

**151. Experiments on the Interaction of Hydroxy-compounds and Phosphorus and Thionyl Halides in the Absence and in the Presence of Tertiary Bases. Part V.**

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(+)Octan-2-ol and phosphorus pentachloride in the presence of respectively ether and carbon disulphide yielded rapidly at  $-10^\circ$  (–)2-chloro-octane and octylene; but the pentabromide under the same conditions afforded phosphoric esters as well as the (–)bromide. It is evident that there is a primary action of the pentahalide and a secondary action of the resulting oxyhalide, the latter action being in certain circumstances ineffective. The function of pyridine chiefly concerns the secondary action of the oxyhalide, which in the presence of sufficient alcohol produces phosphoric ester.

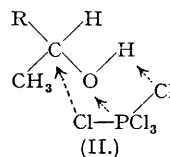
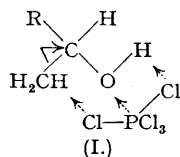
(–)Phenylmethylcarbinol and the pentahalides under conditions described above rapidly gave rise to the (+)halides in large yield but with considerable loss in rotatory power, and thus afforded examples of the reaction represented closely by  $PX_5 + ROH = RX + POX_3 + HX$ . Pyridine appeared to have little influence on the primary action of the pentahalide; but in the presence of sufficient alcohol the secondary action of the oxyhalide gave rise to (+)halide,  $RX$ , having a high rotatory power.

Probable mechanisms in terms of end-on and broadside collisions are suggested.

ALTHOUGH the interaction of hydroxy-compounds and phosphorus pentachloride has been represented by the equation,  $ROH + PCl_5 = POCl_3 + RCl + HCl$ , in the majority of papers referring to this reaction (cf. Clark and Streight, *Proc. Roy. Soc. Canada*, 1929, **23**, 77) the yields of chloride,  $RCl$ , were stated as small or not stated at all. Pierre and Puchot (*Annalen*, 1872, **163**, 253), using the pentachloride (1 mol.), obtained *n*-propyl chloride (29% yield) from the alcohol (4 mols.), and *n*-butyl chloride (31% yield) from the alcohol (5 mols.). It was pointed out (Part II, *J.*, 1945, 106) that the oxychloride may react on its own account and have a considerable influence on the nature and yields of products. The significance of order and speed of mixing will depend on the relative velocities of the primary ( $PCl_5$ ) and subsequent ( $POCl_3$ ) reactions at the prevailing temperature.

(+)Octan-2-ol interacted slowly with the oxychloride (Part II, *loc. cit.*) at  $15^\circ$  and formed (–)2-chloro-octane, and the esters,  $POCl_2OR$ ,  $POCl(OR)_2$ ,  $PO(OR)_3$ , in proportions depending on relative amounts of reagents. It is now shown that (+)octan-2-ol (1 mol.) and the pentachloride (1 mol.) interacted very quickly at  $-10^\circ$  without the intervention of the oxychloride; but instead of the expected theoretical yield of the chloride,  $RCl$  (1 mol.), (–)2-chloro-octane was produced in yield approaching only 50%, the other product noticed being octylene. There was no sign of the formation of phosphoric esters. It is suggested that the

chloride,  $RCl$ , was produced by the end-on mechanism,  $Cl_4PCl \longrightarrow R-OH \longrightarrow ClR + Cl_4P^+ + OH^- \longrightarrow ClR + Cl_4POH \longrightarrow ClR + POCl_3 + HCl$ ; whilst a broadside elimination mechanism (I) would account for the formation of octylene. This elimination mechanism is pictured as being due to a type of hyper-conjugation.



As compared with the oxychloride, the greater ease of reaction of the pentachloride may be attributed to three factors. First, since in most compounds phosphorus is 4-covalent, this number being exceeded only with the halogens, it is to be expected that phosphorus in the 5-covalent state will show a decided tendency to resume the 4-covalent state. Secondly, the trigonal bipyramidal structure of the pentachloride (cf. Mills, *J.*, 1942, 457) appears to confer a high probability of effective orientation on collision. Thirdly, the co-ordinately linked oxygen may be expected to reduce the activity of the chlorine atoms in the oxychloride.

