The Behaviour of 1 : 1 : 1 : 3 : 3 : 3-*Hexachloropropan-2-ol with Inorganic Non-metal Halides.*

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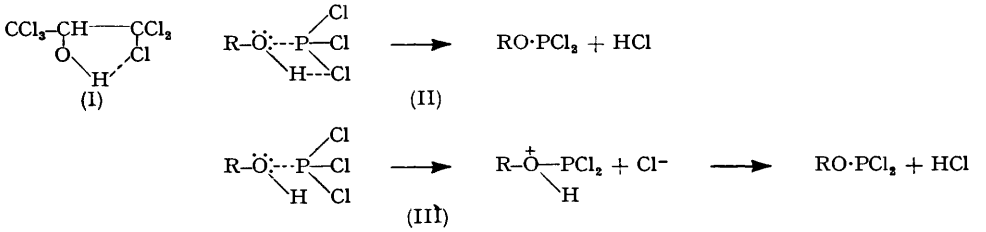
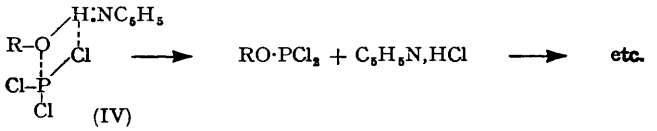
The alcohol did not react with phosphorus trichloride, phosphorus oxychloride, thionyl chloride, silicon tetrachloride, or acetyl chloride, but reacted very slowly with phosphorus pentabromide, tribromide, or oxybromide. In the presence of pyridine, there was formation of esters at −10°. These results appear to be due to a drastic reduction in nucleophilic power of the hydroxyl-oxygen atom by the inductive effect of the substituent chlorine atoms, together with a reduction in the reactivity of the hydrogen atom by internal hydrogen bonding, both effects being compensated by hydrogen bonding with the base, ROH · · · NC_5H_5. Other reactions, including that with boron trichloride, are described.

CERTAIN properties of trichloro-*tert.*-butanol (chloretone) (Gerrard, and Wyvill, *Research*, 1949, **2**, 536) and 2 : 2 : 2-trichloroethanol (Gerrard, Green, and Phillips, *J.*, 1954, 1148) have been described, and it is now evident that 1 : 1 : 1 : 3 : 3 : 3-hexachloropropan-2-ol is an example of the extreme influence of substituent chlorine on the reactivity of an alcoholic hydroxy-group. Under the conditions described the alcohol did not react with phosphorus trichloride, phosphorus oxychloride, thionyl chloride, silicon tetrachloride, or acetyl chloride; but it did so slowly with phosphorus pentabromide, tribromide, or oxybromide in boiling *n*-hexane. This could be due to the drastic reduction of electron availability on the oxygen atom caused by the accumulation of the inductive effect of each of six chlorine atoms, and to the reduction in availability of hydroxyl-hydrogen by internal hydrogen bonding (cf. I). Steric hindrance does not appear as the cause of this low reactivity, for the alcohol reacted readily with the reagents when pyridine was present.



Taking phosphorus trichloride as an example, we adopt the view that the driving force of its primary interaction with an " ordinary " alcohol such as butan-1-ol is the nucleophilic attack of hydroxylic oxygen on phosphorus; but whether the hydroxyl-hydrogen atom is simultaneously removed by a four-centre mechanism (cf. II) involving only one transition state (cf. Gerrard, *J.*, 1939, 99; 1940, 218) or is removed by a subsequent step (III) has not yet been decided.



In the presence of pyridine, the alcohol immediately afforded the trialkyl phosphite and base hydrochloride, and thus showed a remarkable increase in reactivity attributable to co-ordination (cf. IV), which could increase the electron availability on oxygen and break the internal hydrogen bonding. Cleverdon and Smith's dipole-moment work (*Chem. and Ind.*, 1948, 29) supports the view, previously put forward by Gerrard (*J.*, 1939, 99; 1940, 1940, 218), in favour of hydrogen bonding between pyridine and alcohol (R·OH:NC_5H_5).

