CCCXVII.—*The Formation of Triphenylmethylphosphinic Acid from Triphenylmethoxyphosphorus Dichloride. Part II. The Mechanism of the Reaction.*

By Harold H. Hatt.

The action of phosphorus trichloride on triphenylcarbinol leads to the formation of a phosphorus dichloride, to which Boyd and Chignell (J., 1923, **123**, 813) assigned the constitution (I).

$Ph_3C{\cdot}O{\cdot}PCl_2$ (I.) $Ph_3C{\cdot}O{\cdot}P(OH)_2$ (II.) $Ph_3C{\cdot}PO(OH)_2$ (III.)

This compound displays a much greater stability towards hydrolysing agents than analogous compounds derived from aliphatic alcohols, but is nevertheless hydrolysed to the carbinol by hot aqueous acids or alkalis. Alcoholic potash transforms it into an acid to which formula (II) was first assigned. Later Boyd and Smith (J., 1924, **125**, 1477) found that its properties were in better agreement with the phosphinic acid constitution (III); the acid was dibasic and, unlike the phosphorus dichloride (I), the link between the triphenylmethyl group and the phosphorus residue could be broken only with difficulty.

It was thus necessary to suppose that the reaction between alcoholic potash and (I) involved a molecular rearrangement, the triphenylmethyl group migrating from oxygen to phosphorus. Abundant reason for the migration could be found in the tendency for tervalent phosphorus to attain a higher valency state, and the ease with which the triphenylmethyl radical acquires a positive charge should facilitate migration.

The reaction with alcoholic potash is of a complex character. Boyd and Smith found that the product of the reaction contained roughly equal amounts of the acid (III) and its monoethyl ester (reaction i). Subsequent investigation of various triarylmethoxyphosphorus dichlorides (J., 1926, 2323) showed that, besides the production of phosphinic acids, the action of alcoholic potash led to the formation of some carbinol or its ethyl ether as the result of fission at the carbinol carbon atom (reaction ii). The extent to which reactions (i) and (ii) took place depended much on the nature of the triarylmethyl group.

In continuing these investigations it therefore seemed desirable to examine the alcoholysis of the parent dichloride in greater detail, and the progress of the reaction between the phosphorus dichloride (I) and sodium ethoxide in absolute alcohol has been followed. The rate of formation of solid sodium chloride furnishes a measure of the rate of alcoholysis of the phosphorus dichloride. At the same time the phosphorus-containing products of the reaction have been examined by pouring the reaction mixture, after removal of sodium chloride, into water and precipitating the acidic phosphorus compounds by acidification. The table summarises the results obtained when 2·5*N*-alcoholic sodium ethoxide was employed.

Expt.	Time of reaction (minutes).	% of chlorine removed.	Product of the reaction.	Yield calc. as phosphinic acid.
1	3	59	Triphenylmethylphosphinic acid.	85%
2	10	67·5	—	89
3	60	91·2	24% Phosphinic acid, 76% monoethyl ester.	90
4	240	99·8	Monoethyl ester.	93

These experiments show that the removal of the chlorine atoms proceeds in definite stages. The removal of the first atom is rapid, the velocity of the reaction being determined chiefly by the rate of dissolution of the phosphorus dichloride in the alcohol; the second is removed more slowly, and this reaction is complete only after 4 hours. Prolonging the reaction to effect the alcoholysis of the second chlorine atom causes only a small increase in the yield calculated as phosphinic acid (column 5); although it brings about a complete change in the nature of the product isolated (col. 4). The formation of the phosphinic acid, and in such large amounts, in Expt. 1 was unexpected. A *chloro-acid*, $Ph_3C{\cdot}POCl(OH)$ (IV), can be isolated at this stage by acidifying the reaction mixture with alcoholic hydrogen chloride. This substance, having regard to its constitution, is noticeably stable and so far appears to be the only compound of this class that has been isolated. Lange (*Ber.*, 1929, **62**, 786, 793, 1084) has described the isolation of salts of mono- and di-fluorophosphoric acids, but the acids themselves seem to exist only in dilute aqueous solutions. The substance (IV) is stable in cold water and undergoes very slow decomposition in boiling alcohol, from which it can be crystallised. It behaves as a monobasic acid and forms well-defined salts with silver and with organic nitrogen bases. Hot aqueous alkalis bring about complete transformation to the phosphinic acid, whose appearance at this stage is thus explained.

