723. *The Formation of Triarylmethylphosphonic Acids from Triarylmethylphosphonyl Dichlorides.*

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Some new *o*- and *p*-substituted triarylmethylphosphonyl dichlorides have been prepared. They are converted by alcoholic alkali partly into esters of triarylmethylphosphonic acids and partly into triarylmethyl ethers, in relative amounts depending on the substituent and the concentration of the alkali. The mechanisms of the competing reactions are deduced.

Triphenylmethylphosphonyl dichloride with alcohol gives only the ether, the presence of alkali being necessary for alcoholysis to esters of triphenylmethylphosphonic acid. If a hydroxylic compound of lower dissociating power such as methyl salicylate is used, phosphonic esters are produced in absence of alkali.

The reaction between phosphorus trichloride and a triarylmethanol is notable, because the triarylmethyl group becomes directly attached to phosphorus giving rise to a triarylmethylphosphonyl dichloride. As alkylphosphonyl dichlorides these products are remarkably resistant to mild hydrolytic agents, which can therefore be used to free them of phosphorus trichloride, making their isolation in good yield particularly easy (Boyd and Chignell, *J.*, 1923, **123**, 813; Boyd and Smith, *J.*, 1926, 2323; Arbusov and Arbusov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 217; Hatt, *J.*, 1929, 2412; 1933, 776). Nevertheless mild hydrolytic agents slowly attack most of them, and strong hydrolytic agents such as sulphuric acid and alcoholic alkali attack them rapidly. The hydrolytic reactions are of two types: in one the chlorine atoms are replaced by hydroxyl or alkoxyl groups, giving rise to a derivative of the corresponding triarylmethylphosphonic acid; in the other the triarylmethyl and phosphonyl dichloride moieties are separated and the former is incorporated in some phosphorus-free molecule such as the triarylmethanol. The two reactions are in particularly clear competition when alcoholic alkali is the reagent; Boyd and Smith (*loc. cit.*) showed that the nature of the triarylmethyl group influenced the extent to which each reaction occurred with this reagent.

	Yields of phosphonic acid (%)		Basicity of alcohol	Dissociation (%) of hexa-arylethane in 3% solution
Triarylmethyl	With 2·5N-NaOH–EtOH	With 1·8N-NaOH–EtOH		
9-Phenyl-9-fluorenyl	100	98	$\ll 1$	0 [a]
Triphenylmethyl	90	91	1	2·8 [b]
Diphenyl-*p*-tolylmethyl	88	86	2·3	5 [c]
Phenyldi-*p*-tolylmethyl	90	58	4	5·5 [d]
Tri-*p*-tolylmethyl	64	20	6	16 [d]
Diphenyl-*o*-tolylmethyl	59	35	1·5	25 [c], 30 [e]
o-Methoxytriphenylmethyl	26	8	1·8	3·8 [f]
α-Naphthyldiphenylmethyl	—	0 [g]	1·0	34 [e]

[a] Schlenk, Weickel, and Herzenstein, *Ber.*, 1910, **43**, 1754. [b] Preckel and Selwood, *J. Amer. Chem. Soc.*, 1941, **63**, 3397. [c] Marvel, Mueller, Himel, and Kaplan, *ibid.*, 1939, **61**, 2771. [d] Seel, F.I.A.T. Review, Theoretical Organic Chemistry, 1948, I, 89. [e] Byerly, Cutforth, and Selwood, *J. Amer. Chem. Soc.*, 1948, **70**, 1142. [f] Marvel, Whitson, and Johnston, *ibid.*, 1944, **66**, 415. [g] From Boyd and Smith, *loc. cit.*

These hydrolytic reactions have now been studied with a variety of triarylmethylphosphonyl dichlorides. At one extreme, 9-phenyl-9-fluorenylphosphonyl dichloride resists boiling ethanol, acetic acid, or aqueous alkali for hours, and with alcoholic alkali yields no alcohol or simple derivative thereof but is entirely converted into ethyl hydrogen and diethyl 9-phenyl-9-fluorenylphosphonates. At the other extreme *o*-methoxytriphenylmethylphosphonyl dichloride is hydrolysed completely to the alcohol by hot water, and with alcoholic alkali gives the ether as the main product, the amount of phosphonic acid being small unless very concentrated alkali is used. The yields of triarylmethylphosphonic acids obtained with two different concentrations of alkali are given in the annexed Table (yields were reproducible to ±1%).