It is clear that pyridine does not merely react with hydrogen chloride as it is formed, but must take part in removing the hydrogen and the chlorine from the reacting entities.

In the presence of pyridine, thionyl chloride immediately afforded the dialkyl sulphite, but, in marked contrast with the sulphites of ordinary alcohols (cf. Gerrard, *J.*, 1939, 99; 1940, 218; French and Gerrard, *J.*, 1949, 3326), this did not react with thionyl chloride in the presence of pyridine hydrochloride even at 140°. Therefore Darzens's procedure (*Compt. rend.*, 1911, **152**, 1314, 1601) does not give the alkyl chloride.

In the presence of base, silicon tetrachloride readily reacted with the alcohol to the extent of three atoms of chlorine to give an alkoxysilane; but there was difficulty over the fourth. Similar replacement of chlorine in phosphorus oxychloride by alkoxyl in the presence of pyridine was virtually restricted to two chlorine atoms, and even the replacement of the second was very slow. However, when the oxybromide was used, two atoms of bromine were much more readily replaced, but under the conditions employed no further reaction took place. The phosphorobromidate, $POBr(OR)_2$, was obtained as white crystals, and was somewhat resistant to hydrolysis.

The phosphite showed reluctance to be dealkylated by hydrogen chloride and hydrogen bromide. On prolonged heating with hydrogen bromide, the phosphite afforded the alcohol, probably owing to attachment of bromine to phosphorus and of hydrogen to oxygen: $P(OR)_3 + HBr \longrightarrow PBr(OR)_2 + ROH$, etc. The basic function of the lone pair of electrons on the phosphorus atom appears to have been obliterated, and the phosphorus atom has become reluctantly electrophilic. The phosphites of ordinary alcohols quickly give alkyl bromide by a mechanism which is most probably represented by

$$P(OR)_3 + HBr \longrightarrow Br^- + PH^+(OR)_3 \longrightarrow RBr + O{:}PH(OR)_2$$

(Gerrard, *J.*, 1945, 848; Gerrard and Whitbread, *J.*, 1952, 914). This phosphite, like that of 2 : 2 : 2-trichloroethanol (Gerrard *et al.*, *J.*, 1954, 1148), gave the trialkyl phosphate, and not the chloridate, with chlorine. A similar result was obtained with bromine.

The reaction between the alcohol and boron trichloride alone slowly afforded trialkyl borate, but was not rapid enough in the presence of pyridine to compete successfully with the quick formation of pyridine–boron trichloride complex. Ordinary alcohols gave mainly the borate in these circumstances (Gerrard and Lappert, *J.*, 1951, 1020, 2545).

In the presence of base, acetyl chloride readily reacted with the alcohol to give the acetate in good yield.

Preliminary experiments were conducted with ether as solvent and pyridine absent and, since there was no evolution of hydrogen chloride, it was deemed advisable to use *n*-hexane in order to achieve a higher reflux temperature and also to avoid any retention by ether of whatever hydrogen halide was formed. When pyridine was used, a cleaner separation of base hydrochloride was effected with ether as solvent.

In hundreds of experiments on the interaction of alcohols and non-metallic inorganic halides in the presence of pyridine, no difference in reactivity has yet been detected according to whether the solvent was ether, *n*-pentane, or *n*-hexane.

Experimental

All solvents were vigorously dried, all reagents were purified, and liquids were mixed slowly dropwise with vigorous shaking. Base hydrochloride precipitates were analysed.

