223. *Experiments on the Interaction of Hydroxy Compounds and Phosphorus and Thionyl Halides in the Absence and in the Presence of Tertiary Bases. Part III.*

By W. Gerrard.

Whereas addition of phosphorus tribromide (0·33 mol.) to (+)β-octanol slowly formed a high yield, and addition of the alcohol to excess tribromide gave a much lower yield of (−)bromide, RBr, both yields were considerably reduced by the removal of hydrogen bromide by a stream of carbon dioxide. End-on attack of hydrogen bromide on phosphites in the first example (compare action of phosphorus trichloride, Part I, *J.*, 1944, 85) or on bromophosphites in the second (contrast action of the trichloride) appears to be responsible for production of the bromide, RBr.

(+)Phenylmethylcarbinol reacted quickly and gave a good yield of (−)bromide, RBr, by either order of addition, a stream of carbon dioxide having no effect. Ethyl (+)mandelate behaved in an intermediate way.

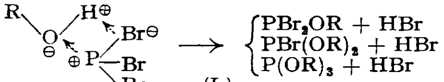
Whereas addition of the tribromide (0·33 mol.) to a mixture of each of these hydroxy compounds in turn (1 mol.) and respectively pyridine, quinoline, dimethylaniline (1 mol.) gave rise to the phosphite $P(OR)_3$ and the hydrobromide of the base, further addition of the tribromide led to formation of (−)β-octyl bromide at 100°, (−)α-bromoethylbenzene at 16°, and almost completely racemised ethyl phenylbromoacetate.

Comparing the results of adding phosphorus tribromide (0·33 mol.) to the alcohol (1 mol.) followed by refluxing for 1 hour, with those obtained when red phosphorus and bromine (equivalent to 0·33 mol. of tribromide) were used, Tseng and Hou (*J. Chinese Chem. Soc.*, 1934, **2**, 57) quote the following yields of bromides, RBr, obtained by them : Me, 34% (33) ; Et, 40 (22) ; Pr, 66·5 (41·7) ; Pr^{β}, 58·7 (43·3) ; Bu, 59·5 (53) ; Bu^{β}, 49·7 (38) ; *tert.*-Bu, 59·4 (43·7)%, the figures in brackets being for the red phosphorus–bromine experiments. As the authors state, these yields are lower than are to be expected if the reaction proceeds as represented by the equation, $PBr_3 + 3ROH = H_3PO_3 + 3RBr$. Reynolds and Adkins, however (*J. Amer. Chem. Soc.*, 1929, **51**, 280), obtained *iso*-butyl, *sec.*-butyl, *tert.*-butyl, *iso*-amyl, *n*-heptyl, and *sec.*-octyl bromides in 80—85% yields by the addition of the tribromide to the alcohol; but quantities and procedure are not stated. In " Organic Syntheses " (1933, **13**, 20) the yields quoted are : Bu^{β}, 60; *sec.*-butyl, 80; Pr, 95; and Pr^{β}, 68%, obtained by addition of the tribromide (0·33 mol.) to the alcohol (1 mol.) at −10°, followed by distillation of the alkyl bromide from the reaction mixture. In contrast, the 29% yield of *sec.*-butyl bromide (Kenyon, Phillips, and Pittman, *J.*, 1935, 1072) obtained by using the tribromide (1 mol.) in ethereal solution, is interesting.

The type and sequence of the reactions which occur during the interaction of phosphorus tribromide and (+)β-octanol, (+)phenylmethylcarbinol, and ethyl (+)mandelate severally, in the absence and in the presence of tertiary bases have now been studied, and these are explained in terms of end-on and broadside collisions between molecules, which on approach are suitably orientated by the mutual interaction of existing or induced relative polarities of parts of the molecules (cf. Part I, *loc. cit.*, and Part II, this vol., p. 106).

