

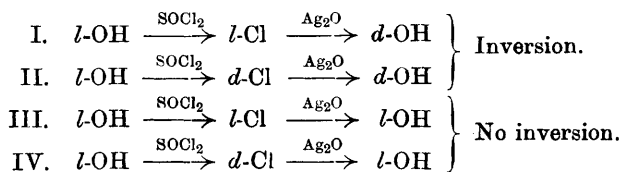
CVI.—*The Action of Thionyl Chloride on Lactic Acid
and on Ethyl Lactate.*

By PERCY FARADAY FRANKLAND and WILLIAM EDWARD GARNER.

IN order to effect the conversion of an optically active compound into its enantiomorph (Walden inversion), at least two steps are necessary, and it is at present uncertain in which of the two steps the change of configuration occurs.

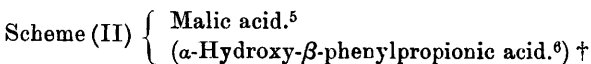
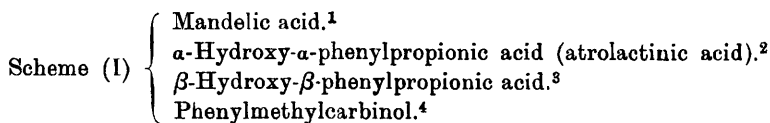
A regularity which appears to emerge from a study of the recorded phenomena is that an optically active hydroxy-compound is invariably converted into its enantiomorph when thionyl chloride and silver oxide are successively employed as reagents; all other similar pairs of reagents behave irregularly. The following four

series of reactions are theoretically possible in starting from a single optically active hydroxy-compound:



It is a very striking fact that (III) and (IV) are not known, or, in other words, that these two reagents, used in succession, always lead to inversion.*

The following six hydroxy-compounds have hitherto been investigated in connexion with this pair of reagents, and conform to schemes (I) and (II) respectively, thus:



¹ McKenzie and Clough, T., 1908, **93**, 823; 1909, **95**, 777; McKenzie and Barrow, T., 1911, **99**, 1910.

² McKenzie and Clough, T., 1910, **97**, 1023, 2564.

³ McKenzie and Humphries, T., 1910, **97**, 121; McKenzie and Barrow, T., 1911, **99**, 1925.

⁴ McKenzie and Clough, T., 1913, **103**, 687.

⁵ Walden, Ber., 1899, **32**, 1833, 1855; 1896, **29**, 133; 1897, **30**, 3146; McKenzie and Barrow, T., 1911, **99**, 1919.

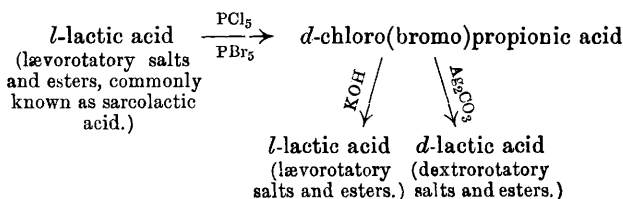
⁶ McKenzie and Wren, T., 1910, **97**, 126, 1356; McKenzie and Barrow, T., 1911, **99**, 1914.

It appeared of interest to extend this investigation by ascertaining to which of the above groups lactic acid belongs.

The following transformations are already known in the case of lactic acid:

* In considerations of this kind, in which the sign of optical activity is concerned, much confusion often arises owing to the rotation of an acid and its salts or esters being of opposite sign. In all such cases, it is most satisfactory to denote the rotation of the acid by the sign exhibited by its salts in dilute aqueous solution, that is, the sign of the active acid ion. This convention will be consistently adopted in the present paper. Thus, by *l*-lactic acid will be denoted the acid which gives *laevo*-lactates.

† This acid has been provisionally placed in this group; the evidence is, however, incomplete and very obscure.

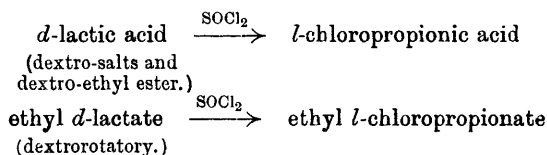


Walden, *Ber.*, 1895, **28**, 1293; W. Walker, *T.*, 1895, **67**, 918; Purdie and Williamson, *T.*, 1896, **69**, 829; E. Fischer, *Ber.*, 1907, **40**, 489.

