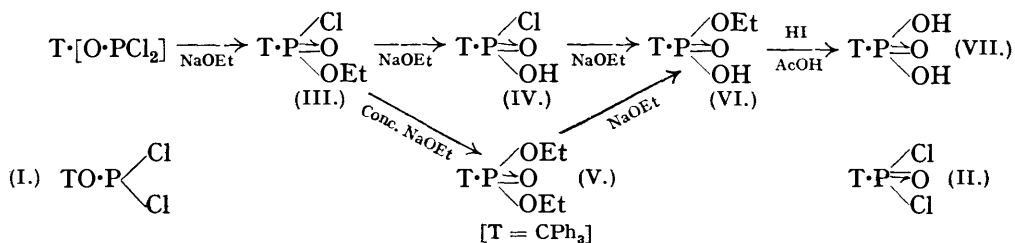


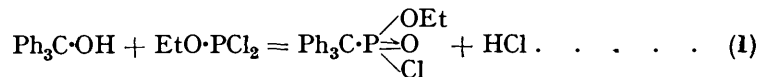
191. *The Constitutions of Some Phosphorus Derivatives of Triphenylmethane.*

BY HAROLD H. HATT.

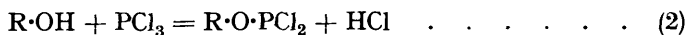
IN a previous paper (J., 1929, 2412) the author showed that the evidence then available did not permit of a decision between the two formulæ (I and II) proposed by Boyd and Chignell (J., 1923, 123, 813) and A. E. and B. A. Arbusov (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 217) respectively for the substance obtained by the action of phosphorus trichloride on triphenylcarbinol: the alcoholysis of the phosphorus dichloride (I or II) was shown to proceed by way of several intermediate products (III, IV, V, and VI), finally to triphenylmethylphosphonic acid, a substance of definite constitution (VII).



Now, if the rearrangement from (I) to (VII) were due to the tendency for phosphorus to acquire the "quinquevalent" state (compare Boyd and Smith, J., 1924, 125, 1477; 1926, 2323: rearrangement was considered to take place during alcoholysis), the reverse change should be difficult, if not impossible; and therefore, starting from (VII), it should be possible to obtain the substance (II). This has not been accomplished, since reagents which appeared likely to replace the hydroxyl groups in (VII) by chlorine either removed the triphenylmethyl group as triphenylchloromethane or brought about condensation to products containing more than one phosphorus atom. Nevertheless, all the intermediate products of alcoholysis (III—VI) have been prepared from (VII) and therefore have the constitutions of phosphonic type indicated in the formulæ. Treatment of the phosphonic acid with phosphorus pentachloride under controlled conditions yields the chloro-acid (IV), from which the chloro-ester (III) is obtained by ethylation. Alternatively, the phosphonic acid can be fully ethylated to give (V), and the latter converted into (VI) by alcoholysis. It can then be shown that the chloro-ester (III) is present in the mixture of products arising from (VI) by treatment with phosphorus pentachloride. Further, the chloro-ester, a substance of phosphonic type, is readily produced by the action of ethoxyphosphorus dichloride on triphenylcarbinol under mild conditions:



The constitution (I) appears to have been assigned originally because there was then no reason to suppose the existence of exceptions to the mechanism given by Menshutkin (*Annalen*, 1866, 139, 343) for the first reaction between phosphorus trichloride and an alcohol (compare, however, Michaelis, *Ber.*, 1901, 34, 1298),



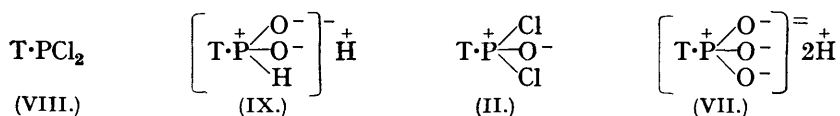
and because the somewhat unexpected stability of the phosphorus dichloride might be due to the special character of the triphenylmethyl group. The definite exception to equation (2) now noticed, equation (1), and in so closely related a case, thus seems sufficient evidence upon which to conclude that the product of the reaction between triphenylcarbinol and phosphorus trichloride has the constitution (II). To maintain now that the phosphorus dichloride has the constitution (I), it would be necessary to assert that migration of the triphenylmethyl group from oxygen to phosphorus accompanies the direct replacement of one chlorine atom by ethoxyl.

Other experiments made to decide the structure of this dichloride comprise its formation by oxidation of *triphenylmethyldichlorophosphine* (VIII).



After unsuccessful attempts to prepare the dichlorophosphine from triphenylmethylsodium and phosphorus trichloride, it was prepared from the triphenylmethylhydrogenphosphonic acid of Fosse (*Compt. rend.*, 1910, **150**, 158; *Bull. Soc. chim.*, 1910, **7**, 321). This acid undoubtedly has the structure (IX; R = H) assigned to it by Fosse: there is no evidence in support of the formula (X) proposed by Schmidlin ("Das Triphenylmethyl," p. 135, F. Enke, Stuttgart, 1914). It yields a neutral *silver* salt and neutral *monomethyl* and *monoethyl* esters (R = Ag, Me, and Et respectively) and is converted quantitatively into the phosphonic acid (VII) by mild oxidising agents. Prolonged refluxing with phosphorus trichloride produces the dichlorophosphine (VIII), and for this reason it seems that the acid must exist to some extent in solution as the phosphinic acid (XI).

