33. *Experiments on the Interaction of Hydroxy-compounds and Phosphorus and Thionyl Halides in the Absence and in the Presence of Tertiary Bases. Part I. Optically Active β-Octanol, Ethyl Mandelate, and Phenylmethylcarbinol.*

By William Gerrard.

During addition of phosphorus trichloride to (+)-β-octanol and to ethyl (−)mandelate, the chloride RCl and the hydrogen phosphite $P(OR)_2 \cdot OH$ were produced; but reversed order of mixing resulted in formation of the *chlorophosphite* $PCl_2 \cdot OR$, which did not decompose into the chloride RCl. (+)-α-Chloroethylbenzene was formed from (−)phenylmethylcarbinol during the actual mixing at 0° in either order, no evidence of formation of the chlorophosphite being discernible. (+)*Tri-β-octyl phosphite* and phosphorus trichloride formed at 15° an equilibrium mixture of the two chlorophosphites, $PCl_2 \cdot OR$ and $PCl(OR)_2$, and the trichloride.

Mixing at 0°, in either order, of thionyl chloride with (+)-β-octanol and with ethyl (−)mandelate resulted in formation of an equilibrium mixture of the chlorosulphinate, OR·SOCl, the sulphite, R_2SO_3, and thionyl chloride, but a little chloride RCl was formed at this stage. (−)-α-Chloroethylbenzene, however, was formed from (−)carbinol during the actual mixing at 0°.

Whereas ethyl (−)mandelate, (+)-β-octanol, and (−)phenylmethylcarbinol formed the corresponding phosphites when mixed with pyridine in ethereal solution and treated with phosphorus trichloride, and the mandelate and β-octanol formed the corresponding sulphites under equivalent conditions, yet (−)phenylmethylcarbinol formed (+)-α-chloroethylbenzene during the actual addition of thionyl chloride, there being no sign of formation of sulphite. On the other hand, ethyl chlorosulphinate used in place of thionyl chloride gave the mixed sulphite, (−)-*α-phenylethyl ethyl sulphite*, which with thionyl chloride gave the non-inverted α-chloroethylbenzene. An equilibrium mixture of chlorosulphinate and unchanged thionyl chloride and sulphite was formed by the action of thionyl chloride and (+)di-β-octyl sulphite. Explanations in terms of mechanisms which depend on oriented collisions on the " front " or on the " back " of the asymmetric carbon atom cannot be disregarded.

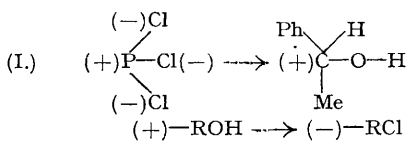
Probable modes of interaction of the compounds stated in the title have been discussed by the author (J., 1936, 688; 1939, 99; 1940, 218, 1464) where full references to literature were given. It is intended to examine in more detail the history of each relevant system from the time when the reagents are mixed to the stage where the C–O bond is broken and the chlorine atom becomes attached; and at the same time to establish a rational connection between the quantities and mode of mixing of the reagents on the one hand, and the nature and yields of products on the other. In this project, the experimental results of Kenyon and Phillips and of McKenzie and their co-workers are of value, but these reactions require detailed attention such as that given (*e.g.*, by Cowdrey, Hughes, Ingold, Masterman, and Scott, J., 1937, 1252) to the counter-process of hydrolysis of the chlorides (RCl).

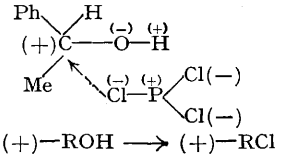
Reactions with Phosphorus Trichloride.—The main effect of adding (+)-β-octanol (Table, A) and ethyl (−)mandelate (Table, B) severally to phosphorus trichloride (>1 mol.) at 0° was the production of chlorophosphites, $PCl_2 \cdot OR$ and $PCl(OR)_2$, and not chloride, RCl. (−)-β-*Octyloxyphosphorus dichloride* and (+)*di-β-octyloxyphosphorus chloride* were distilled without decomposition. The dichloride (b. p. 119°/15 mm.) remained unchanged on standing for 14 days; it decomposed to octylene at 150°/754 mm., but was essentially unaffected by heating with pyridine or its hydrochloride. (−)-α-*Carbethoxybenzyloxyphosphorus dichloride* (b. p. 105—108°/2 mm.) was obtained by distilling the primary mixture obtained from the trichloride and (−)mandelate. It did not yield the chloroacetate on being heated for 30 minutes with pyridine or its hydrochloride.

Continuation of addition of (+)-β-octanol beyond 1 mol. did yield a little (−)-β-octyl chloride, but this was probably formed by the mechanism $PCl(OR)_2 + ROH \longrightarrow P(OR)_3 + HCl \longrightarrow P(OR)_2 \cdot OH + RCl$.

During the addition, at 0°, of the trichloride to (+)-β-octanol and to (−)mandelate, the following reaction appeared to take place: $PCl_3 + 3ROH \longrightarrow P(OR)_3 + 3HCl \longrightarrow P(OR)_2 \cdot OH + RCl$, support for this view being afforded by the readiness with which (+)*tri-β-octyl phosphite* reacted with hydrogen chloride at 0° and afforded (−)-β-octyl chloride and (+)di-β-octyl hydrogen phosphite.

By either order of addition, (−)phenylmethylcarbinol formed (+)-α-chloroethylbenzene during the mixing with the trichloride at 0° (Table, C), and it is possible that the mechanism is one of oriented collision, *e.g.*, mechanisms (I) and (II). In mechanism (II), the (−)Cl becomes attached to the (+)C before the





(+)P can claim the (−)O. With the other two hydroxy-compounds the (+)P becomes attached first, and so forms the stable chlorophosphite. When the trichloride was added to the hydroxy-compound, hydrogen chloride played a significant part; even when the operation was conducted in ethereal solution in the presence of solid potassium carbonate, as was done by Kenyon, Phillips, and Taylor in the case of phenylmethylcarbinol (see Experimental), the hydrogen chloride may not have been removed quickly enough.

The primary product from the addition of the trichloride to (+)-β-octanol and pyridine in ethereal solution appeared to be a good specimen of (+)tri-β-octyl phosphite; distillation, however, afforded both this and

