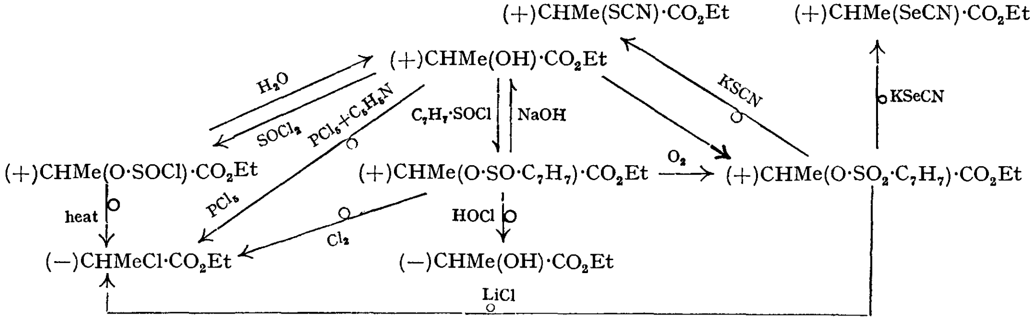
32. *The Replacement of the Hydroxyl Group of Ethyl* (+)*Lactate by Halogens, and the Molecular Dissymmetry of Derivatives of Ethyl Lactate which contain the Sulphin Group.*

By W. Gerrard, J. Kenyon, and H. Phillips.

A number of reactions previously used in the study of substitution at asymmetric carbon atoms in aliphatic compounds have now been applied to optically active ethyl lactate and its derivatives. The results are in harmony with, and may be interpreted in the light of, the mechanisms of these reactions put forward by Kenyon and Phillips (*Trans. Faraday Soc.*, 1930, **26**, 451). It is now shown that the (—)ethyl esters of (+)lactic, (—)α-chloropropionic, and (—)α-bromopropionic acids and the (+)ethyl esters of α-thiocyano- and α-selenocyano-propionic acids all have the same relative configuration.* Certain sulphinoxy-derivatives of ethyl lactate, to the rotatory powers of which an asymmetric sulphur atom may contribute a partial rotation, are also described.

By the interaction of phosphorus pentachloride and ethyl (—)lactate in chloroform solution, Purdie and Williamson (J., 1896, **69**, 820) prepared ethyl (+)α-chloropropionate with α_{5893} + 19·41° (or α_{5790} + 20·70°, since $\alpha_{5790}/\alpha_{5893}$ for this ester is 1·066).

It has now been found that neither the sign nor the magnitude of the rotatory power of this chloro-ester is affected when phosphorus pentachloride and ethyl (—)lactate interact in the presence of either potassium carbonate or the tertiary bases, pyridine, quinoline, and *iso*quinoline, from which it can be concluded that, even in the absence of tertiary bases, association between the reacting molecules takes place almost exclusively in the form which leads to inversion of configuration of the asymmetric carbon atom. Similar considerations apply to the interaction of ethyl (+)lactate and phosphorus pentabromide, for, in the presence of pyridine, quinoline or *iso*quinoline, these compounds yield (—)ethyl α-bromopropionate with $\alpha_{5790}^{17°}$ — 44·1°, whereas Walker (J., 1895, **67**, 914), from the (+)ester in chloroform solution, obtained ethyl (—)α-bromopropionate with $\alpha_{5893}^{17°}$ — 43·59°. These results are illustrated in the accompanying scheme.



Ethyl (+)α-p-*toluenesulphinoxypropionate*, prepared from ethyl (+)lactate and

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* The signs (+) and (—) are used in place of the terms dextrorotatory and lævorotatory; the letters *d*- and *l*- denote configurations. It is assumed that (—)lactic acid has a *d*-configuration and, in the theoretical portion of the paper, that all experiments were made with *d*-compounds. Rotatory powers are given for 1 dm. tubes.

p-toluenesulphinyl chloride in the presence of pyridine, has $\alpha_{5461}^{16^\circ}$ + 31·54°. On oxidation with potassium permanganate it is converted into ethyl (+) α-*p*-toluenesulphonoxypropionate with $\alpha_{5461}^{18\cdot5^\circ}$ + 63·36°, a value in agreement with that recorded (Kenyon, Phillips, and Turley, J., 1925, **127**, 399) for the ester prepared by direct interaction of ethyl (+)lactate and *p*-toluenesulphonyl chloride. By distillation at low pressures, ethyl (+)α-*p*-toluenesulphinoxypropionate [from ethyl (+)lactate] can be separated into fractions of similar composition and refractive index which have rotatory powers varying from $\alpha_{5461}^{20^\circ}$ + 12·0° to $\alpha_{5461}^{20^\circ}$ + 91·4°. These variations in rotatory power must be ascribed to the separation of diastereoisomerides which arise from the asymmetry of the sulphur atom in the molecule (cf. Phillips, J., 1925, **127**, 2552).