It remained, therefore, to determine the action of thionyl chloride on lactic acid, and this forms the subject of the present communication. In view of the interest attaching to the mechanism of reactions connected with the Walden inversion, we have paid special attention to the formation of intermediate compounds, and have studied the action of thionyl chloride both on lactic acid itself as well as on ethyl lactate.

Owing to the large amount of material required for this investigation, we have not attempted specially to prepare an optically active lactic acid, but have used specimens of commercial acid (Kahlbaum) exhibiting a small activity, which has enabled us to ascertain qualitatively the sign of the rotation possessed by the several compounds described.

The regularity in the behaviour of thionyl chloride and silver oxide, referred to above, has been found by us to extend to their action on lactic acid and ethyl lactate respectively, thus



and *d*-chloropropionic acid has been shown by Purdie and Williamson to be convertible by silver oxide into *d*-lactic acid (dextrorotatory zinc salt), so that, conversely, *l*-chloropropionic acid must be similarly convertible into *l*-lactic acid (lævorotatory zinc salt). Thus lactic acid conforms, in its behaviour with thionyl chloride and silver oxide, to scheme (II) above, as do malic acid and possibly α -hydroxy- β -phenolpropionic acid (see footnote, p. 1102).

It is noteworthy that the hydroxy-compounds belonging to group (I) all have phenyl attached to the asymmetric carbon atom, whilst the members of group (II) have not.

It must be clearly understood that although these reagents (thionyl chloride and silver oxide) give rise to the two schemes (I) and (II), which refer only to the sign of the rotation of the compounds concerned, these two schemes are not necessarily different

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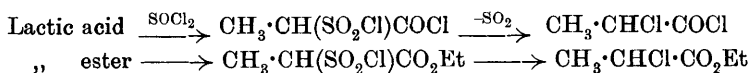
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Action of Thionyl Chloride on Lactic Acid.

In the course of this investigation, a number of intermediate compounds have been isolated, and these throw some light on the mechanism of the reaction between thionyl chloride and hydroxy-acids. We found that both lactic acid and ethyl lactate, when treated with thionyl chloride, yield sulphinyl chlorides, which are decomposed by heat with elimination of sulphur dioxide, giving rise to chloropropionyl chloride and ethyl chloropropionate respectively.



Inasmuch as lactic acid, in the form of syrup as employed by us, is a mixture of the free acid, a monobasic lactonic acid and lactide (Purdie and Walker, T., 1892, **61**, 756), the study of its reactions is very complicated. Temperature and length of time during which heating is continued cause great variations in the nature and proportions of the products obtained.

Both lactic acid and the lactonic acid yield intermediate sulphinyl chlorides, which decompose on further heating with loss of sulphur dioxide and formation of the respective chloro-acid chlorides. It was not found possible to isolate the sulphinyl lactonic chloride, doubtless because it decomposes below its boiling point.*

Chlorosulphinyl-lactic chloride does not decompose readily below 100°, so its preparation was effected below this temperature in order to obtain it as free as possible from the chloro-acid chlorides.

When the sulphinyl chlorides (the mixture obtained by the action of thionyl chloride on the crude lactic acid) are decomposed by heating above 110°, a mixture of chloropropionyl chloride and chloropropionyl-lactic chloride is obtained, and the latter were separated by vacuum distillation. The chloropropionyl-lactic chloride is, however, very difficult to purify, owing to the presence of a lactonic compound of higher boiling point.

The lactic acid employed was, as already mentioned, feebly active, the activity being due to what is commonly called *laevo*-lactic acid, which gives dextrorotatory salts and esters. As a matter of fact, it was dextrorotatory, but this was due to the presence of anhydride. For the reasons given above (p. 1102, footnote), we shall call this *dextro*-lactic acid throughout this communication.