Essentially similar results had previously been obtained by Houssa and Phillips (*J.*, 1932, 108), but it is now shown that, as the reagents were then mixed and refluxed in boiling ether, the temperature was far beyond the minimum requirements of the pentachloride. The two experiments are complementary, however, and show that the production of octylene was not related to the temperature prevailing, and even at the higher temperature phosphorus oxychloride did not intervene. It is evident that a structural factor is concerned in the probability of such intervention. In an exploratory experiment it was found that 1.8 mols. of *n*-butyl alcohol were required to cause the disappearance of the pentachloride (1 mol.) suspended in ether at  $-10^\circ$ , and considerable amounts of phosphoric esters were produced.

Addition of (+)octan-2-ol (1 mol.) to the pentabromide (1 mol.) suspended in ether (or dissolved in carbon disulphide) at  $-10^\circ$  led to the rapid formation of (–)2-bromo-octane (52%) and phosphoric esters.

The function of pyridine depends on the relative proportions of the reagents as well as on conditions. Addition of (+)octan-2-ol (1 mol.) and pyridine (1 mol.) to the pentachloride (1 mol.) in carbon disulphide at  $-10^\circ$  caused the immediate formation of (–)2-chloro-octane in yield approximately the same as, and octylene in much less yield than, when the pyridine was omitted. Pyridine hydrochloride and phosphoric esters were also formed. The base appeared to have little influence on the end-on attack of the pentachloride, but it did facilitate the broadside attack of the oxychloride during the mixing, and so gave rise to phosphoric

esters. Addition of the pentachloride (0.25 mol.) to (+)octan-2-ol (1 mol.) and pyridine (1 mol.) in carbon disulphide solution led to the rapid formation of (–)2-chloro-octane in considerably diminished yield (based on the amount of alcohol), and to the much slower formation of phosphoric ester by the broadside attack of the oxychloride facilitated most probably by the hydrogen bonded base, ROH . . . NC<sub>5</sub>H<sub>5</sub>. Analogous results were obtained when phosphorus pentabromide was used, except that the oxybromide appeared to be more effective in the formation of phosphoric ester.

Hückel and Pietrzok (*Annalen*, 1939, **540**, 250) used pyridine (4 mols.) for each mol. of *l*-menthol and pentachloride in petroleum, and they suggested mechanisms based on the prior formation of ions of the type

(C<sub>5</sub>H<sub>5</sub>N : PCl<sub>5</sub>)<sup>+</sup> Cl<sup>–</sup>, (R – O : P(Cl<sub>4</sub>) : NC<sub>5</sub>H<sub>5</sub>)<sup>+</sup> the former leading to the reaction: Cl<sup>–</sup> → ROH = RCl + OH<sup>–</sup>.

Whereas McKenzie and Clough (*J.*, 1913, **103**, 687) obtained only a viscid oil containing phosphorus by the interaction of the pentachloride and phenylmethylcarbinol under unspecified conditions, Kenyon, Phillips, and Taylor (*J.*, 1931, 382) obtained the (+)chloride, RCl, (with considerable loss in rotatory power) in 53.5% yield by the addition of the (–)alcohol (1 mol.) to ice cold pentachloride (2 mols.) followed by heating on a steam-bath. They obtained the *dl*-chloride, RCl, in 87.5% yield by the addition of an ethereal solution of the *dl*-alcohol to a boiling solution of the pentachloride (2 mols.). It is now shown that the interaction of the (–)alcohol (1 mol.) and respectively the pentachloride and the pentabromide (1 mol.) suspended in ether or dissolved in carbon disulphide is rapid at –10°. Yields of (+)halides, RX, were large, especially for the bromide, but there was still considerable loss in rotatory power. All the phosphorus was found in the aqueous washings; and as it has been shown (Part II, *loc. cit.*) that the interaction of this alcohol and phosphorus oxychloride is slow at 0°, it may be concluded that the equation, ROH + PX<sub>5</sub> = RX + POX<sub>3</sub> + HX, closely represents the reaction. The author suggests that the end-on mechanism accounted for the inversion and a broadside one (II) for the retention of configuration. The elimination mechanism (I) noticed with octan-2-ol was evidently by-passed, because the electron-releasing function of the phenyl group would compensate any electron demand of the reactive carbon atom more readily than would the hyperconjugation mechanism. There was no sign of the intermediate chlorophosphate in these experiments.