With aqueous hypochlorous acid, ethyl (+)α-*p*-toluenesulphinoxypropionate yields ethyl (—)α-chloropropionate, with $\alpha_{5790}^{16^\circ}$ — 18·20°, and also ethyl (—)lactate, with $\alpha_{5790}^{16^\circ}$ — 9·56°. Since the (+)sulphinate has the same configuration as ethyl (+)lactate, the ethyl (—)lactate arises with inversion of configuration. With chlorine water and with bromine in chloroform solution, the (+)sulphinate yields respectively the (—)chloro- and the (—)bromo-ester. The reactions of the (+)sulphinate with hypochlorous acid and with halogens are similar in type, and it is probable therefore that these halogen esters arise with inversion and have the same configuration as ethyl (—)lactate and (+)lactic acid—see above scheme.

Similar reactions of other optically active *p*-toluenesulphinic esters have been described and discussed (Houssa, Kenyon, and Phillips, J., 1929, 1700; Houssa and Phillips, J., 1932, 1232; Kenyon, Phillips, and Shutt, J., 1935, 1663); in the present experiments the formation of the halogen derivatives is attended by less racemisation than in those previously recorded. Attempts to prepare *ethyl α-thiocyano-* and *α-selenocyano-propionate* by the interaction of ethyl (+)α-*p*-toluenesulphinoxypropionate with thiocyanogen and with triselenocyanogen were fruitless. These esters were obtained ($\alpha_{5790}^{20^\circ}$ + 15° and + 1·7° respectively), however, by the interaction of ethyl (+)α-*p*-toluenesulphonoxypropionate and potassium thiocyanate and selenocyanate respectively in alcoholic solution, reactions which may be presumed to take place with inversion of configuration (Kenyon and Phillips, *loc. cit.*; Kenyon, Phillips, and Pittman, J., 1935, 1072).

If ethyl (—)α-chloropropionate has the same configuration as (+)lactic acid, the decomposition of ethyl (+)α-chlorosulphinoxypropionate in the presence of pyridine hydrochloride is also accompanied by inversion, since Frankland and Garner (J., 1914, **105**, 1101) obtained ethyl (—)α-chloropropionate ($\alpha_{5893}^{16^\circ}$ — 3·82°) in this manner. It has been found that this (—)ester can also be obtained (*a*) with $\alpha_{5893}^{16^\circ}$ — 4·4°, by the thermal decomposition of ethyl (+)α-chlorosulphinoxypropionate alone or in the presence of pyridine, and (*b*) with $\alpha_{5790}^{15^\circ}$ — 21·74°, by interaction of ethyl (+)lactate and thionyl chloride in the presence of tertiary bases, followed by heating.

Aqueous hydrolysis of ethyl (+)α-chlorosulphinoxypropionate [from ethyl (+)lactate, $\alpha_{5893}^{16^\circ}$ + 11·30°] yields ethyl (+)lactate with $\alpha_{5893}^{16^\circ}$ + 11·02°, from which it appears that the hydrolysis does not disturb the bonds of the asymmetric carbon atom. The reaction is therefore analogous to the alcoholysis of (—)β-octyl *p*-toluenesulphinate and the saponification of carboxylic esters of optically active alcohols.