The yield of triarylmethylphosphonic acid from the phosphonyl dichloride is clearly a measure of the relative velocities of the two competing hydrolytic reactions, but it affords no measure of the relative rates of hydrolysis of different phosphonyl dichlorides. The evidence is consistent with the view that the two competing reactions are (1*a*) (S_N1 mechanism) and (2) (S_N2 mechanism).

$$\text{R·POCl}_2 \rightleftarrows \text{R}^+ + \text{POCl}_2^- \quad \text{(1}a\text{)}$$

$$\text{R}^+ + 2\text{EtOH} = \text{ROEt} + \text{EtOH}_2^+ \quad \text{(1}b\text{)}$$

$$\text{R·POCl}_2 + \text{OEt}^- = \text{R·PClO·OEt (I)} + \text{Cl}^- \quad \text{(2)}$$

Supporting (1*a*) is the close resemblance of the triarylmethylphosphonyl dichlorides to the triarylchloromethanes, which shows that in many reactions they behave as carbonium salts. They give coloured solutions in dissociating solvents and form strongly coloured complexes with aluminium chloride and with stannic chloride. If the corresponding chloromethane gives a hydroxytetraphenylmethane with phenol, so also will the phosphonyl dichloride. Like the chloromethanes, with aliphatic alcohols they first form the ethers, which are then reduced to the triarylmethanes, if the solutions are sufficiently concentrated to develop high acidity by decomposition of the $POCl_2$ group.

It has been shown (Hatt, *loc. cit.*) that the first isolable intermediate in alkaline alcoholysis to the phosphonic acid or its esters is the ethyl chlorophosphinate (I). Its formation proceeds rapidly and its subsequent conversion into the phosphonic acid or its ethyl ester proceeds quantitatively and relatively slowly. We have found that with the phosphonyl dichlorides which react readily according to (1*a*), the yield of phosphonic acid is very dependent on the concentration of alcoholic alkali. For example, with *o*-methoxytriphenylmethylphosphonyl dichloride, doubling the concentration of alkali from 1·8 to 3·6N raised the yield from 8 to 47%. Such behaviour supports the S_N2 mechanism (2).

The view that (1*a*) and (2) are the competing hydrolytic reactions accords with the order of decreasing yields of phosphonic acids from *p*-substituted phosphonyl dichlorides. Including data reported by Boyd and Smith (*loc. cit.*), the order is NO_2, Cl, H, Me, 2Me, 3Me, MeO. This order is also that of increasing alcohol basicity, of increasing conductance of the triarylchloromethanes in solution (Ziegler and Wollschitt, *Annalen*, 1930, **479**, 90; Ziegler and Mathes, *ibid.*, p. 112), and of increasing rate of chloromethane alcoholysis (Branch and Nixon, *J. Amer. Chem. Soc.*, 1936, **58**, 492). Conductances of the chloromethanes and their rates of hydrolysis have been considered as relative measures of the ease of formation of the triarylcarbonium ion and therefore also of the ease with which reaction (1*a*) occurs. It follows that the influence of the *para*-substituent on the yield of phosphonic acid can be explained entirely through its influence on reaction (1*a*). However this arrangement of the *para*-substituents in the order in which they promote reaction (1*a*) corresponds also to the arrangement of *p*-substituted benzoyl chlorides in order of their decreasing rate of alcoholysis (Branch and Nixon, *ibid.*, p. 2499). It may be that these phosphonyl dichlorides likewise enter less readily into reaction (2) in this order.

