CCCXXXIII.—*Some Reactions of* d-β-*Octyl Chlorocarbonate of Interest from the Standpoint of the Walden Inversion.*

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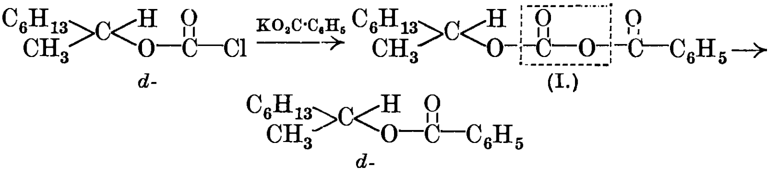
THE reactions of the chlorocarbonates of optically active hydroxy-compounds have hitherto not been utilised in the study of the Walden inversion, although, in some respects, they are eminently suitable for this purpose. For example, they can be prepared, without loss of rotatory power, by the interaction of hydroxy-compounds with carbonyl chloride in the presence of a tertiary base; a method which also ensures that the chlorocarbonate produced has the same configuration as that of the parent hydroxy-compound. Further, they react with alkali salts of carboxylic acids to yield carboxylic esters (Otto and Otto, *Ber.*, 1888, **21**, 1516; Herzog, *ibid.*, 1909, **42**, 2557), with sodium *p*-toluenesulphinate to yield *p*-toluenesulphinic esters (Otto and Rossing, *Ber.*, 1885, **18**, 2504), and with tertiary bases to yield halides (Fry, " The Electronic Conception of Valence," 1921, p. 65). The present communication deals with the reactions of *d*-β-octyl chlorocarbonate * (Hunter, J., 1924, **125**, 1391).

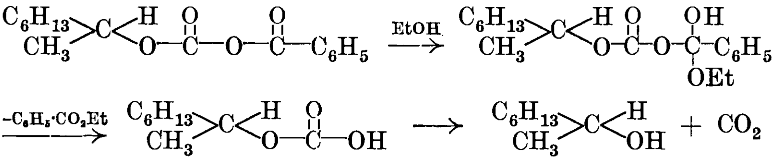
d-β-Octyl chlorocarbonate reacts with potassium acetate and potassium benzoate in what might perhaps be called the normal manner, *i.e.*, according to the equations (in the case of the benzoate)



$$\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}H\\O-\overset{O}{\overset{\|}{C}}-Cl\end{matrix}\xrightarrow{KO_2C\cdot C_6H_5}\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}H\\O-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5\end{matrix}\longrightarrow\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}H\\O-\overset{O}{\overset{\|}{C}}-C_6H_5\end{matrix}$$

d- (I.) *d*-

and, within the limits of experimental error, optically pure *d*-octyl acetate and benzoate are obtained. These results are in agreement with the view that, as an intermediate stage in the reaction, a mixed anhydride is produced which loses carbon dioxide as indicated in (I). In other words, the *d*-β-octyl radical remains attached to an oxygen atom throughout the reaction and hence the bonds of the asymmetric carbon remain undisturbed. That such mixed anhydrides may be formed during these reactions is highly probable, since their isolation is reported (D.R.-P. 117267; Friedländer, " Fortschritte," VI, 146) and, if the reactions described are carried out in ethyl-alcoholic solution, instead of, for example, *d*-β-octyl benzoate, the main products are *d*-β-octanol and ethyl benzoate. This result can be explained on the assumption that the mixed anhydride (I) decomposes as in the scheme :



$$\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}H\\O-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5\end{matrix}\xrightarrow{EtOH}\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}H\\O-\overset{O}{\overset{\|}{C}}-O-\overset{OH}{\underset{OEt}{C}}-C_6H_5\end{matrix}$$

$$\xrightarrow{-C_6H_5\cdot CO_2Et}\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}H\\O-\overset{O}{\overset{\|}{C}}-OH\end{matrix}\longrightarrow\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}H\\OH\end{matrix}+CO_2$$