No.	Order of mixing.†	Reagent, mols.	Main products.	Yield, %.	α_D.	Notes.
		(A) *Reactions of* (+)-β-*octanol*, α_D + 8·0° (1 *mol.*).				
1	⟶	PCl_3, >1	RCl	none	—	—
			PCl_2OR	80	− 34·5°	—
			$PCl(OR)_2$	12	+ 0·7	—
2	⟵	,, ⅓	RCl	27	− 30·4	(1)
			$P(OR)_2$·OH	58	+ 15·8	
3 *	⟵	,, ⅓	RCl	none	—	
			$P(OR)_2$·OH	33	+ 14·5	(2)
			$P(OR)_3$	50	+ 0·8	
4	⟶	$SOCl_2$, 2	RCl	none	—	—
			RO·SOCl	50	—	—
			$SO(OR)_2$	34	− 16·8	(3)
5	⟶	,, 1	RCl	7	—	—
			RO·SOCl	28	—	—
			$SO(OR)_2$	40	− 16·2	—
6	⟵	,, 1	RCl	trace	—	—
			RO·SOCl	29	—	—
			$SO(OR)_2$	43	− 16·5	—
7 *	⟵	,, ½	$SO(OR)_2$	84	− 17·5	—
		(B) *Reactions of ethyl mandelate* (1 *mol.*), α_D −131° *for expts.* 1 *and* 2, +120° *for* 3, 4, *and* 5.				
1	⟶	PCl_3, >1	RCl	none	—	—
			PCl_2OR	28	−117·5	—
			Undist. res.	—	—	(4)
2	⟵	,, ⅓	RCl (Cl, 12·6%)	26	+ 40·5	(1)
			$P(OR)_2$·OH	50	− 93·6	
3	⟶	$SOCl_2$, 1·1	RCl	15	+ 97·7	(5)
			RO·SOCl	80	—	—
			RCl	90	+ 84·2	(6)
4	⟵	,, ½	RCl (Cl, 13·6%)	52	+ 92·6	(1)
			$SO(OR)_2$	24	—	—
5 *	⟵	,, ½	$SO(OR)_2$	88	+124·2	—
		(C) *Reactions of phenylmethylcarbinol* (1 *mol.*), α_D −40·3° *for expts.* 1—4, −41·3° *for* 5, +20·5° *for* 6 *and* 7.				
1	⟶	PCl_3, >1	RCl ‡	75	+ 20·2	(1)
2	⟶	,, 1	RCl ‡	63	+ 19·9	(1)
			$P(OR)(OH)_2$	10·8	—	—
3	⟵	,, ⅓, ⅔, or 1	RCl ‡	60	+ 19·9	(1)
4 *	⟵	,, ⅓	Phosphite (6·7 g. from 7·3 g. ROH)	—	− 65·2	(1)
5	⟶	$SOCl_2$, 1	RCl ‡	80	− 50·9	(1)
6	⟵	,, 1	RCl ‡	66	+ 14·6	(1)
7 *	⟵	,, ⅔	RCl ‡	50	− 22·4	(1)
			Residue (3·5 g. from 12·2 g. ROH)	—	+ 69·6	(1)

* Denotes addition of 1 mol. of pyridine.
† ⟶ Denotes that octanol was added *to* the reagent, and ⟵ *vice versa.*
‡ Formed during mixing.

Notes: (1) After aqueous treatment. (2) After distillation. (3) Estimated by cold aqueous treatment. (4) 4·4 G. from 8·2 g. of mandelate. (5) Primary product. (6) After 4 days, then aqueous treatment.

(+)di-β-octyl hydrogen phosphite, and it has not been ascertained whether the di-ester was present before the distillation. Ethyl (−)mandelate and (−)phenylmethylcarbinol yielded primary products which appeared to have a similar nature to that from β-octanol, but they could not be distilled. An equilibrium mixture of chlorophosphites, tri-β-octyl phosphite, and phosphorus trichloride was formed when the last two were mixed. The phosphite product from (−)phenylmethylcarbinol, however, rapidly yielded (+)-α-chloroethylbenzene when treated with the trichloride.

Reactions with Thionyl Chloride.—By either order of addition at 0°, this reagent produced with (+)-β-octanol an equilibrium mixture of thionyl chloride, (−)di-β-octyl sulphite, and (−)-β-octyl chlorosulphinate, excess of thionyl chloride favouring the last compound. The conclusion that the formation of sulphite is rapid compared with the rate of interaction of thionyl chloride and sulphite is supported by determining the amount of sulphite immediately after mixing, and by observation of the slow rise in rotatory power of a mixture of thionyl chloride and (−)di-β-octyl sulphite (Procedure 10). Heating such a mixture with pyridine hydrochloride [a system similar to that which results when thionyl chloride (1 mol.) is added in the cold to a hydroxy-compound (1 mol.) and pyridine (1 mol.)], probably has two main effects: (1) the rise in temperature increases rate of interaction of the sulphite and thionyl chloride; (2) the hydrochloride facilitates decomposition of the chlorosulphinate by an undetermined mechanism. Preliminary experiments with pyridine hydrobromide and a chlorosulphinate failed to show that the former is a source of bromide ions which might become attached to the asymmetric carbon atom.

The primary product obtained by adding ethyl (+)mandelate (α_D + 120·1°) to thionyl chloride (Procedure 7) was treated in four different ways: (1) Aqueous treatment yielded ethyl (+)mandelate mixed with a little chloroacetate (Cl, 2·7%), and since hydrogen chloride was evolved in quantity during the mixing, the mandelate

must have resulted from the hydrolysis of the chlorosulphinate. (2) During 4 days, the rotatory power and the readily hydrolysed Cl and SO_2 content fell, and aqueous treatment then yielded the (+)chloroacetate, $\alpha_D^{18°}$ +84·2° (Cl, 17·1%). (3) Warming with pyridine hydrochloride followed by aqueous treatment gave the (−)chloroacetate in excellent yield ($\alpha_D^{20°}$ −4·6°) (Cl, 17·8%). (4) Standing for 12 hours with pyridine in ethereal solution followed by aqueous treatment yielded a mixture of mandelate and chloroacetate ($\alpha_D^{22°}$ −20·1°) (Cl, 14·1%), and (+)*bis-α-carbethoxybenzyl sulphite* ($\alpha_D^{22°}$ +108°).

Both (+)-β-octanol and ethyl (−)mandelate gave excellent yields of the corresponding sulphites through the agency of thionyl chloride and pyridine.

(−)Phenylmethylcarbinol yielded, during the mixing with thionyl chloride at 0°, (−)-α-chloroethylbenzene, the (+)isomer being formed if pyridine was also present. Furthermore, (−)-α-chloroethylbenzene was obtained by the action of thionyl chloride on (−)-*α-phenylethyl ethyl sulphite*, prepared from ethyl chlorosulphinate and (−)phenylmethylcarbinol through the agency of pyridine.

Mechanisms similar to (I) and (II), not involving the actual formation of the chlorosulphinate of phenylmethylcarbinol, cannot be disregarded. It is possible that pyridine may form the hydrogen bond, (+)C–O–H·NC_5H_5, and slightly reduce the speed of approach of the thionyl chloride molecule, thus giving some advantage to the "inversion" attack at the back of the molecule. Alternatively, the NC_5H_5 may direct the "non-inversion" attack to itself and again give the inversion attack some advantage.

Experimental.

Rotatory powers were determined in a 50-mm. micro-tube, but are recorded for l = 10 cm. Where aqueous treatment was used it is specified, and all ethereal solutions were dried before evaporation. A solution of sodium carbonate was especially used in extracting the respective dihydrogen phosphite, which was then recovered from the carbonate solution by acidification and extraction with ether.

Procedure (1). *Addition of Hydroxy-compound to Phosphorus Trichloride.*—The hydroxy-compound was added dropwise from a tap funnel fitted to a distillation flask containing the trichloride agitated by a stream of carbon dioxide or hydrogen and kept at 0°. The side tube of the flask was attached to an apparatus for absorbing the hydrogen chloride evolved. When addition was complete, the product was allowed to warm to room temperature, and then treated as specified.

