

8. Behavior of fumaric and maleic acid towards fuming hydrobromic acid. Fittig & Don; Ann. 188, p. 87.

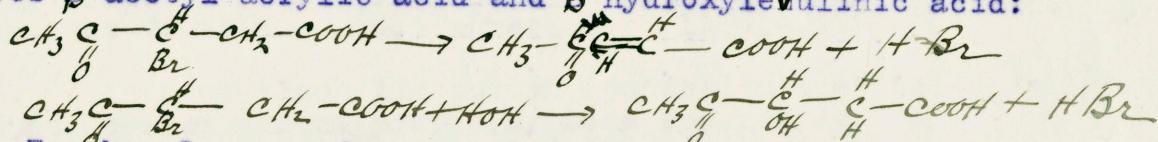
9. Conv. of fumaric acid into malic by means of aqueous sodium hydroxide at 100° Loydl&Linnemann: Ann. 192.80.

10. Form. of crotonic acid by action of alcoholic potash on monobrombutyric ethyl ester.

C. Heil & E. Lauber; Ber. 7, 560-564.

VIII.  $\alpha$  acetyl propionic,  $\beta$  acetyl propionic or levulinic, brom phenylpropionic, phenyl lactic, glycerinic acids.

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



2. Two homologues of acetopropionic acid.

Bischoff & Wislicenus; Ann. 206, 313.

3. A new synthesis of succinic acid with side formation of  $\beta$  acetyl propionic acid.

Noldeke & 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 hydrocumic acid. Glaser; Ann. 143, 343.

9. Über atrolactemsäure and 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.

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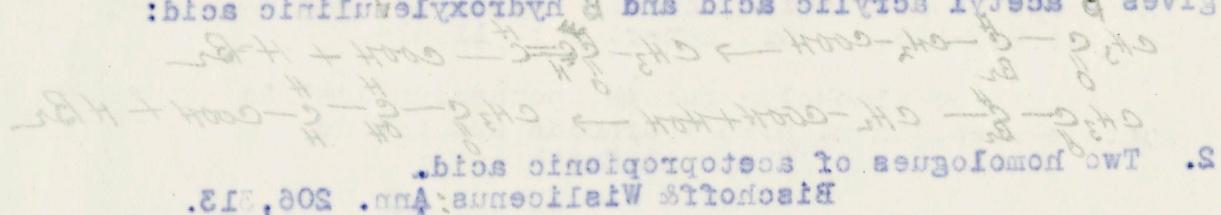
8. Dependence of thermal stability of polymer on temperature and composition of polymer. Littig & Dow, Ann. 188, p. 84.

9. Influence of monomer composition on thermal stability of polymer. H. Kondo, T. Yamada, T. Matsunaga, Ann. 185, 80.

10. Effect of temperature on thermal stability of polymer. C. Hedges & Temperley, J. Polym. Sci., 280-284.

Effect of polymerization conditions on thermal stability of polymer. III

11. Effect of polymerization conditions on thermal stability of polymer. H. Kondo, T. Yamada, T. Matsunaga, Ann. 185, 213.



12. Effect of polymerization conditions on thermal stability of polymer. H. Kondo, T. Yamada, T. Matsunaga, Ann. 185, 222.

13. Effect of polymerization conditions on thermal stability of polymer. G. Hedges & Temperley, J. Polym. Sci., 213.

14. Effect of polymerization conditions on thermal stability of polymer. H. Kondo, T. Yamada, T. Matsunaga, Ann. 185, 208.

15. Effect of polymerization conditions on thermal stability of polymer. H. Kondo, T. Yamada, T. Matsunaga, Ann. 185, 218.

16. Effect of polymerization conditions on thermal stability of polymer. H. Kondo, T. Yamada, T. Matsunaga, Ann. 185, 228.

17. Effect of polymerization conditions on thermal stability of polymer. H. Kondo, T. Yamada, T. Matsunaga, Ann. 185, 243.

18. Effect of polymerization conditions on thermal stability of polymer. H. Kondo, T. Yamada, T. Matsunaga, Ann. 185, 254.

XI. A note on various methods of polymerization. D. Bonnard.

I. Polymerization of styrene by benzoyl peroxide. G. Hedges & Temperley, J. Polym. Sci., 28, 1528.

II. Polymerization of styrene by benzoyl peroxide. G. Hedges & Temperley, J. Polym. Sci., 28, 1481.

III. Polymerization of styrene by benzoyl peroxide. G. Hedges & Temperley, J. Polym. Sci., 28, 1493.

19. Preparation of styrene and other polymers by benzoyl peroxide. H. Kondo, T. Yamada, T. Matsunaga, Ann. 185, 254-274.

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,  $\alpha$ -bromopropionic and  $\alpha$ -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. 1904 p. 555
5. Conc. the speed of the action of alcoholic potash on the halogen derivatives of the fatty hydrocarbons.  
 Meier 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 butyl haloids~~ <sup>in Am. J. Chem. Res. 158, 164</sup>
- ~~9. Action of potassium chloracetate, glacial acetic acid, potassium cyanide, etc.~~  
 10. Relation of opt. active to corresp. dl amylalcohols  
 Marckwald & Golda; Ber. (June 1909) p. 1583.

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

Malic		
Chlorsuccinic	Ber. 28, 1293	Ber. 32, 1833.
Asparaginic	Ber. 29, 135	Ber. 32, 1855.

#### XI

#### Work of Purdie and Williamson on 'Walden Inversion'.

1. Conv. of dextrolactic into laevolactic by means of the action of silver oxide on  $\alpha$ -chlorpropionic 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.'
Brompropionic	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 $\beta$ 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°.

(a)

3. Resistivity of the organic compounds  
George Bentz, T. G. Soc. 31, 460.  
Bro. I. G. Soc. (1908) 24, 88.  
ab. Part III. A same author I. G. Soc. Dec. 1908 b. 1852.  
Resistivity of bromobiphenyl and bromoanisole  
series and water with some other salts
4. Resistivity of Italy with major mistake.  
Burke Donner, T. G. Soc. 1804b. 222
5. Effect of water on the action of some of the  
negotiations between Italy and France  
Metz Wiedemann Zeit. Phys. 8, 69-74.
6. Action of water on the resistance of  
Tengleid Amer. Ch. J. 17, p. 24.
7. Effect of water on the resistance of  
G. H. Muller: Ber. 11, 414.  
lead to 220-222.
8. Action of water on the resistance of  
G. H. Muller: Ber. 11, 414.
9. Effect of water on the resistance of  
G. H. Muller: Ber. 11, 414.
10. Relation of water to the conductivity  
of organic substances: Ber. (Tome 1903) b. 1282.

X. Work of P. Wieden on 'Wieden Invention'.  
Office  
CHJofaranscious Ber. 38, 1833  
Absractins Ber. 36, 1833  
Ber. 30, 3143.

IX

Work of P. Wieden on 'Wieden Invention'.  
I. Com. to deftor of inventioon of a new  
series of water oxides on chlorobiphenyl  
T. G. Soc. 1886 b. 828.

XII. Work of P. Wieden on 'Wieden Invention'.  
Office Ber. 40, 1921, zur Kenntnis der Wiedenische Umrif-  
fne.

Bromobiphenyl Ber. 41, 1886. A study of the  
Ber. 41, 1886. A study of the  
case of deft. series avails  
Ber. 41, 1886. A study of the  
Ber. May 1903 b. 1212. No invention with  
Glycophthalic.  
Ber. Oct. 1903 A fact of Glyc & Cum Bromine  
abnormalities  
Bromobiphenyl also series  
Ber. Jan. 1910 Action of oil on  
series of water for  
at 100

- XIII. Work of MacKenzie on 'Walden Inversion.'
- Mandelic J. L. Ch. Soc.? Anomalous results with potassium hydroxide, silver oxide, etc.
- Phenylchloracetic 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  $\beta$ . bromine.  $\beta$ . Phenylpropionic acid.

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

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

Abstract 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. 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] 669.
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 Muskegonise on "Washen Inveration".  
 Murphy 1. I. Ch. Soc. Amer. Museum L. I. Ch. Soc. Amer. Museum  
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 Pennsylvania Bureau of Geology and Mineral Resources

XIV. Excellent review of work on "Washen Inveration".  
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 H. H. Allen. Washen Inveration. H. H. Allen. Washen Inveration.

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M. McNamee. Morphology of the Washen Inveration. 1. I. Ch. Soc. July 1903.  
 M. McNamee. Morphology of the Washen Inveration. 1. I. Ch. Soc. July 1903.  
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## XVI. On Stereoscopic methods. G. E. Perkins. Ber. 41, 1925.

XVII. Influence of gravity on the rotation of oil. A. C. Cook. July 1903. p. 158.  
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A. C. Cook. Influence of gravity on the rotation of oil. A. C. Cook. July 1903. p. 158.  
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A. C. Cook. Influence of gravity on the rotation of oil. A. C. Cook. July 1903. p. 158.