The relative stability towards hydrolysing agents of triphenylmethyldichlorophosphine (VIII) and the phosphonic acid (IX) is closely comparable with that for triphenylmethylphosphonyl dichloride (II) and the phosphonic acid (VII) (see J., 1929, 2412). The phosphonic acid (IX) is stable towards such hydrolysing agents as hot alkalis, hydrochloric acid, and sulphuric acid; only phosphorus pentachloride converts it into the chloromethane. The dichlorophosphine, on the other hand, yields phosphorus-free derivatives of triphenylmethane with sulphuric acid and with alcoholic potash, and is only converted into the phosphonic acid (IX) by caustic alkali. The stability of the acids relative to the corresponding chlorides may be attributed to the presence on the molecule of the acid, in ionising solvents, of electronegative charges which render the removal of the triphenylmethyl group as a kation difficult. In the corresponding acyl chlorides restraining influences of this kind are much diminished.



If this view is adopted, it is clear from the above formulæ that the relative stabilities of (II) and (VII) and of (VIII) and (IX) should be somewhat similar. The constitution (II) for the phosphorus dichloride thus gains in likelihood by this relationship of the latter's properties with those of the dichlorophosphine (VIII).

The ease with which the carbon-phosphorus link in (VIII) could be broken was especially noticeable in the attempts made to oxidise the dichlorophosphine to the phosphonyl dichloride (II). The usual oxidising agents (chlorine and subsequent hydrolysis; simultaneous treatment with chlorine and sulphur dioxide) removed the triphenylmethyl group:



and the same result was obtained by shaking the dichlorophosphine with a chloroform solution of iodine in presence of aqueous sodium bicarbonate. In ether and benzene the colourless triphenylmethyldichlorophosphine gave markedly yellow solutions which readily took up gaseous oxygen, and so gave rise to appreciable quantities of triphenylmethyl

The same true salt would arise from the triphenylmethoxyphosphorus dichloride, whose ester-like constitution renders such a transformation even more probable, and, under conditions where this ionisation is possible, only the more stable isomeride (II) would be isolated. The conditions necessary for such ionisation are almost certainly present in the reaction between phosphorus trichloride and a triarylcabinol, of which one characteristic is the development of a strong carbonium colour.

So far no substance of the type $T-O-P \begin{matrix} \swarrow A \\ \searrow B \end{matrix}$ has been isolated, but wherever the attempt

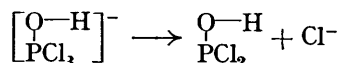
has been made to obtain substances of the isomeric class, $T-P \begin{matrix} \swarrow A \\ \searrow B \\ \text{---} O \end{matrix}$, comparatively little

difficulty has been experienced (compare A. E. and B. A. Arbusov, *loc. cit.*, and *Ber.*, 1929, **62**, 1871; A. E. and I. E. Arbusov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1905). In the case of the chloro-ester (III), the substance described by A. E. and B. A. Arbusov (*loc. cit.*) had a very low melting point (125—126° instead of 137.5—138°). A repetition of their experiments showed that this was not due to isomerism. The melting point of the chloro-ester is much depressed by small amounts of impurities and it has now been found that in every case where the substance obtained melted at about 125° it was impure and by repeated crystallisation ultimately acquired a constant melting point of 140—141°.

Triphenylcarbinol deviates considerably from the typical behaviour of an alcohol, not only in its reaction with phosphorus trichloride, but also in those with phenylhydrazine, aniline, sodium bisulphite (Baeyer and Villiger, *Ber.*, 1902, **35**, 3014), hydroxylamine (Mothwurf, *Ber.*, 1904, **37**, 3150), hypophosphorous acid, cyanoacetic ester, and malonic acid (Fosse, *loc. cit.*; *Compt. rend.*, 1907, **145**, 196); in all of which the triphenylmethyl group becomes attached directly to the reagent residue, and the carbinol hydroxyl group is generally eliminated as water. These reactions led Baeyer and Villiger (*loc. cit.*) to suggest an aldehydic-like constitution for the carbinol and to assign, correctly, a sulphonic acid structure to the product of its reaction with sodium bisulphite. (In this case salts of the unstable isomeric sulphite appear recently to have been obtained; Schmidt-Nickels, *Ber.*, 1929, **62**, 917.) The suggestion of Baeyer can be interpreted as meaning that at one stage in these reactions the triphenylmethyl group appears as a kation. The reaction with phosphorus trichloride would then be expected to give first the addition product, $T \cdot PCl_3 \cdot OH$. Since, however, triphenylchloromethane does not react analogously, it seems that the oxygen of the carbinol takes a more special part in the reaction, as would be the case if the carbinol were supposed to form first an addition compound of the type Sidgwick employs (J., 1924,

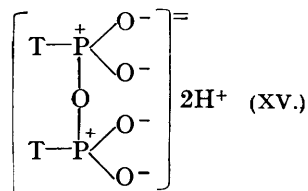
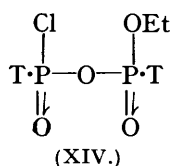
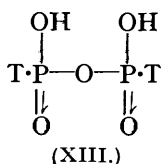
125, 2672) to explain the hydrolysis of phosphorus trichloride:
$$\begin{matrix} R-O-H \\ \downarrow \\ PCl_3 \end{matrix} \quad (XII).$$
 In

the normal Menschutkin reaction, (XII) would undergo simple loss of hydrogen chloride. Triphenylcarbinol may react in this normal way, the -oxyphosphorus dichloride first formed then rearranging itself into the phosphonyl dichloride (II); yet it seems more reasonable, where, as in this example, the alkyl group readily accepts a kationic condition, to suppose that it separates in this condition from the positively charged oxygen atom of (XII) and becomes attached to the phosphorus atom of the resulting anion, either before or after the latter has parted with hydrogen chloride. The formation of triphenylchloromethane, which is always present as a by-product in the reaction, can then be regarded as due in part to an alternative decomposition of the anion:

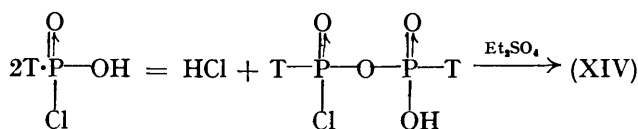


The presence of triphenylmethylphosphonic acid (VII) as a by-product in the reaction between the carbinol and phosphorus trichloride (Boyd and Smith, J., 1924, **125**, 1478) was shown by A. E. and B. A. Arbusov (*loc. cit.*) to depend on some subsequent reaction between the phosphonyl dichloride and the carbinol. Experiments also supporting such an explanation have been reported and discussed elsewhere (Hatt, Thesis, London, 1930).

During the course of this work, some derivatives of triphenylmethylpyrophosphonic acid (XIII) have been obtained.



Ethyl triphenylmethylchloropyrophosphonate (XIV) appears in small quantity during the ethylation in xylene of the chloro-acid (IV). As previously shown (Hatt, *loc. cit.*), the chloro-acid loses hydrogen chloride at its melting point and gives a product, $\text{C}_{19}\text{H}_{15}\text{O}_2\text{P}$. It would be expected that the molecular formula of such a metaphosphonate should be some multiple of this empirical formula (see G. N. Lewis, "Valence and the Structure of Atoms and Molecules," p. 94), the loss of hydrogen chloride from the chloro-acid being an intermolecular process. The compound (XIV) can then be regarded as arising from the ethylation of the first product of such thermal decomposition :



Methyl and *ethyl* esters (XIII, with OR in place of OH) of the pyrophosphonic acid are formed by treatment of the corresponding phosphonic esters with phosphorus pentachloride. Two asymmetric phosphorus atoms should be present and these compounds should therefore exist in two optically inactive forms. The esters are readily freed of all impurities and then show the typical properties of a mixture (indefinite melting point and mixed or indistinct crystalline forms). The mixture of methyl esters has not been separated, but two ethyl esters have been obtained by fractional crystallisation, having the same composition and molecular weight but differing in melting point and in crystalline form. In these compounds the oxygen bridge link between the phosphorus atoms is extremely stable and the esters can therefore be easily converted into the corresponding pyrophosphonic acid. Both isomeric ethyl esters and the mixed methyl esters yield the *same* single *pyrophosphonic acid* (XIII). The isomeric ethyl esters being regarded as the stereoisomeric, internally and externally compensated inactive materials, the formation from them of the same pyrophosphonic acid furnishes strong evidence that the apparent asymmetry of the pyro-acid is destroyed by ionisation or tautomeric shift of the hydroxyl hydrogen atoms (XV). Much the same view has been frequently put forward (Caven, J., 1902, **81**, 1362; Ephraim, *Ber.*, 1911, **44**, 631; A. E. and B. A. Arbusov, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1599) to account for the repeated failure to resolve esters and salts, from optically active bases, of acids having the general formula $\text{R}_1\text{R}_2\text{P}=\text{O}(\text{OH})$ (Caven; Ephraim; A. E. and B. A. Arbusov; also Luff and Kipping, J., 1909, **95**, 1993; Kipping and Challenger, J., 1911, **99**, 626; Pope and Gibson, J., 1912, **101**, 735; Gibson and Johnson, J., 1928, 92; A. E. and I. E. Arbusov, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1909). The fact that on re-ethylation the pyrophosphonic acid yields a mixture which can be separated into the same two isomeric ethyl esters is a further support for this explanation.

EXPERIMENTAL.

Conversion of Triphenylmethylphosphonic Acid into Triphenylmethylchlorophosphonic Acid (IV).—A mixture of the phosphonic acid (5 g.) and phosphorus pentachloride (4.7 g.) was shaken for 2 hours with 10 c.c. of benzene, the whole treated with excess of ice, and the insoluble material washed with water and with benzene, dried in a vacuum, and extracted with 20 c.c. of boiling benzene for 1 hour; the white residue (2.25 g.) had m. p. 219—220° (vigorous decomp.) (229—230° after further purification) and was identified as the chloro-acid by conversion into its aniline and quinoline salts.

When heated with phosphorus pentachloride, the chloro-acid (IV) and the phosphonyl dichloride (II) are completely converted into triphenylchloromethane. Boiling phosphorus trichloride is without action on the chloro-acid. The phosphonyl dichloride (II) is stable towards chlorine, bromine, and iodine in chloroform; a property in agreement with the structure now assigned, but conflicting with the structure (I) (compare Wichelhaus, *Annalen*, 1868, Suppl. VI, 257).

Ethylation of Triphenylmethylchlorophosphonic Acid (IV).—A mixture of the chloro-acid (6.0 g.), anhydrous potassium carbonate (12 g.), ethyl sulphate (7.5 c.c.), and pure xylene (60 c.c.) was refluxed, with exclusion of moisture and occasional shaking, for 2.5 hours. The cooled product was washed with dilute alkali and water and dried, the xylene distilled in a vacuum on a water-bath, and the residual oil dissolved in ether and obtained crystalline by slow evaporation of the solution. The crystals were extracted with petroleum (b. p. 80—100°) (40 + 10 c.c.), 0.72 g. of the almost insoluble pyro-ester (XIV), m. p. 208—216°, remaining undissolved. From the petroleum solution, by evaporation, various crystalline fractions (4.0 g.), m. p. 115—130°, and 1.3 g. of an unidentified oil were obtained. Repeatedly crystallised from benzene and light petroleum (b. p. 40—60°), the former gave the chloro-ester (III), m. p. 140—141°, which was identified by conversion into the chloro-acid (IV) by hydriodic and acetic acids and into the carbinol by sulphuric acid and by a mixed m. p. determination with an authentic specimen.