(+)-β-Octanol (Kenyon, J., 1922, **121**, 2540) ($\alpha_D^{18°}$ +8·0°, 6·5 g., 1 mol.) and the trichloride (13·7 g., 2 mols.) gave, after being at 100°/15 mm. for 2 hours, (−)-*β-octyloxyphosphorus dichloride* (9·2 g.), b. p. 83—84°/2 mm., b. p. 118—119°/17 mm., $\alpha_D^{18°}$ −34·5°, $d_4^{18°}$ 1·0749, $d_4^{26°}$ 1·0683, $d_4^{35°}$ 1·0588, $n_D^{18°}$ 1·4669 (Found: Cl, 30·7; P, 13·5. $C_8H_{17}OCl_2P$ requires Cl, 30·7; P, 13·4%), (+)*di-β-octyloxyphosphorus chloride* (1·0 g.), b. p. 135—140°/2 mm., $\alpha_D^{18°}$ +0·7, $n_D^{20°}$ 1·4430 (Found: Cl, 10·5; P, 9·9. $C_{16}H_{34}O_3ClP$ requires Cl, 10·9; P, 9·6%), and an orange-coloured residue (0·8 g.), but no β-octyl chloride. The dichloride is a colourless liquid which fumes in moist air and is vigorously hydrolysed by water; 4·6 g. were poured on ice, and the ethereal extract, after being washed with a solution of sodium carbonate, gave only 0·2 g. of residue. From the carbonate solution, (+)-*β-octyl dihydrogen phosphite* (2·7 g.), $\alpha_D^{16°}$ +7·0°, $d_4^{15°}$ 1·0210, $d_4^{50°}$ 0·9914, $n_D^{16°}$ 1·4400 (Found: P, 15·9. $C_8H_{19}O_3P$ requires P, 16·0%), was obtained; Houssa and Phillips (J., 1932, 108) found evidence of formation of this phosphite in their experiment with pyridine as a reagent.

After standing at room temperature for 14 days, the dichloride had $d_4^{25°}$ 1·0711, $n_D^{18°}$ 1·4651, $\alpha_D^{18°}$ −31·6°, and 96% of it distilled as dichloride, with original physical properties, and left a residue. No β-octyl chloride was obtained. The dichloride (4·8 g.), when heated at atmospheric pressure, decomposed steadily at 150°. An orange-coloured solid (0·12 g.) was deposited, hydrogen chloride (0·56 g.) evolved, and a colourless distillate (2·3 g.) obtained. The aqueous washing of the last contained hydrochloric acid (0·78 g.) and some phosphite ion, and therefore most of the chlorine in the system was accounted for. The washed distillate was octylene (1·4 g.), b. p. 123°/756 mm. (+)-β-Octanol (6·5 g., 1 mol.) and the trichloride (3·5 g., 0·5 mol.) gave (i) (−)-β-octyl chloride (1·3 g.), b. p. 63°/16 mm., $\alpha_D^{18°}$ −30·2° $n_D^{18°}$ 1·4273; (ii) (−)-β-octyloxyphosphorus dichloride (2·9 g.), b. p. 75°/1 mm., $\alpha_D^{18°}$ −34·1° (Found: Cl, 30·6%); (iii) a mixture of di-β-octyloxyphosphorus chloride and di-β-octyl hydrogen phosphite (3·0 g.), b. p. 130—133°/1—2 mm., $\alpha_D^{18°}$ +4·8°, $n_D^{18°}$ 1·4400 (Found: Cl, 3·7%), from which, after washing with water, (+)di-β-octyl hydrogen phosphite (2·5 g.), b. p. 138—140°/2 mm., $\alpha_D^{18°}$ +15·8°, $n_D^{18°}$ 1·4375, $d_4^{18°}$ 0·9176, was obtained; (iv) residue (0·7 g.).

Procedure 1, carried out with the alcohol (3·0 g.) and the trichloride (4·0 g.) in ethereal solution, gave (−)-β-octyloxyphosphorus dichloride (4·0 g.), b. p. 75—76°/1 mm., 119—119·5°/18 mm., $n_D^{16°}$ 1·4666, $\alpha_D^{16°}$ −33·8° (Found: Cl, 30·6%), as main product, no β-octyl chloride being isolated (see Houssa and Phillips, *loc. cit.*).

(−)Phenylmethylcarbinol (Houssa and Kenyon, J., 1930, 2260) ($\alpha_D^{16°}$ −40·3°, 6·1 g., 1 mol.) and the trichloride (13·75 g., 2 mols.) gave a cloudy liquid, which, after being for 1 hour at 15 mm., was poured on ice. After the ethereal extract had been washed with a solution of sodium carbonate, it yielded (+)-α-chloroethylbenzene (5·3 g.), b. p. 78°/15 mm., $\alpha_D^{15°}$ +20·2°, $n_D^{14°}$ 1·5314 (Found: Cl, 25·0. Calc.: Cl, 25·2%), and an undistilled residue (0·61 g.). The carbonate solution gave an oil (0·05 g.) on acidification. (+)-α-Chloroethylbenzene (4·4 g.), $\alpha_D^{18°}$ +19·9°, a residue (0·5 g.), and, from the carbonate solution, a turbid oil (1·0 g.) [Found: P, 14·2. $P(OH)_2{\cdot}OC_8H_9$ requires P, 16·7%] were obtained when 1 mol. of trichloride was used and the product worked up immediately after mixing. It appears, therefore, that the chloride was formed during the actual mixing at low temperature. McKenzie and Clough (J., 1913, **103**, 687) obtained a 54% yield of (+)-α-chloroethylbenzene, α_D +5·9°, by adding the (−)alcohol, α_D −32·0°, to large excess of the trichloride and fractionating the product without its having previously been washed with water. Kenyon, Phillips, and Taylor (J., 1931, 382) obtained a 17·5% yield of (+)-α-chloroethylbenzene, α_{5461} +10·0°, by adding the (−)alcohol, α_{5461} −52·4°, to excess of the trichloride in ethereal solution, with potassium carbonate in suspension, and distilling the product without aqueous treatment.

Ethyl (−)mandelate was obtained by resolution of mandelic acid by means of *l*-ephedrine (Manske and Johnson, *J. Amer. Chem. Soc.*, 1929, **51**, 1909), followed by esterification by the benzene–alcohol–water ternary mixture method. Owing to the large amount of material required, specimens of mandelate which fell a little short of optical purity had to be used.

The (−)mandelate ($\alpha_D^{16°}$ −131·0°, 9 g., 1 mol.) and the trichloride (13·75 g., 2 mols.) gave a product which attained almost constant weight (14·6 g.) after being in a vacuum for 7½ hours (the theoretical weight for $PCl_2{\cdot}OR$ is 14·05 g.). It then had $\alpha_D^{16°}$ −122·9°, $n_D^{16°}$ 1·5277 (Found: Cl, readily hydrolysed, 26·3; P, 11·5. $C_{10}H_{11}O_3Cl_2P$ requires Cl, 25·2; P, 11·0%), being (−)-*α-carbethoxybenzyloxyphosphorus dichloride*, $PCl_2{\cdot}O{\cdot}CHPh{\cdot}CO_2Et$. (i) 6·8 G. of this product, after being kept at 100°/15 mm. for 1 hour, had $\alpha_D^{16°}$ −136·4°, and as its temperature was raised slowly from 100° to 190° it gave a distillate (0·7 g.), b. p. 138—140°/14 mm., $\alpha_D^{16°}$ −14·8°, $n_D^{16°}$ 1·5200. (ii) 6·8 G. of the product were poured on ice, and the ethereal

extract, after being washed with a solution of sodium carbonate, gave a colourless liquid (1·4 g.), $\alpha_D^{16°}$ −50·7°, containing only a trace of chlorine. From the carbonate solution a thick gum (4·15 g.) (Found : P, 11·0%) was obtained.