Experiments with 1 : 1 : 1 : 3 : 3 : 3-*Hexachloropropan-2-ol and Reagents in Absence of Pyridine.*—The following results are mentioned to show the inertness of the alcohol towards the reagents. The alcohol (4·002 g., 3 mols.) and phosphorus trichloride (0·687 g., 1 mol.) were heated in refluxing *n*-hexane (50 c.c.) for 72 hr. The alkali trap contained chloride ion (0·007 g.). Volatile matter was removed at 15°/20 mm. and trapped (Found: Cl, 0·440 g.), and the residue of alcohol (4·001 g.) had m. p. 87°, mixed m. p. 87°. Similarly the alcohol was quantitatively recovered when it (5·336 g., 2 mols.) was heated in *n*-hexane with thionyl chloride (1·190 g., 1 mol.) for 72 hr. Similarly the alcohol (5·336 g., 4 mols.), m. p. 88°, was recovered after being heated in *n*-hexane with silicon tetrachloride (0·850 g., 1 mol.) for 72 hr. The alcohol (2·668 g., 1 mol.) and acetyl chloride (0·785 g., 1 mol.) were heated in *n*-hexane (20 c.c.) for 72 hr., and the final residue (2·712 g.) gave purified alcohol (2·50 g.), m. p. 86°.

When phosphorus oxychloride (0·767 g., 1 mol.) and the alcohol (4·002 g., 3 mols.) were heated in *n*-hexane (35 c.c.) for 72 hr., no hydrogen chloride was evolved, and all the chlorine of the oxychloride remained easily hydrolysable. The oxybromide (0·717 g., 1 mol.) and alcohol (2·001 g., 3 mols.) under similar conditions afforded about one-sixth of the bromine as hydrogen bromide during 86 hr. Addition of pyridine and ethanol to the resulting solution gave base hydrobromide (Found : Br, 0·404 g.). Similarly the tribromide (0·677 g., 1 mol.) and alcohol (2·001 g., 3 mols.) gave hydrogen bromide (0·182 g.) during 72 hr., and the residue gave base hydrobromide (Found : Br, 0·379 g.). From the alcohol (4·002 g.) and tribromide (1·354 g.), all volatile matter including unchanged tribromide being removed *in vacuo*, the alcohol (1·85 g. after several recrystallisations from *n*-hexane), m. p. 88°, was recovered. The pentabromide (0·431 g., 1 mol.) and alcohol (1·334 g., 5 mols.) under similar conditions afforded hydrogen bromide (0·134 g.) during 86 hr., and the residue contained unchanged pentabromide (Found : Br, 0·276 g.).

Boron trichloride (1·445 g., 1 mol.) in *n*-hexane (100 c.c.) (at −10°) was added to a suspension of the alcohol (9·886 g., 3 mols.) in *n*-hexane (100 c.c.) at −80°. No reaction was apparent until after the mixture had remained at 0° for 2 hr. The mixture was kept at 10° for about 12 hr., whereupon the absorption tubes contained chlorine (0·0631 g.) and boron (0·0032 g.); it was then heated under reflux for 6 hr., and the fresh tubes then contained chlorine (0·9822 g.) and boron (0·0086 g.). The solvent was removed *in vacuo*, and the condensed liquid contained no ionisable chlorine. The residue of *trialkyl borate* (10·024 g. Calc. : 10·236 g.) had m. p. 322° (m. p. 312—313° after repeated recrystallisation from toluene in which it had limited solubility) (Found : C, 14·5; H, 0·9; Cl, 78·4; B, 1·35. $C_9H_3O_3Cl_{18}B$ requires C, 13·35; H, 0·35; Cl, 79·0; B, 1·34%). After being recrystallised from chloroform, the borate had m. p. 325° (Found : C, 14·6; H, 0·7; Cl, 78·9; B, 1·34%), but the m. p. returned to 313° on recrystallisation from toluene. Only 12% was hydrolysed by 0·1N-sodium hydroxide during 7 days, and even after the mixture was heated under reflux for 2 hr. the 7% hydrolysis was accompanied by removal of chlorine from alkyl group. The boron content was determined by heating the ester (*ca.* 1·5 g.) under reflux with methanol (40 c.c.) and concentrated sulphuric acid (2 c.c.) for 2 hr. and then distilling off the trimethyl borate for hydrolysis and titration in the usual way.