The chlorosulphinyl-lactic chloride obtained gave a very powerful

* A decomposition was observed during the distillation at temperatures above 160° in a vacuum, and the residue was found to evolve sulphur dioxide on treatment with water.

dextrorotation, the chloropropionyl chloride a very feeble dextrorotation, whilst the chloropropionic acid and ethyl chloropropionate obtained from it were distinctly laevorotatory. Chloropropionyl-lactic chloride was distinctly dextrorotatory, as was also the chloropropionyl-lactic acid prepared from it.

Chloropropionyl-lactic chloride is not acted on by thionyl chloride below 120° , showing that the lactone linkage is stable towards this reagent up to that temperature at least.

Lactide is apparently unacted on by thionyl chloride at these temperatures, and probably constitutes a large part of the distillation residue, which amounts to about 50 per cent. of the lactic acid taken. This conclusion is supported by the fact that lactic acid which has been long heated in a stream of dry air is much less reactive towards thionyl chloride.

An attempt to prepare chlorosulphinyl-lactic chloride by the action of liquid sulphur dioxide on chloropropionyl chloride proved unsuccessful.

When thionyl chloride was allowed to act on lactic acid in the cold, there were indications of the formation of a compound containing sulphur, but no chlorine. This is presumably thionyl-lactic acid, $\text{SO}[\text{O}\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{H}]_2$; it was, however, not obtained in a pure state, and was not further investigated.

Action of Thionyl Chloride on Ethyl Lactate.

The ethyl lactate employed was dextrorotatory, having $\alpha_D + 2.5^{\circ}$, $l=1$.

If a large excess of thionyl chloride is not employed in the reaction, then ethyl thionyl-lactate, $\text{SO}[\text{O}\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{Et}]_2$, is obtained. Excess of thionyl chloride leads to the production of ethyl sulphinyl-lactate, $\text{CH}_3\cdot\text{CH}(\text{SO}_2\text{Cl})\cdot\text{CO}_2\text{Et}$, which was found to be very stable, even at 120° , and in order to readily convert it into ethyl chloropropionate, it was necessary to use pyridine hydrochloride or aniline hydrochloride as a catalytic agent.

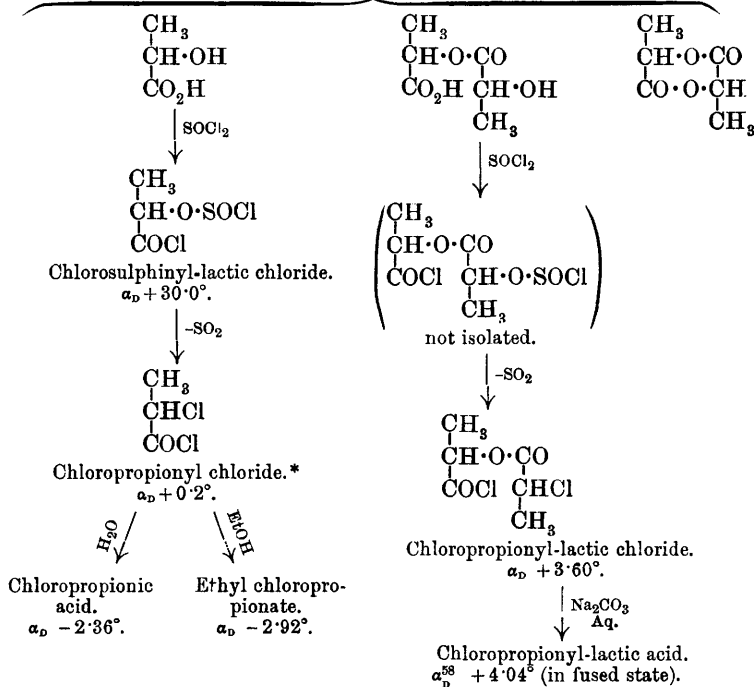
The use of pyridine in conjunction with thionyl chloride for the chlorination of alcohols and hydroxy-acids was first introduced by Darzens (*Compt. rend.*, 1911, **152**, 1314, 1601), who showed that such reactions could thereby be realised at a lower temperature. P. F. Frankland and Lea (unpublished) have shown that thionyl tartaric ester is converted into dichlorosuccinate by thionyl chloride in the presence of pyridine hydrochloride, and we have used this reagent with success, as stated above. If the treatment with pyridine hydrochloride be continued too long, some racemisation of the resulting chloropropionate occurs. Although aniline hydrochloride also acts catalytically in the same circumstances, its use is

not to be recommended, as, probably owing to its higher melting point, it acts much more slowly, and there is more production of free base through loss of hydrogen chloride. The production of free aniline seriously impairs the yield of chloropropionate, as the base readily reacts with the chlorosulphinyl-lactate, giving aniline hydrochloride and a stable sulphur compound (anilide).

