrs. to be sure of complete reaction. No metallic silver was found in the silver residue. The filtrate, heated for seven hours 110-120° under reflux condenser, gave, after distilling off water at reduced pressure (20mm.), heating finally 80-90° 3 hr., gave 2.05 g. stiff gum which titrated only 59.9% as a free acid. After distilling off water at reduced pressure (20mm.), heating finally 80-90° 3 hr., 1.58 g. stiff gum from which nothing crystallized out on standing for two months. (Absence of dilactide). On treatment with an equal volume of phenyl hydrazine and absolute alcohol only 1.19 g. phenyl hydrazone compound were obtained (well washed with ether and dried on clay plate) of m. pt. 98-102° with gas evolution. Silver carbonate in water solution therefore gives exactly the same result as silver oxide.

Acetate-di bromopropionic acid in water solution.

5.27 g. di bromopropionic acid dissolved in 52c.c. of water were treated with 5.8 g. dry silver acetate (1 mol.). Separation of yellow silver bromide was apparent after 10-15 minutes

without appreciable heat evolution. Reaction was allowed to proceed for 29½ hrs. There was obtained, after two hydrolyses of the filtrate at 110°-120°, 2.00 g. of a fairly stiff gum. This gum, however, titrated 93.7% as a free acid. Distillation of remainder of solution at reduced pressure gave 1.7 g. of stiff gum which titrated 87.0% as a free acid. Distillation of water from solution at reduced pressure gave 1.26 g. stiff gum which titrated only 73.6% as a free acid. The remainder of the solution gave 1.07 g. fairly stiff gum, which, on treatment with phenyl hydrazine in absolute alcohol, gave 0.73 g. crude phenyl hydrazine compound (dried over H_2SO_4) which decomposed at 98°-103°. It was necessary in this experiment to separate here from time to time from colloidal silver. The results obtained here are somewhat anomalous compared to those in all of my other experiments with silver oxide and silver salts as well as silver acetate in absolute ether since the gum, obtained here by hydrolysis with water although it possesses only very slight degree of mobility titrates almost entirely as free acid. That it is different from lactic however is shown by the fact that it is readily converted into lactone or anhydride by sweeping over with water. A repetition of this experiment may be advisable.

- summary -

From the results obtained, it is very evident that the product of the action of silver oxide as well as silver salts on bromopropionic acid is not lactic acid but a product which by simply heating in water solution at 120° forms an acid which readily, even by distillation at reduced pressure, goes over into its corresponding anhydride or lactone. This lactone-like body is completely transformed by treatment with acetic anhydride without gain in weight into a non-mobile condensation product insoluble in water. dl lactic, by heating in dry form at 120°-140°, but not in water solution at 120° gives an anhydride lactyl lactic, which by analagous treatment with acetic anhydride gives quantitatively a condensation product insoluble in water. In this connection, it may be said that the work of Wislicenus in regard to the anhydrides of lactic acid was confirmed, with the exception of the statement that crystalline lacted is formed in large yield by drawing a rapid air stream through dl lactic acid at 150° - this experiment was not tried. By heating dl lactic at 120°-140° for 3 hrs., the acid is transformed almost quantitatively into lactyl lactic (lactic anhyd.) as shown by comparison of the results of titration of the material (soluble in water) in the cold and on the boiling water-bath. A small amount (1/5 of total wt.) of the dl lactic acid is thus condensed further into polylactyl lactic acid (insoluble in water but readily soluble in dilute soda solution). Lactyl lactic acid, by heating for six hours in water solution at 120°, is split almost quantitatively giving mobile syrupy lactic acid. That free dl lactic is thus obtained is shown not only by its mobility and the fact that the hydrolyzed gum titrates over 90% as a free acid, but this was also checked by acylation with acetic anhydride. The hydrolysis of lactyl lactic was found to proceed just as well at the temperature of the boiling water-bath. It was found also to be a distinct time reaction similar to the hydrolysis of acetyl lactic as shown by a titration of the material after heating in water solution only one hour on the boiling water-bath.

By heating dl lactic acid to 180° for 3 hrs. (20mm.), a considerable amount of material distills over, while the residual material consisted entirely of lactic acid condensation product, polylactyl lactic, insoluble in water, containing a small amount of soluble

without appreciable heat evolution. Reaction was allowed to proceed for 29 1/2 hrs. There was obtained, after two hydrolyses of the filtrate at 110-120°, 2.00 g. of a fairly stiff gum. This gum, however, titrated 93.7% as a free acid. Distillation of remainder of solution at reduced pressure gave 1.7 g. of stiff gum which titrated 87.0% as a free acid. Distillation of water from solution at reduced pressure gave 1.26 g. stiff gum which titrated only 73.6% as a free acid. The remainder of the solution gave 1.07 g. fairly stiff gum, which, on treatment with phenyl hydrazine in absolute alcohol, gave 0.73 g. crude phenyl hydrazine compound (dried over H_2SO_4) which decomposed at 98-103°. It was necessary in this experiment to separate here from time to time from colloidal silver. The results obtained here are somewhat anomalous compared to those in all of my other experiments with silver oxide and silver salts as well as silver acetate in absolute ether since the gum, obtained here by hydrolysis with water although it possesses only very slight degree of mobility titrates almost entirely as free acid. That it is different from lactic however is shown by the fact that it is readily converted into lactone or anhydride by sweeping over with water. A repetition of this experiment may be advisable.

From the results obtained, it is very evident that the product of the action of silver oxide as well as silver salts on propionic acid is not lactic acid but a product which by simply heating in water solution at 120° forms an acid which readily, even by distillation at reduced pressure, goes over into its corresponding anhydride or lactone. This lactone-like body is completely transformed by treatment with acetic anhydride without gain in weight into a non-mobile condensation product insoluble in water. If lactic by heating in dry form at 120-140°, but not in water solution at 120° gives an anhydride (lactyl lactate), which by analogous treatment with acetic anhydride gives quantitatively a condensation product insoluble in water. In this connection, it may be said that the work of Walford in regard to the anhydrides of lactic acid was confirmed with the exception of the statement that crystalline lactate is formed in large yield by drawing a rapid air stream through dl lactic acid at 120° - this experiment was not tried. By heating dl lactic acid at 120-140° for 3 hrs., the acid is transformed almost quantitatively into lactyl lactate (lactic anhyd.) as shown by comparison of the results of titration of the material (soluble in water) in the cold and on the boiling water-bath. A small amount (1/5 of total wt.) of the dl lactic acid is thus condensed further into poly(lactyl lactate) acid (insoluble in water but readily soluble in dilute soda solution). Lactyl lactate, by heating for six hours in water solution at 120° is split almost quantitatively giving mobile syrupy lactic acid. That free dl lactic is thus obtained is shown not only by its mobility and the fact that the hydrolyzed gum titrates over 90% as a free acid, but this was also checked by acylation with acetic anhydride. The hydrolysis of lactyl lactate was found to proceed just as well at the temperature of the boiling water-bath. It was found also to be a distinct time reaction similar to the hydrolysis of acetyl lactate as shown by a titration of the material after heating in water solution only one hour on the boiling water-bath.