A toluene solution (150 c.c.) of the alcohol (16·008 g., 6 mols.) and boric acid (0·618 g., 1 mol.) was heated under reflux for 5 hr., water being removed by anhydrous copper sulphate in a Soxhlet thimble (cf. Dupire, *Compt. rend.*, 1936, **202**, 2086). More boric acid (0·618 g.) was added, and heating was continued overnight. The borate (6·16 g., 38%) separated from the cooled solvent. After recrystallisation from toluene it had m. p. 310°, and after recrystallisation from chloroform, 324·5°.

Interaction of the Alcohol and Reagents in the Presence of Pyridine.—Phosphorus trichloride. The trichloride (1·375 g., 1 mol.) in ether (10 c.c.) was added dropwise to a well-shaken mixture of the alcohol (8·004 g., 3 mols.) and pyridine (2·373 g., 3 mols.) in ether (20 c.c.) at −10°. Base hydrochloride was immediately precipitated, and after several hours at room temperature the mixture was filtered. The residue (5·236 g.) comprised the phosphite (1·808 g.), m. p. 156°, and base hydrochloride (2·947 g., 2·55 mols.) which was removed by water. The ethereal solution afforded crude phosphite (6·3 g.), m. p. 150°, and after recrystallisation from ethyl acetate the yield of *tris*-1 : 1 : 1 : 3 : 3 : 3-*hexachloroisopropyl phosphite*, m. p. 161°, as white rhombic crystals, was 6·71 g. (81%) (Found : C, 13·35; H, 0·15; Cl, 78·0. $C_9H_3O_3Cl_{18}P$ requires C, 13·05; H, 0·35; Cl, 77·05%).

Phosphorus tribromide. Similarly the alcohol (24·012 g., 3 mols.), pyridine (7·122 g., 3 mols.), and the tribromide (8·123 g., 1 mol.) in ether (90 c.c.) at −20° gave an immediate precipitate of base hydrobromide. After 2 days at room temperature, the mixture was filtered. The residue (21·28 g.) comprised phosphite (8·35 g.), m. p. 158° (recrystallised, m. p. 161°), and base hydrobromide (14·26 g., 2·97 mols.) which was removed by water. Phosphite (16·55 g.), m. p. 158° (recrystallised, m. p. 161°), was obtained from the ethereal filtrate, the total yield being 21·97 g. (78·8%).

Phosphorus oxychloride. The alcohol (8·004 g., 3 mols.) and pyridine (2·373 g., 3 mols.) in ether (40 c.c.) were added to the oxychloride (1·534 g., 1 mol.) in ether (50 c.c.) at −10°. Precipitation of base hydrochloride was slow, and at the end of the mixing (1 hr.) about 1 mol. had separated. After 3 days at room temperature the mixture was filtered. The residue (2·342 g.) comprised alcohol (0·920 g.) and base hydrochloride (1·248 g., 1·08 mols.). This represents one of the three atoms of chlorine in the oxychloride. More salt (0·405 g., 0·35 mol.; mixed with alcohol, 0·210 g.) separated during 10 days. The solution was finally heated under reflux for 20 hr., whereafter from the cooled solution the salt (0·162 g., 0·14 mol.) and an

unidentified substance (0·108 g.), m. p. 140—150°, were precipitated. Removal of ether gave a residue (7·27 g.) of viscous heterogeneous material which has not yet been examined.