The rotatory powers ($\alpha_{5461}^{16^\circ}$ ± 380·3°) of ethyl (+)- and (—)-α-chlorosulphinoxypropionate, and also of methyl (+)α-chlorosulphinoxypropionate, $\alpha_{5461}^{15\cdot5^\circ}$ +265·8° (Patterson and Lawson, J., 1929, 2042), are of much greater magnitude than those of other derivatives of optically active ethyl lactate. This may be due to the formation, as the result of asymmetric induction, of a second active centre in the molecule, since in the production of the chlorosulphinate a mixed sulphoxide group is introduced into a molecule which already contains a centre of asymmetry. It is not unlikely that the partial rotation contributed by such a group would be high, since the specific rotations of sulphoxides and related compounds are high (Harrison, Kenyon, and Phillips, J., 1926, 2079; Clarke, Kenyon, and Phillips, J., 1927, 188; Gajowczyk and Suszko, *Ber.*, 1935, **68**, 1005). This suggestion is strengthened by the observation that distillation of the chlorosulphinate did not result in the separation of fractions with different rotatory powers, which suggests that it contains only one of the two theoretically possible diastereoisomerides, since the distillation of ethyl

(—)α-*p*-toluenesulphinoxypropionate resulted in the partial separation of the diastereoisomeric forms.

Determination of the parachor of the chlorosulphinate provided the expected evidence that the double bond between the sulphur and the oxygen atom is semipolar in character. It appeared possible that if ethyl (+)α-chlorosulphinoxypropionate contains only one of the two possible diastereoisomerides, the interaction of this ester and *n*-amyl alcohol might give only one diastereoisomeric form of *α-carbethoxyethyl* n-*amyl sulphite* and that this would differ in rotatory power from the compound which would be obtained by the interaction of ethyl (+)lactate with *n*-amyl chlorosulphinate and may be presumed to contain two diastereoisomerides. It has been found, however, that these two methods give products which have approximately the same rotatory power and are mixtures of diastereoisomerides, since the sulphite prepared (in larger amount) from ethyl α-chlorosulphinoxypropionate could be separated by distillation into fractions of similar composition but of different rotatory power. These results do not support the view that the sulphur atom in ethyl (—)α-chlorosulphinoxypropionate has given rise to optical activity, but this may be due to racemisation at this centre of optical activity during the interaction of the chlorosulphinate and amyl alcohol. In the absence of knowledge of the optical stability during replacement reactions of the sulphur atom of sulphoxides, the possibility of an asymmetric synthesis during the formation of ethyl (—)α-chlorosulphinoxypropionate must be left undecided.

EXPERIMENTAL.

d(—)-Lactic acid was obtained by the method of Purdie and Walker (J., 1895, **67**, 616), and *l*(+)-lactic acid by that of Patterson and Forsyth (J., 1913, **103**, 2263). Ethyl *d*(+)-[or *l*(—)-] lactate was prepared by slow distillation during 5 hours of a mixture of *d*(—)-lactic acid (1 mol.), ethyl alcohol containing a few drops of sulphuric acid (2 mols.) and benzene (1·2 mols.). After removal of the ternary mixture (bath temp. 96°), the neutralised (calcium carbonate) ethyl *l*(+)-lactate had b. p. 54—56°/11 mm., $n_D^{16^\circ}$ 1·4156, $\alpha_{5893}^{16^\circ}$ + 5·70° (*l*, 0·5). The corresponding ethyl *d*(—)-lactate had $\alpha_{5893}^{18^\circ}$ — 11·15° (*l*, 1·0). Unless otherwise stated, esters with these rotatory powers were used in the experiments described.*

Interaction of Ethyl (—)Lactate and Phosphorus Pentachloride.—(i) *In the presence of potassium carbonate.* Ethyl (—)lactate (5·9 g.) was slowly added with cooling and shaking to a mixture of dry ether (40 c.c.), phosphorus pentachloride (20·4 g., 2 mols.), and potassium carbonate (13·4 g.). The reaction product was poured into ice-water and extracted with ether; the resulting ethyl (+)α-chloropropionate (3·7 g.) had b. p. 143—144°; $\alpha_{5790}^{16^\circ}$ + 20·86° (*l*, 1), $n_D^{16^\circ}$ 1·4166 (Found : Cl, 25·8. Calc. : Cl, 26·0%).

(ii) *In the presence of tertiary bases.* (a) Pyridine. Ethyl (—)lactate (11·8 g.) in pyridine (7·9 g.) was slowly added to cold phosphorus pentachloride (40·8 g., 2 mols.); the mixture, after being maintained at 60° for one hour, was decomposed with ice. The resulting ethyl (+)α-chloropropionate had b. p. 144°, $\alpha_{5790}^{16^\circ}$ + 20·93°, $n_D^{16^\circ}$ 1·4169, $d_{4^\circ}^{20^\circ}$ 1·0725 (Found: Cl, 25·9%). (b) Quinoline. Similar proportions being used, the resulting ethyl (+)α-chloropropionate had b. p. 143—144°, $\alpha_{5790}^{16^\circ}$ + 20·98°, $n_D^{16^\circ}$ 1·4168 (Found: Cl, 25·9%). (c) *iso*Quinoline. Under analogous conditions, the resulting ethyl (+)α-chloropropionate had b. p. 143—144°, $\alpha_{5790}^{16^\circ}$ + 20·90°, $n_D^{16^\circ}$ 1·4167 (Found : Cl, 25·9%).