Holmberg (*Ber.*, 1912, **45**, 997) used the pentabromide in ethereal solution and obtained 1-bromo-1-phenylethane, α<sub>D</sub><sup>14</sup> + 1.5° (from ROH, α<sub>D</sub><sup>17</sup> – 4.4°).

The function of pyridine appears to be twofold. The only influence it appears to have on the primary interaction of the pentahalide is to precipitate the hydrogen halide as C<sub>5</sub>H<sub>5</sub>NHX, and thus to prevent any direct action of this gas. In the experiment of Kenyon, Phillips, and Taylor (*loc. cit.*) (cf. present expt. 10) 1-chloro-1-phenylethane (70%), [α]<sub>5461</sub> + 10.4°, was obtained by the addition of the alcohol, [α]<sub>5461</sub> – 49.8°, (1 mol.) and pyridine (1 mol.) to the pentachloride (2 mols.) at 0° followed by 30 minutes' heating at 50°. It is highly probable that, so far as the direct attack of the pentachloride was concerned, the reaction took place during the actual mixing at 0°, and the rather higher rotatory power of the chloride was due to the suppression of the incidental interaction of the hydrogen chloride and alcohol, PCl<sub>5</sub> + ROH + C<sub>5</sub>H<sub>5</sub>N = POCl<sub>3</sub> + RCl + C<sub>5</sub>H<sub>5</sub>N.HCl. A secondary influence of the base is more fundamental and concerns the subsequent interaction of the oxyhalide and alcohol when the proportions are suitably adjusted. It was shown in Part II (*loc. cit.*) that addition of oxychloride to a mixture of (–)phenylmethylcarbinol, α<sub>D</sub><sup>18</sup> (l = 10 cm.) – 25.6°, and pyridine in ethereal solution at 0° caused production of (+)1-chloro-1-phenylethane, α<sub>D</sub><sup>18</sup> (l = 10 cm.) + 63.0°, from the beginning, and the precipitate had a composition represented by C<sub>5</sub>H<sub>5</sub>N.HCl.C<sub>5</sub>H<sub>5</sub>NPO<sub>2</sub>Cl. Closely similar results have now been obtained with the reagents in carbon disulphide. It is quite clear that the configuration retention mechanism tends to be completely eliminated, probably by the end-on mechanisms suggested in Part II. Now when the pentachloride (0.5 mol.) in carbon disulphide was added at –10° to a solution of (–)alcohol (1 mol.) and pyridine (2 mols.) there appeared to be a rapid formation of some (+)chloride, RCl, (with some loss in rotatory power) by the primary interaction of the pentachloride, followed on standing by a slower secondary interaction of the oxychloride and alcohol, which in the presence of free base yielded the (+)chloride, RCl, having a high rotatory power. The net result was the isolation of (+)chloride, RCl, having α<sub>D</sub><sup>16</sup> (l = 10 cm.) + 78.1°, and a precipitate which appeared to have the composition xC<sub>5</sub>H<sub>5</sub>N.HCl + yC<sub>5</sub>H<sub>5</sub>NPO<sub>2</sub>Cl, where in contrast with the composition stated above, x is appreciably greater than y. Analogous results were obtained with the pentabromide, (–)alcohol, α<sub>D</sub><sup>16</sup> (l = 10 cm.) – 14.8°, yielding the (+)bromide, RBr, having α<sub>D</sub><sup>14</sup> (l = 10 cm.) + 31.1°.

*Loss of Rotatory Power in Substitution Reactions.*—In the systems under consideration there are probably three distinct causes of partial loss in rotatory power. The most probable, in the author's opinion, is the occurrence of end-on inversion mechanisms together with broadside retention mechanisms, the former usually occurring more readily, and therefore preponderant inversion is commonly observed. A second is the occurrence of successive substitutions,  $\bar{X} \rightarrow R \rightarrow \bar{X}$  (Hughes, Juliusburger, Masterman, Topley, and Weiss, *J.*, 1935, 1525), and a third is the symmetrical addition to a planar carbonium cation (Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1196, 1201, 1208, 1236, 1243, 1252; cf. McKenzie and Gow, *J.*, 1933, 705).