By heating dl lactic acid to 180° for 3 hrs. (20 mm.), a considerable amount of material distills over while the residual material consisted entirely of lactic acid condensation product poly(lactyl lactate) insoluble in water containing a small amount of soluble

monomolecular lactyl lactic. The same insoluble condensation product is obtained by heating lactyl lactic 80°-100° with acetic anhydride. To my knowledge, this observation has never been previously recorded in the literature. By hydrolysis of poly lactyl lactic with 5 pts. of water at 120°-130°, it is necessary to heat for 8 hrs. to get oil completely into solution, by heating further for 6 hrs. at 120°, dl lactic was regenerated as a mobile syrup. This observation was checked by titration, as well as by acylation with acetic anhydride.

Crystallizing lactid (of m. pt. 121°-124°³⁵), prepared according to the method of Bischoff and Walden, by dry distillation of sodium brompropionate, was found to be totally different from poly lactyl lactic, obtained as above. The statement in the literature that lactid is formed simply by heating dl lactic to 180°³⁶ was therefore found to be incorrect. Poly lactyl lactic dissolves readily in ether, is non-volatile at 300° (20mm.) and shows absolutely no tendency to crystallize. Lactid (of m. pt. 125°), when recrystallized from absolute alcohol, is a beautiful body crystallizing in transparent square plates which require according to my observation, 100 pts. of cold ether for complete solution. It boils at 255° at ordinary pressure.³⁷ These two bodies are similar only in the respect that they are insoluble in water and both are condensation products of lactyl lactic as well as of dl lactic acid. From its structure, we should expect crystalline lactid to behave as a neutral body but; surprisingly, it goes readily into dilute soda from ether solution. When this soda solution was heated to 100° for six hours, it gave by hydrolysis a mobile acid gum having all the appearance of dl lactic acid. Unfortunately no titration was made of this hydrolyzed material but all of it was converted into crystalline zinc salt difficultly soluble in water. The non-mobile gum insoluble in water, obtained by the action of silver oxide or silver acetate on dl brompropionic acid in absolute ether, goes readily from ether into dilute soda solution. The crude acid product obtained by heating dl lactic to 180° when dissolved in ether and shaken out with 5% soda solution gives a very small amount of neutral material, some dissolves in the soda while a considerable amount was precipitated by addition of the dilute soda solution and required a very large amount of ether to bring it back into solution. It may be added here that in the dry distillation of sodium brompropionate the yield of cryst. lactid was not quantitative, as Bischoff and Walden's statement would indicate, but was only 20% of the theory. Furthermore, although the salt apparently decomposed completely giving large amount of oil at 250°-300°, it was necessary to heat with naked flame (400°+) in order to drive over the oily distillate. The lactid should have distilled here at about 180° since the distillation was carried out at reduced pressure (18mm.). Examination of the remaining oily material (3.0g.) by shaking out with soda from ether solution gave 0.95g. neutral (probably oily lactid) insoluble in water, and 1.75g. stiff gum soluble in water and acid towards soda. This material titrated only 67.0% as a free acid even after heating soda solution 4½ hrs. to 100°. Both the neutral and the acid gum here gave after hydrolysis cryst. zinc salts difficultly soluble in water very similar to zinc lactate. The acid gum, obtained here, has all the properties of the acid material obtained by the action of silver oxide on brompropionic acid. Inasmuch as this is the only case where exactly comparable material was obtained a repetition of the dry distillation of sodium brompropionate will

³⁵ Bischoff & Walden: Ber. 26, 263.

³⁶

³⁷

monomolecular lactic. The same insoluble condensation product is obtained by heating lactic 80-100° with acetic anhydride. To my knowledge, this observation has never been previously recorded in the literature. By hydrolysis of poly(lactic) lactic with 5 pts. of water at 120-130°, it is necessary to heat for 8 hrs. to get oil completely into solution, by heating further for 6 hrs. at 120°, the lactic was regenerated as a mobile syrup. This observation was checked by titration, as well as by acylation with acetic anhydride.

Crystalline lactic (of m. pt. 121-124°), prepared according to the method of Bischoff and Walder, by dry distillation of sodium propionate, was found to be totally different from poly(lactic) lactic, obtained as above. The statement in the literature that lactic is formed simply by heating di lactic to 180° was therefore found to be incorrect. Poly(lactic) lactic dissolves readily in ether is non-volatile at 300° (20 mm.) and shows absolutely no tendency to crystallize. Lactic (of m. pt. 122°), when recrystallized from absolute alcohol, is a beautiful body crystallizing in transparent square plates which require according to my observation, 100 pts. of cold ether for complete solution. It boils at 255° at ordinary pressure. These two bodies are similar only in the respect that they are insoluble in water and both are condensation products of lactic lactic as well as of di lactic acid. From its structure, we should expect crystalline lactic to behave as a neutral body but, surprisingly, it goes readily into dilute soda from ether solution. When this soda solution was heated to 100° for six hours, it gave by hydrolysis a mobile acid gum having all the appearance of di lactic acid. Unfortunately no titration was made of this hydrolyzed material but all of it was converted into crystalline acid salt difficultly soluble in water. The non-mobile gum insoluble in water obtained by the action of silver oxide or silver acetate on di propionic acid in absolute ether, goes readily from ether into dilute soda solution. The crude acid product obtained by heating di lactic to 180° when dissolved in ether and shaken out with 5% soda solution gives a very small amount of neutral material, some dissolves in the soda while a considerable amount was precipitated by addition of the dilute soda solution and required a very large amount of ether to bring it back into solution. It may be added here that in the dry distillation of sodium propionate the yield of cryst. lactic was not quantitative, as Bischoff and Walder's statement would indicate, but was only 20% of the theory. Furthermore, although the salt apparently decomposed completely giving large amount of oil at 250-300°, it was necessary to heat with naked flame (400°) in order to drive over the oily distillate. The lactic should have distilled here at about 180° since the distillation was carried out at reduced pressure (18 mm.). Examination of the remaining oily material (3.0 g.) by shaking out with soda from ether solution gave 0.95 g. neutral (probably oily lactic) insoluble in water, and 1.75 g. acid gum soluble in water (acid towards soda). This material titrated only 67.0% as a free acid even after heating soda solution 4 hrs. to 100°. Both the neutral and the acid gum here gave after hydrolysis crystals which were difficultly soluble in water very similar to zinc lactate. The acid gum obtained here, has all the properties of the acid material obtained by the action of silver oxide on propionic acid. Inasmuch as this is the only case where exactly comparable material was obtained a repetition of the dry distillation of sodium propionate will

be carried out with this modification that, after heating for considerable time as before at 250°-300°, the acid material will be recovered not by distillation at reduced pressure but by thorough ~~EX-~~traction of the salt residue with ether. A careful study will also be made of the products obtained by the action of heat on dl brompropionic acid in dry form as well as in water solution. Preliminary experiment showed that hydrogen bromide was split off readily when the acid was heated for several hours at 180° - no attempt was made, however, to examine the residue.

Examination of the acid material with brucin.