In consideration of the quantum mechanical treatment of a chemical reaction (London, *Z. Electrochem.*, 1929, **35**, 552; Eyring and Polanyi, *Z. physikal. Chem.*, 1931, **12**, 279; Discussion, *Trans. Faraday Soc.*, 1938, **34**, 1) it may be accepted that an end-on approach is most likely for a three-centre system such as the anionic exchange, $\bar{X}\rightarrow C—Y\rightarrow$ to $X—C\ .\ \bar{Y}\rightarrow$, and will lead to an inversion of configuration probably by the mechanism outlined by Lewis (" Valence," 1923, 113; cf. Mills, *J.*, 1944, 340) and Olson (*J. Chem. Phys.*, 1933, 1, 418). According to Eyring, the best manner of approach for the four centre system, $A—B + C—D = AC + BD$, is in one plane, with A approaching C as B approaches D, *i.e.*, a broadside collision, the four atomic centres being in the transition state together. A broadside collision does not favour inversion. There appears to be no evidence, however, that an end-on collision for a four centre system is necessarily prohibited; steric and polar factors might hinder the broadside approach and encourage the end-on collision, *e.g.*, $\oplus H—Br\ominus \rightarrow \oplus R—O—P(OR)_2$, *i.e.*, the " attacking " group need not be an ion; dissociation and subsequent association may occur after collision. (The signs in circles represent partial charges.) The probability of occurrence of effective orientation is involved in the probability factor, *P*, of the equation, Velocity $= PZe^{-E/RT}$ (Hinshelwood, and Winkler, *J.*, 1936, 371), and in order to evaluate the effect of a change in structure, it is desirable to determine in what way the system responds to changes in experimental conditions.

Addition of the tribromide (0·33 mol.) to (+)β-octanol (Table I) below 0° favours the primary formation of phosphorus esters and hydrogen bromide, probably by broadside collision (I), and these then undergo subsequent interaction by the end-on mechanism (II).



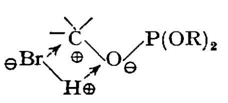
(I.)

$$\overset{\oplus}{H}—\overset{\ominus}{Br}\rightarrow\overset{\oplus}{R}—\overset{\ominus}{O}P(OR)_2 \longrightarrow RBr + \overset{+}{H} + \overset{-}{O}P(OR)_2 \longrightarrow O\leftarrow PH(OR)_2$$

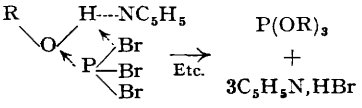
(II.)

Elimination of the first R group is rapid even below 0°; but the second step is much slower; the yield of bromide, RBr, is considerably reduced either by keeping the temperature below 0° or by driving off the hydrogen bromide in a stream of carbon dioxide. When hydrogen bromide is passed into (+)tri-β-octyl phosphite, the formation of (−)β-octyl bromide and (+)di-β-octyl hydrogen phosphite is much more rapid than is the conversion of the latter into (+)β-octyl dihydrogen phosphite. Hydrogen bromide passed into the last compound at 60—70° yielded (−)β-octyl bromide. A reasonable explanation may be found in the cause of the dibasicity of phosphorous acid which appears to have the structure $\overset{-}{O}—\overset{+}{P}H(OH)_2$. In tri-β-octyl phosphite, the lone pair of electrons on the phosphorus atom appears to bring into play a mechanism which can only be available for the replacement of the second R group if the isomerisation $\overset{-}{O}—\overset{+}{P}H(OR)_2 \longrightarrow OH\cdot P(OR)_2$ occurs. Formation of the hydrogen bond, $(RO)_3P\ .\ .\ .\ .\ HBr$, is a possibility, and this or the ionised form, $(RO)_3\overset{+}{P}H + \overset{-}{Br}$, would have the effect of increasing the positive polarity of the active centres of the R groups. Activity of the lone pair is illustrated by the reaction, $P(OEt)_3 + RBr = \overset{+}{P}R(OEt)_3\overset{-}{Br}$, which can be realised. At higher temperatures the latter decomposes into $\overset{-}{O}—\overset{+}{P}R(OEt)_2 + EtBr$ (Kosolapoff, *J. Amer. Chem. Soc.*, 1944, **66**, 109). Then again, chlorine and, for example, tri-*n*-butyl phosphite yield di-*n*-butoxyphosphoryl chloride and *n*-butyl chloride $P(OBu)_3 + Cl_2 = \overset{-}{O}—\overset{+}{P}Cl(OBu)_2 + BuCl$ (Gerrard, *J.*, 1940, 1464; cf. Wichelhaus, *Annalen*, 1868, **6**, 257); but the same halogen and diethyl hydrogen phosphite gave rise to diethoxyphosphoryl chloride and hydrogen chloride, $P(OEt)_2OH + Cl_2 = \overset{-}{O}—\overset{+}{P}Cl(OEt)_2 + HCl$ (McCombie, Saunders, and Stacey, this vol., p. 380), *i.e.*, a second alkyl group was not removed.