The difference in behaviour of phenylmethylcarbinol and octan-2-ol has been of considerable interest, and in the light of the herein reported rotatory power of (+)1-chloro-1-phenylethane, [α]<sub>D</sub><sup>16</sup> + 93.5°, a brief statement on the position is desirable. Thionyl chloride alone and (–)phenylmethylcarbinol afforded (–)1-chloro-1-phenylethane, [α]<sub>D</sub><sup>20</sup> – 50.6° (McKenzie and Clough, *loc. cit.*), and the postulated mechanism to account for

retention of configuration is the intramolecular decomposition of the intermediate chlorosulphinate facilitated by the electron-releasing function of the phenyl group (Kenyon and Phillips; Ingold and Hughes). It now appears that the inversion mechanism must have operated to a significant extent. With phosphorus trichloride the (–)carbinol yielded the (+)chloride,  $[\alpha]_D^{25} + 8.1^\circ$  (McKenzie and Clough) (cf. Part I), indicating only a small preponderance of inversion over retention mechanism.

The high rotatory power reported herein gives added significance to the doubts expressed by Ingold and Hughes concerning the optical purity of the specimens of the methyl and the ethyl ether of phenylmethylcarbinol used as reference material. It follows that some extension of the correlation of steric course and the  $S_N1$  mechanism may be necessary to include examples in which no loss of rotatory power is shown. The preparation of 1-bromo-1-phenylethane having  $\alpha_D^{18} (l = 10 \text{ cm.}) + 131.4^\circ$  has an interesting bearing on the experiments of Levene and Rothen (*J. Biol. Chem.*, 1939, 127, 237; cf. Arcus, *J.*, 1944, 236). The flattening of the molecular rotation curve for the bromide, RBr, prepared at temperatures approaching  $-80^\circ$  has been taken as indicating a maximum rotatory power of  $[M]_{5780}^{25} 90^\circ$ , in benzene. This value, however, is only half the molecular rotation, in benzene, of the bromide, RBr, having  $\alpha_D^{18} (l = 10 \text{ cm.}) 131.4^\circ$ .

#### EXPERIMENTAL.

**General Procedures.**—In the absence of pyridine, the alcohol, dissolved in dry ether or dry carbon disulphide, was mixed dropwise at  $-10^\circ$  with the phosphorus pentahalide, suspended in ether or dissolved in carbon disulphide. A filtering flask fitted with a tap funnel was used, and the side tube was attached to a U tube containing pellets of potassium hydroxide to absorb any hydrogen halide evolved. Unless otherwise stated, ice was added immediately after completion of mixing (15 mins.), and the organic solution was washed with a dilute solution of sodium carbonate, dried quickly with potassium carbonate, and left over sodium sulphate. Phosphate and halide ions were determined quantitatively in the aqueous washings, and the contents of the absorption tube were examined for halide ions.

In the presence of pyridine, the precipitate, which formed during or subsequently to the mixing, was separated by rapid filtration, and kept in a vacuum desiccator for 1 hour before being weighed and analysed. The filtrate was treated as already described except that a washing with a dilute solution of sulphuric acid preceded that with sodium carbonate, and pyridine was determined quantitatively in the aqueous washings.

After removal of the solvent, the residue was distilled.

Rotatory powers are recorded for  $l = 10 \text{ cm.}$

**Interaction of (–)Phenylmethylcarbinol and Phosphorus Pentahalides.**—*Expt. 1.* At the end of the dropwise addition of an ethereal solution (10 c.c.) of the carbinol ( $\alpha_D^{18} -14.8^\circ$ ; 2.44 g.; 1 mol.) to the pentachloride (4.17 g.; 1 mol.) covered with dry ether (10 c.c.), the solid had just disappeared. Ice was added immediately. (+)1-Chloro-1-phenylethane (2.5 g., 89%), b. p.  $64-65.9^\circ/9 \text{ mm.}$ ,  $\alpha_D^{18} + 4.0^\circ$ , was obtained, and there was only a trace of residue. The absorption tube contained a trace of chloroform ion. The aqueous washings contained almost all the phosphorus in the system (Found: P, 0.618 g. Calc.: P, 0.620 g.) and 4/5ths of the chlorine in the system (Found: Cl, 2.82 g.).