Ethyl triphenylmethylchloropyrophosphonate (XIV) is readily soluble in benzene or chloroform and but slightly soluble in ether or light petroleum. After several recrystallisations from benzene-light petroleum it forms colourless lozenges, m. p. 221—222.5° (with slow evolution of a gas), containing solvent of crystallisation which is slowly removed at 100° in a vacuum [Found : loss, 11.3. Found in dried material: C, 71.0*; H, 5.3*; P, 9.4; Cl, 5.2; OEt, 6.8; *M* (in camphor), 630. $C_{40}H_{35}O_4ClP_2C_6H_5$ requires C, 71.0; H, 5.2; P, 9.2; Cl, 5.2; OEt, 6.65%; *M*, 677]. A slow decomposition seems to take place in camphor solution, so that after heating at 160° for $\frac{1}{2}$ hour the depression of the f. p. corresponds to a molecular weight of 570—580. With sulphuric acid the chloropyro-ester yields triphenylcarbinol. This observation, the analyses, and the molecular weight are sufficient evidence for the structure (XIV). In support of the suggested method of formation it was shown that the chloropyro-ester was produced neither by heating the chloro-ester (III) with ethyl sulphate in xylene nor by heating it with the chloro-acid (IV) in xylene solution. It was produced by heating an equimolecular mixture of the chloro-ester and the chloro-acid with ethyl sulphate in xylene solution, but in an amount commensurate with the quantity of chloro-acid present.

Methyl Triphenylmethylphosphonate.—A mixture of the phosphonic acid (25 g.), methyl sulphate (30 c.c.), potassium carbonate (50 g.), and toluene (150 c.c.) was refluxed for 4 hours, the toluene distilled from the washed product in a vacuum, and the crystalline residue recrystallised from benzene and light petroleum, large colourless needles of the methyl ester (22 g.), m. p. 154.5—155.5°, being obtained : there was no evidence of the presence of a second isomeric form (compare Arbusov and Arbusov, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 233) [Found : OMe, 17.5; *M*, in benzene, 348. Calc. for $C_{19}H_{15}OP(OMe)_2$: OMe, 17.6%; *M*, 352].

The ethyl ester can be obtained by a similar process.

Action of Phosphorus Pentachloride on Ethyl Hydrogen Triphenylmethylphosphonate.—Owing to the formation of several by-products the chloro-ester (III) could not be isolated from the products of this reaction. Its presence there was inferred from the isolation from them of the chloro-acid (IV), conditions being used which serve to generate it from the chloro-ester, and the reaction products having previously been freed of all acidic material. The monoethyl ester (VI) (10 g.), phosphorus pentachloride (7.5 g.) and benzene (80 c.c.) were shaken for 5 minutes on a water bath, the product poured on ice and washed with water, and the benzene layer added with stirring to 400 c.c. of hot 2% sodium hydroxide solution. When the benzene had evaporated, the insoluble material was removed, taken up in benzene, and treated with a similar quantity of alkali. The combined alkaline liquors yielded 2.9 g. of acidic material, convertible by hydriodic acid into the phosphonic acid (VII). The neutral materials insoluble in the alkali were refluxed with 40 c.c. of hydriodic acid-acetic acid (2 : 1) and poured into water; the insoluble residue was freed from iodine and acids by washing, dried, and extracted with benzene, which left undissolved 1.5 g. of the chloro-acid (IV), m. p. (after purification) 227—229° (decomp.). Its aniline salt had m. p. 181.5—182°. The benzene-soluble products removed

* The estimations of carbon and hydrogen recorded in this paper were made by Dr. A. Schoeller.

from the chloro-acid on treatment with hydriodic acid, gave triphenylmethane, triphenylmethylphosphonic acid, and other products not identified.

Action of Ethoxyphosphorus Dichloride on Triphenylcarbinol.—(1). The carbinol (5 g.) was added in three portions to the dichloride (7.2 g.), moisture being excluded. After 2 hours' heating on a water-bath, the products were crushed up with ice, and the solid material was ground repeatedly with water, dried in a vacuum (yield, 7.0 g.), and extracted twice for periods of 1 hour with 30 c.c. of dry benzene, 0.5 g. of insoluble material, m. p. 219—220° (decomp.), being left. [This substance was identified as the chloro-acid (IV) in the usual manner. It dissolves to an appreciable extent in the benzene solution of the chloro-ester (III). The total yield of (IV) in these experiments varied from 5 to 7.5%.] The benzene extraction liquors were washed with water, dried, and concentrated somewhat; addition of light petroleum (b. p. 40—60°) then gave 5.1 g. of a crystalline powder, m. p. (after one recrystallisation) 137—139° (later fractions had lower m. p.'s). Further crystallisation gave the pure chloro-ester (III), m. p. 140—141°. No evidence of the existence of a chloro-ester of m. p. 125—126° (compare Arbusov and Arbusov) was obtained. The lower m. p.'s of later fractions were due to the presence of quite other substances. The amounts of such present were estimated approximately by utilising the fact that the chloro-ester and the chloro-acid are completely transformed into (VI) by alcoholic sodium ethoxide. In one experiment the product from 5 g. of triphenylcarbinol, when treated in this way, yielded 0.2 g. of solid organic material insoluble in alkali.