These views of the mechanism of the reaction by which *d*-β-octyl benzoate is produced have been substantiated by the study of the interaction of *d*-β-octyl chlorocarbonate and sodium *p*-toluenesulphinate. The production of *p*-toluenesulphinic esters by the interaction of alkyl chlorocarbonates and sodium *p*-toluenesulphinate is in some ways a unique reaction, since alkyl halides form alkyl *p*-tolyl sulphones with this salt. The preferential formation of alkyl

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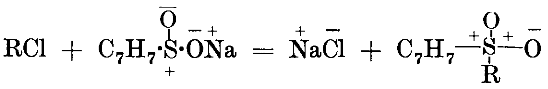
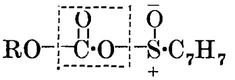
* Actually, in some instances, *l*-β-octyl chlorocarbonate was used, but to avoid confusion it is assumed in the theoretical portion of this paper that *d*-β-octyl chlorocarbonate was used throughout.

p-tolyl sulphones in this manner implies that, of the two different points for attachment which a sulphinoxy-ion presents to an alkyl group, *viz.*, the vacant pair of electrons of the oxygen atoms or the lone pair of electrons of the sulphur atom, the alkyl group selects the sulphur electrons.

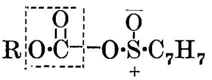


$$RCl + C_7H_7\cdot\overset{\bar{O}}{\underset{+}{S}}\cdot\overset{-+}{O}Na = \overset{+}{Na}\overset{-}{Cl} + C_7H_7\overset{+}{-}\overset{O}{\underset{R}{S}}\overset{+}{-}\bar{O}$$

It follows that, during the interaction of an alkyl chlorocarbonate and sodium *p*-toluenesulphinate, the alkyl group is never able to make this choice. The reason for this must be that the alkyl group remains attached to an oxygen atom throughout the reaction. Assuming, therefore, that the initial stage in the interaction is the elimination of sodium chloride and the formation of a mixed anhydride, it must be concluded that this anhydride decomposes with the evolution of carbon dioxide, as indicated in (II) and not as indicated in (III), in order to explain the absence of sulphone formation.

(II.) 

$$RO-\boxed{\overset{O}{\overset{\|}{C}}\cdot O}-\overset{\bar{O}}{\underset{+}{S}}\cdot C_7H_7$$

 (III.)

$$R\boxed{O\cdot\overset{O}{\overset{\|}{C}}}-O\cdot\overset{\bar{O}}{\underset{+}{S}}\cdot C_7H_7$$

From these considerations it follows that, if R be an optically active radical such as the *d*-β-octyl radical, it cannot be inverted in configuration during the reaction and the *d*-β-octyl *dl*-*p*-toluenesulphinate formed must have the same configuration as the *d*-β-octanol from which the chlorocarbonate was prepared. These conclusions are in agreement with the experimental results obtained with *d*-β-octyl chlorocarbonate. Although, owing to its instability towards heat, *d*-β-octyl *dl*-*p*-toluenesulphinate was not isolated in a state of purity, it yielded *d*-β-octanol on hydrolysis. This reaction was also studied in ethyl-alcoholic solution; ethyl *p*-toluenesulphinate and *d*-β-octanol were then the chief products.

The reaction between *d*-β-octyl chlorocarbonate and pyridine proceeded smoothly and gave lævorotatory β-chloro-octane in good yield. According to Houssa, Kenyon, and Phillips (this vol., p. 1700), lævorotatory β-chloro-octane has the same configuration as *l*-β-octanol, and therefore this reaction was attended by a Walden inversion. In contrast to the reactions previously described, the bonds of the asymmetric carbon atom are disturbed, since the oxygen–carbon linking is broken. The occurrence of a Walden inversion during the formation of the β-chloro-octane is therefore possible. The rotation of the *l*-β-chloro-octane obtained was $\alpha^{20^\circ}_{5461}$ − 31·70° ($l = 1{\cdot}0$), which suggests that the reaction is not attended by any pronounced racemisation, since this chloro-octane has not so far been prepared with a rotation greater than $\alpha_{5461}^{20^\circ}$ $-$ 36·68° ($l = 1·0$) (Houssa, Kenyon, and Phillips, *loc. cit.*).