The product (16·9 g. after 2 hours and 16·0 g. after 3 hours at 15 mm.) obtained from (−)mandelate (9 g.) and trichloride (13·8 g.) was kept for 7 days at 18° and then for 2 hours at 18°/15 mm. It still weighed 16·0 g. and had $\alpha_D^{18°}$ −114·2° (Found : Cl, readily hydrolysed, 29·0%). (i) 5·0 G. of the product were poured on ice. From the ethereal solution, after extraction with a solution of sodium carbonate, a liquid (0·6 g.) (not distilled), $\alpha_D^{18°}$ −55·0°, $n_D^{18°}$ 1·5140 (Found : Cl, 4·1%), was obtained. The carbonate solution gave a viscous residue (1·6 g.), $\alpha_D^{18°}$ −114·0° [Found : P, 11·9. The *dihydrogen phosphite*, $P(OH)_2{\cdot}O{\cdot}CHPh{\cdot}CO_2Et$, $C_{10}H_{13}O_5P$, requires P, 12·7%). (ii) 4·0 G. of the original product, heated at 100°/754 mm. for 1·5 hours, then at 100°/15 mm. for 45 minutes, had $\alpha_D^{18°}$ −129·6° (Found : Cl, readily hydrolysed, 21·3%). From the ethereal solution of this, after extraction with a solution of sodium carbonate, a residue (0·5 g.) (Found : Cl, 4·2%) was obtained. The carbonate solution gave as before a viscous residue (1·2 g.), $\alpha_D^{18°}$ −114·3° (Found : P, 12·0%).

It may be concluded from these experiments (*a*) that the chlorophosphite is formed in some quantity, but (*b*) it does not decompose (or ionise) to give ethyl phenylchloroacetate ; and (*c*) that there is no clue to the mechanism of formation of the small amount of the chloroacetate which appears to be present.

Finally, the (−)mandelate (8·2 g.) and trichloride (11·7 g.) by Procedure (1) gave a product, which, after 1 hour at 50° and ½ hour at 100°/15 mm., had $\alpha_D^{18°}$ −136·8°, and on fractionation yielded a liquid (3·5 g.), b. p. 105—108°/2 mm., d_4^{10} 1·2827, $d_4^{21°}$ 1·2720, $n_D^{21°}$ 1·5259, $\alpha_D^{18°}$ −117·5° (Found : Cl, 25·1 ; P, 10·6%), and a residue of thick gum (4·4 g.).

Procedure (2). *Addition of Phosphorus Trichloride to the Hydroxy-compound.*—Procedure (1) was followed, but with reversed order of addition.

(+)-α-Octanol (4·3 g., 1 mol.) and the trichloride (1·6 g., 0·33 mol.) evolved hydrogen chloride (0·76 g.) during mixing, and on distillation yielded (−)-β-octyl chloride (1·6 g.), b. p. 60—62°/13 mm., $\alpha_D^{18°}$ −29·0°, $n_D^{18°}$ 1·4273, and a residue, which appeared to be a mixture of the di- (1·5 g.) and the mono-octyl phosphite (0·5 g.). In a second experiment with the alcohol (3·2 g.) and trichloride (1·2 g.), hydrogen chloride (0·46 g.) was evolved, and the residue (3·9 g., after being at 15 mm. for 1 hour), was poured into water. After the ethereal extract had been washed with a solution of sodium carbonate, it gave (−)-β-octyl chloride (1·0 g.), b. p. 64°/19 mm., $\alpha_D^{18°}$ −30·4°, $n_D^{18°}$ 1·4275 (Found : Cl, 23·8. Calc. : Cl, 23·9%), and (+)di-β-octyl hydrogen phosphite (2·2 g.), b. p. 135—138°/2 mm., $\alpha_D^{18°}$ +15·8°, $n_D^{19°}$ 1·4370, $d_4^{18°}$ 0·9177 (Found : P, 10·1. Calc. : P, 10·1%). Acidification of the carbonate extract yielded only 0·1 g. of an oil. These results support the scheme $3ROH + PCl_3 \longrightarrow RCl + P(OR)_2{\cdot}OH + 2HCl$.

(−)Phenylmethylcarbinol ($\alpha_D^{16°}$ −40·3°, 3·05 g., 1 mol.) and the trichloride (1·2 g., 0·33 mol.) gave a turbid liquid, the ethereal solution of which, after being washed with a solution of sodium carbonate, yielded (+)-α-chloroethylbenzene (2·05 g.), b. p. 78°/17 mm., $\alpha_D^{22°}$ +19·9°, $n_D^{25°}$ 1·5272 (Found : Cl, 25·0. Calc. : Cl, 25·2%), and a residue (0·7 g.), $\alpha_D^{22°}$ −72·1°, $n_D^{22°}$ 1·5412. The carbonate solution gave but a faint cloudiness on acidification. Essentially the same results were obtained by use of 0·66 mol. or of 1·0 mol. of the trichloride.

Ethyl (−)mandelate (6 g., 1 mol.) and the trichloride (1·6 g., 0·33 mol.) gave a product (6·9 g., after being at 15 mm. for a few minutes), the ethereal solution of which, after being teated with ice and washed with a solution of sodium carbonate, yielded a mixture (1·7 g.) of ethyl (−)mandelate and ethyl (+)phenylchloroacetate b. p. 83—84°/2 mm. (the two substances have similar b. p's.), $\alpha_D^{18°}$ +40·5°, $n_D^{19°}$ 1·5112 (Found : Cl, 12·6. Calc. for the chloroacetate : Cl, 17·9%), and a residue (3·4 g.), $\alpha_D^{18°}$ −93·6°, $n_D^{20°}$ 1·5200 [Found : P, 7·2. (−)*Bis-α-carbethoxybenzyl hydrogen phosphite*, $C_{20}H_{23}O_7P$, requires P, 7·6%]. The carbonate solution deposited an oil (0·3 g.), probably the dihydrogen phosphite, $n_D^{20°}$ 1·5110. Kenyon, Lipscomb, and Phillips (J., 1931, 2275), using 1 mol. of the trichloride and a more rigorous treatment, obtained the chloroacetate (96% RCl), α_{5461} +79·3°, in unstated yield.

Procedure (3). *Addition of Phosphorus Trichloride to the Hydroxy-compound and Pyridine in Ethereal Solution.*—Pyridine hydrochloride was precipitated during the addition of the trichloride in ethereal solution at 0°, the precipitation being complete at the end of the operation. The mixture was filtered rapidly, and the ethereal filtrate evaporated to a residue which was examined as specifically stated.