(2) The reaction was brought about as in (1), but 5 g. of the carbinol and 22 g. of the dichloride were used. After cooling, an equal volume of dry light petroleum was added. After several days, the white crystalline precipitate was washed with light petroleum (moisture was excluded) and dried in a vacuum; it melted at 133—138° (yield, 5.2 g.) and, after a few recrystallisations from benzene-ether, at 140—141°. It was identified as the chloro-ester (III) by a mixed m. p. determination and by conversion into the chloro-acid.

Action of Alcohol-free Sodium Ethoxide on Triphenylmethylphosphonyl Dichloride (II).—The following three experiments show that by varying the conditions of treatment with sodium ethoxide the phosphonyl dichloride may be converted largely into either the chloro-ester (III), ethyl triphenylmethylphosphonate, or ethyl hydrogen triphenylmethylphosphonate. The reactions with the sodium ethoxide seem to be similar to the second process of alcoholysis of the phosphonyl dichloride which takes place with concentrated alcoholic solutions of sodium ethoxide. The pure chloro-ester obtained by this means always had m. p. 140—141°. No evidence could be found for the existence of a chloro-ester of m. p. 125—126°. It follows that the statement (A. E. and B. A. Arbusov, *loc. cit.*) that only one chlorine atom of the phosphonyl dichloride can be removed by alcohol-free sodium ethoxide, and that a chloro-ester (III) of m. p. 125—126° is thus produced, cannot be correct.

Experiment 1. The phosphonyl dichloride (6 g.) was added to powdered sodium ethoxide (3.5 g.) (prepared after the method of Claisen, *Ber.*, 1889, 22, 1010) contained in 30 c.c. of benzene. After 15 hours' refluxing, moisture and carbon dioxide being excluded, 50 c.c. of benzene were added and then excess of water. The liquors were filtered, and the benzene solution washed with dilute aqueous alkali and water and dried. Concentration and addition of light petroleum yielded 3.1 g. of almost pure ethyl triphenylmethylphosphonate (m. p. 121—122° after 2 recrystallisations). The substance was identified by a mixed m. p. determination with the ester obtained by other methods, and by conversion into the phosphonic acid by hydriodic and acetic acids. From the aqueous liquors, on acidification, an acid (2.3 g.) was precipitated which was shown to be a mixture of ethyl hydrogen triphenylmethylphosphonate and the phosphonic acid itself.

Experiment 2. The phosphonyl dichloride (5.3 g.), sodium ethoxide (2.0 g.), and benzene (80 c.c.) were refluxed for 8 hours. The phosphonic acid and its monoethyl ester (0.9 g.) were removed as described in experiment (1). Treatment then of the concentrated benzene solution yielded 3.3 g. of a crystalline powder, m. p. 135—138°, and 140—141° after several recrystallisations; it was identified as the chloro-ester by mixed m. p. and by conversion into the chloro-acid. Only 0.2 g. of crystalline material (m. p. 120—131°) could be obtained from the residues.

Experiment 3. Alcohol-free sodium ethoxide was prepared in 40 c.c. of xylene from 1.56 g. of sodium by the method of Bruhl (*Ber.*, 1902, 35, 3516), 6 g. of the phosphonyl dichloride added, and the mixture refluxed for 4 hours. Proceeding as in the previous experiments, 4.75 g. of ethyl hydrogen triphenylmethylphosphonate (m. p. 250—255° after 1 recrystallisation) were obtained from the aqueous liquors and 0.4 g. of ethyl triphenylmethylphosphonate (m. p. 120—121.5° after crystallisation) from the xylene solution.

Action of Phosphorus Trichloride on Potassium Triphenylcarbinolate.—8 G. of the carbinolate

(compare Blicke, *loc. cit.*) were covered with 50 c.c. of benzene, cooled to 0°, stirred, and treated in an inert atmosphere with 6 g. of phosphorus trichloride. Reaction took place with evolution of heat and the transient appearance of a strong orange colour. After heating for 1 hour on the water-bath, almost all the carbinolate had disappeared and the colourless liquid contained a gelatinous suspension. Water was added, and benzene to maintain solution. By concentration and addition of light petroleum, the benzene liquor yielded 6.3 g. of crystalline material, m. p. 175—184° (187—189° after crystallisation). A mixed m. p. determination established its identity with triphenylmethylphosphonyl dichloride. Subsequent separations from the benzene solution contained the phosphonyl dichloride mixed with carbinol.

Triphenylmethylhydrogenphosphonic Acid (IX).—The acid is obtained purer by the following modification of the method of Fosse. A mixture of triphenylcarbinol (20 g.), acetic acid (80 g.), and sulphuric acid (24 g.) was warmed to 50°, and the resulting clear red liquid treated with a solution (also at 50°) of sodium hypophosphite (12 g.) in acetic acid (50 g.). No brown precipitate appeared and after being kept for 4 hours at 50—60° the whole was treated with excess of water and the crystalline precipitate removed and added to 300—400 c.c. of 0.3*N*-sodium hydroxide. The mixture was boiled and, after cooling to 50°, the solid triphenylmethane was removed and the phosphonic acid precipitated by acidification. Crystallised from glacial acetic acid, it formed colourless needles, m. p. 234—240° [Found : P, 10.0; equiv. (NaOH and phenolphthalein), 302. Calc. for C₁₉H₁₇O₂P : P, 10.05%; equiv., 308]. Stelling (*Z. physikal. Chem.*, 1925, 117, 172) gives m. p. 220—222°. The acid of m. p. 234—240° is practically pure, but by many recrystallisations its m. p. may be raised to 245—248°. At 255—260° the acid undergoes a characteristic decomposition, evolving a gas and becoming first opalescent and then depositing an orange powder. The *silver* salt was obtained as a white caseous precipitate from silver nitrate and a neutral solution of the ammonium salt and dried in a vacuum (Found : P, 7.4; Ag, 25.8. C₁₉H₁₆O₂PAG requires P, 7.5; Ag, 26.0%). The *methyl* ester, obtained by refluxing the acid (10 g.), anhydrous potassium carbonate (15 g.), methyl sulphate (10 g.), and toluene (100 c.c.) for 4 hours, crystallised from toluene, containing a little light petroleum, in colourless needles, m. p. 163—164° (Found : P, 9.8; OMe, 9.5; *M*, in benzene, 330. C₂₀H₁₉O₂P requires P, 9.6; OMe, 9.6%; *M*, 322). The *ethyl* ester, obtained similarly or from the silver salt and ethyl iodide, crystallised in colourless prisms, m. p. 118—121.5° (Found : P, 9.5; OEt, 13.0. C₂₁H₂₁O₂P requires P, 9.2; OEt, 13.4%).