EXPERIMENTAL.

The Interaction of l-β-*Octyl Chlorocarbonate and Potassium Acetate.*—A vigorous evolution of carbon dioxide occurred when a mixture of *l*-β-octyl chlorocarbonate (10 g.) and potassium acetate (7·5 g.; 1·5 mols.) was warmed. From the products, extracted by anhydrous ether from the excess of potassium acetate and the potassium chloride formed, a small fraction, b. p. up to 83°/28 mm., was isolated. It was unsaturated and consisted mainly of octylene. The main fraction (3·7 g.) had b. p. 85—91°/28 mm., $n_D^{23·5^\circ}$ 1·4190, and $\alpha_{5461}^{23^\circ}$ $-2·1°$ ($l = 0·25$). On systematic refractionation it gave two fractions: Fraction I had b. p. 86—90°/31 mm., $\alpha_{5461}^{25^\circ}$ $-2·20°$ ($l = 0·25$), and $n_D^{25^\circ}$ 1·4192. 0·7500 G. required 0·0339 g. of potassium hydroxide for complete hydrolysis (calc. for *l*-β-octyl acetate, 0·2442 g.). This fraction was therefore almost pure *l*-β-octanol, which has $\alpha_{5461}^{20^\circ}$ $-9·60°$ ($l = 1·0$) and $n_D^{20^\circ}$ 1·4256. Fraction II had b. p. 90—91°/31 mm., $\alpha_{5461}^{25^\circ}$ $-2·10°$ ($l = 0·25$), and $n_D^{25^\circ}$ 1·4187. 0·7040 G. required 0·1739 g. of potassium hydroxide for complete hydrolysis (calc. for *l*-β-octyl acetate, 0·2294 g.). This fraction therefore consisted largely of *l*-β-octyl acetate, which has $\alpha_{5461}^{20^\circ}$ $-6·90°$ and $n_D^{17^\circ}$ 1·4168.

It is thought that the presence of the *l*-β-octanol is explained by the interaction of the mixed anhydride with adventitious moisture.

The Interaction of d-β-*Octyl Chlorocarbonate and Potassium Acetate in Ethyl-alcoholic Solution.*—A solution of *d*-β-octyl chlorocarbonate (8·6 g.) and potassium acetate (6·4 g.; 1·5 mols.) in ethyl alcohol (40 c.c.) was heated under reflux on a steam-bath for 1 hour. The reaction mixture was then poured into water, and the product isolated in ether. It consisted (4·2 g.) of *d*-β-octanol, b. p. 83—89°/25 mm., $\alpha_{5461}^{20^\circ}$ $+$ 2·41° ($l = 0·25$), and $n_D^{20^\circ}$ 1·4259. No racemisation had occurred, since the chlorocarbonic ester used was prepared from *d*-β-octanol, $\alpha_{5461}^{22^\circ}$ $+$ 9·51° ($l = 1·0$). In order to prove that the *d*-β-octanol did not arise from the interaction of *d*-β-octyl chlorocarbonate and ethyl alcohol, a solution of the chlorocarbonate in ethyl alcohol was examined after it had stood for 10 days. It then contained *d*-β-octyl chlorocarbonate and *d*-β-octyl ethyl carbonate (Hunter, *loc. cit.*) and was free from *d*-β-octanol.