Since β-octyl bromide (Table I) was produced almost entirely by an inversion (end-on) mechanism, it is evident that the broadside approach of hydrogen bromide, (III), is of low probability, and steric factors (bond distances and valency angles) would appear to be against the four centre broadside approach, with the hydrogen atom towards the phosphorus atom and the bromine atom towards the carbon atom.



(III.)



(IV.)

Addition of (+)β-octanol to the tribromide (2 mols., excess) (Table I) involves mechanism (I) chiefly as far as the first stage, PBr_2OR, and to some extent the second, $PBr(OR)_2$, and since a 29% yield of (−)β-octyl bromide was produced, the hydrogen bromide attacks these bromophosphites by mechanism (II). If the hydrogen bromide be driven away in a stream of carbon dioxide, however, the yield of bromide, RBr, is reduced to 2·5%. Although the bromophosphites PBr_2OR, $PBr(OR)_2$, could not be distilled, their presence in the reaction mixture was indicated by hydrolysing them respectively to the phosphites $POR(OH)_2$, $P(OR)_2\cdot OH$; and, at least below 40°, the bromophosphites showed little tendency to produce the bromide, RBr. This property was also possessed by the reaction mixtures resulting from the addition of appropriate amounts of tribromide to tri-β-octyl phosphite; these mixtures most probably contained bromophosphites.

Addition of the tribromide (0·33 mol.) to (+)β-octanol (1 mol.) in presence of pyridine (1 mol.), quinoline and dimethylaniline respectively caused the rapid precipitation of the hydrobromide of the base; and, since phosphorus esters were obtained from the filtered ethereal extract, the broadside collision mechanism (IV), probably facilitated by hydrogen bond formation, has high probability and is evidently associated with low energy of activation. No bromide, RBr, was formed during this operation, because hydrogen bromide was not produced. Continued addition of the tribromide beyond the 0·33 mol. resulted in the slow interaction of the tribromide and the phosphorous esters formed in the first stage. At 100° (Table II) some (−)β-octyl bromide was produced.

It is seen, therefore, that when pyridine was used the yield of bromide, RBr, was considerably reduced, an observation in accord with the 5·5% yield of β-butyl bromide, obtained also in the presence of pyridine (Kenyon, Phillips, and Pittman, *loc. cit.*), and shows a distinction from the results of Darzens' procedure for thionyl chloride.

During the addition of phosphorus tribromide (0·33 mol.) to (+)phenylmethylcarbinol (1 mol.) at −10°, (−)α-bromoethylbenzene was fairly rapidly formed without the evolution of hydrogen bromide. From the reaction mixture, after it had stood for 30 minutes at −10°, a 68% yield of the bromide, RBr, was obtained, and this was increased to 75% by using slightly more tribromide. Passage of carbon dioxide through the reaction mixture was ineffective in carrying away hydrogen bromide; no change in yield or behaviour was observed. Reversal of order of mixing, tribromide (1 mol.) being used, led to the same results. Since the (−)bromide, RBr, had a high rotatory power, it may be concluded that the end-on mechanism predominates. The main sequence appears to be the formation of the phosphites by the broadside mechanism (I), followed by the subsequent interaction of these and hydrogen bromide by the end-on mechanism (II). Any loss in rotatory power could be due to the interaction of hydrogen bromide and alcohol itself, since this reaction is rapid and gives both configurations to different extents depending on conditions. Whereas Holmberg (*Ber.*, 1912, **45**, 997) found that the interaction of the alcohol and hydrogen bromide led to a completely racemised bromide, RBr, Levene and Rothen (*J. Biol. Chem.*, 1939, **127**, 237) obtained by the same reagents specimens of bromide, RBr, formed by either preponderant inversion or retention according to the temperature. Using hydrogen bromide in benzene, Hughes, Juliusburger, Scott, Topley, and Weiss (*J.*, **1936, 1173**), obtained the bromide (+)RBr, $[\alpha]_D^{20^\circ}$ +12·6° from (−)ROH, $[\alpha]_D^{20^\circ}$ −37·4°, a reaction attended by a considerable loss in rotatory power.