Oxidation of triphenylmethylhydrogenphosphonic acid (IX) to the phosphonic acid (VII) was brought about quantitatively by refluxing it in acetic acid (containing some water) solution with the calculated amount of iodine for 20—30 minutes, or by shaking it with alkaline permanganate. In the latter case 1.22 g. of the acid (IX) gave 1.19 g. of the acid (VII), m. p. 283—283.5°. The latter acid is most conveniently prepared in this way. Hydriodic acid in acetic acid as usually employed converts the esters of the acid (IX) into the phosphonic acid (VII), but the acid (IX) can be obtained from them by refluxing for a short period (in an inert atmosphere) with acetic and hydriodic acids, the latter having been recently freed from iodine by distillation from copper or the acid (IX).

Triphenylmethyldichlorophosphine.—Triphenylmethylhydrogenphosphonic acid (IX) (16 g.) and phosphorus trichloride (22 g.) were heated to refluxing on a water-bath in an atmosphere of dry nitrogen : hydrogen chloride was evolved and later a spongy orange mass, mixed with large colourless crystals, was precipitated. After 8—10 hours a further 18 g. of phosphorus trichloride were added and the mixture was heated until the colourless crystals dissolved; the solution was then filtered (excluding air) from the insoluble orange material (the latter contained phosphorous acid and free phosphorus). The filtrate, treated with an equal volume of light petroleum and kept in an atmosphere of nitrogen, deposited large colourless crystals, which were washed with light petroleum (yield, 12 g.), dissolved in 25 c.c. of boiling phosphorus trichloride and treated with an equal volume of light petroleum. The crystalline product was washed with light petroleum and dried over sodium hydroxide and calcium chloride under reduced pressure in nitrogen. The colourless crystals melted at 138—140° to a light yellow liquid which decomposed at 240° (Found : P, 9.2; Cl, 20.55. C₁₉H₁₅Cl₂P requires P, 9.0; Cl, 20.55%).

Triphenylmethyldichlorophosphine is easily soluble in chloroform or benzene and almost insoluble in ether or light petroleum. Its solutions in benzene and chloroform are less stable than that in phosphorus trichloride, from which crystallisations are best made. The solid phosphine can be ground with cold water without suffering appreciable decomposition. Hot aqueous sodium hydroxide regenerates the phosphonic acid (IX). Unlike the phosphonyl dichloride (II), triphenylmethyldichlorophosphine is converted into triphenylmethane by both 0.5*N*- and 2.5*N*-alcoholic sodium ethoxide and a test of its purity, especially freedom from

oxidation, is the absence of acidic phosphorus compounds in the reaction products. 1.02 G. of the dichlorophosphine and 35 c.c. of 0.5*N*-alcoholic sodium ethoxide after 4 hours' refluxing gave 0.62 g. of triphenylmethane (m. p. 90—92°). Theoretical yield, 0.72 g. Sulphuric acid attacks the dichlorophosphine, producing a solution of the carbonium sulphate, from which the carbinol can be obtained by means of water: 0.875 g. thus gave 0.671 g. of carbinol (m. p. 157—158°; 161° after crystallisation) (theoretical yield, 0.674 g.). During the reaction some hydrogen sulphide is formed.

Oxidation of Triphenylmethyl-dichlorophosphine.—The pure dichlorophosphine (4 g.) and 40 c.c. of dry ether were refluxed for 100 minutes in a stream of oxygen: hydrogen chloride was not evolved and complete solution was never attained. The ethereal solution was filtered from the insoluble crystalline material (A; 1.5 g. after being washed with ether) and washed with water several times (the aqueous solutions reacted strongly acid and contained large quantities of phosphate and chloride ions). Extraction of the ethereal solution with alkali removed an acidic tar and phenol (0.2 g. of tribromophenol, m. p. 91—93°). Concentration of the ethereal solution and addition of light petroleum then gave triphenylcarbinol (0.13 g.). The remaining oil, treated with alkaline alcoholic hydroxylamine, gave 0.27 g. of benzophenoneoxime (m. p. 141—142°, from alcohol). The substance (A) consisted of a mixture of triphenylmethyl peroxide (0.12 g.) and triphenylmethylphosphonyl dichloride. The latter was removed by dissolving it in chloroform and at once precipitating any trace of the peroxide with ether. Afterwards the phosphonyl dichloride crystallised slowly. The peroxide crystallised from carbon disulphide in prisms, m. p. and mixed m. p. 184—186°; the melt was strongly coloured. The phosphonyl dichloride, crystallised from chloroform and ether, melted alone, or mixed with an authentic specimen, at 188—190° (Found: P, 8.6; Cl, 17.3. Calc. for $C_{19}H_{15}OCl_2P$: P, 8.6; Cl, 17.6%). A similar oxidation in benzene solution of 4 g. of the dichlorophosphine yielded 1.45 g. of a mixture of the phosphonyl dichloride and the peroxide: hydrogen chloride was evolved. When the dichlorophosphine (2.0 g.) was shaken with 1.47 g. of iodine in 40 c.c. of chloroform in presence of aqueous sodium hydrogen carbonate, the iodine was rapidly destroyed. Afterwards all the chlorine and phosphorus of the dichlorophosphine were present in the inorganic condition in the aqueous solution. From the chloroform solution triphenylcarbinol (1.03 g.) and a little triphenylmethyl peroxide were isolated. In absence of bicarbonate, iodine has little action on the dichlorophosphine.