Phosphorus oxybromide. This reagent was prepared from phosphorus pentabromide and *iso*propanol as described by Gerrard, Nechvatal, and Wyvill (*Chem. and Ind.*, 1947, 437). Different orders of addition being tried, it was found that precipitation of base hydrobromide was fairly quick at −20°, but involved only two of the three bromine atoms. The mixture was allowed to remain at 15° for 3 days before filtration. The alcohol (8·004 g., 3 mols.) and pyridine (2·373 g., 3 mols.) in ether (40 c.c.) were added to the oxybromide (2·867 g., 1 mol.) in ether (40 c.c.) at −10°. The precipitate comprised base hydrobromide (3·296 g., 2·06 mols.) and a water-insoluble substance (0·592 g.), m. p. *ca.* 100°. Removal of ether at 15 mm. afforded a solid residue (9·17 g.), which was dissolved in hot *n*-heptane and a little ether, washed with water (2 × 40 c.c.), and dried. On removal of solvent, the residue which was insoluble in *n*-heptane had m. p. *ca.* 100°, and the *n*-heptane gave on concentration a solid at 0°, m. p. *ca.* 98°. Repeated recrystallisation of the latter by cooling its solution in boiling ethyl acetate and light petroleum (b. p. 100—120°) afforded a white solid, m. p. 282°, probably the pyrophosphate, $(RO)_2P(:O)\cdot O\cdot P(:O)(OR)_2$. When the primary ethereal filtrate was not washed with water, *bis*-1 : 1 : 1 : 3 : 3 : 3-*hexachloroisopropyl phosphorobromidate* (89% yield), m. p. 120° after recrystallisation from *n*-hexane (Found: C, 11·15; H, 0·4; Cl, 64·1; Br, 12·0; P, 4·2. $C_6H_2O_3Cl_{12}BrP$ requires C, 10·95; H, 0·3; Cl, 64·6; Br, 12·1; P, 4·7%), was obtained as white needles. Bromide ion was only slowly formed by hydrolysis with water; after being in contact with water and acetone for 4 hr. at room temperature, the bromidate was 10% hydrolysed, and the remainder, m. p. 120—121°, was quantitatively recovered. The bromidate reacted slowly with octanol in the presence of pyridine and ether at 15°. After 6 days what was probably the *mixed phosphate*, m. p. 194° after recrystallisation from *n*-hexane (Found: C, 20·1; H, 1·65; Cl, 61·5; P, 4·5. $C_{14}H_{19}O_4PCl_{12}$ requires C, 23·75; H, 2·7; Cl, 60·1; P, 4·4%), was obtained in 15% yield; and much of the bromidate, m. p. 119°, mixed m. p. 119°, was recovered.

Thionyl chloride. There was immediate precipitation of base hydrochloride (6·554 g., 1·89 mol.) when a solution of the alcohol (16·008 g., 2 mols.) and pyridine (4·746 g., 2 mols.) in ether (60 c.c.) was added to thionyl chloride (3·569 g., 1 mol.) in ether (100 c.c.) at −10°. Next morning, the solid was filtered off, and from the ethereal filtrate crude sulphite (quantitative), m. p. 58—62°, was obtained. On recrystallisation from light petroleum (b. p. 100—120°), a white solid, m. p. 64° was obtained, but the sulphite could not be completely freed from the alcohol, into which it appeared to decompose during a number of recrystallisations from *n*-hexane (Found: C, 12·9; H, 0·0; Cl, 74·0; S, 4·95. Calc. for $C_6H_2O_3Cl_{12}S$: C, 12·45; H, 0·35; Cl, 73·4; S, 5·5%).

Heptachloropropane could not be obtained from the sulphite by interaction with thionyl chloride in the presence of base hydrochloride (1 mol. or small amounts). The sulphite (17·20 g., 1 mol.) was mixed with thionyl chloride (3·57 g., 0·5 mol.) and base hydrochloride (0·08 g.). No reaction was apparent at 80° (1 hr.), nor at 100° (1 hr.); and at 140° (2 hr.) thionyl chloride distilled through the column. The distillate was returned, and the mixture kept at 15° overnight and, on being reheated, gave thionyl chloride (3·01 g.). The residue decomposed at 200°/10 mm., and afforded several distillates, from which heptachloropropane could not be isolated.