Interaction of Ethyl (—)Lactate and Phosphorus Pentabromide in the Presence of Tertiary Bases.—(a) *Pyridine.* A mixture of ethyl (—)lactate (3·54 g., 1 mol.) and pyridine (4·7 g., 2 mols.) was added to phosphorus pentabromide (13 g., 1 mol.) covered with benzene. After 3 hours at room temperature, the resulting paste was decomposed with water and yielded ethyl (+)α-bromopropionate (2 g.), b. p. 55—57°/15 mm., $\alpha_{5790}^{17^\circ}$ + 22·05° (*l*, 0·5), $n_D^{18^\circ}$ 1·4458, $d_{4^\circ}^{17^\circ}$ 1·3872.

(b) *Quinoline.* The ester (1 mol.) and base (2 mols.) yielded ethyl (+)α-bromopropionate (2·1 g.), b. p. 55—56°/15 mm., $\alpha_{5780}^{17^\circ}$ + 22·0° (*l*, 0·5), $n_D^{18^\circ}$ 1·4456, $d_{4^\circ}^{17^\circ}$ 1·3875.

(c) iso*Quinoline.* The ester (1 mol.) and base (2 mols.) yielded ethyl (+)α-bromopropionate (1·95 g.), b. p. 56—57°/17 mm., $\alpha_{5790}^{17^\circ}$ + 22·06° (*l*, 0·5), $n_D^{19^\circ}$ 1·4456, $d_{4^\circ}^{16\cdot8^\circ}$ 1·3873 (Found : Br, 44·3. Calc. : Br, 44·2%).

Ethyl (+)α-p-*Toluenesulphinoxypropionate.*—A mixture of ethyl (+)lactate (25 g.), *p*-toluenesulphinyl chloride (35 g.), and pyridine (33 g.) after standing for 12 hours was poured into water, and the precipitated oil extracted with ether. The ethereal solution, after being washed with

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* By calculation from data given by Wood, Such, and Scarf (J., 1923, **123**, 600), the rotation of optically pure ethyl lactate is $\alpha_{5893}^{18\cdot9^\circ}$ 11·65°, $\alpha_{5461}^{20^\circ}$ 13·3° (*l*, 1).

acid and dried (potassium carbonate), yielded *ethyl* (+)α-p-*toluenesulphinoxypropionate* (60% yield), b. p. 110°/<0·1 mm., $\alpha^{16^\circ}_{5790}$ + 12·41°, $\alpha^{16^\circ}_{5461}$ + 14·88°, $\alpha^{16^\circ}_{4358}$ + 24·2° (*l*, 0·25), $n^{16^\circ}_{D}$ 1·5197 $d^{16\cdot4^\circ}_{4^\circ}$ 1·163, $d^{51\cdot6^\circ}_{4^\circ}$ 1·131 (Found, by saponification : *M*, 257·7. $C_{12}H_{16}O_4S$ requires *M*, 256).

Oxidation of Ethyl (+)α-p-*Toluenesulphinoxypropionate.*—To a stirred mixture of the sulphinate (2·56 g.) in acetone (25 c.c.) and magnesium sulphate (0·63 g.) in water (4 c.c.), potassium permanganate (0·63 g.) was added to give a permanent coloration. After addition of water and sulphur dioxide, the precipitated oil was extracted with ether, ethyl (+)α-*p*-toluenesulphonoxypropionate, b. p. 138°/<0·1 mm., $\alpha^{18\cdot5^\circ}_{5461}$ + 15·89° (*l*, 0·25), $n^{16^\circ}_{D}$ 1·5005, being obtained. Kenyon, Phillips, and Turley (*loc. cit.*) give $\alpha^{21^\circ}_{5461}$ + 32·2° (*l*, 0·5), $n^{16\cdot5^\circ}_{D}$ 1·5011, for the optically pure ester.