Whilst (IV) must be regarded as an intermediate product in this alcoholysis, it is not produced directly from the phosphorus dichloride. If the concentration of the sodium ethoxide solution is reduced to 0·2—0·5*N*, the *chloro-ester* $Ph_3C[OPCl(OEt)]$ * (V) is obtained in good yields (85%). With alkali of this concentration, the first chlorine atom is rapidly removed, and the production of (V), at present, may be considered the first stage in the alcoholysis of the phosphorus dichloride.

Heating for a few minutes with 2*N*-sodium ethoxide solution transforms (V) almost entirely into (IV); since also the reaction of the phosphorus dichloride with sodium ethoxide solution is accompanied by the production of diethyl ether, the formation of (IV) may be represented by equation (2). In some experiments the pure diethyl ether isolated represented about 60% of the amount required by this equation. All concentrations of alcoholic sodium ethoxide convert (IV) and (V) by long treatment into the monoethyl ester of the phosphinic acid. This is the final product of complete alcoholysis, the general course of which may be formulated :

$$(1)\quad Ph_3C{\cdot}O{\cdot}PCl_2 \xrightarrow[NaOEt]{} Ph_3C[O{\cdot}PCl(OEt)].$$

$$(2)\quad Ph_3C[O{\cdot}PCl(OEt)] + NaOEt = Ph_3C{\cdot}POCl(ONa) + Et_2O.$$

$$(3)\quad Ph_3C{\cdot}POCl(ONa) \xrightarrow[NaOEt]{} Ph_3C{\cdot}PO(OEt)(ONa).$$

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* The square brackets in this formula indicate that the point of attachment of the triphenylmethyl group has not been decided.

When the phosphorus dichloride is treated for a short time with more concentrated solutions of sodium ethoxide, it is possible to isolate diethyl triphenylmethylphosphinate, $Ph_3C{\cdot}PO(OEt)_2$ (VI). Its yield increases with increasing concentration of the ethoxide solution, and at 4*N* amounts to 20%. The diethyl ester does not normally appear as a product of the alcoholysis of the phosphorus dichloride, because prolonged action of sodium ethoxide solutions causes hydrolysis to the monoethyl ester. The mode of formation of (VI) from the phosphorus dichloride is made clear by the fact that (V) is also partly converted (20%) into (VI) by reaction for a few minutes with concentrated ethoxide solutions. For highly concentrated solutions of sodium ethoxide there exists, therefore, the alternative course :

(4) $Ph_3C[O{\cdot}PCl(OEt)] \xrightarrow[NaOEt]{} Ph_3C{\cdot}PO(OEt)_2$.

(5) $Ph_3C{\cdot}PO(OEt)_2 + NaOEt = Ph_3C{\cdot}PO(OEt){\cdot}ONa + Et_2O$.

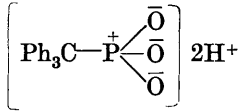
The reaction involving fission at the carbinol carbon atom (reaction ii) is small : values of 2—3% have been obtained.

Difficulty is encountered when an attempt is made to decide the stage in the alcoholysis of the phosphorus dichloride accompanied by rearrangement. The phosphorus dichloride is converted into the carbinol by sulphuric acid and hot aqueous acids or alkalis; formic acid, hydriodic–acetic acid mixtures, and alcoholic sulphuric acid cause reduction to triphenylmethane. These reagents cannot effect the elimination of the triphenylmethyl group from the phosphinic acid or its monoethyl ester, which form the final products of the alcoholysis. Such marked differences in stability are in agreement with the structures already assigned to these compounds, but the phosphinic acid behaves anomalously towards phosphorus pentachloride, triphenylchloromethane being produced instead of the expected phosphinyl dichloride. It is not possible to decide the constitutional formulæ of the intermediate products (IV), (V), and (VI) by a mere reference to their behaviour towards hydrolysing agents, for they display a dual character in this respect.