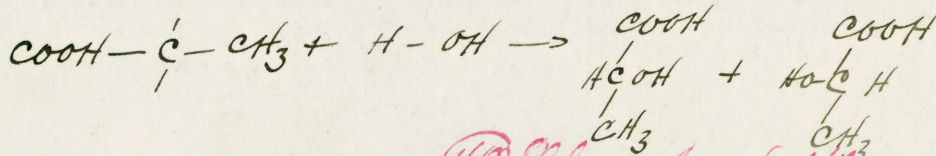
The non-mobile gums, insoluble in water (from the action of silver oxide on dl brompropionic in water and in absolute ether solution) gave, after hydrolysis and treatment with brucin, as indicated above, almost quantitative separation of exactly similar brucin salts in three or four crops from absolute alcohol. The brucin salts thus obtained melted ~~sharply at~~ 200°-212° mainly 208°-211°. Brucin dl lactate melts at sharply 212° but always crystallizes in cubes while the salts, obtained here, crystallized out in the form of large, beautiful, transparent flat slabs made up of plates when they came out slowly, or in the form of fine needles by separating rapidly. A sample from crop II (AgO + Br prop. acid in water solution) melting 200°-211° gave $[\alpha]_D^{20} = -29.36$. The remainder of this crop II dissolved clearly in water. This water solution was now extracted once with fresh chloroform and was re-dissolved in hot absolute alcohol after distilling off water at reduced pressure. By standing over night it gave a large crop which melted 205°-213° and had $[\alpha]_D^{20} = -29.02$. Brucin dl lactate gives $[\alpha]_D^{20} = -29.05$. A sample from crop III (AgO + Br prop. acid in abs. ether) melting at 205°-211° dissolved clearly in water (no free Brucin) and gave $[\alpha]_D^{20} = -32.74$.

Homogeneity of the crude acid product.

That the acid product obtained by the action of silver oxide on brompropionic acid is homogeneous (consists practically entirely of one body) is established by the fact that the phenyl hydrazin ~~compound~~ salt, the zinc salt and the brucin salt crystallize out completely. Several observations seem to afford conclusive evidence that lactic acid is therefore the only reaction product; we have, however, just as conclusive evidence that the reaction product formed here is quite different from lactic. That this acid material is not acrylic acid is proved by analysis and difficult solubility of the zinc salt, the latter property also rigidly excludes the presence of hydracrylic acid (β hydroxypropionic). (41)

Looking at this action from a theoretical standpoint, it is seen that both of these bodies might easily be formed under the conditions of the experiment. ^{formation} Acrylic acid, formed as given before, involves loss of H Br and, by means of rapid action, rearrangement of carboxyethylene (acrylic acid). The acrylic acid formed might afterwards add water but, if it did, it would form exclusively the β substituted propionic acid as addition product. (43)

If the action takes place through intermediatereformation of carboxyethylidene, it does not seem reasonable that this in water solution would not add water to form dl lactic acid. (44)



(38) *Hyf.*
(39) *Hyf.*

(40) *Reich: Ann. Suppl. 2, 128*
(41) *Reichmann: Ann. 171, 292; Ann. 163, 95*
Willigenus: Ann. 166, 6.

just like
dl lactic

why mention
acrylic acid
boils 144° C.P.

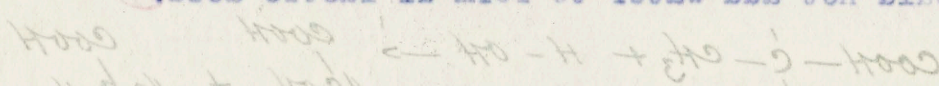
carboxyethylidene

The non-mobile gums, insoluble in water (from the section of silver oxide on di bromopropionic in water and in absolute ether solution) gave after hydrolysis and treatment with brucin, as indicated above, almost quantitative separation of exactly similar brucin salts in three or four crops from absolute alcohol. The brucin salts thus obtained melted sharply at 200-212 mainly 208-211. Brucin di lactate melts at sharply 212 but always crystallizes in cubes while the salts obtained here, crystallized out in the form of large, beautiful, transparent flat plates made up of plates when they came out slowly, or in the form of fine needles by separating rapidly. A sample from crop II (A) Br prop. acid in water solution) melting 200-211 gave 29.36. The remainder of this crop II dissolved clearly in water. This water solution was now extracted once with fresh chloroform and was re-dissolved in hot absolute alcohol after distilling off water at reduced pressure. By standing over night it gave a large crop which melted 205-212 and had 29.02. Brucin di lactate gives 29.02. A sample from crop III (A) Br prop. acid in abs. ether) melting at 205-211 dissolved clearly in water (no free brucin) and gave 32.44.

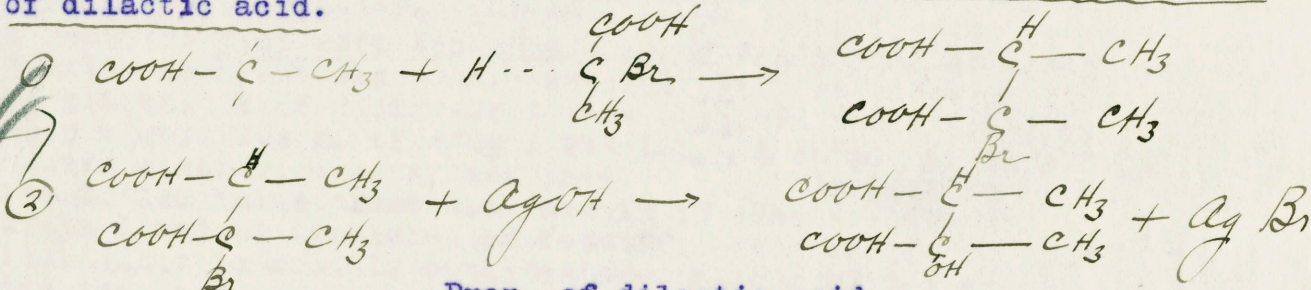
presence of hydroxylic acid (hydroxypropionic). The latter property also rigidly excludes the of the zinc salt; the latter property also rigidly excludes the as not acrylic acid is proved by analysis and difficult solubility formed here is quite different from lactic. That this acid material however, just as conclusive evidence that the reaction product that lactic acid is therefore the only reaction product; we have, completely. Several observations seem to afford conclusive evidence compound, the zinc salt and the zinc salt crystallize out com- of one body) is established by the fact that the phenyl hydrazine on propionic acid is homogeneous (constats practically entirely That the acid product obtained by the action of silver oxide

Looking at this action from a theoretical standpoint, it is seen that both of these bodies might easily be formed under the conditions of the experiment. Acrylic acid formed as given before, involves loss of H Br and, by means of rapid action, rearrangement of carboxyethylene (acrylic acid). The acrylic acid formed might afterwards add water but if it did it would form exclusively the substituted propionic acid as addition product.

If the action takes place through intermediate formation of carboxyethylidene it does not seem reasonable that this in water solution would not add water to form di lactic acid.

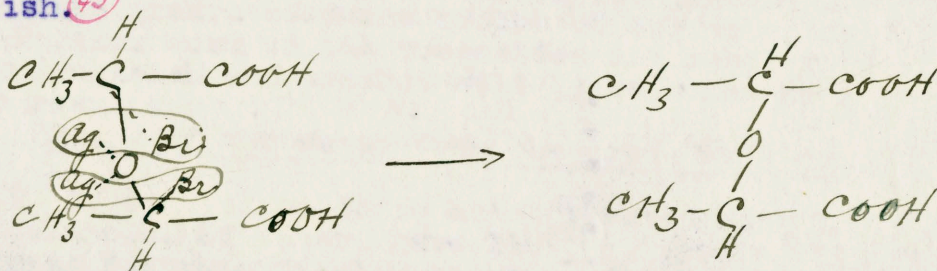


Where the action is carried out in absolute ether, the water formed, in the presence of the large amount of diluent, may add to the unsaturated intermediate product in only a very small measure; as the main reaction we should expect either a formation, by rearrangement, of acrylic acid or some condensation product of acrylic acid or that the intermediate product (carboxyethylidene) would condense with itself or with unchanged bromopropionic acid. As a result of the last idea, we should get readily a structural isomer of dilactic acid.