Addition of the tribromide (0·33 mol.) to an ethereal solution of (+)alcohol (1 mol.) and any of the tertiary bases (1 mol.) at −10° (Table IV) caused the rapid precipitation of the hydrobromide of the base, but no bromide, RBr, was formed, the other product being mainly the phosphite, $P(OR)_3$, a behaviour strictly analogous to that of β-octanol. Continued addition of tribromide (0·66 mol.), however, led at 16° to the slower formation of (−)bromide, RBr, 60% yield, having a high rotatory power. Although it is certain that the main function of the base is to eliminate hydrogen bromide and thus to reduce the configuration-retention mechanism, the identity of the "attacking" group in the end-on collision is not yet discernible. One probability is $Br_2PBr \rightarrow R{-}OP(OR)_2 = RBr + Br_2\overset{+}{P} + \overset{-}{O}P(OR)_2$; but a possibility is the formation of the bromophosphite, PBr_2OR, by the broadside mechanism, followed by the decomposition of this in one or more of several possible ways.

It may be concluded that the behaviour of ethyl (+)mandelate is intermediate between that of the other two hydroxy compounds discussed, except that the specimens of ethyl phenylbromoacetate formed by the agency of a tertiary base and tribromide (1 mol.) were almost completely racemised.

In contrast with the tribromide, phosphorus tri-iodide was without action on an ethereal solution of pyridine and (+)β-octanol. Even after being refluxed for 2½ hours, the ethereal solution yielded almost the theoretical amount of (+)β-octanol, and the ether insoluble part was unchanged tri-iodide. This lack of activity is attributable to the very sparing solubility of the tri-iodide in ether. When the operation was carried out in carbon disulphide solution, pyridine hydrobromide was readily precipitated.

EXPERIMENTAL.

Aqueous Treatment.—Where this was employed it is specified. It comprised the following set of operations: addition to ice, extraction of product with ether, washing this ethereal solution with a dilute solution of sodium carbonate to remove acid and acid phosphorous ester, desiccation of this washed ethereal solution with sodium sulphate, acidification of the carbonate solution to precipitate acid ester, extraction of the latter with ether, the ethereal solution being dried with sodium sulphate and evaporated to obtain the acid ester as an undistilled residue. From the first ethereal solution, any bromide, RBr, was obtained by distillation, and any neutral phosphorous ester was left as residue. Except for use in this aqueous treatment, dry ether, distilled and kept over sodium, was used throughout. Rotatory powers are for $l = 1$ dm.

Interaction of (+)β-Octanol and Phosphorus Tribromide.—(+)β-Octanol (Kenyon, *J.*, 1922, **121**, 2540) ($\alpha_D^{16^\circ}$ +8·0°; 2·6 g., 1 mol.) was mixed dropwise (5 minutes) at −10° with the specified amount of tribromide (Table I), and after the reaction mixture had been allowed to stand as described (experiments are numbered as in Table I) it was given aqueous treatment. β-Octyl bromide had b. p. 81·5°/20 mm. (Calc.: Br, 41·5%) [Calc. for $P(OR)_3$: P, 7·4; for $P(OR)_2{\cdot}OH$: P, 10·1; for $POR(OH)_2$: P, 16·0%].

Expts. 1 and 2. Mixtures were kept at 16° for 12 hours. Expt. 3. Mixture was kept at −10° for 3 hours. At this temperature the formation of phosphorous esters had taken place; but the interaction of these and hydrogen bromide had been considerably reduced in velocity.

Expt. 4. Carbon dioxide was passed through the mixture during the mixing and subsequent standing at 16° for 1 hour. In Expts. 1 and 2 very little hydrogen bromide was evolved (equivalent to 11·0 c.c. 0·1N-$AgNO_3$); but, in Expt. 3, copious fumes of hydrogen bromide were carried away, and its removal reduced the yield of bromide, RBr.