The diethyl ester (VI) has been shown to be diethyl triphenylmethylphosphinate, being obtained also by the action of ethyl iodide on the silver salt of the monoethyl ester.

The properties of the chloro-acid (IV) seem to point to a constitution resembling the phosphinic acid : $Ph_3C{\cdot}POCl(OH)$. It displays marked acid properties although possessing but one hydroxyl group, and is transformed to the phosphinic acid with ease, for example, by boiling with water. On the other hand, it is decomposed by sulphuric acid, producing triphenylcarbinol.

In the chloro-ester (V) the chlorine atom possesses remarkable stability. The substance is unchanged by boiling (4 hrs.) with water, alcohol, or aqueous alkalis. It is attacked by hydriodic–acetic acid mixtures or alcoholic sodium ethoxide, but in each case the chlorine atom is at first untouched, the chloro-acid (IV) being produced. Prolonged action of these reagents produces the phosphinic acid or its monoethyl ester; in view of their peculiar course these reactions can, however, furnish little support for assigning a phosphinic constitution to (V). With sulphuric acid the chloro-ester yields the carbinol and with formic acid undergoes partial reduction to triphenylmethane. Its behaviour is thus ambiguous and its constitution must be regarded as still undecided. For these reasons it is not possible to indicate the stage in the alcoholysis of the phosphorus dichloride accompanied by rearrangement.

If the chloro-acid is assigned the constitution (IV), its instability towards sulphuric acid is unexpected, for this reagent fails to convert the phosphinic acid into the carbonium sulphate. The difference may be explained by the difficulty which would attend the removal of the triphenylmethyl kation from the phosphinic acid, when ionised in solution. The substance  $\left[\mathrm{Ph_3C{-}\overset{+}{P}}\begin{matrix}\bar{\mathrm{O}}\\ \bar{\mathrm{O}}\\ \bar{\mathrm{O}}\end{matrix}\right]2\mathrm{H}^+$ (VII) would be expected to be sulphonated with relative ease and in fact sulphonation takes place rapidly at 70°. The chloro-acid at the same temperature yields the carbonium sulphate. Here the sulphuric acid first effects a loss of hydrogen chloride, and the product, no longer ionisable, is then sulphonated with difficulty, but offers little resistance to the formation of triphenylmethyl kation. Similar arguments would apply in the case of the chloro-ester. The un-ionisable diethyl ester cannot be converted into the carbonium sulphate, no doubt owing to the ease with which the ethoxy-groups are hydrolysed; both are removed by dilute aqueous acids and their removal probably forms the first stage in the action of sulphuric acid, which subsequently effects sulphonation. The production of triphenylchloromethane from the phosphinic acid and phosphorus pentachloride can be explained on the same basis, the un-ionisable phosphinyl dichloride being first produced.

Arbuzov (*Chem. Centr.*, 1929, I, 2729) * has considered the possi-

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* [Note added, October 15th.]—Access to the original work of Arbuzov and Arbuzov (*J. Russ. Phys. Chem. Soc.*, 1929, **61**, 217) was not possible when this paper was written. Those authors did not, as stated in *British Chemical Abstracts*, 1929, **A**, 832, obtain the dialkyl esters of the phosphinic acid by treating the phosphorus dichloride with the sodium derivatives of different alcohols, and the dialkyl esters were obtained from triphenylbromomethane and the trialkyl phosphites, not the dialkyl phosphites.

bility that the phosphorus dichloride might possess the alternative formula $Ph_3C{\cdot}POCl_2$ (VIII). He prepared diethyl triphenylmethylphosphinate from triphenylbromomethane and triethyl phosphite and considered that, if this ester could be obtained by the action of sodium ethoxide on the phosphorus dichloride, the formula (VIII) would be proven. Arbuzov did not obtain this ester by the second method and left the structure of the phosphorus dichloride undecided. The ester, now obtained by the second method, appears to be identical with that of Arbuzov. This cannot be considered as support for the constitution (VIII), for the reason that this second method of preparation utilises precisely that reaction in which Boyd assumed rearrangement to take place.