Separation of the Diastereoisomerides of Ethyl (—)α-p-dl-*Toluenesulphinoxypropionate by Fractional Distillation.*—The ester ($\alpha^{20^\circ}_{5461}$ — 15·72°; *l*, 0·25) was thrice fractionally distilled, b. p. 110—112°/<0·1 mm., seven fractions, having the following constants, being obtained :

Fraction	1	2	3	4	5	6	7
$\alpha^{20^\circ}_{5461}$ (*l*, 0·25)	—3·00°	3·16°	7·13°	10·51°	12·34°	19·67°	22·85°
$n^{20^\circ}_{D}$	1·5165	1·5179	1·5195 *	1·5193	1·5198	1·5199 †	1·5200

* Found : C, 55·8; H, 5·8; S, 12·9 ($C_{12}H_{16}O_4S$ requires C, 56·2; H, 6·25; S, 12·5%).
† Found : C, 56·1; H, 5·9; S, 12·6%.

A second specimen of ester ($\alpha^{16^\circ}_{5461}$ — 15·70°; *l*, 0·25; $n^{17^\circ}_{D}$ 1·5198) was slowly distilled during four hours at 0·1 mm., and three fractions collected (*l*, 0·25).

Fraction.	$\alpha^{19^\circ}_{5790}$.	$\alpha^{19^\circ}_{5461}$.	$\alpha^{19^\circ}_{4358}$.	$n^{19\cdot5^\circ}_{D}$.
1	—2·97°	—3·24°	—3·75°	1·5198
2	11·73	13·34	22·75	1·5199
3	18·10	20·68	—	1·5200

Reactions of Ethyl d(+)-α-p-*Toluenesulphinoxypropionate.*—(a) *With chlorine water.* Ethyl (+)α-*p*-toluenesulphinoxypropionate (5·1 g.; $\alpha^{16^\circ}_{5790}$ + 13·35°; *l*, 0·25) was shaken for one hour with water containing the calculated amount of chlorine. After cooling, the precipitated *p*-toluenesulphonyl chloride (m. p., after crystallisation, 70°; m. p. of amide 137°) was removed by filtration from the reaction mixture, and the filtrate extracted with light petroleum. The petroleum extract contained ethyl (—)α-chloropropionate, b. p. 143—144°; $\alpha^{16^\circ}_{5790}$ — 4·63°; $\alpha^{16^\circ}_{5461}$ — 5·37° (*l*, 0·25) (Found : Cl, 25·85%).

(b) *With bromine.* Bromine (4·8 g.) in chloroform (20 c.c.) was added slowly to ethyl (+)α-*p*-toluenesulphinoxypropionate (7·7 g.) in chloroform (25 c.c.). After 8 days, the solution had become decolorised, and the solvent was removed at ordinary temperature. Trituration of the oily residue with light petroleum separated it into *p*-toluenesulphonyl bromide (amide, m. p. 137°) and ethyl (—)α-bromopropionate, b. p. 55—58°/15 mm., 156—157°/760 mm., $\alpha^{16^\circ}_{5790}$ — 10·91° (*l*, 0·5); $n^{16^\circ}_{D}$ 1·4463 (Found: Br, 44·32%). By the same procedure the (—)sulphinate yielded ethyl (+)α-bromopropionate, $\alpha^{16^\circ}_{5790}$ + 8·95° (*l*, 0·5).

(c) *With hypochlorous acid.* Ethyl (+)α-*p*-toluenesulphinoxypropionate (10·25 g.; $\alpha^{16^\circ}_{5790}$ + 63·28°; *l*, 1·0) was shaken with the calculated amount of hypochlorous acid solution (" Organic Syntheses," Vol. 5, 31) until it no longer produced a permanent coloration with starch–iodide paper. After cooling, the *p*-toluenesulphonyl chloride (m. p. 70°) was filtered off, and the filtrate extracted with light petroleum. The petroleum extract yielded an oil, b. p. 45—56°/14 mm., which, by nine fractional distillations, was separated into ethyl (—)α-chloropropionate, b. p. 42°/14 mm., $\alpha^{16^\circ}_{5790}$ — 9·1° (*l*, 0·5), $n^{16^\circ}_{D}$ 1·4166 (Found : Cl, 25·7%), and ethyl (—)lactate, b. p. 49—51°/14 mm., $\alpha^{16^\circ}_{5790}$ — 4·78° (*l*, 0·5), $n^{16^\circ}_{D}$ 1·4155 (Found, by saponification : *M*, 117·6. Calc. : *M*, 118).