Ethyl Triphenylmethylpyrophosphonates.—Ethyl triphenylmethylphosphonate (V) (25 g.), phosphorus pentachloride (25 g.), and benzene (100 c.c.) were refluxed together for 7 hours and then poured on ice. The benzene liquor was washed with aqueous alkali (only traces of solid acidic material were present) and with water, and, after drying, the benzene was removed in a vacuum. The residue was extracted twice with about 40 c.c. of ether for periods of 1 hour to remove triphenylchloromethane, triphenylcarbinol, and the unchanged phosphonic ester. The insoluble material (12.8 g., m. p. 210—220°) was almost entirely a mixture of the two pyrophosphonic esters, of which one form (α) was present in much the larger quantity. From 11.8 g. of the mixture, 6 g. of the pure α -form were obtained. The isolation of the β -form was more difficult and after long fractional crystallisation from benzene—ether only much smaller quantities were isolated in a state of purity.

Ethyl α -triphenylmethylpyrophosphonate crystallises from benzene—ether (1:2) in clusters of colourless, small, elongated, hexagonal plates, m. p. 222—223°. The m. p. depends slightly on the rate of heating and is probably accompanied by a little decomposition. This ester is very soluble in chloroform, benzene, and toluene, but almost insoluble in ether and light petroleum (Found: C, 73.9; H, 6.1; P, 9.2; OEt, 12.8; *M*, in benzene, 660, 678; *M*, in camphor, 653, 632. $C_{42}H_{40}O_5P_2$ requires C, 73.4; H, 5.9; P, 9.05; OEt, 13.1%; *M*, 686).

Ethyl β -triphenylmethylpyrophosphonate, when crystallised slowly from benzene and ether, separates in highly refractive, stout, polyhedral crystals which often have re-entrant faces, probably due to the formation of twin crystals. Thrown out from solution more rapidly, it forms small crystals of octahedral appearance. The crystals sometimes contain solvent of crystallisation, but the conditions favouring such an occurrence have not been determined. In one case 0.0742 g. of the ester lost 0.0077 g. at 100° in a vacuum (theo. loss for 1 mol. of benzene, 0.0076 g.); whereas another sample of 0.1065 g. lost only 0.0003 g. In both cases the m. p. was 228—231°, but the first substance, before drying, underwent partial fusion if plunged into a bath at 175°. The two samples when mixed had the same m. p. and each when mixed with the isomeric α -ester melted at 209—223°, a m. p. approximately the same as that of the original mixture of esters first isolated (Found: C, 73.1; H, 5.9; P, 8.7; OEt, 12.45%; *M*, in camphor, 698).

Methyl Triphenylmethylpyrophosphonate.—Methyl triphenylmethylphosphonate (10 g.), phosphorus pentachloride (10 g.), and benzene (40 c.c.) were refluxed together for 7 hours (with shorter times much of the phosphonic ester is left unchanged; prolonged action leads to the formation of triphenylchloromethane). On cooling, some *methyl triphenylmethylpyrophosphonate* crystallised and was removed and washed with benzene and water. The benzene liquors were worked up as described in the case of the ethyl esters, and the crude products were freed of impurities by extraction several times with ether (150 c.c.). 7.5 G. of the almost pure (mixed?) methyl triphenylmethylpyrophosphonates were obtained, m. p. 220—230°. This substance is very soluble in toluene and chloroform, moderately easily soluble in benzene and methyl alcohol, and almost insoluble in ether and light petroleum. After 4 recrystallisations from chloroform and ether it melted at 227—233° (Found: P, 9.4; OMe, 9.4; M, in camphor, 628, 600. $C_{46}H_{38}O_5P_2$ requires P, 9.4; OMe, 9.4%; M, 658).

Triphenylmethylpyrophosphonic Acid.—0.30 G. of the corresponding α -ethyl ester was dissolved in 7.5 c.c. of acetic acid, 2.5 c.c. of hydriodic acid (d 1.7) added, and the mixture refluxed for $\frac{1}{2}$ hour. The *pyrophosphonic acid* commenced to crystallise after 2—3 minutes. After the addition of water and removal of acids and iodine from the insoluble material, the latter, dried at 100°, melted at 266—268° (yield, 0.27 g.). From benzene and ether it was obtained as a crystalline powder, m. p. 267—270°. In like manner from 0.20 g. of the pure β -ethyl ester there was obtained 0.165 g. of the acid, m. p. (after recrystallisation) 266—270°, and from the mixed methyl triphenylmethylpyrophosphonate, an acid, m. p. 266—269°. Mixtures of these three products had the same m. p. The m. p. of the acid always extended over a noticeable range, usually from 266° to 270°, and at about 280° visible decomposition set in (Found: C, 72.4; H, 5.1; P, 10.1. $C_{38}H_{32}O_5P_2$ requires C, 72.4; H, 5.1; P, 9.8%). The acid is recovered unchanged after being heated for 20 hours in hydriodic acid—acetic acid (1 : 2). 0.3 G. of the acid was heated with 12 c.c. of 2*N*-hydrochloric acid in a sealed tube at 200° for 8 hours, and 0.295 g. was recovered, m. p. 264—266°.