(−)-β-Octanol ($\alpha_D^{20°}$ −8·0°, 26 g., 1 mol.), pyridine (15·8 g., 1 mol.), and the trichloride (9·2 g., 0·33 mol.) yielded pyridine hydrochloride (22·5 g.) (Found : Cl, 30·3. Calc. : Cl, 30·7%) and a residue (27·5 g.), $\alpha_D^{16°}$ −3·1°, $d_4^{18°}$ 0·8784, $n_D^{16°}$ 1·4432 (Found : P, 7·5%), results in good accord with the scheme $3ROH + 3C_5H_5N + PCl_3 \longrightarrow P(OR)_3 + 3C_5H_5N,HCl$. On distillation, however, the following were obtained : β-octanol (2·0 g.), b. p. up to 88°/18 mm., (−)di-β-octyl hydrogen phosphite (7·5 g.), b. p. 142—144°/2 mm., $\alpha_D^{20°}$ −14·5°, $n_D^{21°}$ 1·4391, $d_4^{21°}$ 0·9133 (Found : P, 10·0. Calc. : P, 10·1%), a mixture of the latter substance and tri-β-octyl phosphite (8·0 g.), b. p. 145—155°/2 mm., $\alpha_D^{20°}$ −8·0°, $n_D^{21°}$ 1·4420, $d_4^{21°}$ 0·8969 (Found : P, 8·7%), which were gradually separated by prolonged fractionation, and (−)*tri-β-octyl phosphite* (8·5 g.), b. p. 162—164°/2 mm., $\alpha_D^{20°}$ −0·8°, $n_D^{22°}$ 1·4449, $d_4^{22°}$ 0·8843 (Found : P, 7·5. $C_{24}H_{51}O_3P$ requires P, 7·4%). Essentially the same results were obtained when pyridine was replaced in turn by quinoline and dimethylaniline

These results compare with those obtained from the addition of an ethereal solution of (−)-β-octyloxyphosphorus dichloride (5·7 g., 1 mol.), $\alpha_D^{18°}$ −34·2°, from (+)-β-octanol, $\alpha_D^{18°}$ +8·0°, to (+)-β-octanol (6·5 g., 2 mols.) and pyridine (3·95 g., 2 mols.) in ether. Precipitation of pyridine hydrochloride (5·5 g.) (Found : Cl, 30·0. Calc. : Cl, 30·7%) was complete at the end of the addition, and the filtered solution yielded : β-octanol (1·2 g.), b. p. 80—82°/14 mm., $n_D^{16°}$ 1·4271, $\alpha_D^{16°}$ +1·0; the hydrogen phosphite (2·5 g.), b. p. 138—145/2 mm., $\alpha_D^{16°}$ +14·1°, $n_D^{16°}$ 1·4381 ; the phosphite (3·3 g.), b. p. 159—162°/2 mm., $\alpha_D^{16°}$ +8·4°, $n_D^{16°}$ 1·4415 ; residue (0·2 g.).

(−)Phenylmethylcarbinol ($\alpha_D^{22°}$ −41·1°, 7·32 g., 1 mol.), pyridine (4·75 g., 1 mol.), and the trichloride (2·75 g., 0·33 mol.) gave pyridine hydrochloride (7·17 g. Calc. : 6·93 g.) (Found : Cl, 29·2%), all the chlorine thus being accounted for, and a residue (6·7 g.) obtained by evaporation, finally for 3 hours in a vacuum, of the washed and dried ethereal solution (Found : P, 7·8%), $\alpha_D^{18°}$ −65·2°, $n_D^{17°}$ 1·5350, probably mainly the normal phosphite, but it could not be distilled.

Ethyl (+)mandelate ($\alpha_D^{16°}$ +120·1°, 18·0 g., 1 mol.), pyridine (7·9 g., 1 mol.), and the trichloride (4·6 g., 0·33 mol.) gave pyridine hydrochloride (11·3 g. Calc. : 11·6 g.) (Found : Cl, 29·7%), and on evaporation the washed and dried ethereal solution left a residue [16·8 g. Calc. for $P(OR)_3$: 18·9 g.], $\alpha_D^{18°}$ +101·0°, $n_D^{18°}$ 1·5091.

Procedure (4). *Behaviour on Heating the Chlorophosphite with Pyridine or with Pyridine Hydrochloride.*—(−)-β-Octyloxyphosphorus dichloride ($\alpha_D^{18°}$ −34·2°, 5 g.) in ethereal solution did not evolve heat when treated with pyridine (3·9 g., 2 mols.) in ether. There was no sign of reaction during 24 hours at 18° and 1 hour at 50°, the ether being allowed to distil, but there was vigorous reaction when the product was poured on ice ; some hydrogen chloride escaped, but the wash water contained ⅞ of the chlorine in the system. The ethereal extract after being washed with a solution of sodium carbonate gave a residue (0·52 g.), $n_D^{23°}$ 1·4378, $\alpha_D^{16°}$ +10·1°, and acidification of the carbonate solution yielded (+)-β-octyl dihydrogen phosphite (2·9 g.), $\alpha_D^{16°}$ +5·0°, $n_D^{16°}$ 1·4388 (Found : P, 15·7. Calc. : P, 16·0%). The dichloride (3 g.), heated with pyridine (2 g.) in absence of ether for 2 hours at 70—80° and worked up as in the preceding experiment, yielded, from carbonate-washed ether, 0·05 g. of residue and from the carbonate solution afforded (+)-β-octyl dihydrogen phosphite (1·8 g.), $\alpha_D^{16°}$ +5·8°, $d_4^{15°}$ 1·0210, $d_4^{50°}$ 0·9913 (Found : P, 16·0. Calc. : P, 16·0%). Heating the chlorophosphite with pyridine hydrochloride gave essentially the same results.

Procedure (5). *Addition of Phosphorus Trichloride to the Phosphite.*—(−)Tri-β-octyl phosphite (5·9 g., 1 mol.), $\alpha_D^{18°}$

$-0{\cdot}8°$, from (−)-β-octanol, $\alpha_D^{18°}$ $-18{\cdot}0°$, was treated with the trichloride (4 g., 2 mols.) at 0°. Two hours after the mixing, the liquid had $\alpha_D^{20°}$ $+4{\cdot}8°$, unchanged after 24 hours' standing at 20°. After being at 20°/15 mm. for 2 hrs. and at 30°/15 mm. for 1 hr., the product (8·1 g.) (Found : Cl, readily hydrolysed, 26·6%) was treated as follows. (i) 3·5 G., heated at 100° for 1 hour, poured on ice, and extracted with ether gave, after the latter had been washed with a solution of sodium carbonate, the (−)hydrogen phosphite (0·85 g.), b. p. 136°/2 mm., $\alpha_D^{20°}$ $-14{\cdot}5°$, $n_D^{23°}$ 1·4370 (Found : P, 10·0. Calc. : P, 10·1%), and a residue (0·5 g.). The carbonate solution yielded impure dihydrogen phosphite (0·59 g.) (Found : P, 13·9%). (ii) 3·5 G. mixed with pyridine (1·5 g.) and heated at 100° for 1 hour gave almost exactly the same results, (−)hydrogen phosphite (0·85 g.), $\alpha_D^{18°}$ $-14{\cdot}2°$, $n_D^{20°}$ 1·4385 (Found : P, 9·8%), residue (0·4 g.), and impure dihydrogen phosphite (0·58 g.) (Found : P, 13·8%). It is significant that no β-octyl chloride was formed in these circumstances; an equilibrium mixture of the chlorophosphites appeared to form, and these hydrolysed to the hydrogen and the dihydrogen phosphite.