Silicon tetrachloride. With the tetrachloride (1·699 g., 1 mol.), pyridine (3·164 g., 4 mols.), and the alcohol (10·672 g., 4 mols.) in *n*-pentane (70 c.c.) at 20—25°, there was an immediate precipitation of base hydrochloride, which was estimated as 3·3 mols., whereas the alcohol (about 1·7 g.) was recovered. Little could be done with the thick oil (8·61 g.) left by the evaporated solvent. When the alcohol (8·004 g.) and pyridine (2·373 g.) were restricted to 3 mols. for 1 mol. of tetrachloride (1·699 g.) only 2·2 mols. of base hydrochloride were precipitated from ethereal solution. Again the sticky residue (7·89 g.) from the ether was intractable.

In attempts to obtain crystalline solids, octyloxychlorosilanes were used. These were prepared by the addition of octan-1-ol (65 g., 1 mol.) in ether (40 c.c.) to silicon tetrachloride (85 g., 1 mol.) in ether (25 c.c.) at 0°, nitrogen being passed into the mixture. After 1 hr., volatile matter was removed at 15°/15 mm., and after protracted fractionations the following liquids together with mixtures were obtained: octyloxytrichlorosilane (84·0 g.), b. p. 105°/9 mm., $n_D^{20\cdot5}$ 1·4315 (Found: Cl, 40·3. Calc. for $C_8H_{17}OCl_3Si$: Cl, 40·35%); dioctyloxydichlorosilane (21·4 g.), b. p. 138—140°/0·5 mm., $n_D^{20\cdot5}$ 1·4360 (Found: Cl, 19·95. Calc. for $C_{16}H_{34}O_2Cl_2Si$: Cl, 19·85%), and trioctyloxychlorosilane (9·1 g.), b. p. 175—180°/0·5 mm., $n_D^{20\cdot5}$ 1·4373 (Found: Cl, 9·7. Calc. for $C_{24}H_{51}O_3ClSi$: Cl, 8·15%).

The trichlorosilane (2·637 g., 1 mol.) in ether (20 c.c.) was added to the alcohol (8·004 g.,

3 mols.) and pyridine (2·373 g., 3 mols.) in ether (50 c.c.) at −20°. Base hydrochloride was immediately formed. Next morning the precipitate was filtered off, and it comprised hydrochloride (2·589 g., 2·24 mols.) and the alcohol (1·337 g.), m. p. 86°. The ethereal filtrate gave a viscous oil (9·03 g.). Similarly the dichlorosilane (3·574 g., 1 mol.), pyridine (1·582 g., 2 mols.), and the alcohol (5·336 g., 2 mols.) gave base hydrochloride (2·243 g., 1·94 mol.), unchanged alcohol (0·152 g.), and a residue (8·02 g.), which, after being redissolved in ether, washed, and dried, afforded a liquid, probably the mixed *di*-n-*octyloxydi*-1 : 1 : 1 : 3 : 3 : 3-*hexachloro*iso*propoxysilane* (Found : Cl, 52·1; Si, 3·5. $C_{22}H_{36}O_4Cl_{12}Si$ requires Cl, 51·9; Si, 3·45%).

Boron trichloride. The analysis of this system was protracted. The trichloride (1·058 g., 1 mol.) in *n*-hexane (20 c.c.) was added to the alcohol (7·224 g., 3 mols.) and pyridine (2·142 g., 3 mols.) in *n*-hexane (50 c.c.) at 20° (at lower temperatures the alcohol separates). Next morning the precipitate was filtered off, and the filtrate gave a viscous liquid (6·46 g.) which slowly solidified (several days). It afforded pyridine (0·77 g.) and the alcohol (5·45 g., 75·4% recovery), m. p. and mixed m. p. 87°. The precipitate (2·488 g.) comprised pyridine hydrochloride (0·705 g.) and a water-insoluble material (2·349 g.) which softened at 75°, melted with decomposition at 210°, and appeared to comprise pyridine–boron trichloride complex (1·119 g.) and some alkoxyboron chloride.