At present the evidence is not sufficient to enable a final decision to be made with regard to the formula of the phosphorus dichloride. Formula (I) offers an explanation of its properties and is in agreement with the manner of preparation. On the other hand, the gradation of properties shown by the chloro-ester, chloro-acid, and phosphinic acid indicates that a phosphinyl dichloride (VIII) might possess properties not unlike those of the known dichloride.

Experiments are in progress which it is hoped will furnish a solution of this problem.

EXPERIMENTAL.

The data recorded in the table were obtained as follows: 2 g. of powdered triphenylmethoxyphosphorus dichloride and 13·3 c.c. (6 mols.) of a 2·5*N*-solution of sodium ethoxide in 99·7% alcohol were placed in a flask provided with a reflux condenser and calcium chloride guard tube. The mixture was heated rapidly on a water-bath, and the reaction assumed to commence at the first appearance of a vigorous ebullition. After refluxing for the desired time, the mixture was cooled rapidly to 16°. The precipitated sodium chloride was collected in a Gooch crucible, washed with a saturated solution of sodium chloride in absolute alcohol, and estimated volumetrically. The values obtained were corrected for the solubility of sodium chloride in absolute alcohol at 16°. A small quantity of the phosphorus dichloride remained unchanged if the reaction was interrupted after a short time, but when the phosphorus dichloride employed was finely divided the amount recovered never exceeded 0·5%.

The alcoholic filtrates from the sodium chloride were poured into water, the alcohol was removed by boiling, and the solution was filtered to remove neutral phosphorus compounds and acidified. The precipitate was collected, washed with hydrochloric acid until free from inorganic phosphorus compounds, and dried to constant weight at 100°. It consisted of a mixture of triphenylmethylphosphinic acid and its monoethyl ester; its yield was computed as phosphinic acid, based on a determination of its phosphorus content. Many experiments show that the values thus obtained are trustworthy to within 2%.

Almost pure triphenylmethylphosphinic acid was formed when the phosphorus dichloride was refluxed with the sodium ethoxide solution for 3 minutes; it contained 9·7% of phosphorus (theory requires 9·6%), and after crystallisation from benzene melted at 274—276°, alone or mixed with the pure phosphinic acid. Prolonged action of sodium ethoxide solution produced practically pure monoethyl ester of the phosphinic acid. At intermediate times, in agreement with the observations of Boyd and Smith (*loc. cit.*), mixtures of the acid and its ester were obtained, whose compositions could be calculated approximately from their phosphorus content.

Ethyl Hydrogen Triphenylmethylphosphinate.—This *ester* forms the sole acid phosphorus product after 6 hours' heating, 9·4 g. being obtained from 10 g. of triphenylmethoxyphosphorus dichloride. It is difficultly soluble in most organic solvents. Crystallised from benzene, it melts at 259°. It dissolves in sulphuric acid, but produces no colour: hydriodic–acetic acid mixtures convert it into the phosphinic acid (Found: P, 8·7. $C_{21}H_{21}O_3P$ requires P, 8·8%).

The *silver* salt was obtained as a crystalline white precipitate by the addition of silver nitrate to a hot aqueous solution of the ammonium salt (Found, after drying to constant weight at 110°: P, 6·8; Ag, 22·8. $C_{21}H_{20}O_3PAg$ requires P, 6·8; Ag, 23·5%).