Prep. of dilactic acid

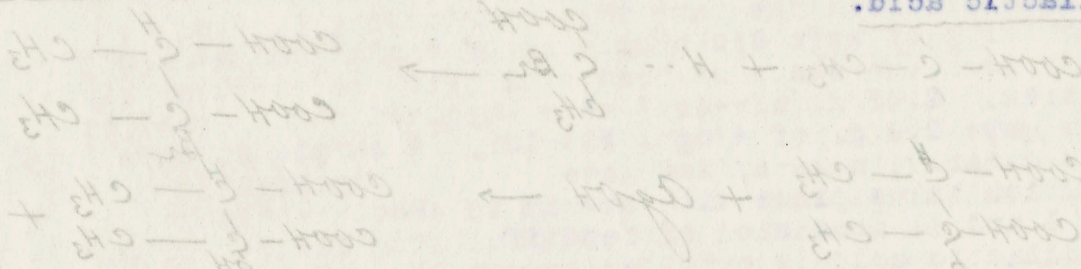
As a result of a simple metalepsis, we might expect to get in absolute ether solution dilactic acid which has been studied by Jungfleisch. ⁽⁴⁵⁾



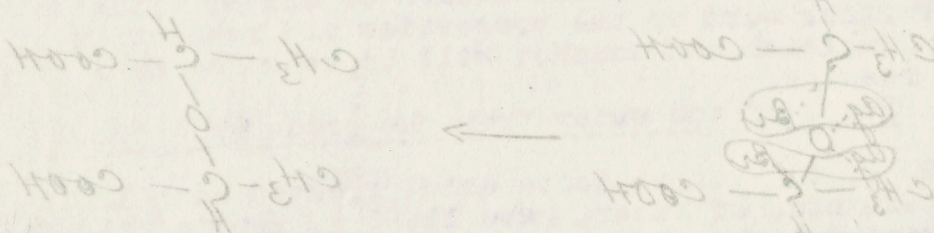
Dilactic acid was prepared according to the latest method ⁽⁴⁶⁾ by the action of sodium ethyl lactate on dl bromopropionic ethyl ester in absolute ether solution. Dilactic diethyl ester, thus obtained, boiled at 121°-136° (24mm) and gave when hydrolyzed with alcoholic sodiumhydroxide, a sodium salt which crystallized in large quantity from absolute alcohol. There was no difficulty in getting dilactic acid in solid form but it was difficult to find a suitable solvent from which to purify it. Water, alcohol, ether and acetic ethyl ester dissolve the acid too easily to be used as recrystallizing solvents. The acid dissolves fairly readily in hot benzol, but comes out partly gummy on cooling. On standing, however, without solvent the free acid seems to crystallize completely. The brucin salt of dilactic acid crystallizes readily and fairly completely from an equal volume of absolute alcohol in the form of beautiful glistening, transparent, long needles melting from 110°-138°. 10.5 g. brucin salts gave 2.27g. Crop I (air-dry) of dc. pt. 125°-138°. The dried salt gave $[\alpha]_D^{20} = -32.16$, clear solution in water (no brucin). 1.65 g. (air-dry) were obtained as Crop II of d'cpt. 119°-126°. Sample from this crop gave clear solution in cold water and 32.08. The filtrate from this second crop distilled off at reduced pressure gave 6.17 g. salts which when dissolved in an equal volume and allowed to stand several days without seeding gave only a very small amount of crystalline material. This observation seemed to favor the idea that a resolution had occurred here with brucin in alcohol solution.

- ⁽⁴⁵⁾ Jungfleisch & Godehat: Centralblatt, 1907 II, 136.
⁽⁴⁶⁾ Jungfleisch & Godehat: Comptes Rendus, 144, 949 [May 1907].
⁽⁴⁷⁾ Jungfleisch & Godehat: Comptes Rendus, 146, 26-29.

Where the action is carried out in absolute ether, the water formed in the presence of the large amount of diluent may add to the unsaturated intermediate product in only a very small measure; as the main reaction we should expect either a formation, by rearrangement, of acrylic acid or some condensation product of acrylic acid or that the intermediate product (carboxystyrene) would condense with itself or with unchanged bromopropionic acid. As a result of the last idea, we should get readily a structural isomer of dilactic acid.



Prep. of dilactic acid
As a result of a simple metathesis we might expect to get in absolute ether solution dilactic acid which has been studied by Jungfleisch.



Dilactic acid was prepared according to the latest method by the action of sodium ethyl lactate on di bromopropionic ethyl ester in absolute ether solution. Dilactic diethyl ester, thus obtained, boiled at 121-122 (24mm) and gave when hydrolyzed with alcoholic sodium hydroxide, a sodium salt which crystallized in large quantity from absolute alcohol. There was no difficulty in getting dilactic acid in solid form but it was difficult to find a suitable solvent from which to purify it. Water, alcohol, ether and acetic ether ester dissolve the acid too easily to be used as recrystallizing solvents. The acid dissolves fairly readily in hot benzol, but comes out partly gummy on cooling. On standing, however, without solvent the free acid seems to crystallize completely. The product salt of dilactic acid crystallizes readily and fairly completely from an equal volume of absolute alcohol in the form of beautiful glistering, transparent, long needles melting from 110-118. 10.5 g. bromin salts gave 2.27 g. Cryst. (air-dry) of d.p. 125-138. The dried salt gave 32.16, clear solution in water (no precip.). 1.65 g. (air-dry) were obtained as Cryst. of d.p. 119-126. Sample from this crop gave clear solution in cold water and 32.08. The filtrate from this second crop distilled off at reduced pressure gave 6.17 g. salts which when dissolved in an equal volume and allowed to stand several days without seeding gave only a very small amount of crystalline material. This observation seemed to favor the idea that a resolution had occurred here with pinon in alcohol solution.

Handwritten notes:
Jungfleisch's method: Compound benzene, 144, 94 g (1907)
Jungfleisch's method: Compound benzene, 144, 25-29

Such a resolution frequently takes place readily in water solution; but from absolute alcohol the brucin salt tends to come out rather in the dl (racemate) form. That resolution occurred ^{here} was made doubtful, however, from the fact that by standing for two months longer, a heavy crop of soft disks made up of small needles was formed which finally took the shape of beautiful heavy rectangular slabs made up of plates. 2.45 g. (air-dry) were obtained which (dried over H_2SO_4 in vacuum) gave 2.4 g. of d'cpt. $110^\circ-128^\circ$. A sample of this crop III dissolved clearly in water and gave $[\alpha]_D^{20} = -30.4^\circ$. Apparently a very slight resolution takes place with brucin in absolute alcohol solution. Crops I and II consisted of beautiful long slender prisms. The fact that dilactic acid is obtained crystalline with the greatest ease and that the brucin salt of dilactic acid has d'cpt. varying from $110^\circ-138^\circ$ instead of $200^\circ-213^\circ$ and gives $[\alpha]_D^{20} = -32.16^\circ$ instead of -29.02° proves conclusively that this body is not present in appreciable amount in the products of the action of silver oxide on brompropionic acid. Further work on the properties and resolution of dilactic acid by Jungleish and Godchot will be welcomed as a confirmation of these results.