Reactions with the Phosphite.—At room temperature there was a period of 30 min. before chlorine reacted with the phosphite, and then a vigorous, exothermic reaction ensued. The dry gas was passed into a solution of the phosphite (2·073 g.) in ether at −10° for 1·5 hr.; but no absorption occurred. During the evaporation of the solvent *in vacuo* at room temperature (10 min.) the vigorous reaction again occurred, and a phosphine-like odour was detected. More ether was added, and complete saturation with gas at room temperature was effected. Volatile matter was removed *in vacuo*, and the white *tris*-1 : 1 : 1 : 3 : 3 : 3-*hexachloro*iso*propyl phosphate* (1·82 g.) had m. p. 182° unchanged on recrystallisation from *n*-hexane (Found : C, 13·05; H, 0·75; Cl, 75·5; P, 3·7. $C_9H_3O_4Cl_{18}P$ requires C, 12·8; H, 0·35; Cl, 75·6; P, 3·65%). By means of carbon dioxide bromine vapour was passed into the phosphite (2·156 g.) at room temperature. Removal of volatile matter *in vacuo* afforded a residue (2·12 g.), m. p. 182° unchanged on recrystallisation from *n*-hexane (Found : C, 13·05; H, 0·55; Cl, 73·85; P, 3·7%). The m. p. was undepressed by the previous specimen of phosphate. There was no easily hydrolysable halogen present.

The phosphite (4·145 g., 1 mol.) was recovered, m. p. and mixed m. p. 160°, after it had been heated with ethyl iodide (0·780 g., 1 mol.) in chloroform (10 c.c.) for 40 hr. at 100°.

Dry hydrogen chloride was passed into the phosphite (4·145 g.) in ether (10 c.c.) for 10 hr. at 20°. After removal of volatile matter, the residue (4·13 g.), m. p. 148°, was dissolved in hot *n*-hexane and treated with charcoal, and the solution was filtered and cooled. Phosphite (2·3 g., 55·5%), m. p. 160°, and, from the mother-liquor, more phosphite (1·2 g.) were obtained, the total recovery being 84·5%.

Dry hydrogen bromide was passed into the phosphite (3·481 g.) in ether (10 c.c.) for 3 hr. at 20°. Removal of volatile matter *in vacuo* gave a solid (3·285 g.), m. p. 142°, which, after repeated recrystallisation from *n*-hexane, gave the phosphite (0·61 g.), m. p. 158° (Found : C, 13·35; H, 0·15; Cl, 78·2. Calc. : C, 13·05; H, 0·35; Cl, 77·05%). A solution of the phosphite (6·004 g.) in ether (200 c.c.) was saturated with hydrogen bromide (6·5 hr.) and stored for 2 days. It was heated under reflux for 6 hr., and volatile matter was removed at 20°/20 mm. The red fuming liquid (7·38 g.) afforded the alcohol (3·95 g.), m. p. 87—88° (Found : C, 13·85; H, 0·85; Cl, 80·3. Calc. for $C_3H_2OCl_6$: C, 13·5; H, 0·75; Cl, 79·75%), which was extracted by hot *n*-hexane. The residue contained bromine.

The Alcohol, Acetyl Chloride, and Pyridine.—The alcohol (4·002 g., 1 mol.) and pyridine (1·187 g., 1 mol.) in ether (50 c.c.) were added to acetyl chloride (1·177 g., 1 mol.) in ether (100 mm.) at −15°. Base hydrochloride was formed at once, and the precipitate comprised alcohol (0·325 g.) and hydrochloride (1·711 g., 0·987 mol.). The filtrate residue (4·635 g.) had m. p. 42°, m. p. 45° after repeated recrystallisation from light petroleum (b. p. 100—120°), and was the *acetate* (white platelets) (Found : C, 19·65; H, 1·45; Cl, 68·5. $C_5H_4O_2Cl_6$ requires C, 19·45; H, 1·3; Cl, 68·9%).