(d) *With thiocyanogen.* Ethyl (—)α-*p*-toluenesulphinoxypropionate (10 g.; α_{5893} — 21·5°; *l*, 0·5) was added slowly to the calculated amount of thiocyanogen (Kaufmann, *Analyst*, 1926, **51**, 157) dissolved in acetic acid. When the reaction mixture gave no coloration with starch–iodide paper, water was added, and the mixture extracted with light petroleum. The oil (4 g.) thus obtained decomposed when heated.

(e) *With triselenocyanogen.* A mixture of this compound (14 g.) and ethyl (—)α-*p*-toluenesulphinoxypropionate (10 g.) in chloroform solution was heated under reflux for several days. In this case also the oil extracted by light petroleum decomposed when distillation was attempted.

Ethyl (—)α-*Thiocyanopropionate.*—A solution of ethyl (—)α-*p*-toluenesulphonoxypropionate (8·2 g.; $\alpha^{20^\circ}_{5893}$ — 27·5°; *l*, 0·5) and potassium thiocyanate (4 g.) in absolute alcohol (50 c.c.) was heated under reflux for six hours, cooled, and diluted with dry ether. After removal of the precipitated potassium *p*-toluenesulphonate, the filtrate yielded *ethyl* (−)*α-thiocyanopropionate*, b. p. 119°/20 mm., $\alpha^{20^\circ}_{5790}$ − 7·51° (*l*, 0·5), $n^{20^\circ}_{D}$ 1·4657 (Found: C, 45·2; H, 5·7. $C_6H_9O_2NS$ requires C, 45·3; H, 5·7%).

Ethyl (−)*α-Selenocyanopropionate.*—A solution of ethyl (−)α-*p*-toluenesulphonoxypropionate (10 g.) and potassium selenocyanate in absolute alcohol (50 c.c.) was heated under reflux for six hours, diluted with water (300 c.c.), and extracted with ether. *Ethyl* (−)*α-selenocyanopropionate* was obtained, b. p. 63—64°/<0·1 mm., $\alpha^{17\cdot5^\circ}_{5790}$ − 0·85°, $\alpha^{17\cdot5^\circ}_{5461}$ − 0·91°, $\alpha^{17\cdot5^\circ}_{4358}$ − 1·38° (*l*, 0·5), $n^{17\cdot5^\circ}_{D}$ 1·4905 (Found : Se, 38·0. $C_6H_9O_2NSe$ requires Se, 38·3%).

Interaction of Ethyl (+)*Lactate and Thionyl Chloride in the Presence of Tertiary Bases.*—(i) *Pyridine.* To a cold solution of ethyl (+)lactate (4·7 g.) in pyridine (3·2 g., 1 mol.), thionyl chloride (4·8 g.) was added slowly; after being heated to 60° for one hour, the mixture was poured into ice-water, and the ethyl (−)α-chloropropionate extracted with ether. The ester (3·8 g.) had b. p. 45°/19 mm., $\alpha^{17^\circ}_{5893}$ − 19·56°, $\alpha^{17^\circ}_{5790}$ − 20·87°, $\alpha^{17^\circ}_{5461}$ − 23·38°, $\alpha^{17^\circ}_{4358}$ − 44·8° (*l*, 1·0); $n^{20^\circ}_{D}$ 1·4166, $d^{15^\circ}_{4^\circ}$ 1·0853.

(ii) *Quinoline.* By the same procedure as in (i), but with quinoline (6·0 g.) in place of pyridine, the ethyl(−)α-chloropropionate (3·9 g.) obtained had b. p. 40·5°/12 mm., $\alpha^{16^\circ}_{5893}$ − 19·36°, $\alpha^{16^\circ}_{5790}$ − 20·60°, $\alpha^{16^\circ}_{5461}$ − 23·0°, $\alpha^{16^\circ}_{4358}$ − 44·0° (*l*, 1·0), $n^{20^\circ}_{D}$ 1·4166, $d^{15^\circ}_{4^\circ}$ 1·0854 (Found: Cl, 25·9%); [*P*] 291·7 (Calc., from constants given by Sugden, " Parachor and Valency," 292·2).