A. E. and B. A. Arbusov (*J. pr. Chem.*, 1931, 130, 103, 126) believed they had obtained ethyl triphenylmethylpyrophosphonate, as a wax-like material, by the action of triphenylbromomethane on tetraethyl pyrophosphite. With hydrochloric acid at 200° it yielded triphenylmethylphosphonic acid. As shown in the following experiment, ethyl triphenylmethylpyrophosphonate yields the pyrophosphonic acid under such conditions, whence it would seem that the substance of Arbusov and Arbusov probably has some other constitution.

Ethyl α -triphenylmethylpyrophosphonate (0.4 g.) and 2*N*-hydrochloric acid (14 c.c.) were heated for 8 hours in a sealed tube at 195—200°. The solid product consisted of fine silky needles and a white cake, m. p. (dried) 245—260° (yield, 0.375 g.). The product was completely soluble in hot aqueous ammonia and was precipitated on acidification. Crystallised from glacial acetic acid, the first fraction melted at 266—268° (mixed m. p. with the pyrophosphonic acid, 266—268°; with triphenylmethylphosphonic acid, 220—270°). Later fractions melted at 200—240°, apparently because of incomplete hydrolysis, since by treatment with hydriodic and acetic acids these fractions gave the pyrophosphonic acid. No triphenylmethylphosphonic acid could be detected. A similar incomplete hydrolysis was obtained at 225—230°.

Triphenylmethylpyrophosphonic acid forms crystalline salts of low solubility with ammonia and the alkali metals. Its insoluble *silver* salt has a strong tendency to associate with excess of the acid or of silver nitrate. It may be prepared as follows: The acid (1 g.) and 175 c.c. of 0.02*N*-ammonia in 70% aqueous ethyl alcohol were refluxed until nearly all the acid had dissolved; the hot filtered solution was added to 1 g. of silver nitrate in 100 c.c. of 90% alcohol. The silver salt separated as a white crystalline powder (prisms, about 0.01 mm. in length), which was dried at 100° (Found: P, 7.5; Ag, 24.9. $C_{38}H_{30}O_5P_2Ag_2$ requires P, 7.35; Ag, 25.5%). The pyrophosphonic acid can be regenerated unchanged from the silver salt.

Alkylation of Triphenylmethylpyrophosphonic Acid.—(I) The acid (1 g.), methyl sulphate (2.2 c.c.), potassium carbonate (3 g.), and xylene (20 c.c.) were refluxed for 5 hours, excess of xylene added, and the liquor well washed with dilute aqueous alkali and with water. After evaporation of the xylene liquors and crystallisation of the residues from xylene—ether, 0.9 g. of colourless crystalline material was obtained, every fraction of which melted within the range 227—235°. Mixed with the already described methyl esters, it melted at 227—233°.

(II) Ethylation, by a like process, of 1.5 g. of the acid yielded, from the xylene solution, 0.21 g. of crystalline material (m. p. 217—227°), and, as sparingly soluble material, 1.26 g. of the potassium salt of the acid. By fractional crystallisation the 0.21 g. was separated into the α (m. p. 221—223°) and β (m. p. 227—233°) ethyl triphenylmethylpyrophosphonates. A third substance seems to be formed in the ethylation, since in the fractional crystallisation, the less

soluble (α) fractions contained small amounts of a substance appearing as wisps of fine hair-like crystals. The α -ester could only be freed of these by repeated crystallisation. Both the α - and the β -ester obtained here yielded the original pyrophosphonic acid on treatment with hydriodic and acetic acids. They were identified by means of mixed melting points.

The Addition Compound, $[\text{Ph}_3\text{C}\cdot\text{PO}(\text{OH})_2]_2, \text{POCl}_3$.—Phosphoryl chloride (8 c.c.), cooled to 0° , was treated with 3 g. of dry and finely powdered phosphonic acid. After being kept at 0° for 3 hours, the excess of phosphoryl chloride was sucked off and the crystalline addition *product* was washed repeatedly by distilling light petroleum from sodium on to it. The product was left in a vacuum over sodium hydroxide and calcium chloride for 24 hours. Throughout the operations moisture was carefully excluded (Found : P, 11.65. $\text{C}_{38}\text{H}_{34}\text{O}_7\text{Cl}_3\text{P}_3$ requires P, 11.6%). The substance is decomposed at once by water. The following analytical data were obtained by decomposing the substance with hot water, collecting the phosphonic acid produced, and estimating chloride and phosphate in the aqueous solution. The last two estimations are reported as the corresponding amounts of phosphorus and chlorine in the original material [Found : phosphonic acid, 80.46; Cl, 12.4; P (hydrolysable), 3.86. Cl : P in aqueous solution, 2.82. $(\text{C}_{19}\text{H}_{17}\text{PO}_3)_2, \text{POCl}_3$ requires phosphonic acid, 80.88; Cl, 13.2; P (hydrolysable), 3.87%; Cl : P, 3.00]. The low chlorine content is probably due to the ease with which the addition product loses hydrogen chloride. The addition product is partly converted into the carbinol by sulphuric acid.

The author thanks the Chemical Society for a grant, and the Department of Scientific and Industrial Research for a research award, during the tenure of which at University College, Southampton, some of the experimental work was carried out.

EAST LONDON COLLEGE, UNIVERSITY OF LONDON.

[Received, April 22nd, 1933.]