Preparation of Hexachloroacetone.—Difficulty has been experienced in our attempts to prepare hexachloroacetone by procedures described in the literature. By passing chlorine into monochloroacetone at temperatures up to 100° (F.P. 816,956, *Chem. Zentr.*, 1938, I, 2216; F.P. 837,741, *Chem. Zentr.*, 1939, II, 228), little better than the tetrachloroacetone was obtained. Granacher, Usteri, and Geiger (*Helv. Chim. Acta*, 1949, **32**, 703) had a similar experience. Edwards, Evans, and Watson (*J.*, 1937, 1942) did not give quantities of reactants or yields

of product in describing their procedure; but Dr. H. B. Watson kindly gave us the necessary information. Chlorine was passed into a refluxing and stirred mixture of tetrachloroacetones (1425 g.) (prepared by chlorinating acetone), acetic acid (90%, 1·72 l.), and sodium acetate (71 g.) under ultra-violet light for 55 hr., and then without it for a further 54 hr. Water (5 l.) was added; the oil was dried (Na_2SO_4) and distilled (b. p. 80—110°/13 mm.). Extraction of the aqueous layer with chloroform (5 × 150 c.c.; and then continuously for 10 hr.), followed by low-pressure removal of solvent from the dried solution, afforded a distillate, b. p. 60—200°/13 mm., which was combined with the former distillate; the whole was fractionated through a 75 × 2·5 cm. column packed with single-turn glass helices, jacketed electrically, and fitted with a variable take-off, total reflux head. Hexachloroacetone (520 g., 35%), b. p. 110°/40 mm., n_D^{20} 1·5103 (Found : C, 13·55; Cl, 80·5. Calc. for C_3OCl_6 : C, 13·6; Cl, 80·3%), and pentachloroacetone (16%) were obtained, and tetrachloroacetone (30%) was recovered.

Reduction of Hexachloroacetone (cf. Geiger, Usteri, and Granacher, *Helv. Chim. Acta*, **1951**, **34**, 1335).—The ketone (26·5 g.) in ether (50 c.c.) was added (1 hr.) to a suspension of lithium aluminium hydride (1·2 g.) in ether (50 c.c.). Mixing being complete (−10°), the mixture was stirred for 2 hr. at 0° and then cautiously added to ice (200 g.) and 2N-sulphuric acid (100 c.c.). The ethereal layer was separated, the aqueous layer extracted several times with ether, and the combined solution, after being dried (Na_2SO_4), afforded 1 : 1 : 1 : 3 : 3 : 3-hexachloropropan-2-ol (95%), b. p. 124°/10 mm., needles, m. p. 87—88° (Found : C, 13·45; H, 0·75; Cl, 79·3. Calc. for $C_3H_2OCl_6$: C, 13·5; H, 0·75; Cl, 79·75%). When the reduction was carried out at 35°, the yield was 81%. Information about two patents by Woolf and Gilbert (U.S. 2,635,117—8/1953) concerning the preparation of polychloroacetones has recently become available.

Choice of Solvent.—So far as solubility is concerned, ether is a more convenient solvent than *n*-hexane; but as preliminary experiments with ether as solvent gave no sign of reaction, it was deemed desirable to use *n*-hexane in order to achieve a higher reflux temperature and at the same time considerably reduce any retention of hydrogen chloride which would be formed if reaction had occurred to any appreciable extent. The following result illustrates the behaviour when ether was used as solvent. Hexachloropropan-2-ol (4·002 g., 3 mol.) in dry ether (35 c.c.) was added to phosphorus trichloride (0·687 g., 1 mol.), and the mixture was heated under reflux for 72 hr. No hydrogen chloride was absorbed in the trap containing potassium hydroxide. Unchanged phosphorus trichloride was removed *in vacuo* with the ether and condensed in a liquid-nitrogen trap (Found : Cl, 0·507 g. Cl in system : 0·532 g.). The residue (4·008 g.) had m. p. 85—86°, alone or mixed with hexachloropropan-2-ol. Thus recovery of the alcohol was 100%.

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