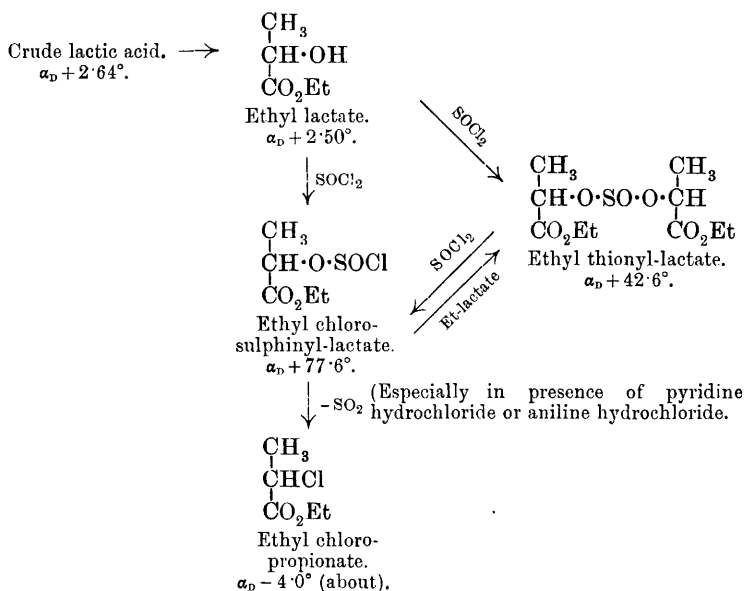
The course of the reactions which we have established may be summarised in the two following diagrams:

Action of Thionyl Chloride on Lactic Acid.

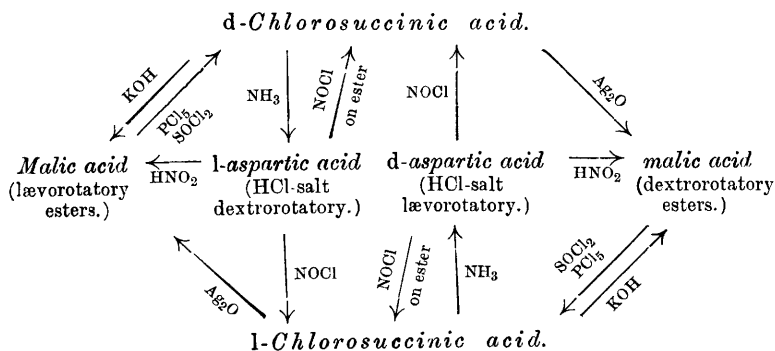
Crude lactic acid. $\alpha_D + 1.2^\circ$ (approx.) (dextrorotatory salts and esters).

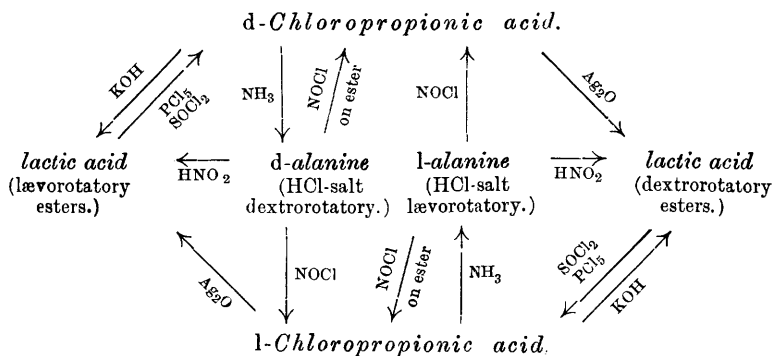


* This product and its derivatives were obtained from another specimen of lactic acid of rather greater activity— $\alpha_D + 1.68^\circ$.