S. H. Bowditch. Description of the Washen Inveration. 1. I. Ch. Soc. 89, 1903.

S. H. Bowditch. Description of the Washen Inveration. 1. I. Ch. Soc. 89, 1903.

XX. Color. The rule for the selection of mineral compounds of interest. M. McNamee. 1. I. Ch. Soc. 89, 1903. Vol. 10, p. 157.

XXX. Action of some minerals on iron-lead salts. B. B. Bishop. Ber. 35, 1915.  
 Ber. 35, 1915.

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 &amp; 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.

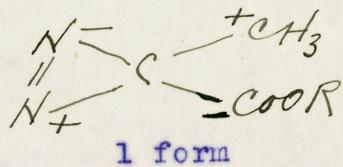
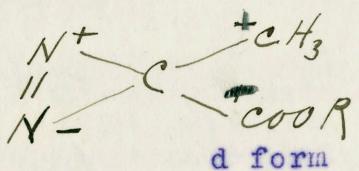
Fittig&Prehn: Ann. 188,142.

12. Also Ann. 188.87 Fittig&Horn  
 Ann. 143,343 Glaser Classed under other  
 Ann. 206.27 Fittig&Kast divisionss.

- XXXII. Studies in Oligocene Age
- Kellogg, Ann. Supply. I. 192-193  
Ann. Supply. S. 82.
- XXXIII. Studies of Unstabilized Ages
- Mifflin and Gifford  
Decomposition of the newer lava rocks  
with water.
1. Studies in unconsolidated soils  
Mifflin, Ann. 200. SI.
  2. Littig & Thompson, Ann. 200. 72.
  3. Properties of metamorphic soils  
Mifflin & Mengele, Ann. 200. 62.
  4. Hydrosoilogenesis and soiliness,  
Littig, Stahl, Lundeberg, and Mengele, Ann. 200. 45.
  5. Benthosologenesis,  
Bredt & Mifflin, Ann. 200. 28.
  6. Geog. the soils of the Colorado Plateau,  
Miffling & Palmer, Ann. 192, 193.
  7. Pseudomyelogenesis soils,  
Miffling & Palmer, Ann. 192, 193.
  8. Pseudomyelogenesis,  
Purcell, Ann. 200. 21.
  9. Abundance of mycorrhizal fungi,  
Miffling & Palmer, Ann. 208. 88.
  10. Terrestrial soils and pedogenesis,  
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  11. The colonization of soils resulting from glaciogenesis and mass wasting,  
Miffling & Palmer, Ann. 188, 192.
  12. Allo. Ann. 188. 82. Miffling & Palmer  
Ann. 143, 343 Glaser  
Ann. 206. 24 Miffling & Kast

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 ~~the~~ these compounds are not equivalent. The preparation of ~~the~~ diazo fatty acid esters is no easy matter ~~and~~ and besides it was necessary first to become thoroughly familiar with the properties of the optically active acids of the C<sub>3</sub> series.

propionic

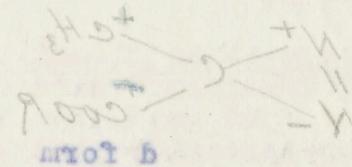
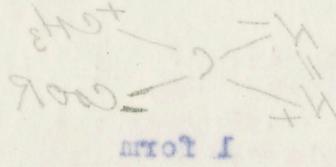
Optically active alanin was prepared according to Fisher's method by resolution of benzoyl alanin by means of brucin in aqueous solution. Benzoyl l alanin made in this way melted 147 - 149 degrees. The free base (l alanin) was made from the benzoyl derivative according to the directions of Fisher and Raske 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 Raske 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 decm tube; p = 1.020;  $[\alpha]_D^{29.5} = + 24.36$  degrees. The rotation given by Warburg for purest 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 | ⑤ Fisher & Warburg  
 ② C. J. G. C. J. G. 38, 401; Ber. 18, 1294 | Am. 340, 571  
 ③ E. Fischer & students: J. Pr. Ch. 2, 38, 401; Ber. 18, 1294 | ⑥ Fisher & Raske  
 ④ E. Fischer & Raske: Ber. 32 II, 2454. | ⑦ J. Pr. Ch. 2, 44, 564; Ber. 18, 1298 | Ber. 39, 3988  
 ⑧ E. Fischer & Raske: Ber. 32 II, 2451; Ber. 38, 487; Ber. 19, 850 | ⑨ J. Pr. Ch. 2, 44, 559; Ber. 19, 850 | Warburg:  
 Am. 340, 168

REPORT ON WORK ON THE MALLDEN IMMERSION.

There is a large number of people here who have been working on the project. The work is progressing well, and we are making good progress. The team is composed of experienced professionals from various fields. We are currently working on the final stages of the project, and we expect to complete it by the end of the month. The team consists of approximately 50 members, including engineers, scientists, and technicians. The work is being carried out in a coordinated manner, with each member contributing their expertise to the overall success of the project. The team is highly motivated and dedicated to the completion of the project. We are grateful for the support and cooperation of all involved in the project.



The project has been progressing well, and we are on track to meet our goals. The team is working hard and is committed to the success of the project. We are grateful for the support and cooperation of all involved in the project. The work is being carried out in a coordinated manner, with each member contributing their expertise to the overall success of the project. The team is highly motivated and dedicated to the completion of the project. We are grateful for the support and cooperation of all involved in the project.

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$$\frac{2}{2} \times 2 = 2$$

The above preparation of d brompropionic acid contains, therefore, 4.38% of the optical antipode as against 3% usually obtained by Fisher.

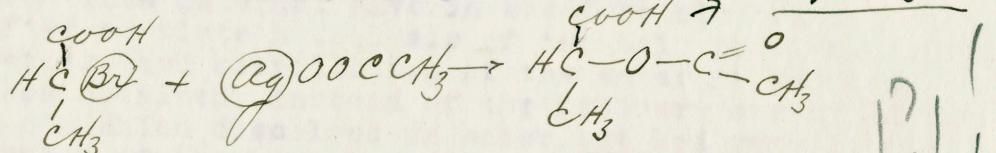
Inasmuch as nearly all of the experiments where an inversion was observed had been carried out in water solution, we set out to determine whether or not the same inversion could be obtained in non-aqueous solution. In order to establish first of all the influence of the solvent and to avoid also the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

Agacetate (1 mol) on d brompropionic 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 bromide. Silver bromide had to all appearances separated out quantitatively in 50-60 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 Miss Denis' directions proved that it consisted almost entirely of silver bromide and contained only the slightest trace of metallic silver.

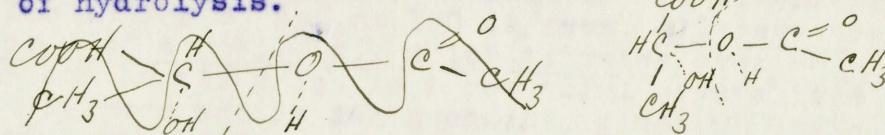
From the standpoint of metalepsis, we should expect to obtain in the ethereal filtrate  $\alpha$  acetyl propionic acid.

Action I



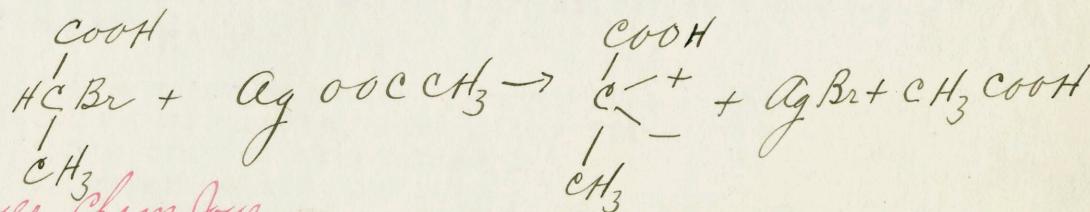
d brompropionic      d acetyl propionic  
 which would have the structure as given if no inversion accompanies the change. Such an acid according to Bischoff does not exist but would lose carbon dioxide spontaneously, just as  $\alpha$  aceto acetic acid does, and would yield acetic ethyl ester ( $\text{CH}_3\text{C}=\overset{\text{O}}{\underset{\text{CH}_3}{\text{O}}} \text{CH}_3$ ) which would then be subsequently hydrolyzed to give acetic acid.

If, however,  $\alpha$  acetyl propionic acid is capable of existence, just as much as  $\beta$  acetyl propionic acid (laevulinic) 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 bromide giving silver bromide and setting free acetic acid.

Action II



① Doctor's thesis: Amer. Chem. Soc.

② Bischoff-Wellicenus: Ann. 206, 313.