Triphenylmethylchlorophosphinic Acid (IV).—Triphenylmethoxyphosphorus dichloride (4 g.) and 26·6 c.c. of a 2·5*N*-solution of sodium ethoxide in absolute alcohol were heated under reflux for 3 minutes and cooled rapidly, and 30 c.c. of a solution of concentrated hydrochloric acid in absolute alcohol ($N = 1·86$) slowly added, the mixture being shaken and cooled. Water was then added until the mixture became clear, any unchanged phosphorus dichloride remained insoluble and was removed, and 300 c.c. of water, strongly acidified with hydrochloric acid, were added to the filtrate. An oil separated which, after solidifying, was washed with water, dried at 100°, powdered, and extracted twice for 2 hours with 15—20 c.c. of boiling dry benzene. The *product* (3·03 g.; yield, 80%) melted at 226—227° (Found: P, 9·0; Cl, 10·3. $C_{19}H_{16}O_2ClP$ requires P, 9·1; Cl, 10·35%).

The substance is almost insoluble in non-hydroxylic solvents. The melting point varies with the rate of heating and fusion is accompanied by complete decomposition into hydrogen chloride and a vitreous residue; the pure crystallised product usually melts at 233—234°. Complete hydrolysis to the phosphinic acid is effected by heating with formic acid, acetic acid, or water.

On addition of the theoretical amount of aniline to a solution of triphenylmethylchlorophosphinic acid in absolute alcohol, the *aniline* salt was precipitated as a crystalline white powder, m. p. 182—182·5° (151—156° by rapid heating). It contained one molecule of alcohol of crystallisation, which was expelled by heating at 100° under reduced pressure; under similar conditions at 60°, the alcohol was retained (Found: N, 2·8; P, 6·5; C_2H_6O, 9·8. $C_{25}H_{23}O_2NClP,C_2H_6O$ requires N, 2·9; P, 6·45; C_2H_6O, 9·6%).

The *quinoline* salt, prepared in like manner, formed large colourless crystals, m. p. 181·5—182·5° (Found: P, 6·6; Cl, 7·2. $C_{28}H_{23}O_2NClP$ requires P, 6·6; Cl, 7·5%).

The Chloro-ester (V).—A mixture of 2 g. of triphenylmethoxyphosphorus dichloride and 66 c.c. of a 0·5*N*-solution of sodium ethoxide in absolute alcohol was refluxed for 3 minutes, cooled rapidly, and the solution filtered to remove any unchanged dichloride. Water (400 c.c.) was added with stirring and, after 1 hour, the crystalline material which had separated was collected, washed, and dried at 100°. Yield, 1·7 g. (83%). Crystallised many times from benzene and light petroleum (b. p. 40—60°), it formed colourless crystals, m. p. 137·5—138°. Alternatively the *chloro-ester* may be isolated by pouring the filtered alcoholic solution into excess of hot water (85°) and after 30 minutes collecting the crystalline material; the product, m. p. 135—137°, is obtained in smaller yield, but is free from the phosphinic acid, traces of which are present when the first method is employed (Found: P, 8·1; Cl, 9·7; EtO, 11·45; *M*, cryoscopic in benzene, 367, 385. $C_{21}H_{20}O_2ClP$ requires P, 8·4; Cl, 9·6; EtO, 12·15%; *M*, 371). When heated at 50—60° for 10 minutes with a 3 : 1 mixture of sulphuric and acetic acids, the chloro-ester is converted quantitatively into triphenylcarbinol.

Arbuzov (*loc. cit.*) has described a chloro-ester (m. p. 125—126°) which is probably identical with the substance now described.

Conversion of the Chloro-ester (V) *into Triphenylmethylchlorophosphinic Acid* (IV). (1) *By alcoholic sodium ethoxide.* The chloro-ester (2·053 g.) and 13·3 c.c. of a 2·08*N*-solution of sodium ethoxide in absolute alcohol were heated to refluxing for 3 minutes. The subsequent procedure was the same as described in the preparation of (IV). The product, purified by extraction with hot benzene, consisted of almost pure triphenylmethylchlorophosphinic acid, m. p. 229—229·5°. Yield, 1·407 g. (74%).