*Expt. 2.* The same quantities of reagents in carbon disulphide solution (50 c.c.) afforded (+)1-chloro-1-phenylethane (2.21 g., 80%), b. p.  $73^\circ/13 \text{ mm.}$ ,  $\alpha_D^{18} + 9.4^\circ$  (Found: Cl, 25.2. Calc.: Cl, 25.2%), and the remaining data were essentially the same.

*Expt. 3.* The same carbinol (2.44 g.; 1 mol.) in ethereal solution (10 c.c.) was added to phosphorus pentabromide (8.60 g., 1 mol.) covered with ether (10 c.c.) at  $-10^\circ$  (15 mins.); by the end of this operation the pentabromide had disappeared. Ice was immediately added. By distilling the ethereal solution, (+)1-bromo-1-phenylethane (2.90 g.; 79%), b. p.  $85.5^\circ/9 \text{ mm.}$ ,  $\alpha_D^{18} + 11.8^\circ$  (Found: Br, 43.0. Calc.: Br, 43.2%), and a residue (0.6 g.) were obtained. The absorption tube contained only a trace of bromide ion; all the phosphorus and 4/5 of the bromine in the system were found in the aqueous washings.

*Expt. 4.* When the reagents were used in carbon disulphide, the bromide, RBr, (93%), had b. p.  $89^\circ/14 \text{ mm.}$ ,  $\alpha_D^{18} + 9.4^\circ$  (Found: Br, 43.5%), the remaining data being essentially the same.

*Expt. 5.* The pentachloride (2.6 g.; 0.5 mol.) dissolved in carbon disulphide (50 c.c.) was added at  $-10^\circ$  to a solution of (–)carbinol ( $\alpha_D^{18} -44.0^\circ$ ; 3.05 g.; 1 mol.) and pyridine (4.0 g.; 2 mols.) in the same solvent (10 c.c.). Formation of a white solid commenced immediately, and proceeded slowly at  $-10^\circ$ . After the mixing was complete (15 mins.) the mixture was kept at  $15^\circ$  for 12 hours. From the filtered solution, (+)1-chloro-1-phenylethane (1.86 g.; 53%) b. p.  $69^\circ/11 \text{ mm.}$ ,  $\alpha_D^{18} + 78.1^\circ$  (Found: Cl, 25.0%), and a residue (decomp.) (0.65 g.) were obtained. The white solid (5.43 g.) dissolved slowly but completely in water (Found: Cl, 28.3; P, 6.6;  $C_6H_5N$ , 54.8%), and was probably a mixture of rather more than one mol. of pyridine hydrochloride and less than one of the compound  $C_6H_5NPO_2Cl$ , together with a small amount of quaternary compound,  $C_6H_5NRHX$ , where X is an acid radical. Nearly all the phosphorus in the system was found in the solid (0.360 g. compared with 0.387 g.); the remainder was in the aqueous washings. Of the 4 g. of pyridine used, 2.98 g. were found in the solid, and 0.760 g. in the aqueous washings; the difference, 0.26 g., had probably gone to form the quaternary compound the presence of which was demonstrated by the precipitation of the ferrocyanide (Gerrard *J.*, 1936, 688).

*Expt. 6.* Repetition of expt. 5, except that 8 g. of pyridine (4 mols.) were used, led to the formation of a white solid (6.20 g.) (Found: Cl, 25.9; P, 6.1;  $C_6H_5N$ , 53.8%). (+)1-chloro-1-phenylethane (2.0 g.; 57%), b. p.  $71.5^\circ/13 \text{ mm.}$ ,  $\alpha_D^{18} + 83.4^\circ$  (Found: Cl, 25.2%), and a residue (0.4 g.). Since the aqueous washings contained 4.18 g. of pyridine, it follows that again rather less than 2 mols. of pyridine have reacted for each mol. of carbinol. Details of results are similar to those recorded for expt. 5.