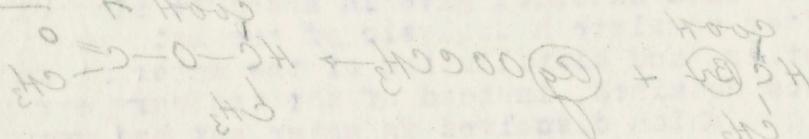
③ Grote & Tollens: Ber. 11, 2177; Wellicenus: Ann. 149, 328

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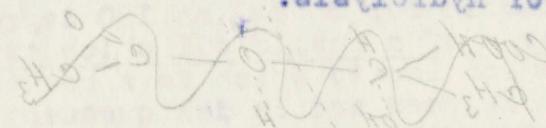
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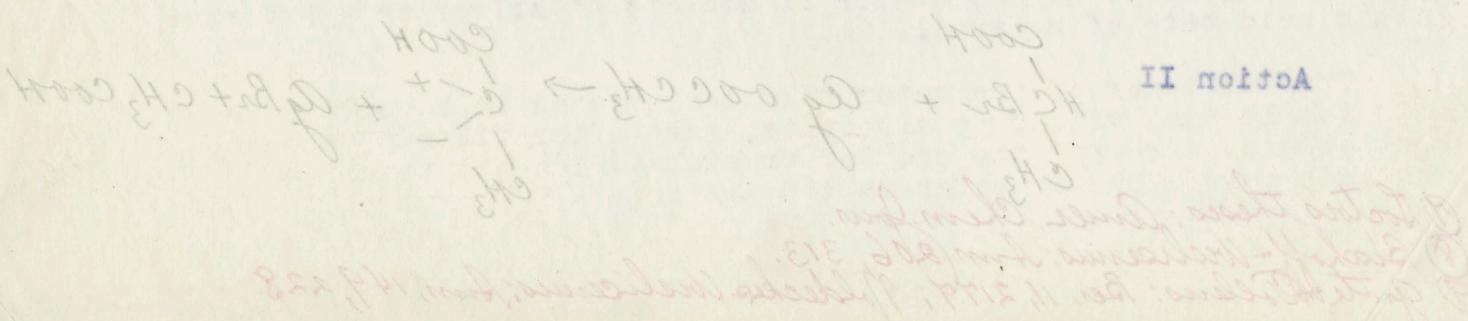
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II noisios

It is impossible to get any acrylic acid from & bromo 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 ( $\alpha$ -hydroxypropionic) acid. Any acrylic acid by 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 0.4g gum remained sticking to the silver bromide which was subsequently extracted with absolute alcohol. This material gave in absolute alcohol solution  $\alpha_{D}^{20} = +9.5$ . 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  $\alpha_{D}^{20} = +20.57$  degrees. The lack of mobility of the hydrolyzed gum found further confirmation in the fact that when it was titrated with  $\text{KOH}$  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 socalled oily lacticid 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 lacticid 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  $\alpha$ -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

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

(3) Glimenko: Ber. 23c, 325-48905  
(4) Pelouze:

(5) Wislicenus: Ann. 167, 302.

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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 H<sub>2</sub>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  $\alpha$ -bromopropionic acid very probably gives complete information as to zinc content of these zinc salts. As for 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°; 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°. Some <sup>racemization</sup> reaction 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.  $\alpha$  lactate, mixed with 89.15% of Zn. dl lactate. (7)

*how do you know  
what salt present?* 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°; p = 1.029;  $[\alpha]_{D}^{28} = +3.37^{\circ}$ . percent of active material  $= \frac{3.37}{7.7} = 45.54$ .

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 H<sub>2</sub>O demands 18.18% of crystal-water, while Zn d or l lactate 2 H<sub>2</sub>O requires only 12.76%. (9)

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  $\alpha$ -bromopropionic 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 bromopropionic acid (1 mol.) and 1.71 g. silver acetate (1 mol.) in water solution as a check gave an altogether similar result - much less racemation 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°;  $[\alpha]_{D}^{28} = +3.33^{\circ}$ . This experiment gave therefore

$$\frac{3.33}{7.7} = 43.22\% \text{ Zn } \alpha \text{ lactate}$$

$$71.61\% \text{ Zn dl lactate}$$

*Other percentages of active material are calculated from the constants established by Gmelin and adopted by Emil Fischer. Ganglisch finds values considerably different from these.*

Purdie  
Purdie  
R. Marckwald, Ph.D., Berlin, 1909, p. 1583.

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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 (2), 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 (2), 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 that the inversion takes place only with silver hydroxide, water and analogous 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 grains) titrated rapidly with  $\text{AgNO}_3$  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 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 filtered, obtaining 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  $2.37^{\circ}$  (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.

(2) N.Y. J. Am.

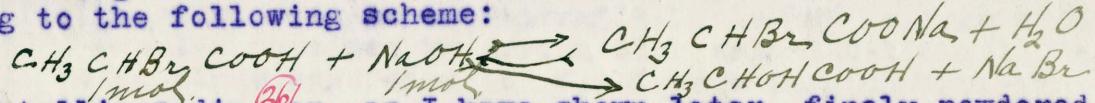
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Action of very dilute sodium hydroxide (0.1%) in water solution on d brompropionic acid.

1.5727 g. d brompropionic ( $\text{K}_{\alpha}^{29.5^{\circ}} = +24.36^{\circ}$ ) dissolved in 88 c.c. of 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 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  $+0.24^{\circ}$ .  $\text{K}_{\alpha}^{24^{\circ}} = +2.66^{\circ}$ .  $\frac{366}{873} = 30.47\%$  lactic acid lactate  $69.53\%$  zinc lactate

Titration of the salt residue rapidly with  $\frac{1}{10}$  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  $+0.25^{\circ}$ . 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  $\alpha$  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  $\alpha$  brompropionic 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  $\alpha$  brompropionic 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 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)

Bischoff Walden: Ber. 26, 263.

(25) Senter: Trans. R. Soc. 91, 460  
Proc. U.S. Soc. 1908, 24, 87  
4. J. Am. Chem. Soc. 1909, p. 1877

(26) Pitty: Ann. 200, 87

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

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.

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*in doubtful*  
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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.

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 (more properly acetyl propionic acid), as I have found, dissolves readily in water, both crystallized lacticid and the body previously described as polylactyl lactic, although insoluble in water, give by hydroly-

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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<sup>refractionating</sup> several times, no constant boiling material could be obtained. But by allowing the higher boiling fraction, 4.76 g.<sup>155-175</sup> 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 Anschutz and Bertrand<sup>29</sup> 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<sup>30</sup> who gives it as 134°(15mm.).

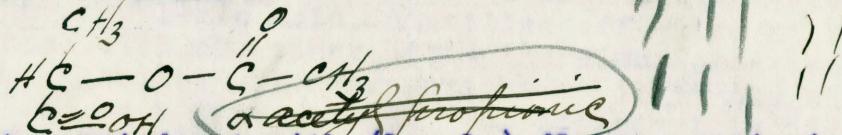
Just how the water causes such a transformation, as noted above, is hard to explain since very little acid material is swept over in the volatile distillate when the water added is distilled off at reduced pressure- this negates the idea that acetyl lactic acetate is formed as the first product. That 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 <sup>small</sup> amount of oil (4.1 g.) boiling above 180°(20mm.) and 43.5 g. non-nolatile 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

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also be accounted for by the amount of lactyl lactic present in the lactic as a result of standing. If acetic anhydride replaces the alcohol hydroxyl ( $\text{OH}$ ) 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 ( $1\frac{1}{2}$  mols.) silver acetate (17.72g.) in absolute ether 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 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  $140^{\circ}$ - $152^{\circ}$  (19mm.) for acetyl lactic: the main portion boiled from  $152^{\circ}$ - $190^{\circ}$  (19mm.) mainly  $170^{\circ}$ - $180^{\circ}$ . 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  $100^{\circ}$  (20mm.) 36.05g. crude acylated gum. 32.5g. of this material, heated further over metal bath  $140^{\circ}$ - $160^{\circ}$ , gave 2.81g. of acetic acid and acetic anhydride of B.pt  $64^{\circ}$ - $72^{\circ}$  (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  $140^{\circ}$ - $150^{\circ}$  (20mm.) or by sweeping over water in case the acylated gum does not split readily with water, as is the case with acetyl lactic.

#### Action of 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 brompropionic acid (10g).

After a short period of induction, as in the previous experiment with silver acetate, 7.68g. silver oxide ( $\frac{1}{2}$  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 d brompropionic in absolute ether. This gum (200c.c. ether) was shaken out with soda (100c.c. 5% soda solution) from ether.