Prep. of the ester from the crude acid gum.

19.95 g. dl Brompropionic acid, treated with 15.14 g. silver oxide in 420 c.c. of water, gave 11.95 g. mobile oil after distilling off ethereal filtrate finally at reduced pressure. After dissolving oil in 12 c.c. absolute alcohol, a continual stream of dry HCl gas ^{hydrogen chloride} was passed into solution for 4 hrs.-allowed to stand one night in the ice-chest- then passed in HCl gas for $6\frac{1}{2}$ hrs. longer and again allowed to stand over night as before. Solution was now saturated with hydrogen chloride. Added 300 c.c. of water but only small amount 3-4 g. of oil separated out. There was then added in small portions 13.6 g. dry sodium carbonate which gave finally a very slightly alkaline ^{solution}. This slightly alkaline ^{mixture} was extracted six times with ether using about 150 c.c. ether each time. The ether solution after being dried twice with $CaCl_2$ of calcium was distilled off finally at reduced pressure (20 mm), heating only to $50^\circ-60^\circ$. 11.65 g. crude oil were thus obtained. By fractional distillation this gave:

8.47 g. of B.pt. $58^\circ-62^\circ$ (14 mm).

1.83 g. of B.pt $108^\circ-140^\circ$ (12 mm).

0.35 g. non-volatile.

Fract. a, 8.47 g. of B. pt. $58^\circ-62^\circ$ (14 mm.), gave by redistillation ^{fract. a'} 8.27 g. of B. pt $55^\circ-57^\circ$ (15 mm.) 6.5 g. of fract. a [boiling at $55^\circ-57^\circ$ (15 mm.)] treated with 7 c.c. of water, gave by shaking 3.1 c.c. insoluble oil which on redistillation gave 2.55 g. boiling constantly $52^\circ-53^\circ$ (15 mm.) To recover the ester soluble in water, the water solution was extracted three times with ether etc. gave finally 2.2 g. of B. pt. $55^\circ-58^\circ$ (15 mm.) mainly $56^\circ-57^\circ$. This ester when boiled with alcoholic sodium hydroxide gives fair amount of silver chloride by subsequent treatment with silver nitrate. It gave a strong irritating odor and red-brown color exactly like that of crotonaldehyde resin when it was heated with strong aqueous sodium hydroxide. This same observation has been previously made when acrolein is heated with strong aqueous sodium

Such a resolution frequently takes place readily in water solution; but from absolute alcohol the pruin salt tends to come out rather in the diacetate form. That resolution occurred was made doubtful, however, from the fact that by standing for two months longer, a heavy crop of soft disks made up of small needles was formed which finally took the shape of beautiful heavy rectangular plates made up of plates. 2.45 g. (air-dry) were obtained which dried over H₂O in vacuum gave 2.4 g. of d'opt. 110-128. A sample of this crop of disks solved clearly in water and gave 2.4 g. of d'opt. 110-128. Apparently a very slight resolution takes place with pruin in absolute alcohol solution. The fact that diacetic acid is obtained crystallizing with the greatest ease and that the pruin salt of diacetic acid has d'opt. varying from 110-138 instead of 200-213 and gives 32.16 instead of 29.02 proves conclusively that this body is not present in appreciable amount in the products of the action of silver oxide on bromopropionic acid. Further work on the properties and resolution of diacetic acid by Jungbluth and Goddard will be welcomed as a confirmation of these results.

Prep. of the ester from the crude acid form.

19.95 g. of bromopropionic acid, treated with 15.14 g. silver oxide in 420 c.c. of water, gave 11.95 g. mobile oil after distilling off ethereal filtrate finally at reduced pressure. After dissolving oil in 120 c.c. absolute alcohol, a continual stream of dry H₂Cl gas was passed into solution for 4 hrs. - allowed to stand over night in the ice-chest - then passed in H₂Cl gas for 6 hrs. longer and again allowed to stand over night as before. Solution was now saturated with hydrogen chloride. Added 300 c.c. of water but only small amount 3-4 g. of oil separated out. There was then added in small portions 13.6 g. dry sodium carbonate which gave finally a very slightly alkaline solution. The slightly alkaline solution was extracted six times with ether using about 150 c.c. ether each time. The ether solution after being dried twice with chloride of calcium was distilled off finally at reduced pressure (20 mm). Heating only to 50-60. 11.65 g. crude oil were thus obtained. By fractional distillation this gave:

8.47 of B.pt. 58-62 (14 mm).
1.83 g. of B.pt 108-140 (12 mm).
0.35 g. non-volatile.

Fract. 8.47 of B. pt. 58-62 (14 mm.) gave redistillation 8.27 of B. pt. 58-62 (14 mm.) treated with 7 c.c. of water gave by shaking 3.1 c.c. insoluble oil which on redistillation gave 2.55 g. boiling constantly 52-53 (15 mm.). To recover the ester soluble in water, the water solution was extracted three times with ether etc. gave finally 2.8 g. of B. pt. 52-58 (15 mm.) mainly 56-57. This ester when boiled with alcoholic sodium hydroxide gives fair amount of silver chloride by subsequent treatment with silver nitrate. It gave a strong irritating odor and red-brown color exactly like that of crotonaldehyde resin when it was heated with strong aqueous sodium hydroxide. This same observation has been previously made when crotonaldehyde is heated with strong aqueous sodium

hydroxide and therefore points strongly to the fact that acrylic acid or one of its condensation products may be present here. Lactic ethyl ester, which is soluble in water and which was found to give with same thermometer boiling point $54^{\circ}\text{--}57^{\circ}(14\text{--}15\text{mm.})$, dissolves when heated with strong aqueous sodium hydroxide without any noticeable odor or coloration.

The oil, obtained above, insoluble in water of B.pt. $52^{\circ}\text{--}53^{\circ}(15\text{mm.})$ sharp odor affecting the eyes and nose after heating with alcoholic sodium hydroxide; it gave a very large amount of silver chloride by subsequent treatment with silver nitrate-clear solution and no odor of crotonaldehyde on heating with aqueous sodium hydroxide.

The high-boiling $[108^{\circ}\text{--}140^{\circ}(12\text{mm.})]$ ester was found to be insoluble in water and gave only traces of silver chloride by heating with alcoholic sodium hydroxide and subsequent treatment with silver nitrate. A sharp odor unlike that of crotonaldehyde but no brown-red resin was obtained by heating with aqueous sodium hydroxide. On distillation of ethyl lactat (Kahlbaum product), a very small amount was found to have B.pt. $100^{\circ}\text{--}140^{\circ}(14\text{--}15\text{mm.})$ but dissolved readily in an equal volume of water. The main product had B.pt. of $52^{\circ}\text{--}53^{\circ}(15\text{mm.})$ and was insoluble in water, and therefore had all the properties of α or β chlorpropionic ethyl ester (B.pt. $55^{\circ}\text{--}58^{\circ}(15\text{mm.})$), which is also formed in large amount and which has same solubility in water and exactly the same boiling point as lactic ethyl ester, differs from the latter in that it appears to contain a fair amount of halogen and gives a characteristic red resin when heated with strong aqueous alkali. In view of the fact that in this experiment lactic ethyl ester, first formed, might be transformed with fuming hydrochloric acid into chlorpropionic ester or to its derivatives, this esterification experiment may to advantage be repeated under different conditions, using only limited small amount of HCl gas according to Fisher's latest directions, by heating the crude acid in sealed tube with absolute alcohol alone or in the presence of a trace of sulphuric acid.