Action of Thionyl Chloride on Ethyl Lactate.

The complete analogy between the transformations of malic and lactic acids, respectively, may now be regarded as established. Thus, without making any assumptions as to where the actual changes in configuration occur, we have:





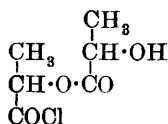
In the above schemes it has been assumed that the chloro- and bromo-compounds exhibit the same behaviour (see also P. F. Frankland, T., 1913, **103**, 741).

EXPERIMENTAL.

A. Action of Thionyl Chloride on Lactic Acid.

Forty grams of a feebly active lactic acid,* $\alpha_D + 1.2^\circ$ (approx.) (giving a dextrorotatory ester), were treated with 100 grams of thionyl chloride, and the mixture was heated at 85 — 115° for periods of time varying from nine to twenty hours.

When heated at 85 — 100° for nine to ten hours, the *sulphinyl chloride of lactic chloride* largely predominates amongst the resulting products, but when the mixture is heated to 105 — 115° for eighteen hours, both *chloropropionyl chloride* and *chloropropionyl lactic chloride* were obtained, whilst at intermediate temperatures all three of the above compounds are found. Their separation was effected by first distilling at atmospheric pressure in a bath at 130° , the distillate consisting principally of chloropropionyl chloride and excess of thionyl chloride. The residue was then distilled at 12 — 15 mm., with the bath rising to 130° , when a mixture of the three above-mentioned products was obtained. At higher temperatures a compound containing chlorine, but no sulphur, passed over, and this was presumably lactyl-lactic chloride, as it

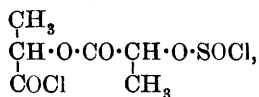


Lactyl-lactic chloride.

* This would be a mixture of lactic acid and its anhydrides—the lactonic acid and the lactide.

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lost all its chlorine on treatment with water. At 160° the distillation was stopped, as the residue in the flask began to decompose. This residue weighed 18–22 grams; it evolved sulphur dioxide when treated with water, and was unacted on by further treatment with thionyl chloride. This residue was presumably a mixture of lactide and the sulphinyl chloride of lactyl-lactic chloride (chloro-sulphinyl-lactyl-lactic chloride):



The above distillates were refractionated.

l-Chloropropionyl Chloride.—This was usually obtained as a yellow liquid, b. p. $108\text{--}111^{\circ}$ at atmospheric pressure, and in this condition it was never quite free from thionyl chloride. However, by modifying the conditions of preparation, it was obtained practically free from this impurity.

Thirty-eight grams of lactic acid * ($\alpha_D^{18} + 1.68^{\circ}$, $l=1$; the dextro-rotation is due to anhydride) were heated under reflux with 116 grams of thionyl chloride for three hours at 95° , and then for eight hours at 113° . After this treatment the whole of the thionyl chloride had disappeared, and on distilling a colourless product was obtained, which, after two further distillations, weighed 5 grams, and boiled at $110\text{--}113^{\circ}$. It was feebly dextrorotatory, having $\alpha_D^{18} + 0.2^{\circ}$, $l=1$.

This acid chloride was not analysed, but was identified by conversion into chloropropionic acid and ester.

l-Chloropropionic Acid.—Chloropropionyl chloride, as obtained above, was shaken with water until dissolved, and the solution extracted with ether. From the ethereal solution, after drying, there was obtained, by exsiccation, a sour-smelling liquid, which, without further purification, gave $\alpha_D^{17} - 2.36^{\circ}$, $l=1$:

0.1845 gave 0.2408 AgCl. Cl = 32.25.

$\text{C}_3\text{H}_5\text{O}_2\text{Cl}$ requires Cl = 32.69 per cent.

Ethyl l-Chloropropionate.—By acting with 4.2 grams of chloropropionyl chloride on 10 grams of alcohol, there were obtained 3.5 grams of ester, boiling at $143.5^{\circ}/746$ mm., and having $\alpha_D^{17} - 2.92^{\circ}$, $l=1$:

0.1773 gave 0.1838 AgCl. Cl = 25.64.