*Expt. 7.* The quantities specified in expt. 6, but with the pentachloride suspended in ether, gave rise to (+)chloride, RCl, (2.0 g.), b. p.  $68^\circ/10 \text{ mm.}$ ,  $\alpha_D^{18} + 66.1^\circ$ , and a solid (5.69 g.) (Found: Cl, 28.8; P, 6.7;  $C_6H_5N$ , 48.4%). More than half the pyridine in the system (4 mols.) was found in the aqueous washings. Again nearly all the phosphorus was in the solid.

*Expt. 8.* The pentabromide (3.5 g.; 0.4 mol.) was added slowly to an ethereal solution (20 c.c.) of the alcohol ( $\alpha_D^{18} -14.8^\circ$ ; 2.44 g.; 1 mol.) and pyridine (4.8 g.; 3 mols.) at  $-10^\circ$ . Precipitation of solid proceeded slowly, and particles of the pentabromide persisted in suspension for some time, even when the mixture was removed from the cooling bath and occasionally shaken for 3 hours at  $15^\circ$ . After being at  $15^\circ$  for 12 hours the mixture was filtered. The solid (5.554 g.) [Found: Br, 41.8; P, (as  $PO_4$ ), 2.8;  $C_6H_5N$ , 42.9%] contained half the pyridine in the system. The aqueous washings contained only a trace of phosphate ion (Found: Br  $\equiv 10.1 \text{ c.c. of } 0.1N\text{-}AgNO_3$ ;  $C_6H_5N$ , 2.13 g.). From the ethereal solution, (+)1-bromo-1-phenylethane (1.52 g., 41%), b. p.  $84^\circ/9 \text{ mm.}$ ,  $\alpha_D^{18} + 31.1^\circ$  (Found: Br, 43.4. Calc.: Br, 43.2), and a residue, which decomposed at the end of the distillation, were obtained.

*Expt. 9.* With the same reagents dissolved in carbon disulphide, precipitation of solid (4.910 g.) (Found: Br, 38.7;



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P, 3.3;  $C_5H_5N$ , 49.7%) proceeded slowly, but much more quickly than in expt. 8. Aqueous washings contained traces of bromide and phosphate ions and 2.27 g. of pyridine, *i.e.*, 1.5 mols. of base had reacted. 1-Bromo-1-phenylethane (1.95 g.), b. p.  $84-85^\circ/9$  mm.,  $n_D^{25} + 30.1^\circ$  (Found, Br, 43.3%), was obtained.

*Expt. 10.* (+)-1-Chloro-1-phenylethane (1.90 g., 68%), b. p.  $70-71^\circ/12$  mm.,  $n_D^{25} + 12.4^\circ$  (Found: Cl, 25.1%), and a decomposed residue (0.55 g.) were obtained by the addition (15 mins.) of the pentachloride (4.2 g.; 1 mol.) to the alcohol ( $n_D^{25} = 16.0^\circ$ ; 2.44 g.; 1 mol.) and pyridine (1.6 g.; 1 mol.) in carbon disulphide at  $-10^\circ$ , followed by immediate filtration and work-up. The precipitate (3.20 g.) (Found: Cl, 40.7; P, 6.7;  $C_5H_5N$ , 48.1%) appeared to be a mixture of pyridine hydrochloride and possibly the substance,  $PCl_5ONHC_5H_5$ .

*Interaction of (+)Octan-2-ol ( $n_D^{25} + 8.0^\circ$ ) and Phosphorus Pentahalides.—Expt. 1.* At the end of the addition (15 mins.) of (+)octan-2-ol (3.25 g.; 1 mol.) in ether (10 c.c.) to the pentachloride (5.21 g.; 1 mol.) suspended in ether (10 c.c.) at  $-10^\circ$ , the solid had just disappeared. Ice was immediately added. Octylene and (–)-2-chloro-octane (1.80 g.; 48%), b. p.  $63^\circ/15$  mm.,  $n_D^{25} - 29.8^\circ$  (Found: Cl, 23.8. Calc.: Cl, 23.9%), but no residue, were obtained. The aqueous washings contained: P, 0.725 g.; Cl, 3.62 g. (System contained: Cl, 4.44 g.; P, 0.775 g.). No oil was formed when the carbonate washings were acidified. During the addition, no hydrogen chloride passed into the absorption tube; and even when, during the following 15 mins., dry hydrogen was passed through the solution at  $-10^\circ$ , an insignificant amount of hydrogen chloride (equivalent to 3.4 c.c. of 0.1N- $AgNO_3$ ) was collected. When the solution was allowed to warm to  $15^\circ$  (15 mins.) and then agitated by a stream of hydrogen, the amount of hydrogen chloride evolved in 15 mins. was equivalent to 25.6 c.c. of 0.1N- $AgNO_3$ .