When the tribromide was added quickly there was a rise in temperature and a copious evolution of hydrogen bromide with a consequent reduction in yield of bromide, RBr.

Expt. 5. As for 4, except that carbon dioxide was passed through the mixture for 8 hours at 16°.

Expt. 6. As for 4, but carbon dioxide was passed for 2 hours at 16° and then mixture was set aside at 16° for 12 hours. It would appear that the final stage, $PBr(OR)_2 + ROH = P(OR)_3 + HBr$, is sufficiently slow to be incomplete after 2 hours at 16°, and so hydrogen bromide was generated after the passage of carbon dioxide had been discontinued.

Expt. 7. Mixture stood at 15° for 2 hours. Expt. 8. Carbon dioxide was passed for 2 hours at −10°. Expt. 9. As for No. 7, then the mixture was warmed at 40° for 2 hours.

It is seen that in the presence of excess of the tribromide, the alcohol reacts with a molecule of tribromide to form the bromophosphite, PBr_2OR, rather than with the latter to form the monobromophosphite, $PBr(OR)_2$. Hydrogen bromide apparently attacks these somewhat slowly, so that the passage of carbon dioxide is sufficient to drive it away before it can react. The result is a low yield of bromide, RBr, but a high yield of β-octyl dihydrogen phosphite which has resulted from the hydrolysis of the corresponding bromophosphite, PBr_2OR.

TABLE I.

			Ethereal solution.						Carbonate extract.		
			Distillate.			Residue, mainly $P(OR)_2OH$.			Mainly $POR(OH)_2$.		
Expt.	Order of mixing.	PBr_3 mols.	Yield RBr, %.	Br, %.	$\alpha_D^{16°}$ (−).	Wt., g.	P, %.	$\alpha_D^{16°}$ (+).	Wt., g.	P, %.	$\alpha_D^{16°}$ (+).
1	⟵ *	0·33	73	41·4	38·2°	0·15	—	—	0·21	—	—
2	⟵	0·66	78	41·4	37·8	0·10	—	—	0·13	—	—
3	⟵	0·33	20	41·4	42·0	1·10	9·0	9·5°	0·30	15·9	—
4	⟵	0·33	28·5	41·4	42·5	0·91	9·3	10·8	0·47	15·6	—
5	⟵	0·36	30·0	41·3	42·4	0·70	—	—	0·62	—	—
6	⟵	0·36	40·5	41·2	42·6	0·45	—	—	0·69	—	—
7	⟶ †	2	29	41·3	40·0	0·36	—	—	1·45	15·9	4·1°
8	⟶	2	2·5	41·0	—	0·3	—	—	1·85	16·2	6·2
9	⟶	2	2·5	—	—	0·15	—	—	2·00	15·9	6·0

* signifies addition of PBr_3 to alcohol; † signifies the reverse procedure.

Interaction of (+)β-Octanol and Phosphorus Tribromide in Presence of Tertiary Bases.—Dropwise addition of the tribromide (9·1 g., 0·33 mol., in 10 c.c. of ether) to (+)β-octanol (13 g., 1 mol.) and pyridine (7·9 g., 1 mol.) in ethereal solution at −10° caused the immediate precipitation of pyridine hydrobromide, 16·0 g. (after 2 hours under reduced pressure; calc.: 16·0 g.) (Found: Br, 48·5. Calc.: Br, 50·0%), and from the filtered ethereal solution the following 4 fractions were obtained: b. p. 56—71°/2 mm. (1·0 g.), $n_D^{23°}$ 1·4367; b. p. 140—147°/2—3 mm. (3·8 g.), $n_D^{25°}$ 1·4371, $\alpha_D^{20°}$ +13·6° (Found: P, 9·95. Calc. for di-octyl hydrogen phosphite: P, 10·1%); b. p. 150—165°/2—3 mm. (2·3 g.), $n_D^{25°}$ 1·4397, $\alpha_D^{20°}$ +8·9°; b. p. 167—169°/2—3 mm. (4·3 g.), $n_D^{23°}$ 1·4419, $\alpha_D^{20°}$ +4·0° (Found: P, 7·7. Calc. for tri-octyl phosphite: P, 7·4%). Essentially the same results were obtained when pyridine was replaced in turn by quinoline and dimethylaniline and furthermore these results are similar to those obtained when phosphorus trichloride was used in place of the tribromide (Part I, *loc. cit.*).

