163. *The Conversion of* l-*Phenylmethylcarbinol into Dextrorotatory and Lævorotatory α-Chloroethylbenzene.*

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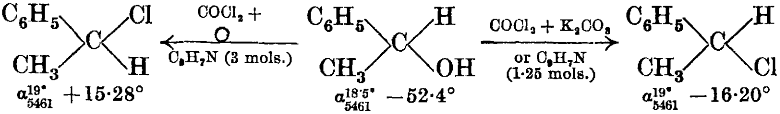
By the action of carbonyl chloride on *l*-phenylmethylcarbinol in the presence of either potassium carbonate or quinoline (1·25 mols.), lævorotatory α-chloroethylbenzene is obtained, whereas in the presence of quinoline (3·0 mols.) the chloride obtained is dextrorotatory:

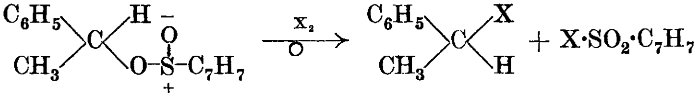


(All observed rotations in 1 dcm. tube.)

These results are similar to those obtained with ethyl *l*-α-chloroformoxymandelate (Kenyon, Lipscomb, and Phillips, J., 1931, 2275) and also with *d*-β-octyl chloroformate (Houssa and Phillips, this vol., p. 108). Phenylmethylcarbinyl chloroformate, the initial stage in the interaction of the alcohol with carbonyl chloride, was not used in the above experiments, because it is much less stable than the other chloroformates, and therefore difficult to isolate free from α-chloroethylbenzene.

In the presence of excess of quinoline (3 mols.) the chloride probably arises by the decomposition of an addition compound formed between the chloroformate and the quinoline. This addition compound would contain the entering chloro-atom as an anion and therefore its decomposition would lead to the formation of α-chloroethylbenzene with inversion. When only one molecular proportion of quinoline was used, it was converted into quinoline hydrochloride by the hydrogen chloride liberated during the formation of the chloroformate. Under these experimental conditions this ester undergoes its usual type of decomposition, during which the optically active radical assumes the anionic state, which leads to the production of the chloride without inversion (Houssa and Phillips, *loc. cit.*).

These contentions are based, to some extent, on the production of *l*-β-octanol and its lævorotatory chloride when *d*-β-octyl *p*-toluenesulphinate is allowed to react respectively with aqueous solutions of hypochlorous acid and chlorine (Houssa, Kenyon, and Phillips, J., 1929, 1700). This *d*-sulphinate has the same configuration as *d*-β-octanol and therefore an inversion occurs during its interaction with hypochlorous acid. Further, since the chlorine probably reacts with the sulphinate in a similar manner to the hypochlorous acid, it is assumed that the lævorotatory chloride obtained is also produced with inversion. The behaviour of compounds containing an α-phenyl group may, however, diverge from that shown by purely aliphatic compounds, and for this reason the interaction of *l*-phenylmethylcarbinyl *p*-toluenesulphinate with aqueous solutions of chlorine, bromine, and hypochlorous acid has been studied. The sulphinate did not react smoothly with these reagents: it was partly hydrolysed, and partly oxidised to the unstable sulphonate, and only a small proportion was converted into the corresponding halide according to the equation:



The pure chloride and bromide obtained in this manner were very slightly dextrorotatory. Although a considerable amount of *p*-toluenesulphonyl chloride was obtained by the action of an aqueous solution of hypochlorous acid on the *l*-sulphinate, very little phenylmethylcarbinol was produced. Apparently the reaction which might have given rise to the alcohol led to the formation of styrene. A small quantity of α-chloroethylbenzene with a low dextrorotation was isolated from this reaction: it was probably produced by the interaction of the *l*-sulphinate with the chloride present in the solution of hypochlorous acid used. The reaction between the *dl*-sulphinate and iodine monochloride proceeded more smoothly, the main products being *p*-toluenesulphonyl iodide and α-chloroethylbenzene.

It can be concluded that, with halogens, *l*-phenylmethylcarbinyl *p*-toluenesulphinate, like *d*-β-octyl *p*-toluenesulphinate, gives rise to halides with a change in sign of rotation. Since, however, phenyl-added to an ice-cold solution of carbonyl chloride (1·25 mols.) in toluene (50 g., 12·5% solution), *l*-phenylmethylcarbinol (Houssa and Kenyon, J., 1930, 2260: 6·1 g., $\alpha_{5461}^{18\cdot5^\circ}$ − 13·1°, $l = 0{\cdot}25$) was added from time to time in small quantities. The reaction mixture, after being kept for 3 hours, was heated on a steam-bath for 1 hour and then washed with water, dilute hydrochloric acid, and finally with water. The toluene (dried with sodium sulphate) was removed by distillation, and the residual lævorotatory α-chloroethylbenzene, b. p. 70°/13 mm., repeatedly distilled until the refractive index remained unaltered (Found: Cl, 25·3. Calc., 25·2%). It (2·2 g.) then had $n_D^{22^\circ}$ 1·5280 and $\alpha_{5461}^{19^\circ}$ − 4·05° ($l = 0{\cdot}25$).