*Expt. 2.* By the same procedure, but with carbon disulphide (50 c.c.) as solvent, octylene, (–)-2-chloro-octane (1.81 g.), b. p.  $63^\circ/15$  mm.,  $n_D^{25} - 29.0^\circ$ , but no residue, were obtained. During the mixing and subsequent passage of hydrogen (15 mins.) at  $-10^\circ$ , hydrogen chloride (0.805 g.) was evolved. The aqueous washings contained: Cl, 2.862 g.; P, 0.722 g.

*Expt. 3.* The alcohol (2.6 g.; 1 mol.) was added to a suspension of pentabromide (8.6 g.; 1 mol.) in ether (20 c.c.) at  $-10^\circ$ . A little pentabromide remained unreacted at the end of the addition (15 mins.). Ice was immediately added. From the ethereal solution, (–)-2-bromo-octane (2.0 g.; 52%), b. p.  $69^\circ/8$  mm.,  $n_D^{25} - 34.9^\circ$  (Found: Br, 41.8. Calc.: Br, 41.45%), a fraction, b. p.  $90-105^\circ/8$  mm. (0.43 g.), and a residue (0.33 g.) (Found: P, 4.6%) were obtained. No hydrogen bromide was evolved during the mixing, a little (equiv. to 2.8 c.c. of 0.1N- $AgNO_3$ ) was carried off in a stream of hydrogen (15 mins.) at  $-10^\circ$ , and rather more (equiv. to 18.1 c.c. of 0.1N- $AgNO_3$ ) at  $15^\circ$  (15 mins.). The aqueous washings contained: Br, 6.04 g.; P (as  $PO_4$ ), 0.49 g. (in system, Br, 8.00 g.; P, 0.620 g.), and the carbonate extract afforded a trace of oil.

*Expt. 4.* Essentially the same results were obtained when carbon disulphide was used in place of ether. No hydrogen bromide was evolved at  $-10^\circ$ , and in a stream of hydrogen at  $-10^\circ$  some of the former gas (equiv. to 19.1 c.c. of 0.1N- $AgNO_3$ ) was carried away in 15 mins.

*Expt. 5.* The pentachloride (2.09 g.; 0.25 mol.) in carbon disulphide (30 c.c.) was added to the alcohol (5.2 g.; 1 mol.) and pyridine (3.2 g., 1 mol.) in the same solvent (10 c.c.) at  $-10^\circ$ . Precipitation of pyridine hydrochloride began immediately, but was far from complete at the end of the addition, and after being at  $15^\circ$  for 48 hours the mixture was filtered. The solid (4.10 g. Calc. for  $C_5H_5NHCl$ , 1 mol.: 4.62 g.) (Found: Cl, 32.1;  $C_5H_5N$ , 65.9. Calc.: Cl, 30.7;  $C_5H_5N$ , 68.4%) was pyridine hydrochloride contaminated by a substance, possibly  $C_5H_5NHOPCl_4$ . The aqueous washings of the carbon disulphide solution contained only traces of chloride and phosphate ions. From the solvent, (–)-2-chloro-octane (0.90 g.), b. p.  $63-64^\circ/15$  mm.,  $n_D^{25} - 20.9^\circ$ , the alcohol, b. p.  $78-80^\circ/10$  mm. (0.65 g.), and a residue (oil-bath at  $140^\circ$ ) (2.5 g.) (Found: P, 7.2. Calc. for  $OP(OR)_3$ : P, 7.1%) were obtained. The carbonate extract yielded a trace of oil.