Dropwise addition of the tribromide (5·4 g., 1 mol.) to a mixture of the octanol (2·6 g., 1 mol.) and base (1 mol.) at −10°, in absence of ether, followed by heating for 30 minutes at 100°, led to the results stated in Table II. The cold semi-solid mass was extracted with ether, and the ethereal solution was given aqueous treatment.

TABLE II.

	Ethereal solution.					Carbonate.	
	Distillate, b. p. 71°/13 mm.			Residue $P(OR)_2OH$.		Extract $POR(OH)_2$.	
Tertiary base.	Yield RBr, %.	Br, %.	$\alpha_D^{16°}$ (−).	Wt., g.	P, %.	Wt., g.	P, %.
Pyridine	19·5	41·4	40·5	0·24	—	1·45	15·7
Quinoline	35·0	41·3	40·5	0·35	—	0·90	15·9
Dimethylaniline	25·0	41·2	35·1	0·85	9·4	0·74	15·7

Interaction of Phosphorous Ester and Phosphorus Tribromide.—Tri-β-octyl phosphite (2·09 g., 1 mol.) was mixed with tribromide [2·7 g., 2 mol., quantities related to the reaction, $P(OR)_3 + 2PBr_3 = 3PBr_2OR$] and kept at 40° for 2 hours. After aqueous treatment, a distillate (0·4 g.), b. p. 74°/16 mm., and a residue (1·1 g.) were obtained. The carbonate extract yielded only a trace of oil, from which it may be concluded that the second stage, $PBr(OR)_2 + PBr_3 = 2PBr_2OR$, is slow.

In the same way, the tri-ester (2·09 g., 1 mol.) and tribromide (0·7 g., 0·5 mol.) yielded distillate (0·2 g.), b. p. 75 °/16 mm., and a residue (1·2 g.).

The tribromide (5 g.) was added to the phosphite residue (Table IV; 2·6 g.) at −10° and allowed to stand at 16° for 12 hours before being given aqueous treatment. (−)α-Bromoethylbenzene (2·0 g.), b. p. 92—94°/18 mm., $\alpha_D^{22°}$ −68·3°, was obtained. By the same procedure, from the phosphite residue (3·0 g.) from ethyl mandelate (Table VI) impure ethyl phenylbromoacetate (0·70 g.), b. p. 80—82°/1 mm. (Found: Br, 29·8%), a residue (0·30 g.) (Found: P, 7·6. Calc. for $P(OR)_2OH$: P, 7·6%) and from the carbonate extract a residue (0·35 g.) (Found: P, 10·6. Calc. for $POR(OH)_2$: P, 12·7%) were obtained.

Interaction of Hydrogen Bromide and Phosphorous Ester.—Through tri-β-octyl phosphite [$\alpha_D^{16°}$ +3·1°, from (+)ROH, $\alpha_D^{16°}$ +8·0°; 4·3 g.] hydrogen bromide was passed, the ester not being cooled. The liquid soon became warm, and it was kept at 16° whilst the gas was passed for 3 hours. Aqueous treatment yielded (−)β-octyl bromide (1·61 g.), b. p. 79°/18 mm., $\alpha_D^{16°}$ −35·0° (Found: Br, 41·2%), a residue (0·78 g.) (Found: P, 9·7%), and from the carbonate extract, the mono-octyl ester (1·2 g.) (Found: P, 15·6%). Passage of the hydrogen bromide through the tri-ester (2·8 g.) at −5° to 0° for 2 hours led to the formation of (−)β-octyl bromide (0·6 g.), $\alpha_D^{20°}$ −34·0° (Found: Br, 41·1%), and a residue (1·8 g.), $\alpha_D^{20°}$ +8·6° (Found: P, 9·5%), the carbonate extract giving only a trace of oil.