The " phosphite " product [Procedure (3), (3 g.) from (−)phenylmethylcarbinol, $\alpha_D^{18°}$ $-41{\cdot}1°$] and the trichloride (5 g.) were mixed at 0° and kept for 16 hours at 15°, 2 hours at 15°/15 mm., and finally ½ hour at 70° before being poured on ice. The washed ethereal extract gave (+)-α-chloroethylbenzene (2·5 g.), b. p. 76°/14 mm., $n_D^{17°}$ 1·5302, $\alpha_D^{18°}$ $+36{\cdot}8°$ (Found : Cl, 25·0. Calc. : Cl, 25·2%).

The product (5·6 g.) obtained from ethyl (+)mandelate by procedure (3) was mixed with trichloride (4 g.), and after being in a vacuum for 5 hours the product (8·16 g.) had $\alpha_D^{18°}$ $+115{\cdot}2°$ (Found : Cl, 21·0; P, 11·5%), and yielded on aqueous treatment products which did not contain any chlorine and were too viscous for observation of rotatory power. The residue from the carbonate-washed ether weighed 1·1 g., $n_D^{22°}$ 1·5130; that from the carbonate solution weighed 1·41 g., $n_D^{21°}$ 1·5089 (Found : P, 10·8%).

Procedure (6). *Passage of Hydrogen Chloride through Phosphite.*—(−)Tri-β-octyl phosphite (3·1 g.), [$\alpha_D^{16°}$ 1·1°, from (−)-β-octanol, rapidly absorbed hydrogen chloride at 0—5°, and after aqueous treatment there were obtained (+)-β-octyl chloride (0·65 g.), b. p. 66—67°/20 mm., $\alpha_D^{18°}$ $+20{\cdot}3°$, $n_D^{23°}$ 1·4265; (−)di-β-octyl hydrogen phosphite (1·56 g.), b. p. 133—135°/2 mm., $\alpha_D^{22°}$ $-14{\cdot}8°$ (Found : P, 10·1%), and a residue (0·8 g.).

(−)Di-β-octyl hydrogen phosphite ($\alpha_D^{20°}$ $-14{\cdot}5°$, 3·3 g.) was recovered, except for trace of β-octyl chloride, when hydrogen chloride was passed through it for 3 hours at 15°. After aqueous treatment the (−)hydrogen phosphite (2·3 g.) had b. p. 134—136°/2 mm., $\alpha_D^{22°}$ $-14{\cdot}6°$, $d_4^{21°}$ 0·9177, $n_D^{23°}$ 1·4376 (Found : P, 10·2%). Passage of hydrogen chloride at 50° for 1 hour yielded after aqueous treatment (+)-β-octyl chloride (0·7 g.), b. p. 63°/17 mm., $\alpha_D^{18°}$ $+19{\cdot}9°$, unchanged hydrogen phosphite (0·86 g.), b. p. 123°/1 mm., $\alpha_D^{18°}$ $-14{\cdot}8°$, $n_D^{15°}$ 1·4388 (Found : P, 9·6%), and, from the carbonate extract of the ethereal solution, impure dihydrogen phosphite (0·8 g.) (Found : P, 12·2%).

Procedure (7). *Addition of the Hydroxy-compound to Thionyl Chloride.*—Evidence of the formation of β-octyl chlorosulphinate and α-carbethoxybenzyl chlorosulphinate has already been given (Gerrard, *loc. cit.*), but uncertain results were obtained for phenylmethylcarbinol. The difficulty lies in the complete removal of the excess thionyl chloride before the chlorosulphinate (if formed) decomposes, and in spite of many experiments it can only be assumed that α-phenylethyl chlorosulphinate if formed at all has but transitory existence.

Procedure (7) was conducted as for procedure (1). (+)-β-Octanol ($\alpha_D^{18°}$ $+8{\cdot}0°$, 6·5 g., 1 mol.) and thionyl chloride (6·0 g., 1 mol.) at 0° evolved hydrogen chloride (nearly 1 mol.) but no sulphur dioxide. After 2 hours at 15°/15 mm., the product had $\alpha_D^{16°}$ $-34{\cdot}2°$. Half of this was poured on ice, and β-octyl chloride (0·3 g.), (+)-β-octanol (0·9 g.), b. p. 78—81°/16 mm., $\alpha_D^{16°}$ $+6{\cdot}3°$, and (−)di-β-octyl sulphite (1·5 g.), b. p. 134—135°/2 mm., $\alpha_D^{16°}$ $-16{\cdot}2°$, $n_D^{14°}$ 1·4450 (Found : SO_2, 20·9. Calc. : SO_2, 20·9%), were obtained. After 12 hours, and then 2 hours at 15°/15 mm., the other half had $\alpha_D^{18°}$ $-33{\cdot}5°$ and on aqueous treatment gave essentially the same products as the first half. With thionyl chloride (2 mols.) and the alcohol (6·5 g., 1 mol.), aqueous treatment applied within one hour after mixing afforded (+)-β-octanol (3·3 g.), b. p. 80—81°/17 mm., $\alpha_D^{16°}$ $+7{\cdot}7°$, and di-β-octyl sulphite (2·6 g.), b. p. 134°/2 mm., $\alpha_D^{16°}$ $-16{\cdot}8°$, $n_D^{14°}$ 1·4451 (Found : SO_2, 20·8%) (cf. Levene and Mikeska, *J. Biol. Chem.*, 1924, **59**, 45).

(−)Phenylmethylcarbinol ($\alpha_D^{16°}$ $-41{\cdot}3°$, 3·0 g., 1 mol.) and thionyl chloride (3·0 g., 1 mol.) gave, during mixing, hydrogen chloride (1·1 g.) and sulphur dioxide (1·4 g.), and the product gave after aqueous treatment (−)-α-chloroethylbenzene (2·8 g.), $\alpha_D^{17°}$ $-50{\cdot}9°$, $n_D^{18°}$ 1·5279 (Found : Cl, 25·0. Calc. : Cl, 25·2%) (cf. McKenzie and Clough, *loc. cit.*).