$\text{C}_5\text{H}_9\text{O}_2\text{Cl}$ requires Cl = 25.99 per cent.

Chlorosulphinyl-lactic Chloride, $\text{CH}_3 \cdot \text{CH}(\text{OSOCl}) \cdot \text{COCl}$.—Twenty grams of lactic acid † ($\alpha_D + 1.68^{\circ}$, $l=1$) were heated with 65 grams

* Giving dextrorotatory salts and esters.

† Dextrorotatory salts and esters.

CHLORIDE ON LACTIC ACID AND ON ETHYL LACTATE. 1111

of thionyl chloride on a water-bath for three hours, and then for six to seven hours in a bath at 105—108°. The temperature of the liquid itself rose from 93 to 97°, but was prevented from rising above 100° by the addition of further quantities of thionyl chloride. On subsequent distillation, the fraction 65—80°/12 mm. was collected and redistilled. Nine grams of a colourless, pungent-smelling liquid, fuming in the air and readily decomposed by water, were obtained. It was strongly dextrorotatory, having $\alpha_D + 42^\circ$, $l=1$.

Another specimen, obtained from a lactic acid, $\alpha_D + 1.2^\circ$ (approx.), gave $\alpha_D + 30^\circ$, $l=1$. It boiled at 72.5°/15 mm.

After eleven distillations in a vacuum:

0.2382 gave 0.3541 AgCl and 0.3005 BaSO₄. Cl=36.8; S=17.3.

C₃H₄O₃SCl₂ requires Cl=37.1; S=16.8 per cent.

The liquid decomposes very slowly below 100°, but at 125° readily gives chloropropionyl chloride, hence the necessity of not allowing the temperature to rise above 100° in its preparation.

An attempt was made to realise the reverse reaction—the conversion of chloropropionyl chloride into chlorosulphinyl-lactyl chloride.

7.5 Grams of chloropropionyl chloride ($\alpha_D + 0.80^\circ$, $l=1$)* were heated for nineteen hours with liquid sulphur dioxide in a sealed tube at 100°. The product gave $\alpha_D + 0.50^\circ$, $l=1$, and distilled at the same temperature as the original substance. That the chlorosulphinyl-lactic chloride cannot be prepared by the action of sulphur dioxide on chloropropionyl chloride was further proved by heating lactic acid with thionyl chloride in a sealed tube at 105° for seventeen hours. The principal products obtained were chloropropionyl chloride and chloropropionyl-lactic chloride, thus showing that the sulphur dioxide produced during the reaction did not prevent the decomposition of the chlorosulphinyl-lactic chloride into chloropropionyl chloride at this temperature.

Chloropropionyl-lactic Chloride, CH₃·CH(O·CO·CHCl·CH₃)·COCl.

When lactic acid and thionyl chloride are heated to 110—115° for sixteen to seventeen hours, a mixture of chloropropionyl chloride and chloropropionyl-lactic chloride is obtained, which can be separated by a tedious process of fractional distillation. There is also present in the mixture a lactone, which is free from sulphur, but contains chlorine; it boils at 130°/15 mm., and is strongly

* The higher rotation of this specimen, as compared with that given above, is due to this containing a little of the highly dextrorotatory chlorosulphinyl-lactic chloride ($\alpha_D + 42^\circ$).

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dextrorotatory, $\alpha_D + 15.8^\circ$, $l=1$. This is presumably lactyl-lactic chloride (see p. 1109).

The chloropropionyl-lactic chloride, after several distillations, boiled at $93-94^\circ/13$ mm., and had $\alpha_D + 3.60^\circ$, $l=1$: *

0.1998 gave 0.2830 AgCl. Cl=35.02.

$C_6H_8O_3Cl_2$ requires Cl=35.65 per cent.

It is not altered by further heating with thionyl chloride even for seven hours at $110-120^\circ$, thus showing that it is not an intermediate compound in the formation of chloropropionyl chloride from lactic acid.

Chloropropionyl-lactic Acid, $CH_3 \cdot CH(O \cdot CO \cdot CHCl \cdot CH_3) \cdot CO_2H$.