(31)

edt ni tneaqeq qitlosi lytosl to fhuoms edt vd rot bejnuccos ed oais  
edt aecisqet ebirbyins citoes ti .gnibnata to fhuas ~~is~~ abjollosi  
-vos tqeqxe bluoda ew ,bios citoes ni quora (.R.O) lyxorbys lonoobs  
:siunrot evsd of citoes betsl

~~1988-01-24~~  
bios citoiqorqmoib ib (.fom 1) dtiw tuo bejriro tneaqeqe na  
redte etufoads ni (.357.71) etajecos revlia (.afom 1) bns (30.01)

.358.8 vianylo dtiw ejmifit laekete tlo gnillitalb revlia evag  
.359.1 dtiw bejserj .360.8 aint .bios citoes .360.9 bns mug ebrio  
-ni mug tilita .361 evag ,etajecos 21-01 rot neksa bns jctsw bios to  
tuo neksa ,mug eldufoani edT .eldufoe .362.8 ,jctsw ni eldufoa  
-loa edT .mug bios tilita .363.8 evag ,noitcoca rehje mort aboa dtiw  
et jafolitallitalb vd evag ,tneaqeqe rastaf a vd bevomq as ,mug eldu  
lafirejam to .364.0 tuoda vino noitiaoquocob nomi dtiw etnaseq beonb  
beliod noitq niam edt :citoes lyxorbys (.mmef) 365.1 anilled  
niam edt jatit berjatidatse gniyal .365-01-01 vliniam (.mmef) 001-21  
// bios citoal betslvcs ton asw tneaqeqe aint ni touborq noitcoca  
vrev vlinetra qd jatit bns ,aiguelatam elqna vd tqeqxe bluoda ew as  
dtiw enob asw rehjeut gniyalton ,benriot asw bios citoes eert elttif  
-rebianco ton ro redterw ,revewon ,noitcoca a ait .lafirejam aint  
tneaqeqe aint marit tneaqeq vlinetra asw bios citoes etom vldas  
a mort vlinetra rehje vrb edt tlo gnillitalb revlia ,erehw bewoda  
nqf a rot bejser asw lafirejam bios edt ,vianylo gniyal dtad-jctsw  
evrb of (.mmos) dtad jctsw gniyod edt to erufareqmet edt ja emit  
tauflit na as evres lliw tneaqeqe gniyoffot edT .citoes edt revo  
citoes dtiw tennam lanaq edt ni bejser citoes ib .365.8 :noitcoca  
ebrio .366.8 (.mmos) 001 ja evoda as noitallitalb vd evag ebirbyins  
lafirejam revo tennat betsel lafirejam ait to .367.8 mug betslvcs  
tq.8 to ebirbyins citoes bns bios citoes to .368.8 evag 190-190-190  
neea at ti aint .bios citoes to vjilidom bns robo- (.mmos) 19-19-19  
gnibnata amamer ayawla bios citoes to fhuoms eldsriebianco vrev jatit  
nqfah gniyod vd bevomer ed vino nso hoiaw mug betslvcs ebrio edt of  
mug betslvcs edt easo ni rehje revo gniqeeva vd to (.mmos) 001-01  
citoes lyxorbys dtiw easo edt ai as ,jctsw dtiw vlinetra jifqa ton asob  
.rehe .ada ni bios citoiqorqmoib ib no ebixo revlia to noitcoca  
bios edt to erufan edt vlinetra etom vldas of rehje ni  
vlinetra rot eldaavha bejser asw ti ,aiguelatam vd beniatdo mug  
,dtiw evoda as ton redte etufoads ni tneaqeqe edt tuo vldas of  
,redte etufoads ni tneaqeqe edt tuo vldas of  
-teqxe anolwerq edt ni as ,noitcoca to boiteq trida a rehje  
-vd tlo zifq (.fomg) ebixo revlia .369.7 ,etajecos revlia dtiw tneaqeqe  
ni bejlosaib (.fom 1) bios citoiqorqmoib ib 21.01 mort ebimoid nezotb  
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-nqmax .tuor eno to ebiant ebimoid revlia to noitcoca etelqmc a  
-llatam on bewoda noitcoca rehje eldsriebianco gniyig rehje edt to noitcoca  
noitabixo to fhuoms eldsriebianco on jatit betslvcs hoiaw revlia of  
-lit laekete edt mort beniatdo erehw mug to .370.8 .eoifq neksj bns  
-redte etufoads emosed ,emit trida a rot gnibnata vd ,mug aint .redte  
beniatdo jatit as emsa edt asw ,aecostaqeqa lls of ,bns elidom-nq  
b as lliw as citoiqorqmoib ib no etajecos revlia to noitcoca edt vd  
neksa asw (redte .o.000) mug aint .redte etufoads ni citoiqorqmoib  
-redte mort (noitcoca aboa 25.0.001) aboa dtiw tuo

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. 3.1 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.), 13.0g. 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 ( $\frac{1}{2}$  mol.) silver oxide (7.68g) 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 + $3H_2O$ )
% Zn. in anhyd. salt	26.96	26.39	26.89 (Zn. dl lactate)

3.0g. of gum gave thus by treatment with zinc carbonate etc. 3.69 g. first crop, 0.7423 g. <sup>(air-dry)</sup> as 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 <sup>(of crop I)</sup>, 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

(10)

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to aseoxe figila njiw beserit nerit isid ḡ tot 001 ja beseri aw  
beoubet ja tetaw to helleitaib, bios okioobiyd eftib brabnaja  
awit beniatdo awt erenit - oje renje vib njiw beseritke ,stusaeq  
nolitw bns vifidom figila vire vino bad dolitw mug s to .3 82.4  
beserit ,oitoal lytoal to .3 1.82 bios eft s as 20.74 vino beserit  
001 ja emitulos emisais ni beseri bns aboa njiw vsw xalimia s ni  
beserit nolitw mug elidom vifist to .3 82.5 evag .oje axon xia tot  
vd beisagerq ,oitoal lytoal ebuto .3 82.01 .bios eft s as 20.87  
.o.3 8.02 ni vlibser bevisatib .sin 3 tot 041-051 oitoal ib gnijsen  
00-208 .sin ḡ beseri awt etuukim alit nerit .ebibydnas oitoos to  
oitoos to aseoxe bns bios oitoos to gniilitaiib reftis ,evag ji  
ebuto .30.81 ,(.in ḡ tot 001 ot vifanit gnijsen) .nn 82 ja ebibydnas  
-tetam alit ,tetaw bios .o.3 81 njiw tnefisit vH .touborg beisagerq  
tetaw ni elidoua .3 82.4 bns tetaw ni elidouani mug .3 80.7 evag lai  
etelqmooc reftis ,evag mug elidouani eft to .3 84 .(oitoos motl eft)  
s as 21.08 beserit nolitw llo elidom .3 80.4 ,tetaw njiw alyvitydn  
.sin ḡ tot noitulos tetaw ni gnijsenja reftis 20.40 bns bios eft

oitoigotqmoit ib no n itufos tetaw ni ebiko revifa to noitulos  
.bios

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-fts to noitulos biqst , (etumim 81-01) noitulos to beisagerq tnefisit  
vd awt nolitw noitulos to eftib vifist s ,etusaeq beoubet ja  
tuo melada awt mug alit .tetaw ni elidoua vifefiqmoo awt nolitw  
abo eft (.o.3 002) tento motl noitulos aboa 20 .o.3 001 njiw  
vire njiw gnijsen vH .sin ḡ tot 001 ja beseri nerit awt noitulos  
to gniilitaiib, bios okioobiyd eftib brabnaja to aseoxe figila  
.3 82.8 .oje ,tento vib njiw beseritke ,etusaeq beoubet ja  
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omis to aseoxe njiw gniilitaiib vd atisa omis otni beisagerq awt  
atisa omis ,emiflataylo ,elidoua vififisitib evag bns etamodiso  
omis to seorit ot foegaei vire ni xalimia alyvitydn evag nolitw  
njiw tnefisitqke eft motl beniatdo aqoic owt to alyvianA .etatosi  
evag noitulos tetaw ni ebiko revifa  
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-ni +isa omis oiasd to seorit s beniatdo ,beisagerq as ,qoto njiw  
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eemit gnijsen plesvietni tnefisit ja vifefisit gnijsenja vd noitulos  
tentor wof ai omis to etuulads eft tsit befon ed of ai tI .motw

*(than)* 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  $150^{\circ}$  in place of  $100^{\circ}$  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  $105^{\circ}$ - $115^{\circ}$ . When 5 c.c. dl lactic (88.1%) or the product (obtained after heating dl lactic in water solution at  $120^{\circ}$  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 hydrazin *sulf* 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  $100^{\circ}$ - $114^{\circ}$  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  $110^{\circ}$ - $120^{\circ}$ , 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. 5 c.c. dl lactic (88.1% Kahlbaum product) titrated 80.2% as a free acid; when another 5 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. When 11.5 c.c. dl lactic (88.1% Kahlbaum product) is heated for four hrs.  $90^{\circ}$ - $100^{\circ}$  (20mm.), 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. dl lactic (88.1% Kahl. prod.) was heated for 6 hrs. with 50 c.c. water in an oil bath kept at  $110^{\circ}$ - $120^{\circ}$ . 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 Liebig's Annalen,*

bios oitoalib bios oifysas tafit viflora yiev aefasibni hofiw dafid  
tmeesib tom eis (atouborq noitisa ebco isilimia resto as Ifew as)  
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taff evoda raf my Iffw onis to agatneceq eit tadt tuo hnt van  
-tied ni befatiqicetq asw onis eit reTA . aefasib onis tot behnaneb  
bios elidom vifist to .g 3.1 , ebifqun negevibd ntiw noitufos gni  
lynerq to emifov laupe na ntiw tneutserit no hofiw benistdo eiew my  
neefit mi vlefelqmc bekillatayc forocla etufoads bios omisibynd

ai touborq bios eit tafit consibve gnotra yiev ai aint . aefunim

bns tafit ntiw Ifew ymidaw , tto ynfifit reTA . aeoenegeonm  
erev bnuoqmc emiasibynd lynerq eburo to .g 30.2 etafq yaflo no gntib  
eit to (31.88) oitoal ib .o.od 001-001 ja gniffem benistdo touborq  
ot 001 to noitufos tafaw ni oitoal ib gniffem tafit benistdo touborq  
exuaaqb becuber ja tafaw tto gniffitab vlfneupeadus bns aifon xia  
-tibynd lynerq to emifov laupe na ntiw tennam isilimia s ni befaerit ai  
noitufos tafit benistdo vifist as aw etafq , forocla etufoads bns enis  
-rejifit tafit reTA . aefunim neefit ni bnuoqmc nissibynd lynerq eburo to  
eburo eit , etafq yaflo no gntib bns tafit ntiw Ifew ymidaw , gni