Ethyl (+)mandelate ($\alpha_D^{18°}$ $+120{\cdot}1°$, 9 g., 1 mol.) and thionyl chloride (6·5 g., 1·1 mols.) gave off hydrogen chloride (1·26 g.) but only a trace of sulphur dioxide during the mixing. After one hour at 15 mm., the product attained constant weight (13·3 g. Calc. for R·O·SOCl : 13·2 g.) and had $\alpha_D^{18°}$ $+97{\cdot}7°$, $n_D^{20°}$ 1·5245 (Found, by cold alkali hydrolysis : Cl, 15·0; SO_2, 19·8. Calc. for R·O·SOCl : Cl, 13·6; SO_2, 24·4%). Although the nature of the material prevents purification, there seems little doubt that the chlorosulphinate was present in quantity. 3·7 G. of the product on aqueous treatment yielded a mixture of ethyl (+)mandelate and the chloroacetate (2·7 g.), b. p. 139—141°/16 mm., $\alpha_D^{20°}$ $+113{\cdot}2°$, $n_D^{19°}$ 1·5144 (Found : Cl, 2·7%). 3·7 G. of the first product, after standing for 12 hours at room temperature and 15 mm., had $\alpha_D^{18°}$ $+89{\cdot}6°$ (Found, cold hydrolysis : Cl, 6·8; SO_2, 12·6%), and after 4 days at room temperature it had $\alpha_D^{18°}$ $+72{\cdot}9°$, $n_D^{20°}$ 1·5075. After aqueous treatment it yielded ethyl (+)phenylchloroacetate (2·6 g.), b. p. 138°/13 mm., $\alpha_D^{18°}$ $+84{\cdot}2°$, $n_D^{19°}$ 1·5150 (Found : Cl, 17·1%) (cf. McKenzie and Barrow, J , 1911, **99**, 1910). 5·0 G. of another specimen when heated to 70° (1 hour) with pyridine hydrochloride (2 g.) yielded, after aqueous treatment, ethyl (−)phenylchloroacetate (3·0 g.), b. p. 137°/12 mm., $\alpha_D^{20°}$ $-5{\cdot}2°$, $n_D^{20°}$ 1·5149 (Found : Cl, 17·8%). 5·0 G. of this second specimen, when treated with pyridine (1·5 g.) in ethereal solution at 15°, yielded impure chloroacetate (1·2 g.), $\alpha_D^{22°}$ 20·1° (Found : Cl, 14·1%), and sulphite (1·5 g.), $\alpha_D^{22°}$ $+110°$ (Found : SO_2, 15·2%).

Procedure (8). *Addition of Thionyl Chloride to the Hydroxy-compounds.*—The operation was the same as in procedure (2). (+)-β-Octanol ($\alpha_D^{18°}$ $+8{\cdot}0°$, 4·1 g., 1 mol.) and thionyl chloride (4 g., 1 mol.) evolved hydrogen chloride (1·85 g.) but no sulphur dioxide. After being for 1 hour at 15°/15 mm., the product gave on aqueous treatment a trace of β-octyl chloride, (+)-β-octanol (1·2 g.), b. p. 77—80°/15 mm., $\alpha_D^{15°}$ $+6{\cdot}8°$, and (−)di-β-octyl sulphite (2·2 g.), b. p. 134°/2 mm., $n_D^{14°}$ 1·4449, $\alpha_D^{16°}$ $-16{\cdot}5°$ (Found : SO_2, 20·8%).

(+)Phenylmethylcarbinol ($\alpha_D^{17°}$ $+20{\cdot}5°$, 4 g., 1 mol.) and thionyl chloride (4 g., 1 mol.) steadily evolved hydrogen chloride and sulphur dioxide (0·025 g.-mol. of each) during mixing. The product was immediately treated with water, and afforded (+)-α-chloroethylbenzene (3·1 g.), b. p. 75—76°/15 mm., $\alpha_D^{18°}$ $+14{\cdot}6°$, $n_D^{18°}$ 1·5278 (Found : Cl, 24·9%). Repetition with the alcohol (3 g.), mixed with pyridine hydrochloride (2 g.), and thionyl chloride (3 g.) caused during mixing a steady evolution of hydrogen chloride (1·01 g. Calc. : 0·91 g.) and sulphur dioxide (1·04 g. Calc. : 1·6 g.). (Pyridine hydrochloride appears to retain sulphur dioxide.) The product, after aqueous treatment, gave (+)-α-chloroethylbenzene (3·2 g.), b. p. 75—76°/15 mm., $\alpha_D^{17°}$ $+11{\cdot}9°$, $n_D^{18°}$ 1·5289 (Found : Cl, 25·0%).

Ethyl (+)mandelate ($\alpha_D^{18°}$ $+120{\cdot}1°$, 4·5 g., 1 mol.) and thionyl chloride (1·5 g., 0·5 mol.), gave hydrogen chloride (0·52 g.) and a residue which after 2 hours at 15 mm. had $\alpha_D^{20°}$ $+114{\cdot}1°$, $n_D^{22°}$ 1·5218, and on aqueous treatment gave impure chloroacetate (2·6 g.), b. p. 138—139°/14 mm., $\alpha_D^{24°}$ $+92{\cdot}6°$, $n_D^{24°}$ 1·5120 (Found : Cl, 13·6%), and a residue (1·2 g.), probably α-carbethoxybenzyl sulphite, b. p. 215—225°/2 mm. (slight decomp.) (Found : SO_2, 15·0%).

Procedure (9). *Addition of Thionyl Chloride to the Hydroxy-compound in Presence of Pyridine.*—The details are the same as for Procedure (3). (−)-β-Octanol ($\alpha_D^{20°}$ $-8{\cdot}1°$, 26·0 g., 2 mols.), pyridine (15·8 g., 2 mols.), and thionyl chloride (11·9 g., 1 mol.), all in ethereal solution, yielded pyridine hydrochloride (23·0 g. Calc. : 23·0 g.) (Found : Cl, 30·5; C_5H_5N, 68·8.

Calc.: Cl, 30·7; C_5H_5N, 68·7%), and from the washed ethereal solution, (+)di-β-octyl sulphite (25·1 g., 84%), b. p. 128—129°/1 mm., $\alpha_D^{22°}$ +18·0°, $d_4^{16°}$ 0·9275, $n_D^{22°}$ 1·4436 (Found: S, 10·5. Calc.: S, 10·5%). Hunter (J., 1924, **125**, 1389) prepared (−)di-β-octyl sulphite, $\alpha_{5890}^{17°}$ −18·43°, by addition of thionyl chloride to (+)-β-octanol in petroleum, followed by distillation without aqueous treatment.

With (+)phenylmethylcarbinol ($\alpha_D^{18°}$ +20·3°, 12·2 g., 1 mol.), pyridine (8·0 g., 1 mol.), and thionyl chloride (9 g., 0·75 mol.) in ether an entirely different result was obtained. The (−)-α-chloroethylbenzene was formed during the actual addition, it being necessary to use 0·75 mol. of thionyl chloride to effect complete precipitation of pyridine. Furthermore, there was no evidence that di-α-phenylethyl sulphite was formed at all. The white precipitate (12·1 g.) (Found: Cl, 28·2; C_5H_5N, 65·7; SO_2, 4·8%) was filtered off immediately, and the ethereal solution after being washed gave (−)-α-chloroethylbenzene (7·0 g.), b. p. 74°/15 mm., $\alpha_D^{18°}$ −22·4°, $n_D^{15°}$ 1·5300 (Found: Cl, 25·0%), and a residue (oil-bath, 160°) (3·5 g.), $\alpha_D^{18°}$ +69·6°, which did not respond to the usual analysis of sulphites but yet with thionyl chloride gave (+)-α-chloroethylbenzene (2·4 g.), b. p. 78—80°/18 mm., $\alpha_D^{18°}$ + 20·5°. In another experiment procedure (9) gave, from (−)alcohol, $\alpha_D^{18°}$ −37·2°, (+)-α-chloroethylbenzene, $\alpha_D^{18°}$ +41·6°. In a previous experiment on inactive material, already reported, this peculiar behaviour was not detected, for difficulty was experienced in handling the precipitate, attributed to a solvent action of the "sulphite," and so the precipitate was assumed to be pyridine hydrochloride. The residual ethereal solution was not worked up, but was treated with more thionyl chloride, the action of which was assumed to be the formation of the chloroethylbenzene from the sulphite.