(iii) iso*Quinoline.* Procedure as in (ii) gave ethyl (−)α-chloropropionate (3·1 g.), b. p. 40·5°/12 mm., $\alpha^{17^\circ}_{5790}$ − 20·13°, $\alpha^{17^\circ}_{5461}$ − 22·51° (*l*, 1·0), $n^{20^\circ}_{D}$ 1·4167, $d^{20^\circ}_{4^\circ}$ 1·0855.

Ethyl (+)*α-Chlorosulphinoxypropionate.*—(i) *Preparation.* Ethyl (+)lactate (14·5 g.) was slowly added to cold thionyl chloride (22 g.) and, after the initial vigorous reaction, the mixture was heated (2 hours) on the steam-bath, then (2 hours) at 90°/15 mm., and finally distilled. Ethyl (+)α-chlorosulphinoxypropionate, b. p. 43—45°/<0·1 mm., was obtained, $\alpha^{16^\circ}_{5790}$ + 83·0°, $\alpha^{16^\circ}_{5461}$ + 95·08°, $\alpha^{16^\circ}_{4358}$ + 172·4° (*l*, 0·25), $n^{16^\circ}_{D}$ 1·4583, $d^{13^\circ}_{4^\circ}$ 1·2819; [*P*] 380·5 (Calc. : 380·4).

(ii) *Thermal decomposition.* Ethyl (+)α-chlorosulphinoxypropionate (15 g.; $\alpha^{16^\circ}_{5790}$ + 83·94°; *l*, 0·25), distilled slowly at atmospheric pressure, gave ethyl α-chloropropionate contaminated with undecomposed chlorosulphinate which was removed by sodium carbonate solution. The ethyl (+)α-chloropropionate (7·5 g.) then had b. p. 143—145°, $\alpha^{16^\circ}_{5893}$ − 2·2° (*l*, 0·5), $n^{17^\circ}_{D}$ 1·4168.

(iii) *Interaction with pyridine.* Pyridine (15·8 g., 1 mol.) was added slowly to a cold solution of ethyl (+)α-chlorosulphinoxypropionate (40 g.; $\alpha^{16^\circ}_{5461}$ + 190·2°; *l*, 0·5) in dry ether (50 c.c.). A white precipitate (0·4 g.) was removed, and the filtrate kept in a closed vessel. A yellow oil, which slowly turned red, was deposited, and after 2 days was separated and washed with dry ether. A portion (50 c.c.) of the combined ethereal filtrate and washings (total vol., 108 c.c.) was washed with dilute hydrochloric acid, dried (potassium carbonate) and distilled. It gave a liquid (5·5 g.) from which ethyl (−)α-chloropropionate (4 g.) was obtained, b. p. 143—144°, $\alpha^{15^\circ}_{5790}$ − 10·87° (*l*, 0·5), $n^{16^\circ}_{D}$ 1·4169, $d^{15^\circ}_{4^\circ}$ 1·0855 (Found : Cl, 25·8%).

The residual oil, insoluble in ether, was optically inactive in aqueous solution (Found : Cl, 14·4; SO_2, 19·0. $C_{10}H_{14}O_4NClS$ requires Cl, 12·7; SO_2, 22·9%). With picric acid in aqueous-alcoholic solution, this N-*chloropyridinium* N-*α-carbethoxyethyl sulphinate* (6 g.) gave N-*α-carbethoxyethylpyridinium picrate* (4·5 g.), needles, m. p. 95°, from acetone (Found : C, 46·9; H, 3·9; N, 13·8. $C_{16}H_{16}O_9N_4$ requires C, 47·0; H, 3·9; N, 13·8%. Cf. Gerrard, J., 1936, 688).

(iv) *Interaction with water.* Ethyl (+)α-chlorosulphinoxypropionate (8·9 g.; α_{5790} + 82·0°; *l*, 0·25) was shaken with water for 5 minutes. Extraction of the aqueous solution with ether gave ethyl (+)lactate (2 g.), b. p. 49°/12 mm., $n^{15^\circ}_{D}$ 1·4155, $\alpha^{16^\circ}_{5893}$ + 11·02° (*l*, 1·0). The ethyl (+)lactate from which the chlorosulphinate had been prepared had $\alpha^{16^\circ}_{5893}$ + 11·3°.