. noitufos asg ntiw 001-001 ja beffem bns .g 31.0 beffew tles

lyne oitoal ton mott tisa eburo eit exifisatayc ot tqmefja nA  
.oafq doot laifetam to aefi eldsarebianco as houm as ni befaerit tafaw  
ai laifetam eit to tafitup eno tafit vlfneupeadus tneutreque eit  
-dasw elqmi . bevoromi ton ai tafit gniffem eit bns beffewocer aint

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-tibynd lynerq eit . yofoc woffey tafit vifist as vlfneupeadus bns  
-tibynd tafit vifist as vlfneupeadus bns tafit vifist as vlfneupeadus bns  
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on to ed vlfneupeadus ntiw evitatiqnaup jaomia eit , revewom  
bios v xo isilimia resto to noitufos eit tot si fi hnt eau etom

biof vlfneupeadus eit tot si fi hnt eau etom  
. bns tafit vlfneupeadus eit tot si fi hnt eau etom

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(.tom 1 ) bios oinoidoqmcot ib .g 3.01 . tafit etufoads ni tafit  
taff etufoads .o.o 001 ni (.tom 1 ) ebixho revilia .g 37.7 ntiw beffew  
nfiw elidom-non vlfneupeadus aemoced hofiw myg bios eburo .g 3.8 evaq  
.o.o 7.0 ntiw aet nif net tot neidam , laifetam aint to .g 38.4 blos  
taff .g 39.0 vlfneupeadus bios tafaw ni eldufoani myg .g 38.3 evaq , tafaw to  
vlfneupeadus bios tafaw ni eldufoani myg .g 38.2 evaq , tafaw to  
vlfneupeadus bios tafaw ni eldufoani .g 3.5 eit s as 3.82

hofiw noitufos bios na evaq , 001-001 ja tafaw to aifaq evit ntiw  
eit tto gniffitab reTA . bios eit s as 3.0.3 beffew , bios hofiw  
.g 3.5 (.mm 2S) exuaaqb becuber ja noitufos tafaw eit to rebniamet  
bios eit s as 3.5.6 vlfneupeadus hofiw benistdo eiew myg tifit to  
-hofiso onis ntiw noitufos tafaw ni beffew , laifetam aint to .g 38.0  
eit 111 ynfifit tisa onis exifisatayc eldufoa vlfneupeadus s evaq , etas  
touborq muqifial (31.88) oitoal ib .o.od . etasof onis to aefunimreque  
ni beffewocer aw .o.od rebniamet hofiw , bios eit s as 3.0.8 beffew  
exuaaqb becuber ja tafaw tto gniffitab tafit bns tafaw to .o.o 08  
. bios eit s as 3.1.8 beffew , bios hofiw qifva elidom to .g 3.1.8 evaq  
. etasof onis to beffew , (touborq muqifial (31.88) oitoal ib .o.od .  
ti tafit bios eit tot noitufos tafit vifista etefqmc emos (.mm 05) 00-100

taff . tafit vifista etefqmc emos (.mm 05) 00-100

(.31.88) oitoal ib .g 38.11 tneutreque tafit tafit vifista etefqmc emos (.mm 05)  
00-100 ja tafit tafit vifista etefqmc emos (.mm 05) 00-100

water at reduced pressure, 9.45 g. mobile oil. By heating with 3 pts. of acetic anhydride  $80^{\circ}$ - $100^{\circ}$  for 7 hrs. and distilling off acetic acid and excess of acetic anhydride at reduced pressure (20mm.) heating finally to  $100^{\circ}$  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 <sup>the</sup> water and remaining acetic acid at reduced pressure, 12.45 g. of acylated gum were left. This gave by fractional distillation @  $6.83^{\circ}$  g. of B. pt.  $133^{\circ}$ - $137^{\circ}$  (18mm.) mainly  $134^{\circ}$ - $6^{\circ}$ -acetyl lactic, 4.0 g. boiling  $137^{\circ}$ - $180^{\circ}$  (18mm.) mainly  $140^{\circ}$ - $160^{\circ}$ , @ 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 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  $134^{\circ}$ - $136^{\circ}$  (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.  $80^{\circ}$ - $90^{\circ}$  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. total), insoluble in water, was hydrolyzed twice with water in oil bath kept at  $110^{\circ}$ - $120^{\circ}$  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 g. 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 <sup>this manner</sup> 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 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  $110^{\circ}$ - $120^{\circ}$ . After distilling off water at reduced pressure, heating finally  $80^{\circ}$ - $90^{\circ}$  for  $\frac{1}{2}$  hr., 3.88 g. of gum were obtained which possessed very little mobility. This material titrated only 55.9% 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-

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(13)

bile on standing several days. This material was then heated with 3 pts. of acetic anhydride  $80\text{--}90^\circ$  7 hrs., and gave, after distilling off acetic acid and excess of acetic anhydride at reduced pressure (20mm.) [heating finally at  $100\text{--}\frac{1}{2}\text{ hr.}$ ] 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  $100^\circ$ ), 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. 5/6 of the solution (cont. 3.1 g. acid) obtained by hydrolysis of the total insoluble gum, <sup>was</sup> ~~gave~~ <sup>reheated</sup> 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 acid obtained by hydrolysis <sup>has</sup> properties totally different from ~~the~~ mobile syrupy lactic acid.

### as carbonate + dl brompropionic acid in water solution

In order to repeat exactly the experiment of Fisher and Walden, <sup>(33)</sup> 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  $110\text{--}120^\circ$  under reflux condenser, gave, after distilling off water at reduced pressure (20mm.) [heating finally  $80\text{--}90\text{--}\frac{1}{2}\text{ hr.}$ ] 2.05 g. stiff gum which titrated only 59.9% as a free acid. After distilling off water at reduced pressure (20mm.) [heating finally  $80\text{--}90\text{--}\frac{1}{2}\text{ hr.}$ ] <sup>this material</sup> 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.  $95\text{--}102^\circ$  with gas evolution. Silver carbonate in water solution therefore gives exactly the same result as silver oxide.

### Agacetate + 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

<sup>(33)</sup> P. Walden,  
E. Fisher;

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"mix up" or meas.

without appreciable heat evolution. Reaction was allowed to proceed for  $29\frac{1}{2}$  hrs. There was obtained, after two hydrolyses of the filtrate at  $110^{\circ}\text{-}120^{\circ}$ , 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  $\text{HgSO}_4$ ) which decomposed at  $98^{\circ}\text{-}103^{\circ}$ . 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

*heating only 80°* 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  $120^{\circ}$  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  $120^{\circ}\text{-}140^{\circ}$ , but not in water solution at  $120^{\circ}$  gives an anhydride lactyl lactic, 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 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  $150^{\circ}$  this experiment was not tried. By heating dl lactic at  $120^{\circ}\text{-}140^{\circ}$  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  $120^{\circ}$ , is split almost quantitatively giving mobile syrupy lactic acid. That free dl lactic is thus obtained is shown not only by the 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  $180^{\circ}$  for 3 hrs. (20mm.), a considerable amount of material distills over, while the residual material, however, consisted entirely of lactic acid condensation product <sup>mostly</sup> ~~mostly~~ polylactyl lactic, insoluble in water <sup>but</sup> containing <sup>also</sup> a small amount of soluble

(34) Wislicenus: Ann 167, 302.

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monomolecular lactyl lactic. The same insoluble condensation product is obtained by heating lactyl lactic  $80^{\circ}$ - $100^{\circ}$  with acetic anhydride. To my knowledge, this observation has never been previously recorded in the literature. By hydrolysis of polylactyl lactic with 5 pts. of water at  $120^{\circ}$ - $130^{\circ}$ , it is necessary to heat for 8 hrs. to get oil completely into solution, by heating further for 6 hrs. at  $120^{\circ}$ , 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.  $121^{\circ}$ - $124^{\circ}$ )<sup>(35)</sup>, prepared according to the method of Bischoff and Walden, by dry distillation of sodium brompropionate, was found to be totally different from polylactyl lactic, obtained as above. The statement in the literature that lactid is formed simply by heating dl lactic to  $180^{\circ}$ <sup>(36)</sup> was therefore found to be incorrect. Polylactyl lactic dissolves readily in ether, is non-volatile at  $300^{\circ}$  (20mm.) and shows absolutely no tendency to crystallize. Lactid (of m. pt.  $125^{\circ}$ ), 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  $255^{\circ}$  at ordinary pressure.<sup>(37)</sup> 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  $100^{\circ}$  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  $180^{\circ}$  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  $250^{\circ}$ - $300^{\circ}$ , it was necessary to heat with naked flame ( $400^{\circ}$ ) in order to drive over the oily distillate. The lactid should have distilled here at about  $180^{\circ}$  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 <sup>and</sup> acid towards so soda. This material titrated only 67.0% as a free acid even after heating soda solution  $4\frac{1}{2}$  hrs. to  $100^{\circ}$ . 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.