It is noteworthy that, whereas addition of (+)phenylmethylcarbinol to excess acetyl chloride led to formation of α-chloroethylbenzene with almost entire loss of activity (McKenzie and Clough, *loc. cit.*), yet it is now found that the (+)alcohol ($\alpha_D^{18°}$ +9·4°, 4·07 g., 1 mol.) and pyridine (2·63 g., 1 mol.), in ethereal solution, treated with acetyl chloride (2·6 g., 1 mol.) gave little but (+)-α-phenylethyl acetate (3·55 g.), b. p. 99°/13 mm., $\alpha_D^{18°}$ +18·0°. Furthermore, addition of ethyl chlorosulphinate (8·7 g., 1 mol.) to an ethereal solution of (−)phenylmethylcarbinol ($\alpha_D^{18°}$ −37·2°, 8·1 g., 1 mol.) and pyridine (5·27 g., 1 mol.) yielded pyridine hydrochloride (7·3 g. Calc.: 7·6 g.) (Found: Cl, 30·4%) and (−)-*α-phenylethyl ethyl sulphite* (88% yield), b. p. 93°/2—3 mm., $\alpha_D^{20°}$ −94·5° (Found: SO_2, 29·5. $C_{10}H_{14}O_3S$ requires SO_2, 29·9%).

Ethyl (+)mandelate ($\alpha_D^{18°}$ +120·3°, 9 g., 1 mol.), pyridine (4 g., 1 mol.), and thionyl chloride (3 g., 0·5 mol.) yielded pyridine hydrochloride (5·75 g. Calc.: 5·75 g.) (Found: Cl, 30·3%), and a residue (8·8 g., from the washed ethereal solution), $\alpha_D^{18°}$ +124·2°, $n_D^{26°}$ 1·5237. A small portion of this was distilled, b. p. 218—221°/2 mm., $\alpha_D^{22°}$ +124·1°, $n_D^{24°}$ 1·5272 [Found: SO_2 15·4. (+)*Bis-α-carbethoxybenzyl sulphite*, $C_{20}H_{22}O_7S$, requires SO_2, 15·8%].

Procedure (10). *Addition of Thionyl Chloride to Sulphite.*—(+)Di-β-octyl sulphite ($\alpha_D^{22°}$ +18·0°, 7·61 g., 1 mol.) and thionyl chloride (3·0 g., 1 mol.) were kept together at 22°. The mixture attained maximum rotation after 10 hours: 0 hr., +15·4°; 1 hr., 19·9°; 2 hrs., 24·1°; 4 hrs., 29·3°; 5 hrs., 30·8°; 6 hrs., 32·0°; 9 hrs., 33·2°; 10 hrs., +33·4°. After aqueous treatment, the following fractions were obtained: (+)-β-octyl chloride (0·9 g.), b. p. 64—67°/18 mm., $\alpha_D^{19°}$ +5·9°, $n_D^{19°}$ 1·4260; (−)-β-octanol (1·8 g.), b. p. 78—81°/18 mm., $\alpha_D^{19°}$ −0·6°, $n_D^{19°}$ 1·4268; and (+)di-β-octyl sulphite (3·6 g.), b. p. 185°/18 mm., $\alpha_D^{19°}$ +13·7°, $n_D^{20°}$ 1·4435 (Found: S, 10·40. Calc.: S, 10·46%). From this it appears that an equilibrium mixture of thionyl chloride, chlorosulphinate, and sulphite was formed. Another specimen of this mixture from 4 g. of sulphite gave with pyridine (2 g.) in ethereal solution a dark-red oil (about 1 g.; Gerrard, *loc. cit.*), and from the ether, (+)-β-octyl chloride (2·5 g.), b. p. 64°/19 mm., $n_D^{22°}$ 1·4259, $\alpha_D^{20°}$ +25·6°, was obtained.

(−)-α-Phenylethyl ethyl sulphite [3·2 g., 1 mol., $\alpha_D^{20°}$ −94·5°, from (−)-alcohol, $\alpha_D^{20°}$ −37·2°], used in place of di-α-phenylethyl sulphite which could not be obtained in the usual way, and thionyl chloride (1·8 g., 1 mol.) were mixed at 0°, and after 7 hours at 15°, the product was poured on ice. (−)-α-Chloroethylbenzene (1·9 g.), b. p. 85°/25 mm., $\alpha_D^{23°}$ −45·7°, $n_D^{25°}$ 1·5260 (Found: Cl, 25·0%), was isolated. Thionyl chloride (1·8 g., 1 mol.) added to a mixture of (−)sulphite (3·2 g.) and pyridine (2·4 g., 2 mols.) yielded, without being heated, (+)-α-chloroethylbenzene (0·6 g.), b. p. 85°/25 mm., $\alpha_D^{20°}$ +2·4° (Found: Cl, 24·9%).

(+)Bis-α-carbethoxybenzyl sulphite (5·5 g.), $\alpha_D^{18°}$ +124·2°, from (+)mandelate, $\alpha_D^{18°}$ +120·1°, and thionyl chloride (2·5 g.), after standing for 5 days at 17°, had $\alpha_D^{13°}$ +56·5° and had liberated sulphur dioxide (0·7 g.). One half of the product gave after aqueous treatment ethyl (+)phenylchloroacetate (1·5 g.), b. p. 137°/12 mm., $\alpha_D^{20°}$ +75·6, $n_D^{20°}$ 1·5146 (Found: Cl, 17·6%), and a residue (0·8 g.) of sulphite. The other half, after being heated at 100° for 2 hours, and then given aqueous treatment, yielded (+)chloroacetate (2·0 g.), b. p. 137°/12 mm., $\alpha_D^{20°}$ +76·2°, $n_D^{20°}$ 1·5149 (Found: Cl, 17·9%), and a residue (0·3 g.) of sulphite. Thionyl chloride (1·5 g., 0·5 mol.) was added to an ethereal solution of (+)mandelate (4·5 g., 1 mol., $\alpha_D^{18°}$ +120·1°) and pyridine (2 g., 1 mol.). To the mixture of sulphite and pyridine hydrochloride which remained when the ether was evaporated, thionyl chloride (1·5 g., 0·5 mol.) was added, and the product heated at 80° for 2 hours. Ether extraction left a white solid (2·8 g., theoretical for pyridine hydrochloride) and on aqueous treatment the ethereal solution yielded (−)chloroacetate (3·5 g.), b. p. 138°/13 mm., $n_D^{19°}$ 1·5147, $\alpha_D^{18°}$ −35·0° (Found: Cl, 17·8%). Kenyon, Lipscomb, and Phillips (J., 1930, 415) heated the ethereal solution for 30 mins. and got a product containing 63% of chloroacetate (Cl, 11·3%). The presence of ethyl mandelate in this product was due, not to its failure to react, but to the hydrolysis of the chlorosulphinate which under the conditions (pyridine hydrochloride as a separate phase) had not decomposed.

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