(v) *Fractional distillation.* By two fractional distillations ethyl (+)α-chlorosulphinoxypropionate was divided into the following fractions, all with b. p. 43—44°/<0·1 mm. (rotations for l = 0·5) :

Fraction	1	2	3	4	5	6
α_{5790}	+ 82·11°	+ 82·75°	+ 82·97°	+ 83·00°	+ 83·46°	+ 83·46°
α_{5461}	+ 94·16°	+ 95·05°	+ 95·16°	+ 94·95°	+ 95·96°	+ 95·96°
α_{4358}	+168·86°	+170·76°	+170·96°	+172·36°	+172·89°	+172·89°
$n^{19^\circ}_{D}$	1·4584	1·4583 *	1·4583	1·4583	1·4583	1·4583 †

* Found : S, 15·85 ($C_5H_9O_4ClS$ requires S, 16·0%). † Found : S, 15·94%.

The rotatory powers of fractions 2 and 6 were unchanged after 2 weeks.

α-Carbethoxyethyl n-*Amyl Sulphite.*—(i) *From* n-*amyl chlorosulphinate and ethyl lactate.* *n*-Amyl chlorosulphinate, prepared from *n*-amyl alcohol (12·6 g.) and thionyl chloride (30 g.)

and redistilled until its refractive index became constant, had b. p. 71·5—71·75°/13 mm., $n_D^{17°}$ 1·4568, $d_{4°}^{11°}$ 1·1259, [*P*] 355·4 (Calc.: 354·6). It (2·1 g.) was added to ethyl (—)lactate (1·5 g.) dissolved in a mixture of pyridine and ligroin. After removal of the precipitated pyridine hydrochloride (1·46 g.), water was added, and the *α-carbethoxyethyl* n-*amyl sulphite*, b. p. 140—142°/13 mm., $\alpha_{5893}^{16°}$ — 37·15° (*l*, 0·5), $n_D^{16°}$ 1·4377 (Found: S, 12·8. $C_{10}H_{20}O_5S$ requires S, 12·7%), isolated with ether.

(ii) *From ethyl* (—)*α-chlorosulphinoxypropionate and* n-*amyl alcohol*. The sulphinoxypropionate (10 g.; $\alpha_{5790}^{16°}$ — 83·2°; *l*, 0·5) was added slowly to a solution of *n*-amyl alcohol (4·4 g.) and pyridine (4 g.) in ligroin (20 c.c.). After removal of pyridine hydrochloride (5·8 g.), addition of water and extraction with ether gave α-carbethoxyethyl *n*-amyl sulphite (12 g.), b. p. 140—142°/13 mm., $\alpha_{5893}^{16°}$ — 39·14° (*l*, 0·5); [*P*] 558·6 (Calc. : 558·2) (Found : S, 12·8%).

By two redistillations, the sulphite was separated into the following fractions :

Fraction	1	2	3	4	5	6
B. p./13 mm.	135—136°	137°	139°	143—144°	144—145°	146°
$\alpha_{5461}^{15°}$ (*l*, 0·5)	−15·12°	−18·81°	−24·31°	−30·32°	−35·70°	−48·31°
$n_D^{15°}$	1·4373	1·4375	1·4376	1·4374	1·4374	1·4376
S, %	12·81	12·85	12·81	12·85	12·77	12·72

The attempted preparation of α-carbethoxyethyl *n*-amyl sulphite by methods similar to (i) and (ii) but in the absence of pyridine gave products which could not be distilled to constancy of refractive index.

n-*Amyl sulphite*, prepared by heating thionyl chloride (5 g.) and *n*-amyl alcohol (7 g., 2 mols.) to 50° for 2 hours, had b. p. 129·5°/12 mm., $d_{4°}^{16°}$ 0·9822, $d_{4°}^{40°}$ 0·9543 (Found: S, 14·3. $C_{10}H_{22}O_3S$ requires S, 14·4%).

(+)*α-Carbethoxyethyl sulphite*, prepared in the same way from thionyl chloride and ethyl (+)lactate (2 mols.), has b. p. 111—112°/<0·1 mm., b. p. 161°/14 mm., $\alpha_{5790}^{15°}$ + 49·60°, $\alpha_{5461}^{15°}$ + 56·14°, $\alpha_{4358}^{15°}$ + 96·0° (*l*, 0·25), $n_D^{18°}$ 1·4402 (Found : S, 11·4. $C_{10}H_{18}O_7S$ requires S, 11·4%).

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BATTERSEA POLYTECHNIC, S.W. 11.

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