*Expt. 6.* The pentabromide (4.31 g.; 0.25 mol.) in carbon disulphide solution (30 c.c.) was added to the alcohol (5.2 g.; 1 mol.) and pyridine (3.2 g.; 1 mol.) in the same solvent (20 c.c.) at  $-10^\circ$ . Precipitation of the hydrobromide of the base commenced immediately but continued subsequently at  $15^\circ$  (48 hours). The solid (6.44 g. Calc.: 6.4 g.) (Found: Br, 49.0;  $C_5H_5N$ , 49.2. Calc.: Br, 50.0;  $C_5H_5N$ , 49.4%) was separated, and from the carbon disulphide solution (–)-2-bromo-octane (1.20 g.), b. p.  $69^\circ/9$  mm.,  $n_D^{25} - 28.1^\circ$  (Found: Br, 41.6%, and a residue (3.81 g.) (oil-bath  $140^\circ$ ) (Found: P, 7.0%) were obtained. Aqueous washings contained only traces of bromide and phosphate ions.

Addition (15 mins.) of a solution of the alcohol (4.4 g.; 1 mol.) and pyridine (2.7 g.; 1 mol.) in carbon disulphide to the pentachloride (7 g.; 1 mol.) in the same solvent at  $-10^\circ$  caused the immediate precipitation of a white solid (4.622 g.) (Found: Cl, 42.7; P, 3.1;  $C_5H_5N$ , 51.4%). Phosphorus pentabromide behaved analogously.

Houssa and Phillips (*loc. cit.*) added an ethereal solution of the alcohol [ $n_D^{20} + 9.62^\circ$  ( $l = 1.0$ ); 1 mol.] and pyridine (2 mols.) to the pentachloride (1 mol.) and then heated the mixture for 30 mins. An unspecified amount of 2-chloro-octane,  $n_D^{25} - 34.86^\circ$  ( $l = 1.0$ ), and considerable amounts of phosphoric esters were obtained.

*Rotatory Powers of 1-Halogeno-1-phenylethanes.*—In repetition of an experiment described in Part II (*loc. cit.*) but with carbon disulphide instead of ether as solvent, phenylmethylcarbinol ( $n_D^{25} - 44.0^\circ$ ; 3.66 g.; 1 mol.), pyridine (4.8 g.; 2 mols.), and phosphorus oxychloride (3.07 g.; 0.67 mol.) were used. The white precipitate (7.24 g.) (Found: Cl, 19.1; P, 7.9;  $C_5H_5N$ , 45.7%) closely resembled that (7.38 g.) (Found: Cl, 19.2; P, 7.9;  $C_5H_5N$ , 46.3%) previously described, and the other product isolated was (+)-1-chloro-1-phenylethane, b. p.  $72.5^\circ/12$  mm.,  $n_D^{25} - 99.6^\circ$  (Found: C, 68.6; H, 6.6; Cl, 25.1. Calc.: C, 68.3; H, 6.4; Cl, 25.2%).

By repeating expt. 5, Table IV, Part III (*J.*, 1945, 848), but with carbon disulphide as solvent, 1-bromo-1-phenylethane, b. p.  $83^\circ/9$  mm.,  $n_D^{25} + 131.4^\circ$  (from ROH,  $n_D^{25} - 44.0^\circ$ ) (Found: C, 52.1; H, 5.1; Br, 43.1. Calc.: C, 51.9; H, 4.9; Br, 43.2%), was obtained.

*Rotatory Power of 2-Bromo-octane.*—Repetitions of expt. 6, Table I, Part III (*loc. cit.*), but with hydrogen instead of carbon dioxide to agitate the liquid, led to uniform results: 2-bromo-octane, b. p.  $70.5^\circ/10$  mm.,  $n_D^{25} - 42.6^\circ$  (from ROH,  $n_D^{25} + 7.92^\circ$ ) (Found: C, 50.0; H, 8.8; Br, 41.2. Calc.: C, 49.7; H, 8.8; Br, 41.45%), was obtained.

Phenylmethylcarbinol was resolved by the procedure of Downer and Kenyon (*J.*, 1939, 1156), octan-2-ol by that of Kenyon (*J.*, 1922, 121, 2540).

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