The Interaction of l-β-*Octyl Chlorocarbonate and Potassium Benzoate.*—*l*-β-Octyl chlorocarbonate (10 g.) and potassium benzoate (10 g.; 1·2 mols.) were heated together on a steam-bath for 6 hours and the mixture was then cooled and extracted with anhydrous ether. From the ethereal extract, an oily residue was obtained which did not contain unsaturated products and on distillation separated into two fractions: Fraction I (2·8 g.), b. p. 80—90°/28 mm., $n_{\mathrm{D}}^{25°}$ 1·4255, $\alpha_{5461}^{24°}$ − 2·87° ($l = 0·25$); fraction II (3·8 g.), b. p. 175—177°/28 mm., $n_{\mathrm{D}}^{24°}$ 1·4824, $\alpha_{5461}^{24°}$ −8·68° ($l = 0·25$). Fraction II was *l*-β-octyl benzoate and after further purification by distillation had b. p. 105—110°/1 mm., $n_{\mathrm{D}}^{25°}$ 1·4840, $\alpha_{5461}^{25°}$ −9·27° ($l = 0·25$); 1·0426 g. required 0·2481 g. of potassium hydroxide for complete hydrolysis (calc. for *l*-β-octyl benzoate, 0·2484 g.). Pickard and Kenyon (J., 1915, **107**, 122) record the following constants for *d*-β-octyl benzoate: b. p. 171°/20 mm., $n_{\mathrm{D}}^{20°}$ 1·4887, $\alpha_{5461}^{20·5°}$ + 38·06° ($l = 1·0$). It may be concluded, therefore, that this ester was obtained from *l*-β-octyl chlorocarbonate without loss of rotatory power.

Fraction I on redistillation was separated into fraction (*a*) (1·2 g.), b. p. up to 89°/30 mm., $n_{\mathrm{D}}^{24·5°}$ 1·4241, $\alpha_{5461}^{25°}$ − 3·32° ($l = 0·25$), and fraction (*b*) (1·3 g.), b. p. 89—91°/30 mm., $n_{\mathrm{D}}^{25·5°}$ 1·4256, $\alpha_{5461}^{25°}$ − 2·42° ($l = 0·25$). Fraction (*b*) was pure *l*-β-octanol and gave a hydrogen phthalic ester, m. p. 75°, $[\alpha]_{5461}^{25°}$ − 55·9° ($l = 2·0$; $c = 5·5250$) in ethyl-alcoholic solution. Fraction (*a*) also consisted mainly of *l*-β-octanol, but it contained chlorine.

The Interaction of d-β-*Octyl Chlorocarbonate and Potassium Benzoate in Ethyl-alcoholic Solution.*—After 48 hours at the ordinary temperature, the reaction between *d*-β-octyl chlorocarbonate (8·6 g.) and potassium benzoate (10·8 g.; 1·5 mols.) in ethyl alcohol (60 c.c.) was completed by heating the mixture under reflux for 3 hours. The products were isolated in ether and on systematic fractionation gave (*a*) *d*-β-octanol (2·5 g.), b. p. 86—88°/24 mm., $n_{\mathrm{D}}^{18°}$ 1·4335, $\alpha_{5461}^{18°}$ +2·23° ($l = 0·25$), which yielded a hydrogen phthalic ester, m. p. 74°, $[\alpha]_{5461}^{18°}$ + 55·9° ($l = 2·0$; $c = 6·2000$) in ethyl-alcoholic solution; and (*b*) impure ethyl benzoate, b. p. 102—104°/27 mm. and $n_{\mathrm{D}}^{19°}$ 1·4909. 0·9554 G. of this ethyl benzoate required 0·3448 g. of potassium hydroxide for complete hydrolysis (calc., 0·3568 g.). An authentic specimen of ethyl benzoate was found to have $n_{\mathrm{D}}^{17°}$ 1·5080. The ethyl benzoate isolated was contaminated with an optically active compound, since it had $\alpha_{5461}^{19°}$ + 0·30° ($l = 0·25$). It was not found possible to remove this optical activity by treating the ester with phthalic anhydride in pyridine solution. On the other hand, it was found that a mixture of two solutions, (1) ethyl benzoate (20 c.c.) containing *d*-β-octanol (1·052 g.) and having $\alpha_{5461}^{26°}$ + 1·37° ($l = 2·0$) and $n_{\mathrm{D}}^{21·5°}$ 1·5005 and (2) ethyl benzoate (20 c.c.) containing *d*-β-octyl chlorocarbonate (1·1236 g.) and having $a_{5461}^{26°}$ +2·92° ($l = 2·0$) and $n_{\mathrm{D}}^{21°}$ 1·5001, could be freed from optically active material by treatment with phthalic anhydride and pyridine. The ethyl benzoate isolated was therefore not contaminated with either β-octanol or β-octyl chlorocarbonate. The nature of this optically active impurity remains obscure.