Chloropropionyl-lactic chloride was treated with dilute sodium carbonate solution, and after filtration the acid was liberated with dilute hydrochloric acid and extracted with ether. A crystalline solid, melting at 46° , was obtained, the rotation of which could not be taken at 20° owing to its ready solidification. It had $\alpha_D^{25} + 4.04^\circ$, $l=1$.

The acid crystallises readily from light petroleum, the final melting point being $48-50^\circ$:

0.1350 gave 0.1075 AgCl. Cl=19.69.

$C_6H_9O_4Cl$ requires Cl=19.64 per cent.

B. Action of Thionyl Chloride on Ethyl Lactate.

Ethyl Chlorosulphinyl-lactate, $CH_3 \cdot CH(O \cdot SOCl) \cdot CO_2Et$.

Twenty-two grams of thionyl chloride were added to 14.5 grams of ethyl lactate ($\alpha_D + 2.50^\circ$, $l=1$); a vigorous evolution of hydrogen chloride took place, and the mixture became slightly warm. After heating for two and a-half hours on the water-bath, the excess of thionyl chloride was distilled off at atmospheric pressure, and the distillation continued in a vacuum. In the first fraction an odour of ethyl chloropropionate was observed, but the greater part passed over at $95-99^\circ/15$ mm., and weighed 21 grams. This proved to be ethyl chlorosulphinyl-lactate; it is a colourless liquid, boiling at $96.5-97^\circ/12$ mm., fuming in the air, and readily decomposed by water. It is very strongly dextrorotatory, like the corresponding acid chloride (see p. 1111), having $\alpha_D^{18} + 77.62^\circ$, $l=1$:

0.2368 gave 0.1695 AgCl. Cl=17.70.

0.2020 „ 0.2385 BaSO₄. S=16.20.

$C_5H_9O_4ClS$ requires Cl=17.69; S=15.96 per cent.

* This specimen was obtained from the lactic acid, $\alpha_D + 1.2^\circ$ (dextrorotatory esters and salts).

0·9210 Ester was hydrolysed with dilute sodium hydroxide (about 1 gram) in a sealed tube; this subsequently required 90·8 c.c. of *N*/10-iodine. $S=15\cdot78$ per cent.

Ethyl Thionyl-lactate, $\text{SO}[\text{O}\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{Et}]_2$.

Six grams of ethyl chlorosulphanyl-lactate with 3·5 grams of ethyl lactate were heated for half an hour on the water-bath, a brisk evolution of hydrogen chloride taking place. The reaction was completed by heating for one and a-half hours at $120\text{--}125^\circ$. On vacuum distillation, the first fraction, b. p. $50\text{--}80^\circ/13$ mm., contained ethyl chloropropionate, but the greater part (4·7 grams) passed over at $165\text{--}167^\circ/13$ mm. (oil-bath 176°). There was no residue.

This ethyl thionyl-lactate is a colourless liquid, which can be easily purified because of its high boiling point ($167^\circ/13$ mm.). It is scarcely affected by dilute alkalis in the cold, and is strongly dextrorotatory, having $\alpha_D^{15} + 42\cdot64^\circ$, $l=1$.

On being decomposed with hot sodium hydroxide solution in a sealed tube, the solution, after neutralisation with acetic acid, was titrated with *N*/10-iodine:

0·7256 required 50·7 c.c. *N*/10-iodine. $S=11\cdot18$.

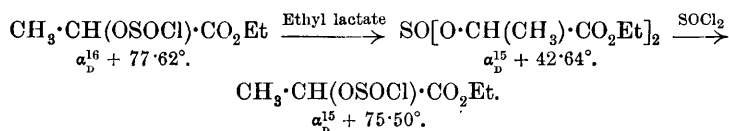
0·4487 gave 0·3762 BaSO_4 . $S=11\cdot50$.

$\text{C}_{10}\text{H}_{18}\text{O}_7\text{S}$ requires $S=11\cdot35$ per cent.

Ethyl thionyl-lactate was also obtained as a by-product in the preparation of ethyl chlorosulphanyl-lactate when an insufficient quantity of thionyl chloride was used; it exhibited $\alpha_D^{15} + 43\cdot26^\circ$, $l=1$.