Passage of hydrogen bromide into the mono-ester $POR(OH)_2$ (2·6 g.) (obtained from carbonate extracts) kept at 60—

70° caused the separation of a water soluble, ether insoluble, lower layer, and, after 2 hours, aqueous treatment led to the isolation of (−)β-octyl bromide (2·1 g.), b. p. 79°/18 mm., $\alpha_D^{20^\circ}$ −15·3° (Found : Br, 41·4%), the carbonate extract giving only a cloudiness on acidification.

When hydrogen bromide was passed at 16° through the phosphite residue (Table IV; 3·0 g.), a water soluble lower layer separated in about 15 mins. Aqueous treatment then led to isolation of (−)α-bromoethylbenzene (2·4 g.), b. p. 86°/11 mm., $\alpha_D^{22^\circ}$ −40·6° (Found : Br, 43·1. Calc. : Br, 43·2%). On being re-distilled, its rotatory power remained unchanged.

Interaction of (+)*Phenylmethylcarbinol and Phosphorus Tribromide.*—In Table III are recorded the results obtained by mixing the (+)carbinol (2·44 g., 1 mol.) ($\alpha_D^{16^\circ}$ +38·6°) with the tribromide. In experiments 1 and 2 the reagents were mixed and kept at −10° for 30 minutes. No hydrogen bromide was evolved. The mixture was then given aqueous treatment; no oil was obtained when the carbonate extract was acidified. In experiment 3, the procedure followed was that of experiment 1, except that carbon dioxide was passed through the mixture.

TABLE III.

Expt.	Order of mixing.	PBr_3 mols.	Yield RBr, %.	B. p.	Br, %.	$\alpha_D^{16^\circ}$ (−).	Residue, g.
1	⟵	0·33	66·3	88°/14 mm.	43·2	38·4	0·3
2	⟶	1·0	67·7	,,	43·2	37·2	0·2
3	⟵	0·37	74·3	,,	42·9	40·8	0·2

Interaction of Phenylmethylcarbinol and Phosphorus Tribromide in Presence of Tertiary Bases.—In experiments 1, 2, 3, Table IV, the tribromide (1·81 g., 0·33 mol.) in ethereal solution (10 c.c.) was added dropwise to an ethereal solution (15 c.c.) of the carbinol (2·44 g., 1 mol.), $\alpha_D^{16^\circ}$ +40·1°, and base (pyridine, Pyr., quinoline, Q, and dimethylaniline, D.M.A., 1 mol.) at −10°. After being kept for an hour at 16°, the solution was filtered and the solid kept under reduced pressure for 2 hours before being weighed. The ethereal solution was washed rapidly with water only, dried with sodium sulphate and evaporated, the residue being then kept at 50°/16 mm. for 30 minutes [Calc. for the tri-ester, $P(OR)_3$: P, 7·9%. Calc. for the hydrobromides of the tertiary bases in order stated above : Br, 50·0, 38·1, 39·6%].

In experiments 4, 5, 6 the operation described for 1, 2, 3 was repeated; but, before filtering the solution, phosphorus tribromide (3·6 g., 0·66 mol.) was added at −10°, the mixture kept for 12 hours at 16°, and then, after filtration from the solid, aqueous treatment was given. In this way, the bromide, RBr, was produced by a reaction subsequent to that which went on during the addition of the first 0·33 mol. of tribromide (Calc. for α-bromoethylbenzene : Br, 43·2%).

Certain specimens of α-bromoethylbenzene quickly lost rotatory power on being redistilled. One specimen, for example, b. p. 96°/20 mm., $\alpha_D^{20^\circ}$ −106·2°, was distilled, and the large middle fraction (90%) had $\alpha_D^{23^\circ}$ −68·5°, and when the whole of this was distilled, b. p. 96°/20 mm., the distillate had $\alpha_D^{23^\circ}$ −4·3°. Values recorded in Table IV are for redistilled specimens.

TABLE IV.