The Interaction of d-β-*Octyl Chlorocarbonate and Sodium* p-*Toluenesulphinate.*—A mixture of *d*-β-octyl chlorocarbonate and anhydrous sodium *p*-toluenesulphinate was kept for 10 days. The product was then diluted with 100 c.c. of ether and filtered, and the ethereal extract dried with anhydrous sodium sulphate. After removal of the ether by distillation, the oily product gave a fraction, b. p. 40—50°/0·1 mm., which was unchanged *d*-β-octyl chlorocarbonate; the residue showed signs of decomposition and the distillation was therefore discontinued. The dark-coloured residue was impure *d*-β-octyl *p*-toluenesulphinate. It was hydrolysed with alcoholic sodium hydroxide and the liberated *d*-β-octanol was isolated in the usual manner. It had b. p. 86—87°/23 mm., $n_D^{19°}$ 1·4256, and $\alpha_{5461}^{20°}$ + 8·60° (l = 1·0). The *d*-β-octanol from which the *d*-β-octyl chlorocarbonate was prepared had $\alpha_{5461}^{20°}$ + 9·63° (l = 1·0) and $n_D^{20°}$ 1·4263. It can be concluded, therefore, that *d*-β-octyl chlorocarbonate reacts with sodium *p*-toluenesulphinate to yield *d*-β-octyl *dl*-*p*-toluenesulphinate, and that slight racemisation of the optically active octyloxy-radical may occur during the reaction.

The Interaction of l-β-*Octyl Chlorocarbonate and Sodium* p-*Toluenesulphinate in Ethyl-alcoholic Solution.*—After a mixture of *l*-β-octyl chlorocarbonate (32 g.), anhydrous sodium *p*-toluenesulphinate (40 g.; 1·3 mols.), and ethyl alcohol (160 c.c.) had stood for 3 days, it was heated under reflux for 1 hour. The reaction mixture was then poured into water and the oily product which separated was extracted with ether. The lower-boiling product obtained on distillation was *l*-β-octanol, b. p. 80—85°/17 mm., $n_D^{20°}$ 1·4247, and $\alpha_{5461}^{20°}$ −2·31° (l = 0·25). The higher-boiling fractions consisted of mixtures of ethyl *p*-toluenesulphinate, *l*-β-octyl ethyl carbonate, and probably *l*-β-octyl *p*-toluenesulphinate.

The Interaction of l-β-*Octyl Chlorocarbonate with Pyridine.*—Carbon dioxide was evolved when *l*-β-octyl chlorocarbonate (6 g.) [$\alpha_{5461}^{20°}$ − 28·94° (l = 1·0)] was heated with pyridine (24 g.) on a steam-bath for 1 hour. The product was poured into dilute hydrochloric acid and the oil which separated was extracted with ether. The ether was removed from the dried extract by distillation; the residual oil, *d*-β-octyl chloride, after repeated distillation, had b. p. 65—66°/19 mm., $\alpha_{5461}^{20°}$ + 31·70° (l = 1·0), and $n_D^{20°}$ 1·4265.

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