(2) *By hydriodic–acetic acid mixture.* 2 G. of the chloro-ester were heated under reflux with a mixture of hydriodic acid (6 c.c.) (b. p. 126°) and glacial acetic acid (12 c.c.) for 8 minutes, the product was cooled, and the crystalline material collected, washed with dilute sulphurous acid and water, dried at 100°, and extracted twice

with hot benzene; 1·47 g. (80%) of pure triphenylmethylchlorophosphinic acid (m. p. 233—234°) were obtained (Found : P, 9·1; Cl, 10·1. Calc. : P, 9·1; Cl, 10·35%).

Diethyl Triphenylmethylphosphinate (VI).—A mixture of 20 g. of triphenylmethoxyphosphorus dichloride and 82 c.c. of 4*N*-alcoholic sodium ethoxide was refluxed for 3 minutes, the reaction mixture poured at once into excess of water, and the alcohol expelled by heating on a water-bath. The insoluble material was removed, washed, and dried at 100° (yield, 3·62 g.; 17·2%). Crystallisation from ether and light petroleum (b. p. 40—60°) yielded a white crystalline powder, m. p. 120—121°.

The reaction between the phosphorus dichloride and concentrated sodium ethoxide is vigorous and difficult to control, and the product is contaminated with small amounts of material resulting from fission at the carbinol carbon atom. The diethyl ester was more conveniently prepared by heating together 3·5 g. of the chloro-ester and 12 c.c. of 3·5*N*-alcoholic sodium ethoxide for 2·5 minutes, 0·65 g. (21%) being obtained; crystallised from ether and light petroleum, it melted at 120—121° [Found : P, 8·25; EtO, 23·1. Calc. for $C_{19}H_{15}PO(OEt)_2$: P, 8·15; EtO, 23·7%]. The substance has the same melting point as the diethyl triphenylmethylphosphinate described by Arbuzov (*loc. cit.*) and is probably identical therewith.

When the diethyl ester is heated with concentrated sulphuric acid at 40° or 130°, no triphenylcarbinol is produced, but complete sulphonation takes place. Treatment with hot aqueous sulphuric acid causes hydrolysis, the monoethyl ester being first formed and finally the phosphinic acid itself. A quantitative conversion into the phosphinic acid is brought about by heating with hydriodic–acetic acid mixtures.

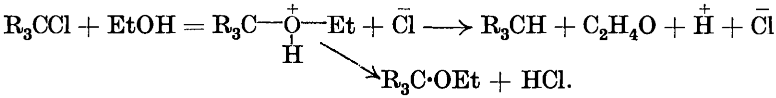
Action of alcoholic sodium ethoxide. 0·441 G. of the diethyl ester was heated for 4 hours with 4·8 c.c. of 2·5*N*-alcoholic sodium ethoxide. The mixture was then poured into water and the phosphorus acids were isolated in the usual way. They consisted of the practically pure monoethyl ester of the phosphinic acid (0·407 g.; m. p. 254—257°).

Diethyl triphenylmethylphosphinate has also been obtained as follows : Silver monoethyl triphenylmethylphosphinate (7·2 g.), ethyl iodide (3·2 g.), and 30 c.c. of carefully dried benzene were shaken together for a week in a flask protected from light. The silver iodide was removed and the benzene evaporated under reduced pressure; 5·8 g. of white crystalline material remained, m. p. 118—120° after crystallisation from ether. Towards hydrolysing agents it exhibited the same properties as the diethyl ester already described; a mixed melting point established their identity.