Other possibilities of interpretation.

Lactic acid first formed might by auto-alkylation in the presence of silver oxide, acting as contact agent, form readily lactyl lactic (an ester) as well as polylactyl lactic or cryst. lactid. But lactyl lactic, polylactyl lactic (obtained by heating dl lactic to 180°) and crystalline lactid of m.pt 125° all give mobile syrupy dl lactic acid by hydrolysis. The hydrolysis of lactyl lactic with boiling water, which is practically complete in six hours, gives a very interesting comparison to that of the corresponding ester, acetyl lactic the hydrolysis of which, with water is still very incomplete after boiling with water for hours. Having ascertained that the hydrolyzed product had properties different from those of dl lactic, the three bodies mentioned above due to auto-alkylation of lactic acid first formed are removed from consideration. Dilactic acid has also been rigidly excluded. There are, however, a number of other condensations possible depending on the intermediate formation of carboxyethylidene which may condense with other material as such or may first give active acrylic acid which is also capable of adding various reagents. It is not at all improbable that carboxyethylidene is the result of a rapid action may rearrange to carboxethylene (active acrylic acid) just as ethylidene rear-

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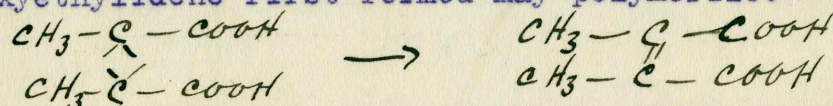
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The high-boiling $108-140^{\circ}\text{C}$ (15°mm) ester was found to be insoluble in water and gave only traces of silver chloride by heating with alcoholic sodium hydroxide and subsequent treatment with silver nitrate. A sharp odor unlike that of crotonaldehyde but no brown-red resin was obtained by heating with aqueous sodium hydroxide. On distillation of ethyl lactate (Kahlbaum product) a very small amount was found to have B.pt. $100-140^{\circ}\text{C}$ ($14-15^{\circ}\text{mm}$), but dissolved readily in an equal volume of water. The main product had B.pt. of $52-53^{\circ}\text{C}$ (15°mm) and was insoluble in water, and therefore had all the properties of or B chloropropionic ethyl ester (B.pt. $55-58^{\circ}\text{C}$ (15°mm)), which is also formed in large amount and which has same solubility in water and exactly the same boiling point as lactic ethyl ester, differs from the latter in that it appears to contain a fair amount of halogen and gives a characteristic red resin when heated with strong aqueous alkali. In view of the fact that in this experiment lactic ethyl ester first formed might be transformed with fuming hydrochloric acid into chloropropionic ester or to its derivatives, this esterification experiment may to advantage be repeated under different conditions, using only limited small amount of HCl gas according to Fisher's latest directions, by heating the crude acid in sealed tube with absolute alcohol alone or in the presence of a trace of sulphuric acid.

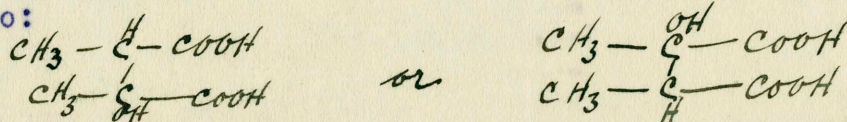
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ranges to ethylene, or as oxyethylidene to oxyethylene (vinyl alcohol.) Compare Nef. ⁵⁴ Before going ahead on this basis, however, two very plausible ideas already advanced remain to be tested out. Carboxyethylidene first formed may polymerize:



which by the addition of water at the double bond may go over, in part, into:



These same space isomeric bodies which are structurally isomeric to dilactic acid (a true ether) may be formed directly, as already indicated, by direct addition of unchanged brompropionic acid to carboxyethylidene. We should expect these bodies to have properties closely allied to those of dilactic as well as dl lactic acid. Because of the presence of the alcohol group we should expect them to be easily transformed into an $\alpha\beta$ or 1,2 lactone.

Action of silver oxide on dl brompropionic ethyl ester in absolute ether solution.

Because of the fact that hydrolysis takes place when simple esters of brompropionic acid are treated with silver oxide in water solution, Fisher was forced to establish the action of silver oxide on the esters of halogen acids by means of an isolated case with a complex ester optically active brompropionyl glycin. ⁵⁵ By use of absolute ether, absolute alcohol or other solvents different from water, we are enabled to carry out the action of silver oxide on various esters without danger of hydrolysis. A remarkable difference was observed, however, between free brompropionic acid and its corresponding ethyl ester. While the acid shows a tremendous activity toward silver oxide at ordinary temperature, the activity of the ester under the same conditions is practically nil. 20.75 dl brompropionic ethyl ester of B. pt. 95°-96° (85-90°) were treated with 13.28 g. of dry silver oxide in 100 c.c. of absolute ether. After allowing mixture to stand at ordinary temperature for 24 hrs. and filtering, 13.07 g. brown silver oxide were recovered unchanged. The ethereal filtrate gave 19.5 g. as residue which by fractional distillation gave 18.99 g. of unchanged brompropionic ethyl ester of B. pt. 68°-70° (23-27 mm.) and 0.43 g. higher boiling.

By heating together dl brompropionic ethyl ester and silver oxide the main product is dilactic diethyl ester just as in the action of sodium ethyl lactate on brompropionic ester. 20.2 g. brompropionic ethyl ester, treated with 13.07 g. dry silver oxide and heated for 3½ hrs. 120°-125°, gave after filtration, 18.98 g. silver bromide, silver oxide and metallic silver. After treatment with an excess (about 400 cc. in all) dilute ammonia (of sp. g. 0.97) 16.83 g. silver bromide and metallic silver were recovered. This shows that the splitting off of hydrogen bromide is complete since practically no silver oxide is recovered unchanged. By further treatment with 80 c.c. 28.6% potassium cyanide solution and washing with 40 c.c. more of solution of same strength, 0.88 g. metallic silver was obtained. After distilling off ether, 11.11 g. of mobile oil (theory for dilactic diethyl ester = 11.33 g.) were obtained which gave the following fractions:

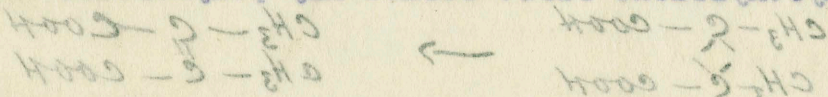
@ 4.2 g. 68°-100° (21-23 mm.)