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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 brom-propionic 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.

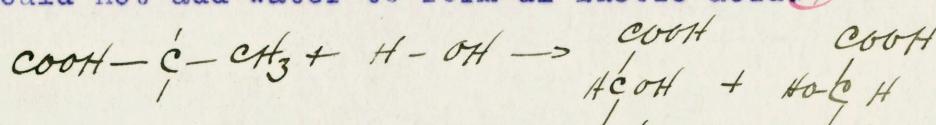
The non-mobile gums, insoluble in water (from the action of silver oxide on dl brompropionic in water and in absolute ether solution) gave, after hydrolysis and treatment with brucin, as indicated above, almost quantitative separation of exactly similar brucin salts in three or four crops from absolute alcohol. The brucin salts thus obtained melted ~~sharply~~ <sup>at</sup> ~~from~~ 200°-212° mainly 208°-211°. Brucin dl lactate melts ~~at~~ sharply <sup>at</sup> 212° <sup>(38)</sup> 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 ( $\text{AgO} + \text{Br}$  prop. acid in water solution) melting 200°-211° gave  $\Delta T_f = -29.36^\circ$ . 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  $\Delta T_f = -29.02^\circ$ . Brucin dl lactate gives  $\Delta T_f = -29.05^\circ$ . A sample from crop III ( $\text{AgO} + \text{Br}$  prop. acid in abs. ether) melting at 205°-211° dissolved clearly in water (no free Brucin) and gave  $\Delta T_f = -32.74^\circ$ .

#### 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, 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 hydroacrylic acid (B hydroxypropionic). <sup>(40)</sup>

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. <sup>Formation</sup> 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 B substituted propionic acid as addition product. <sup>(41)</sup>

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 dl lactic acid. <sup>(42)</sup>



<sup>(38)</sup> *De laus: Am. Symp. 2, 128*  
<sup>(39)</sup> *Ginsenam: Ann. 171/293; Ann. 163, 95*  
<sup>(40)</sup> *Wielicinski: Ann. 166, 6.*

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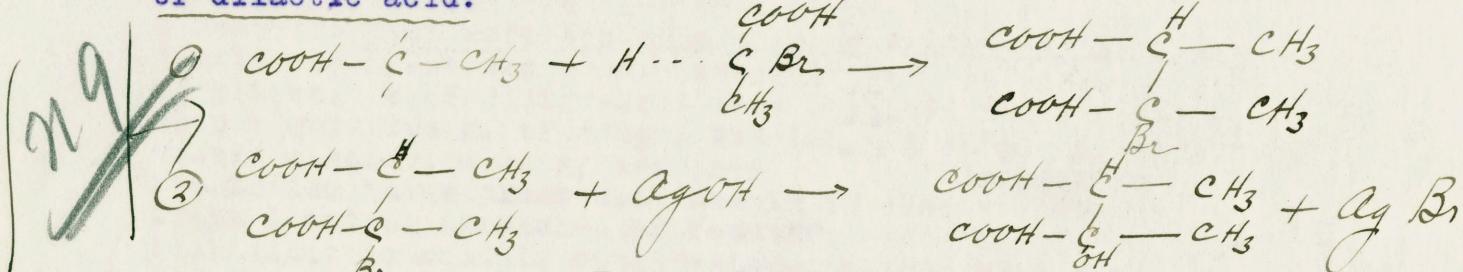
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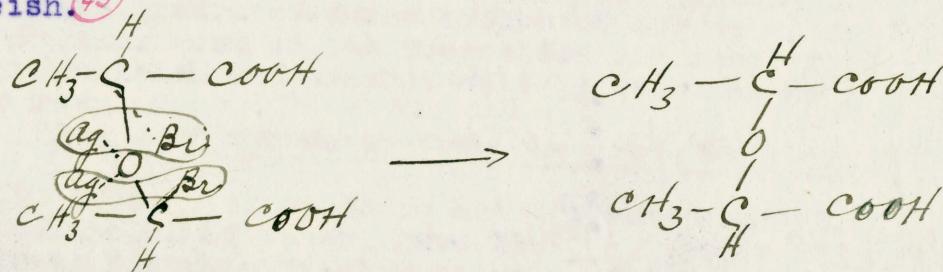
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Where the action is carried out in absolute ether, the water formed in the presence of the large amount of diluent, may add to the unsaturated intermediate product in only a very small measure; as the main reaction we should expect either a formation, 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 brompropionic 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.<sup>45</sup>



Dilactic acid was prepared according to the latest method by the action of sodium ethyl lactate on dl brompropionic ethyl ester in absolute ether solution. Dilactic diethyl ester, thus obtained, boiled at 121°-136°(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 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 II (air-dry) of d.cpt. 125°-138°. The dried salt gave  $\Delta_{D}^{20} = -32.16$ , 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.

<sup>45</sup> Jungfleisch & Godchot: Centralblatt, 1907 II, 136.

<sup>46</sup> Jungfleisch & Godchot: Comptes Rendus, 144, 979 (May 1907).

<sup>47</sup> Jungfleisch & Godchot: Comptes Rendus, 146, 26-29.



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 <sup>here</sup> 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  $\Delta D = -30.47^{\circ}$ . 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  $\Delta D = -32.16^{\circ}$  instead of  $-29.02^{\circ}$  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 12c.c. absolute alcohol, a continual stream of dry  $HCl$  gas (<sup>hydrogen chloride</sup>) 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 300c.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 <sup>solution</sup>. This slightly alkaline solution was extracted six times with ether using about 150c.c. ether each time. The ether solution after being dried twice with <sup>chloride</sup> of calcium was distilled off finally at reduced pressure (20mm), heating only to  $50^{\circ}-60^{\circ}$ . 11.65 g. crude oil were thus obtained. By fractional distillation this gave:

8.47 g. of Bpt.  $58^{\circ}-62^{\circ}$  (14mm).

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

0.35 g. non-volatile.

Fract. @ 8.4% of B. pt.  $58^{\circ}-62^{\circ}$  (14mm.), gave by redistillation 8.27 g. of B.pt  $55^{\circ}-57^{\circ}$  (15mm.) <sup>fact. a'</sup> 6.5 g. of fract. a boiling at  $55-57$  (15mm.) treated with 7 c.c. of water, gave by shaking 3.1 c.c. insoluble oil which on redistillation gave 2.55g. boiling constantly  $52^{\circ}-53^{\circ}$  (15mm.). To recover the ester soluble in water, the water solution was extracted three times with ether etc. <sup>it</sup> gave finally 2.2 g. of B. pt.  $55^{\circ}-58^{\circ}$  (15mm.) 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



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  $54^{\circ}-57^{\circ}$  (14-15mm.), dissolves when heated with strong aqueous sodium hydroxide without any noticeable odor or coloration.

The oil, obtained above, insoluble in water of B.pt.  $52^{\circ}-53^{\circ}$  (15mm.) ~~had~~<sup>sharp</sup> 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  $108^{\circ}-140^{\circ}$  (12mm.) 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  $\alpha$ -ethyl lactate (Kahlbaum product), a very small amount was found to have B.pt.  $100^{\circ}-140^{\circ}$  (14-15mm.) but dissolved readily in an equal volume of water. The main product had B.pt. of  $52^{\circ}-53^{\circ}$  (15mm.) and was insoluble in water, and therefore had all the properties of  $\alpha$  or  $\beta$  chlorpropionic ethyl ester (B.pt.  $55^{\circ}-58^{\circ}$  (15mm.)). The ester soluble in water of B.pt.  $55^{\circ}-58^{\circ}$  (15mm.), 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~~ <sup>after</sup> 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 poly-lactyl lactic or cryst. lactid. But lactyl lactic, poly-lactyl lactic (obtained by heating dl lactic to  $180^{\circ}$ ) and crystalline lactid of m.pt  $125^{\circ}$  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 <sup>52</sup> 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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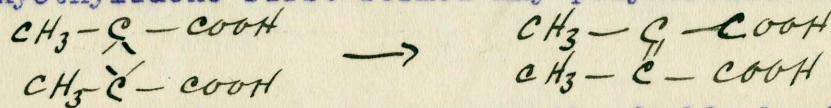
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njiw gntiseb xetla eson bns aye ent gntsebli robo qisnia (.mmf)  
xetlia to tnuoma eyris krev a evsg ti ebixorbyd muibos oiforcois  
muifofos xsefo-etsatin xetlia njiw tneatser tneareadua vd ebixorbyd  
-xetbyd muibos aueups njiw gntiser no ebvnebli nolo ro robo on bns  
. ebi