Conversion of Triphenylmethylphosphinic Acid into Triphenylchloromethane.—5 G. of the phosphinic acid and 10 g. (3 mols.) of phosphorus pentachloride were heated together at 70°. A vigorous evolution of hydrogen chloride took place at first and ceased suddenly, leaving a yellow liquid containing much unchanged pentachloride. During the subsequent 1½ hours' heating the remaining pentachloride went slowly into solution without any noticeable evolution of hydrogen chloride. Benzene was then added and the solution was rapidly extracted with water and dried. Evaporation of the benzene yielded 3·92 g. (91%) of triphenylchloromethane, m. p., after crystallisation from benzene, 106—109°.

Action of Alcohol on the Phosphorus Dichloride.—Boyd and Chignell (*loc. cit.*) stated that with ethyl alcohol the phosphorus dichloride yields triphenylmethyl ethyl ether. This statement has been confirmed : 1 G. of the phosphorus dichloride, when refluxed for an hour with 10 or 100 c.c. of absolute alcohol, yields chiefly the carbinyl ether. Schmidlin and Garciá Banús (*Ber.*, 1912, **45**, 3189) described the reduction of triphenylcarbinol by means of ethyl alcohol–sulphuric acid (1 : 1). This reagent causes considerable decomposition and it is preferable to employ much less acid. 1 G. of the carbinol, when refluxed for ½ hour with 23 c.c. of ethyl alcohol–sulphuric acid (4 : 1), or for 2 hours with 20 c.c. of an 8 : 1 mixture, produces almost pure triphenylmethane. The same reagent reduces the phosphorus dichloride to the methane. In alcohol the phosphorus dichloride decomposes and liberates hydrogen chloride, and with very little alcohol the acidity developed suffices to cause reduction : 1 g. of the phosphorus dichloride, when refluxed for 2 hours with 2 c.c. of alcohol, yielded a considerable amount of triphenylmethane.

The course of this reduction is illustrated by a consideration of the behaviour of tri-*p*-tolylchloromethane towards ethyl alcohol. In this case short boiling with alcohol (15 minutes) yields tri-*p*-tolylmethyl ethyl ether; prolonged boiling (2 hours) produces tritolylmethane. By similar treatment with alcoholic hydrochloric acid, the corresponding carbinol can be converted into its ethyl ether or reduced to the methane.



$$R_3CCl + EtOH = R_3C{-}\underset{H}{\overset{+}{O}}{-}Et + \overset{-}{Cl} \longrightarrow R_3CH + C_2H_4O + \overset{+}{H} + \overset{-}{Cl}$$
$$\searrow R_3C{\cdot}OEt + HCl.$$

The statement of Arbuzov (*loc. cit.*) that the phosphorus dichloride is converted into the carbinol by boiling with alcohol could not be confirmed. When 1 g. of the phosphorus dichloride was refluxed with 100 c.c. of absolute alcohol it was possible to isolate a very small amount of triphenylcarbinol, but the ethyl ether formed the chief product. Alcoholic hydrogen chloride of the same strength as that finally produced in the foregoing experiment behaved towards triphenylchloromethane and towards the carbinyl ether in the same way, the product being the carbinyl ether associated with a little carbinol. The following experiment illustrates the ease with which the carbinyl ether is hydrolysed by dilute aqueous acids and may offer an explanation of the production of carbinol in Arbuzov's experiments. 1 G. of the phosphorus dichloride was refluxed with 100 c.c. of absolute alcohol for 1 hour, 100 c.c. of water were added, and the mixture was warmed gently until just clear. On cooling, almost pure triphenylcarbinol (0·6 g.) crystallised, m. p. 157—160°. It was identified by means of a mixed melting point. In a similar experiment where, prior to the addition of water, the solution was neutralised by the addition of aqueous sodium carbonate, 0·66 g. of the carbinyl ether was obtained, m. p., after crystallisation from aqueous ethyl alcohol, 82—83°. A very little carbinol was present.

Boiling methyl alcohol converts the phosphorus dichloride into methyl triphenylmethyl ether. 2 G. of the phosphorus dichloride and methyl alcohol (10 c.c.), after boiling for 2 hours, yielded 1·45 g. of a product, m. p. 82—83° after crystallisation from methyl alcohol.

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