54 Nef: Ann. 298,

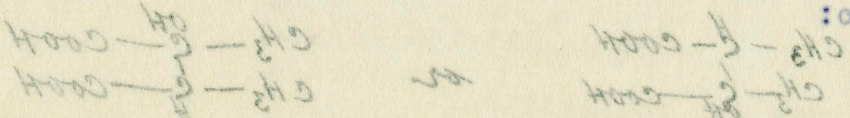
55 E. Fisher: Ber. 40, 1051

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ranges to ethylene, or as oxethylidene to oxethylidene (vinyl also-
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which by the addition of water at the double bond may go over, in
 part, into:



These same space isomeric bodies which are structurally isomeric
 to dilactic acid (a true ether) may be formed directly, as already
 indicated, by direct addition of unchanged propionic acid to
 carboxethylidene. We should expect these bodies to have properties
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 Because of the presence of the alcohol group we should expect them
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 solution, Fisher was forced to establish the action of silver oxide
 on the esters of halogen acids by means of an isolated case with a
 complex ester optically active bromopropionyl glycin. By use of
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 various esters without danger of hydrolysis. A remarkable differ-
 ence was observed, however, between free propionic acid and its
 corresponding ethyl ester. While the acid shows a tremendous activ-
 ity toward silver oxide at ordinary temperature, the activity of the
 ester under the same conditions is practically nil. 20.75 g.
 propionic ethyl ester of B. pt. 98-99 (88-90) were treated with
 13.28 g. of dry silver oxide in 100 c.c. of absolute ether. After
 allowing mixture to stand at ordinary temperature for 24 hrs. and
 filtering, 13.07 g. brown silver oxide were recovered unchanged.
 The ethereal filtrate gave 19.5 g. as residue which by fractional
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 B. pt. 68-70 (23-27 mm.) and 0.43 g. higher boiling.

By heating together di propionic ethyl ester and silver ox-
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 dilactic diethyl ester = 11.33 g.) were obtained which gave the
 following fractions:

68-100 (21-23 mm.) 4.2 g.

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① 0.41 g.	100°-115° (21 mm.)
② 3.69 g.	115°-140° (21 mm.)
③ 1.47 g.	170°-215° (21 mm.)
④ 1.05 g.	non-volatile.

By redistillation

Fract ^{4.2g gave} 3.37 g. 63°-80° (20 mm.) mainly 65°-69°

Fracts. b c ^{4.1g gave} 2.99 g. 115°-140° (20 mm.)

Fract d was not redistilled.

A similar experiment, carried out with 28.59 g. brompropionic ethyl ester and 18.3 g. dry silver oxide in 200 c.c. absolute ether, gave no action on standing in the cold for 18½ hrs. By heating at 120°-130° for 10 hrs. (after distilling off ether), there was obtained, after extraction with dry ether, 27.85 g. silver bromide, silver oxide, metallic silver. By treatment with an excess (about 600 c.c.) of dilute ammonia (sp.g. 0.97), 24.62 g. of silver bromide and metallic silver were recovered. By further treatment with 100 c.c. 28.6% potassium cyanide and washing with 50 c.c. more of cyanide solution of same strength, 0.82 g. metallic silver remained undissolved. 16.15 g. of mobile gum were obtained by distilling off ethereal filtrate finally at reduced pressure heating finally 50°-60° (20 mm.) which gave by fractionation:

① 1.22 g.	65°-74° (25-30) Br. prop ethyl ester
② 1.68 g.	74°-108° (25 mm.)
③ 4.68 g.	108°-138° (25 mm.)
④ 0.83 g.	138°-145° (25)
⑤ 3.68 g.	170°-220° (25 mm.) together with very slight decomposition.

1.5 g. non-volatile.

By Redistillation: gave
Fracts. a b (2.90 g), having slight stinging odor, gave:
[Br prop. ethyl ester, lactic ethyl ester, pyruvic ethyl ester all would boil 60°-80° (20 mm.)]
I - 1.87 g. 71°-79° (25-27 mm.)
0.46 g. 80°-115° (25 mm.)

Fracts. c d gave:

II 4.59 g. 100°-135° (23-25 mm.) mainly 128°-9°

Fract e gave

III 2.71 g. 158°-228° (25 mm.) mainly 160°-200° of phenol-like odor.

All three final fractions were completely insoluble in water-at least to all appearances.

1.87 g. of the low boiling ester 71°-79° (25-27 mm.) dissolved in ether and shaken out with soda, gave back 1.8 g. mobile oil. 3.91 g. of ester boiling at 128° (25 mm.) to [dilactic diethyl ester], dissolved in ether and shaken out with soda, gave 3.7 g. mobile neutral ester.

By redistillation this gave:-

0.30 g. of b. pt 95°-110° (23 mm.)

2.59 g. of b. pt. 110°-126° (23 mm.)

0.55 g. higher boiling rest containing cryst. solid.

100-115 (21 mm.)	0.41 g.
115-140 (21 mm.)	3.69 g.
170-215 (21 mm.)	1.47 g.
non-volatile.	1.05 g.

By redistillation

Tract a 3.37 g. 63-80 (20 mm.) mainly 65-69

Tract b 2.99 g. 115-140 (20 mm.)

Tract d was not redistilled.

A similar experiment carried out with 28.59 g. bromopropionic ester and 18.3 g. dry silver oxide in 200 c.c. absolute ether gave no action on standing in the cold for 18 hrs. By heating at 120-130° for 10 hrs. (after distilling off ether) there was obtained after extraction with dry ether 27.85 g. silver bromide, silver oxide, metallic silver. By treatment with an excess (about 600 c.c.) of dilute ammonia (sp. g. 0.97) 24.62 g. of silver bromide, metallic silver were recovered. By further treatment with 100 c.c. 28.6% potassium cyanide and washing with 50 c.c. more of cyanide solution of same strength 0.82 g. metallic silver remained undissolved. 16.15 g. of mobile gum were obtained by distilling off etheral filtrate finally at reduced pressure heating finally 50-60° (20 mm.)

which gave by fractionation:

65-74 (25-30) Br. prop ethyl ester	1.22 g.
74-108 (25 mm.)	1.68 g.
108-138 (25 mm.)	4.68 g.
138-145 (25)	0.83 g.
170-220 (25 mm.) together with very slight decomposition	3.68 g.

1.3 g. non-volatile.

Redistillation gave:

Tract a b (2.90 g.) having slight stinging odor. Br prop. ethyl ester, lactic ethyl ester, pyruvic ethyl ester all would boil 60-80 (20 mm.)

1.87 g. 71-79 (25-27 mm.)	I
0.46 g. 80-115 (25 mm.)	I

Tract c d 4.59 g. 100-135 (23-25 mm.) mainly 128-29

Tract e 2.71 g. 158-228 (25 mm.) mainly 160-200° of phenol-like odor.

All three final fractions were completely insoluble in water-at least to all appearances.

1.87 g. of the low boiling ester 71-79 (25-27 mm.) dissolved in ether and shaken out with soda, gave back 1.8 g. mobile oil. 3.91 g. of ester boiling at 128 (25 mm.) to lactic distillate, dissolved in ether and shaken out with soda, gave 3.7 g. mobile neutral ester.

By redistillation this gave:-

0.30 g. of b. pt. 95-110 (23 mm.)
2.59 g. of b. pt. 110-126 (23 mm.)

0.55 g. higher boiling rest containing cryst. solid.

In the preparation of dilactic diethyl ester according to Jungfleish and Godchots' ⁵² method, the same three fractions are obtained as in the above experiment only that the middle fraction contains far more material than the other two. For example: 24.45 g. crude ester made from dl brompropionic ethyl ester by the action of sodium ethyl lactate gave

3.47 g. 65°-70°(25mm.)

0.74 g. 90°-125°(25mm.)

19.13 g. 110°-140°(22mm.)

mainly 125°-130° mostly 128°-9°

3.12 g. 160°-190°(22mm.) cont. considerable ^{crystalline} material.

1.1 g. non-volatile.