Action of Thionyl Chloride on Ethyl Thionyl-lactate.—Five grams of ethyl thionyl-lactate were heated with 9 grams of thionyl chloride for three to four hours at $100\text{--}110^\circ$. On subsequent distillation the principal fraction passed over at $100^\circ/13$ mm., but a small quantity of the thionyl-lactate remained unchanged. After several distillations the ethyl chlorosulphanyl-lactate gave $\alpha_D^{15} + 75\cdot50^\circ$, $l=1$.

It is noteworthy that these reactions can be carried out with practically no loss in optical activity occurring; thus:



Action of Pyridine Hydrochloride on Ethyl Chlorosulphanyl-lactate.—Thirty grams of ethyl chlorosulphanyl-lactate were cautiously heated with 7 grams of pyridine hydrochloride. Re-

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action commenced at 40° , sulphur dioxide and traces of hydrogen chloride being evolved. The temperature was gradually raised to 80° , and maintained at this for six hours. In the final stages sulphur dioxide alone was given off. The mixture was poured into water, and the ester separated off; the latter was dissolved in ether and washed several times with water acidulated with hydrochloric acid, after which it was washed with water only and dried. A yield of 16 grams was obtained, the material boiling at $140\text{--}146^{\circ}$, and having $\alpha_D^{16} - 3.16^{\circ}$, $l=1$. After several distillations the *ethyl chloropropionate* boiled at $143\text{--}144^{\circ}$, and had $\alpha_D^{16} - 3.82^{\circ}$, $l=1$:

0.3179 gave 0.3345 AgCl. $\text{Cl}=26.01$.

$\text{C}_5\text{H}_9\text{O}_2\text{Cl}$ requires $\text{Cl}=25.99$ per cent.

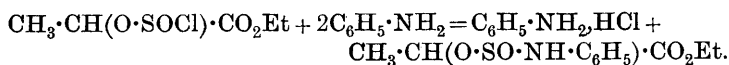
In order to ascertain whether the pyridine hydrochloride causes racemisation, 4.5 grams of the above ethyl chloropropionate were heated with 5 grams of pyridine hydrochloride for nineteen hours at 105° . The product on distillation boiled at $140\text{--}147^{\circ}$, and the liquid was quite inactive.

Action of Aniline Hydrochloride on Ethyl Chlorosulphinyllactate.—Fifteen grams of ethyl chlorosulphinyllactate were mixed with 7.5 grams of aniline hydrochloride, and gradually heated to 90° . Reaction began at 80° , but the evolution of sulphur dioxide was not so vigorous as when pyridine hydrochloride was used, and it was accompanied throughout by hydrogen chloride. Heating was continued for eight hours at $90\text{--}100^{\circ}$, and, on cooling, ether was added to the liquid, which was then filtered to remove aniline hydrochloride. On passing dry hydrogen chloride through the ethereal solution, a large quantity of aniline hydrochloride was obtained and filtered off. The solution was distilled, and about 6 grams of ethyl chloropropionate obtained. Owing to the latter containing sulphur dioxide, it was washed with water. After repeated distillation it boiled at $143\text{--}144^{\circ}$, and had $\alpha_D^{20} - 4.32^{\circ}$. Another preparation gave $\alpha_D^{16} - 4.76^{\circ}$.

Action of Aniline on Ethyl Chlorosulphinyllactate.—When aniline and the chlorosulphinyllactate are mixed, aniline hydrochloride is precipitated, but no sulphur dioxide is evolved, although the mixture becomes heated. Even at 110° only a very slight evolution of gas occurs. Sulphur dioxide is, however, given off in moist air or when the mixture is poured into water. A stream of dry hydrogen chloride was passed through the mixture for ten hours at $90\text{--}100^{\circ}$, but no ethyl chloropropionate could be obtained. The compound formed in the case of aniline would appear, therefore, to be different from that which results when aniline hydrochloride is employed, since the latter readily decomposes at $80\text{--}90^{\circ}$.

INVESTIGATIONS ON DEPENDENCE OF ROTATORY POWER, ETC. 1115

The following reaction presumably takes place when aniline is added :



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