	Reagents.		α-Bromoethylbenzene.				Solid.				Phosphite.		
Expt.	PBr_3 mols.	Base mols.	Yield, %.	B. p.	$\alpha_D^{17^\circ}$ (−).	Br, %.	Wt., g.	Br, %.	Base, %.	P, %.	Wt., g.	P, %.	$\alpha_D^{16^\circ}$ (+).
1	0·34	1 Pyr.	—	—	—	—	3·20	48·9	50·2	—	2·5	7·8	105·7°
2	0·34	1 Q.	—	—	—	—	4·11	37·7	—	—	2·40	7·3	103·3
3	0·34	1 D.M.A.	—	—	—	—	3·80	39·4	—	—	2·60	7·4	104·1
4	1·0	1 Pyr.	62	88—89°/15 mm.	89·3°	43·0	3·40	39·4	40·6	4·1	—	—	—
5	1·0	2 Pyr.	48	88°/14 mm.	105·4	43·1	5·20	44·5	34·2	—	—	—	—
6	1·0	1 Q.	55	97—97·5°/21 mm.	108·1	43·2	4·32	32·8	—	5·7	—	—	—
7	1·0	1 D.M.A.	55	,, ,,	108·0	43·2	4·00	36·1	—	4·0	—	—	—

Interaction of Ethyl (+)*Mandelate and Phosphorus Tribromide.*—The (+)ester (3·6 g., 1 mol.), $\alpha_D^{16^\circ}$ +121·1°, was mixed with the tribromide at −10°, kept at 20° for 3 hours, and then given aqueous treatment. Results are recorded in Table V (Calc. for ethyl phenylbromoacetate : Br, 32·9%).

TABLE V.

			Ethereal solution.					Carbonate extract, $POR(OH)_2$.	
			Distillate, b. p. 88°/1 mm.			Residue.			
Expt.	Order of mixing.	PBr_3 mols.	Yield, RBr, %.	Br, %.	$\alpha_D^{20^\circ}$ (−).	Weight, g.	P, %.	Weight, g.	P, %.
1	⟵	0·34	54·0	32·9	80·3°	0·22	7·0	0·40	11·1
2	⟶	1·0	44·2	32·8	82·4	0·38	7·2	0·38	10·9
3	⟶	2·0	39·0	32·8	82·4	0·56	7·3	—	—
4	(CO_2) ⟶	2·0	17·5	—	—	0·70	7·2	0·62	12·3
						For $P(OR)_2OH$, Calc.	7·6	Calc.	12·7

Interaction of Ethyl (+)*Mandelate and Phosphorus Tribromide in Presence of Tertiary Bases.*—The tribromide (1·81 g., 0·33 mol., in 10 c.c. ether) was added dropwise at −10° to an ethereal solution (10 c.c.) of the ester (3·6 g., 1 mol.; $\alpha_D^{20^\circ}$ +52·3°) and tertiary base (1 mol.). During the mixing, a white precipitate separated and this was collected after the mixture had stood at 18° for 1 hour. The residue from the ethereal solution was kept for 1 hour at 100°/15 mm., and the solid was kept under reduced pressure for 1 hour before examination. The results are recorded in Table VI (Calc. for tri-ester; $P(OR)_3$: wt., 3·79; P, 5·46%).

The tribromide (1 mol.) was added to a mixture of the (+)mandelate (3·6 g., 1 mol.; $\alpha_D^{16^\circ}$ +152·2°) and tertiary base (1 mol.) at −10°, followed by heating for 30 minutes at 100°. The semi-solid mass was extracted with ether, and the ethereal solution was given aqueous treatment. The ethyl phenylbromoacetate obtained was almost completely racemised. The ether insoluble solids contained approximately one-third of the bromine in the system. Weights of solid and bromide, RBr, for the respective bases are as follows : pyridine, 4·96, 1·51; quinoline, 4·76, 2·3; dimethylaniline, 6·56, 2·0 g.

TABLE VI.

Base B.	Precipitate, BHBr.				"Phosphite" residue.		
	Wt., g.	Calc.	Br, %.	Calc., %.	Wt., g.	$\alpha_D^{20^\circ}$ (+).	P, %.
Pyr.	3·21	3·20	49·1	50·0	3·45	48·3°	5·4
Q.	4·18	4·20	37·2	38·1	3·56	48·8	5·3
D.M.A.	4·00	4·04	39·4	39·6	3·56	48·1	5·4

THE NORTHERN POLYTECHNIC, HOLLOWAY, N.7.

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