Hydrolysis of the three fractions.

3.37 g. from Expt. I of B. pt. 63°-80°(20mm.), treated with an excess of alcoholic sodium hydroxide for 3 hrs., gave no separation of sodium salts from alcohol and finally 1.68 g. mobile oil which by distillation yielded 1.29 g. of b. pt. 58°(40 mm.) and 0.1 g. fore-runner. The 1.29 g. oil dissolved readily in 1c.c. of water without any considerable heat evolution. When the aqueous solution was treated with nitric acid and silver nitrate it gave a very large amount of silver bromide precipitate. The free acid here is evidently a brom-acid of some sort, ^{aqueous} but brompropionic acid boils at 110°(20 mm.) and would presumably lose its halogen on treatment with alcoholic soda or potash.

2.67 g. of the high boiling ester 170°-220°(20mm.) gave by hydrolysis as above considerable separation of sodium salt from alcohol and finally 2.13 g. oil possessing only fair degree of mobility. Treatment with 10 pts. of water gave a small amount of insoluble unchanged ester of sweet odor. The filtrate was heated for 6 hrs. 110°-120° under reflux condenses and gave after distilling off water at reduced pressure (25 mm.) 1g. 38g. non-mobile gum which titrated 91.6% as a free acid. The remainder of the solution distilled off at reduced pressure gave 1.2 g. stiff gum from which no crystals separated out on standing for three months. On treatment with 5.2 g brucin, 7.55 g. Br. salts were obtained which gave as first crop 0.51g from absolute alcohol of dc'pt. 115°-130°(not sharp). This fact and also the observation that a considerable amount of the sodium salt obtained here separates out from absolute alcohol leads us to believe that this high boiling ester is for the most part simply a condensation product of dilactic diethyl ester.

5.58 g. of ester of b. pt. 115°-140°(20-25 mm.), dilactic diethyl ester, hydrolyzed as above with an excess of alcoholic sodium hydroxide, gave a very large separation of sodium salt from absolute alcohol and finally, after treatment with standard dilute hydrochloric acid etc., 3.85 g. of mobile gum. By treatment with 10 pts. of water a small amount of unchanged ester of sweet odor was recovered. The filtrate was heated under reflux condenser for six hours at 110°-120° and gave after distilling off water at reduced pressure (25mm.) 2.36 g. non-mobile gum which gave considerable amount of crystalline material by standing 2-3 days. Titration showed that 95% of material was in the form of a free acid. By again distilling off water at reduced pressure, 2.1 g. stiff gum were obtained which again gave crystals on standing. The crystals were very fine not like the beautiful long needles of dilactic acid and besides about one-half of the material remained gummy. It was therefore treated with 9.2 g. Brucin giving 11.93 g. Brucin salts which, when crystallized

56 h.c. cit

In the preparation of dilactic diethyl ester according to Jungfleisch and Godchaux method, the same three fractions are obtained as in the above experiment only that the middle fraction contains far more material than the other two. For example: 24.45 g. crude ester made from di brompropionic ethyl ester by the action of sodium ethyl lactate gave

3.47 g. 83-90(25mm.)
0.74 g. 90-133(25mm.)
19.13 g. 110-140(25mm.)

mainly 125-130 mostly 128-9

3.12 g. 180-190(25mm.) cont. considxx mat.

1.1 g. non-volatile.

Hydrolysis of the three fractions.

3.37 g. from Expt. I of B. pt. 83-80(20mm.) treated with an excess of alcoholic sodium hydroxide for 3 hrs. gave no separation of sodium salts from alcohol and finally 1.68 g. mobile oil which by distillation yielded 1.29 g. of b. pt. 58(40 mm.) 0.1 g. fore-runner. The 1.29 g. oil dissolved readily in 10 c.c. of water without any considerable heat evolution. When the aqueous solution was treated with nitric acid and silver nitrate it gave a very large amount of silver bromide precipitate. The free acid here is evident ly a brom- acid of some sort but brompropionic acid boils at 110° (20 mm.) and would presumably lose its halogen on treatment with alcoholic soda or potash.

2.67 g. of the high boiling ester 170-220(20mm.) gave by hydrolysis as above considerable separation of sodium salt from alcohol and finally 2.13 g. oil possessing only fair degree of mobility. Treatment with 10 pts. of water gave a small amount of insoluble unchanged ester of sweet odor. The filtrate was heated for 6 hrs. 110-120° under reflux condenses and gave after distilling off water at reduced pressure (25 mm.) 1.38 g. non-mobile gum which crystallized at 91.6° as a free acid. The remainder of the solution distilled off at reduced pressure gave 1.2 g. stiff gum from which no crystals separated out on standing for three months. On treatment with 5.2 g. brucine 7.55 g. Br. salts were obtained which gave as first crop 0.2 g. from absolute alcohol of b. pt. 115-130(not sharp). This fact and also the observation that a considerable amount of the sodium salt obtained here separates out from absolute alcohol leads us to believe that this high boiling ester is for the most part simply a condensation product of dilactic diethyl ester.

2.58 g. of ester of b. pt. 115-140(20-25 mm.) dilactic diethyl ester, hydrolyzed as above with an excess of alcoholic sodium hydroxide, gave a very large separation of sodium salt from absolute alcohol and finally, after treatment with standard dilute hydrochloric acid etc., 3.85 g. of mobile gum. By treatment with 10 pts. of water a small amount of unchanged ester of sweet odor was recovered. The filtrate was heated under reflux condenser for six hours at 110-120° and gave after distilling off water at reduced pressure (25mm.) 2.36 g. non-mobile gum which gave considerable amount of crystalline material by standing 2-3 days. Titration showed that 92% of material was in the form of a free acid. By again distilling off water at reduced pressure, 2.1 g. stiff gum were obtained which again gave crystals on standing. The crystals were very fine not like the beautiful long needles of dilactic acid and besides about one-half of the material remained gummy. It was therefore treated with 9.2 g. Brucine giving 11.93 g. Brucine salts which, when crystallized

in the usual way from absolute alcohol, gave as first crop large amount of voluminous soft fine needles in one hour after seeding with dilactic brucin. 2.75 g. brucin salts (air-dry), obtained as first crop, which yielded 2.55 g. (dried in vacuum over H_2SO_4) which dissociate completely 110° - 128° . Here and also in fract III (high boiling ester), given above, a very small second crop was obtained melting also around 110° . The boiling point of the ester, the fact that the sodium salt crystallizes almost completely from absolute alcohol, the fact that the free acid contains a large amount of crystal needles and that the brucin salt has the same appearance and decomposition point as dilactic brucin leaves very little doubt that dilactic acid is one of the main products when brompropionic ester is heated with silver oxide.

in the usual way from absolute alcohol, gave as first crop large amount of voluminous soft fine needles in one hour after seeding with dilactic bromine. 2.75 g. bromine salts (air-dry) obtained as first crop which yielded 2.55 g. (dried in vacuum over P_2O_5 which dissociate completely 110-128°. Here and also in first III (high boiling ester), given above, a very small second crop was obtained melting also around 110°. The boiling point of the ester, the fact that the sodium salt crystallizes almost completely from absolute alcohol, the fact that the free acid contains a large amount of crystalline needles and that the bromine salt has the same appearance and decomposition point as dilactic bromine leaves very little doubt that dilactic acid is one of the main products when bromopropionic ester is heated with silver oxide.