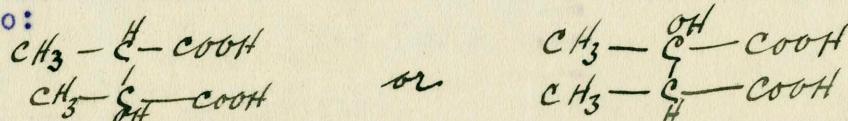
-foam ed of bnyot asw xetaw (.mmf) 108-140 ymlii-pofit emT  
njiw gntiser vd ebixorbyd xetlia to aecot vly evsg bns xetaw ni eldu  
xetlia njiw tneatser tneareadua bns ebixorbyd muibos oiforcois  
-nwoed on bns ebvnebli nolo ro to xetli emT emT ro qisnia A . etstint  
nlo ebixorbyd muibos aueups njiw gntiser vd benisido asw niaer hei  
tnuoma krev a (touborg musmif) tafatj lynde to noitalaffitaih  
ni vlybser nevlosaib jnd (.mmf-41) 14-140 (14-140) tq.B. evan of bnyot asw  
(.mmf-82-82) to . tq.B. bas tnebont nif . tq.B. to emtov laupe ns  
to aetfregorq ent lls bad eftelerent bns , xetaw ni eldufoam asw bns  
ni eldufoz xetaw emT (. . tq.B. xetaw lynde oiforcois qisnia  
tnuoma eyris ni bennot oals ai hoifw (.mmf-82-82) tq.B.  
gntliod emsa ent vlytakse bns xetaw ni vlytakse emsa asd hoifw bns  
-qs ti jast ni xetla ent mort xetli xetaw lynde oitczi as  
oitalaffitaih a evig bns nevlosa to tnuoma krev a niaer of aiz  
ent to weiv ni . ilaliz aueups ymoxia njiw betsed neww niaer hei  
tngim bennot xatil xetaw lynde oitczi tneatserq ent ni jast jost  
oimoiqeqiofio ojnt bios oiforcois ymlii njiw bennotansit ed  
of yam tneatserq ent oitczi tneatserq ent , nevlosaib ati to ro xetaw  
betimif vlyo ynlia , omoitbnoz tneatserq xebnu betseger ed eyatavba  
yda , smoitbnoz jaetal a'nsa' emtov of ymlii aza (.N) to tnuoma llsma  
emola forcois xtuofia njiw edut belsea ni bios ebuto ent gntiser  
. bios oitcziqura to esot a to esotserq ent ni ro  
noitsiocoz to aetfregorq oitczi

-seig ent ni noitalaffitaih oitczi vd tngim bennot xatil bios oitczi  
lytakse vlybser nriot , tneas tneatser as ymlios , ebixo xetlia to eson  
. bios . tayro to oitczi lytakse as llyew as (xetaw na) oitczi  
ot oitczi lls gntiser vd benisido oitczi lytakse llyew , oitczi lytakse jnd  
lls yqurya elidom evig lls 881 tq.m to bios emtov bns (081  
njiw oitczi lytakse to aitayforbyd emT . aitayforbyd vd bios oitczi  
a evig amn xia ni etelqmoz vlytakse as hoifw xetaw gntliod  
xetaw ymlii oitczi ent ni jast ot noitalaffitaih ymlii  
-ni ymlii ai xetaw njiw to aitayforbyd ent oitczi lytakse  
benisatoes ymlii . tneatser rof xetaw njiw gntliod xetla etelqmoz  
to esot mort tneatserq aetfregorq bas touborg beayforbyd ent jast  
noitalaffitaih oitczi ot eub evoda bennotnem aelbod esot ent , oitczi lls  
-xetion . Difis-  
-tneatserbiamos mort hevomer eis bennot xatil bios oitczi to  
tneatser s reweom eis ent . ebvnebli vlybser need oals as bios oit  
-tot ejasibemnefni ent no ymlii oitczi aetfregorq ait ymlii  
tneatser tneatser njiw esatnebnoz yam hoifw emtov ymlii to noital  
-tneatser oals ai hoifw bios oiforcois evitos evig xatil yam ro nraa as  
xatil eftedorqmi lls ja tom ai fi . atmegaser aotisav ymlii  
-tneatser yam noital bios biqer a lo tneatser ent ai emtov ymlii  
-tneatser emtov ymlii as xatil (bios oiforcois evitos) emtov ymlii

ranges to ethylene, or as oxyethylidene to oxyethylene (vinyl alcohol.) Compare Nef<sup>54</sup> 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 ~~anab~~ 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 glycine.<sup>55</sup> 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°(85-90mm.) were treated with 13.28 g. of dry silver oxide in 100c.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°(23-27mm.) 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, 18.98g. silver bromide, silver oxide and metallic silver. After treatment with an excess (about 400c.c. 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 80c.c. 28.6% potassium cyanide solution and washing with 40c.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 Fisher: Ber. 40, 1051

-cossia kytiv (Kytiv) efti asxekylyamec as to asxekylyamec aszgaz  
 owt, nevezet, paveret, aint no hasek aszgaz. Before this time (Kytiv)  
 betasz ed of niamer bezevba aszgaz bialiansipq  
 :exizmey vam bezrot tarit asxekylyamec aszgaz  
 Cariboo - 2 - 2000 CH<sub>3</sub>  
 Cariboo - 2 - 2000 CH<sub>3</sub> ←  
 Cariboo - 2 - 2000 CH<sub>3</sub>

ni, revo ob vam bnow eldich enf ts retez to noitibbs enf vyd molnir  
 :otni, bslt.



oktymosai villositorita eis holdw asibod oktymosai eosqa emsa esent  
 vbsatil as, villositora bezrot ed vam (repte entt a)bios oktymosai  
 of bios oktymosai bezenom to noitibbs tsent vyd, betzok  
 zelit evan of asibod esent tsogke bluora ew .asxekylyamec aszgaz  
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 ment tsogke bluora ew quorl iforocls enf to esenesq enf to esenesq  
 .esnotol S.I to B.bns otm bezrotansit vifase ed of

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.noitibbs tenfle etuocads

ebixia nerw esolt asibod asayforbyd tarit jast enf to esenesq  
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 ebixo retilia to noitibbs enf natiyaet of bezrot asw retez, noitibbs  
 a ntiw easo bezrosl as to ansem vyd abias negold to esenesq enf no  
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 ati bus bios oktymosai eest neewted, rewevod, beveado asw some  
 -vitcs zuebmennet a zwora bios enf elidw .retez fynto gyldvozaet  
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 ntiw betzert ewew 00-58-33 .B. B. To retez fynto oktymosai  
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 bus .A.S tot esmelszturq vianibio ja bns of esutkim gniwoell  
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 to retez fynto oktymosai bezenom to .g 80.81 evag noitallitib  
 .g 88.0 .g 77.0 bus (.mm-53-80) .B.g .88-83 .B.  
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 .g 5.05 .retez oktymosai no etzitlit fynto mubos to noitibbs  
 ebixo retilia vif .g 70.81 ntiw betzert, retez fynto oktymosai  
 -lia .g 80.81 ,noitallitib retilia evag .180-150 .A.S tot betzen bus  
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 .benistdo asw retilia offisatem .g 88.0 ,benignom berenccer at noitibbs  
 zof zkoenf )lio elidom to .g 11.11 ,repte tho gntifig retez  
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 .anoitosei gniwoell  
 (.mm 88-100(81-83 mm .g 8.82

1963-02-22

1963-02-22

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

By redistillation

Fract. <sup>4.2g gave</sup> 3.37 g. 63°-80°(20 mm.) mainly 65°-69°

Fracts. b c <sup>4.1g gave</sup> 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 <sup>and</sup> metallic silver. By treatment with an excess (about 600 c.c.) of dilute ammonia (sp.g. 0.97), 24.62 g. of silver bromide <sup>and</sup> 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 <sup>silver</sup> remained undissolved. 16.15 g. of mobile gum were obtained by distilling off ethereal filtrate finally at reduced pressure <sup>heating finally</sup> 50°-60°(20 mm.) which gave by fractionation:

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

1.5 g. non-volatile.

By Redistillation: gave

Fracts. a b (2.90 g), having slight stinging odor, <sup>gave</sup>:  
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 <sup>gave</sup>:

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

Fract. e <sup>gave</sup>

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 <sup>neutral</sup> 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 <sup>3.7g fract. II</sup> 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.