(b) *In the presence of potassium carbonate.* *l* + *dl*-Phenylmethylcarbinol (10 g.; $\alpha_{5461}^{24^\circ}$ − 15·58°, $l = 0{\cdot}5$) was added slowly to a solution of carbonyl chloride (1·3 mols.) in toluene (90 g., 12·5% solution) containing potassium carbonate (11·5 g.; 2 mols.). When the evolution of carbon dioxide had ceased, the solution was filtered and distilled. After removal of the toluene, the residue was separated into two fractions, both of which consisted of lævorotatory α-chloroethylbenzene contaminated with *l* + *dl*-phenylmethylcarbinyl chloroformate. Fraction I, b. p. 71—76°/15 mm. (Found: Cl, 20·5%), had $n_D^{25^\circ}$ 1·5253 and $\alpha_{5461}^{21^\circ}$ − 11·29° ($l = 0{\cdot}25$), whilst fraction II, b. p. 80—95°/15 mm. (Found: Cl, 22·7%), had $n_D^{25^\circ}$ 1·5257 and $\alpha_{5461}^{21^\circ}$ − 6·14° ($l = 0{\cdot}25$). This experiment was repeated with larger quantities of the *dl*-alcohol and it was found that the *chloroformate* (Found: Cl, 13·2. $C_9H_9O_2Cl$ requires Cl, 13·8%) was slowly converted into α-chloroethylbenzene when distilled at 80—90°/13 mm.

The Conversion of 1-*Phenylmethylcarbinol into Dextrorotatory α-Chloroethylbenzene.*—(c) *By the action of quinoline* (3 *mols.*) *on* 1-*phenylmethylcarbinyl chloroformate.* *l*-Phenylmethylcarbinol (6·1 g.; 1 mol.) was added to a toluene solution of carbonyl chloride (1 mol.) and quinoline (3 mols.), and the α-chloroethylbenzene was isolated as described in (a). After repeated distillation, the dextrorotatory α-chloroethylbenzene (2 g.) (Found: Cl, 24·9%) had b. p. 68—69°/11 mm., $n_D^{22\cdot5^\circ}$ 1·5288, and $\alpha_{5461}^{19^\circ}$ + 3·82° ($l = 0{\cdot}25$).

(d) *By the action of an aqueous solution of hypochlorous acid on* 1-*phenylmethylcarbinyl* p-*toluenesulphinate.* *l*-Phenylmethylcarbinyl *p*-toluenesulphinate (26 g., prepared by the method of Kenyon and Phillips, J., 1930, 1681, from *l*-alcohol with $\alpha_{5461}^{20^\circ}$ − 12·72°, $l = 0{\cdot}25$) was shaken with 135 c.c. of a 4·015% solution of hypochlorous acid ("Organic Syntheses," V, 31) and kept at 0° for 12 hours. The white solid which had separated was removed, washed with ice-cold light petroleum, and recrystallised from this solvent. It then had m. p. 69°, alone and when mixed with *p*-toluenesulphonyl chloride. The filtrate from the white crystals was extracted with the light petroleum with which the crystals had been washed, and the extract was washed with dilute sodium hydroxide solution and water, dried, and distilled. After removal of the solvent, two fractions were obtained : fraction I, (3 g.), b. p. 42—46°/17 mm., which consisted mainly of styrene; fraction II, b. p. 79—80°/18 mm., which consisted of impure α-chloroethylbenzene. When purified by repeated distillation, fraction II gave α-chloroethylbenzene (1 g.), b. p. 74—76°/16 mm., $n^{17°}$ 1·5335, and $\alpha_{5461}^{19°}$ + 0·90° (l = 0·5). On cooling, the non-volatile residue which remained after these fractions had distilled set to a semi-solid mass, but it could not be induced to yield a pure product.

(e) *By the action of chlorine water on* l-*phenylmethylcarbinyl* p-*toluenesulphinate.* The experiment was conducted in a similar manner to (d), with a solution of chlorine (7·1 g.) in water (1450 c.c.). *p*-Toluenesulphonyl chloride was again obtained, but the volatile product contained far less styrene. It (3·7 g.) consisted almost entirely of α-chloroethylbenzene contaminated with lævorotatory alcohol produced by the hydrolysis of the *l*-sulphinate. Its rotatory powers after three successive distillations were severally − 0·21° − 0·15°, and − 0·10° (l = 0·25). The chlorine content was still low (Found : Cl, 23·3%), but the product could not be redistilled owing to its small volume. A non-volatile residue similar to that obtained in (d) remained unidentified.

The Action of Iodine Monochloride on dl-*Phenylmethylcarbinyl* p-*Toluenesulphinate.*—The *dl*-sulphinate (19 g.) was shaken with a solution of iodine monochloride (12·8 g.) in water (250 c.c.) prepared by the method of Orton (J., 1900, **77**, 830). The products, isolated as described in (d), consisted of *p*-toluenesulphonyl iodide, m. p. and mixed m. p. 86°, and α-chloroethylbenzene, b. p. 72—73°/14—15 mm. and $n_D^{25°}$ 1·5250.

The Conversion of l + dl-*Phenylmethylcarbinyl* p-*Toluenesulphinate into Dextrorotatory* α-*Bromoethylbenzene.*—The *l* + *dl*-sulphinate (26 g., prepared from *l* + *dl*-alcohol with $\alpha_{5461}^{23°}$ − 5·28°, l = 0·25) was treated with a solution of bromine (16·9 g.) in water (500 c.c.). The products isolated as described in (d) consisted of *p*-toluenesulphonyl bromide (14 g.), m. p. and mixed m. p. 97°, a very small quantity of styrene, b. p. 70—80°/23 mm., and α-bromoethylbenzene (Found : Br, 43·3. Calc., 43·2%), b. p. 86—88°/15—16 mm., $n_D^{25·2°}$ 1·5595, and $\alpha_{5461}^{19°}$ + 0·10° (l = 0·25).

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