(IS)

100-112(SI mm)	.3 41.0
112-140(SI mm)	.3 38.0
130-170(SI mm)	.3 43.0
non-mon-	.3 30.0

BA ~~reheisitzaibet~~

• 3.23 g. 83-80(SI mm) ~~Reiset~~

(.mm 80(SI mm) 112-140(SI mm) ~~Reiset~~

bellitzaiber tom saw h ~~Reiset~~

oimotqomord .3 ed.88 njiw tuo beiriso tneqeqe xamia A  
xente etufoads .3.0 ni ebiko revilia vrb .3.81 bns xetaf xet  
ja gnisad vB .3.82 tot blio ent ni gnihsata no hoitoz om eva  
benistdo asw erext (xente tho gnihsatah xetla). xnt Of tot ISO-130°tot  
revilia ebimord revilia .3 28.72 xetla vrb njiw noitositxke xetla  
.3.008 tuoda aaseoxe na njiw tneqeqe vB .revilia offlatem ebiko  
offlatem ebimord revilia to .3 28.48 (.3.0 .3.0) zinomus etufo  
28.82 .3.0 100 njiw tneqeqe xetla vB .benetocer etew revilia  
noitulos ebinsyo to etew .3.00 njiw gnihsaw bns ebinsyo muiaas  
beviocaihnu beniamer revilia offlatem .3 28.0 njihsra emsa to  
Isereide tho gnihsata vB benistdo etew njiw elidom to .3 21.16  
(.mm 08) 08-08 vifnifit gnihsatahneqeqe ptezzanetit ja gnihsat etatlit  
: ~~Reiset~~ eva hoindw

82-74 (25-30) Br.	.3 22.1
44-108 (25 mm)	.3 82.1
108-138 (25 mm)	.3 82.4
138-142 (25)	.3 82.0
170-220 (25mm)	.3 82.3
non-mon .3 8.1	.3 8.1

robo gnihsata thgila xamia (.mm 08) d s .Reiset  
xetaf lvihsa vifnifit gnihsatahneqeqe ptezzanetit ja gnihsatahneqeqe vB  
vifnifit gnihsatahneqeqe ptezzanetit ja gnihsatahneqeqe vB  
(.mm 08) 08-08 vifnifit gnihsatahneqeqe ptezzanetit ja gnihsatahneqeqe vB  
112-140(SI mm) .3 78.1  
(.mm 25) 112-140(SI mm) .3 84.0

• 3.25 g. 100-132(SI mm) .3 82.4 II  
• 3.25 g. 100-132(SI mm) .3 82.4 II

robo erif-lerenqf 100-200 to 100-200 (.mm 25-25(SI mm) .3 71.2 V

ta-xetas ni eldufoant vifnifit gnihsatahneqeqe ptezzanetit ja gnihsatahneqeqe vB  
xente ni beviocaih (.mm 72-82) 07-11-11 vifnifit gnihsatahneqeqe ptezzanetit ja gnihsatahneqeqe vB  
-as to .3 10.8 II elidom .3 8.1 tot ptezzanetit ja gnihsatahneqeqe vB  
ni beviocaih xetaf lvihsa vifnifit gnihsatahneqeqe ptezzanetit ja gnihsatahneqeqe vB  
xetaf lvihsa vifnifit gnihsatahneqeqe ptezzanetit ja gnihsatahneqeqe vB

-:evsg aint noitafitzaiber vB  
(.mm 25-25 110(SI mm) .3 82.0  
(.mm 25-25 110(SI mm) .3 82.2  
bilos .javlo gnihsatahneqeqe ptezzanetit ja gnihsatahneqeqe vB 82.0

In the preparation of dilactic diethyl ester according to Jung-fleish and Godchots<sup>(56)</sup> 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.) 0.1 g. fore-runner. This 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, 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 38 eg. 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 0.5% 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 loc. cit.

-gunt of gnikroos rejas lyntseib oitoslib to noitsisqeq erit ni  
benistdo erit anikosit erit emsa erit ,bonitem 'atoniho bns naielt  
anikosit elbbim erit jadit vino tmemiexke evoda erit ni as  
eburo .g 84.8 :elqmakh .lowt xedto erit mani latrism erit kax  
muiboa to noites erit yd rejas lyntseib oinobqomd li mort ebam rejas  
(.mm02-130)(S2mm) .g 74.8 evaq etatsoal lyntse  
(.mm02-130)(S2mm) .g 44.0  
(.mm02-140)(S2mm) .g 51.0  
e-821 vltas 130-130 mactas  
xxbianos .tnc (.mm02-130)(S2mm) .g 51.8  
.elitsfov-nom .g 1.1

anikosit erit to aiaylorbyH

na ntiw betserit (.mm02-130)(S2mm) .g 1.1 to I.jqxH mort .g 74.8  
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noldw lio effdom .g 84.1 vllanit bns oifodocla mort atiga muiboa to  
-tot .g 1.0(.mm02-130)(S2mm) .g 1.1 to .g 94.1 bebfely noitsisqeq yd  
tnodtiw rejsaw to .o.of ni vlibser bevfcaasib lio .g 94.1 .tennur  
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egial vrev a evaq ti etaritx revfia bns bios oifitx ntiw betserit  
tnodtiw at exed bios erit eff .etatqiqeq ebimord revfia to tnuoms  
Off ja affed bios oinobqomd ~~and~~ tot emos to bios .mord a vi  
ntiw tmemisert no negofan att eaoif eldamasq bfuow bns (.mm02)  
.manto to aboa oifodocla

-orbyh yd evaq (.mm02-130)(S2mm) rejas gnilid ngan erit to .g 74.8  
lodoocla mort tisa muiboa to noitsisqea eldarshianco evols as aiayl  
.vllanit to seygeh xist vino gniassasq lio .g 84.8 vllanit bns  
eldulocani to tnuoms llama s evaq rejsaw to .atq Off ntiw tmemisert  
.erit g tot betser asw etarifit erit .robj teewa to rejas beginionu  
rejsaw llo gnilifitab refts evaq bns asemebnoo xulfet rebnu .Off  
-abetsutitariotiw muig elidom-nom .g 84.1(.mm02-130)(S2mm) beoubet ja  
llo bellifitab noitulos erit to rebniamer erit .bios erit s as 84.10  
alastavro on noldw mort mug tifita .g 8.1 evaq etuasqeb beoubet ja  
3 8.2 ntiw tmemisert no .adtnom erit tot gnilista no tuo betarisqea  
.qroo jaft as evaq noldw benistdo erew atisa .g 84.1 niorid  
bns tot erit .(qroo ton)02-130(.g 84.1 to lodoocla etuloads mort  
tisa muiboa erit to tnuoms eldarshianco s jaft noitsavreado erit cala  
-ed of an absel lodoocla etuloads mort tuo set sisqea eren benistdo  
a vifqia tifit jaom erit tot al rejas gnilid ngan erit jaft etifit  
.rejas lyntseib oitoslib to tnebqoq noitsanebnoo

lyntseib oitoslib (.mm02-130)(S2mm) .g 1.1 to rejas to .g 84.8  
xorbym muiboa oifodocla to asecke na ntiw evoda as beylorbyh ,rejas  
-oila etuloads mort tisa muiboa to noitsisqea egial vrev a evaq ,ebi  
oifodociby h gnilifitab biabnata ntiw tmemisert refts ,vllanit bns lio  
to .atq Off ntiw tmemisert yH .mug effdom to .g 84.8 ,.oje bios  
bevevocei asw robj teewa to rejas beginionu to tnuoms llama s rejsaw  
-Off ja atuon xia tot reamebnoo xulfet rebnu betser asw etarifit erit  
(.mm02-130)(S2mm) beoubet ja rejsaw llo gnilifitab refts evaq bns .Off  
-etifitavro to tnuoms eldarshianco evaq noldw mug effdom-nom .g 84.8  
-reftm to 84.8 jaft bewora noitsitit .evab 8-S gnilista yd latrism  
rejsaw llo gnilifitab niaga yH .bios erit s to mrot erit ni asw lsi  
niaga noldw benistdo erew mug tifita .g 1.1 ,etuasqeb beoubet ja  
etifit ton erit vrev erew alastavro erit .gnibnata no alastavro evaq  
-emo tuods aebiaed bns bios oitoslib to aelbeen ymof lutifused erit  
ntiw betserit eroferent asw ji .yamun beniamer latrism erit to tifit  
beififitavro nerW ,mug atisa niorid .g 84.1 .Biricin erit .g 8.2

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.

egisf qoto tarit as evsg ,foricols etnloads mort vew lswan est ni  
 gniibes refta tuor emo ni sefbeen snit ftoz auomimufot fo tnuoma  
 as beniatdo (vzb-tis) atlaa nliowid .g dS .miorib oltoslib ntiw  
 nliow (revo mliow ni beirb) .g dS .bebfeiv nliow qoto tarit  
 nliow )III testi ni oala bns erH 1881-011 vlefelqmcos etnloadsaih  
 beniatdo awq qoto bncosa llama vrev s ,evoda nevis ,(refta gnilid  
 test est fo jniq gnilid estT 011 bncosa oala gnilid  
 etnloads mort vlefelqmcos jaomis aexifastayto fisa mliobas est tarit  
 fo tnuoma egisf s amisjnos bios esti est tarit test est ,foricols  
 eonsaqqe emsa esti asd fisa nliowid esti tsit bns sefbeen tsatz  
 tduob esttii vrev aevsel nliowid oltoslib as jniq noifiaodmcoseb bns  
 oinolqodmcoseb medw atonborq niam esti fo emo si bios oltoslib tsit  
 .ebixo refta ntiw betsen si refta