When the substituent occupies an *ortho*-position other factors must participate in controlling the yield of phosphonic acid. With *o*-methoxyphenyl, *o*-tolyl, and α-naphthyl the basicities of the alcohols are low, that of α-naphthyldiphenylmethanol being the same as triphenylmethanol (Ziegler and Boye, *Annalen*, 1927, **458**, 229; Conant and Hall, *J. Amer. Chem. Soc.*, 1927, **49**, 3062). Where measured, the conductances of the triarylchloromethanes are low (*o*-methoxyphenyl, α-naphthyl) and the rate of alcoholysis slow (α-naphthyl) and in agreement with these low basicities. Such properties would correspond in the *para*-series to 90% yields of phosphonic acids, but, instead, the yields are low and in one example nil. The basicities and allied properties show that the new effect cannot be upon reaction (1*a*). It is suggested that for *o*-tolyl and α-naphthyl the effect is one of steric opposition to the approach of the ethoxyl ion for reaction (2). These two *ortho*-groups are among the most potent in increasing the degree of dissociation of hexa-arylethanes (see table) and their influence on this property has been explained as steric in character. An explanation of this kind cannot be used for the *o*-methoxy-group, for the yield of phosphonic acid, although below that expected from its basicity and related properties, is above the yield from the *p*-methoxy-isomer. In the hexa-arylethanes also its presence appears to introduce no detectable steric effect. A single methoxyl group in either the *ortho*- or *para*-position has little stabilising influence on the triarylmethyl, but, if anything, this is greater in the *para*-position (Marvel, Whitson, and Johnson, *loc. cit.*).

If the competing hydrolytic reactions are of types (1*a*) and (2), the second should be favoured in media of low dissociating power and with their use it might be possible to obtain products from a reaction of type (2) proceeding in absence of alkali. It has been found that, whereas in alcohol (ε_{20} 25·8) little or no phosphonic acid is produced in absence of alkali, with phenol or *p*-cresol (ε_{20} 10·3) triphenylmethylphosphonyl dichloride gives appreciable quantities of the monophenyl and monotolyl esters of the acid (Boyd and Hardy, *J.*, 1928, 635). With methyl salicylate (ε_{21} 8·8) the phosphorus compounds obtained are exactly analogous to those obtained with alcohol in presence of alkali. *o*-Carbomethoxyphenyl triphenylmethylchlorophosphinate, $Ph_3C{\cdot}PClO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2Me$ has been prepared in this way.

EXPERIMENTAL

M. p.s are not corrected.

Triarylmethanols.—9-Phenylfluoren-9-ol was prepared from fluorenone in 80% yield by reaction in ether with phenylmagnesium bromide (3 mols.). The remaining alcohols were prepared in 80—90% yield from the ethyl ester of the appropriate aromatic acid and an arylmagnesium bromide (4 mols.).

The basicities were measured by Baeyer and Villiger's method but, as recommended by Ziegler and Boye (*loc. cit.*), titration was to a faint yellow colour. Several determinations were needed to discover the desired end-point.

Triarylmethylphosphonyl Dichlorides.—The method employed was essentially that of Boyd and Chignell (*loc. cit.*), modified to suit the stability of the particular phosphonyl dichloride. To freshly distilled phosphorus trichloride (2 mols.) at 0°, the finely powdered alcohol was added in small portions with frequent shaking, during 0·5 hour, allowed to reach room temperature, and then heated for 4—5 hours at 60—70°. After cooling, the strongly coloured mixture was decomposed with crushed ice. 9-Phenyl-9-fluorenylphosphonyl dichloride is stable towards hot aqueous ammonia and hot water, and was purified by digestion with these reagents, filtration, and re-crystallization from aqueous acetone. The remaining compounds, particularly those containing *ortho*-substituents, were rapidly converted into the alcohol by these reagents and were purified by grinding them for a short time with cold dilute ammonia and with water, filtering, washing with a little light petroleum, and then drying rapidly at room temperature under reduced pressure. The pure compounds were colourless, but the less stable among them became strongly coloured in light and slowly decomposed. Their properties are tabulated.

Triarylmethylphosphonyl dichlorides.

Triarylmethyl	M. p.*	Yield (%)	Molecular formula	Found, %		Required, %	
				P	Cl	P	Cl
9-Phenyl-9-fluorenyl	153°	50	$C_{19}H_{13}OCl_2P$	8·7	19·4	8·7	19·7
Phenyldi-*p*-tolylmethyl	171·5	75	$C_{21}H_{19}OCl_2P$	8·0	18·1	8·0	18·2
Tri-*p*-tolylmethyl	177·5	75	$C_{22}H_{21}OCl_2P$	7·8	17·5	7·7	17·6
Diphenyl-*o*-tolylmethyl	124—125	60	$C_{20}H_{17}OCl_2P$	8·3	18·9	8·3	18·9
o-Methoxytriphenylmethyl ...	171·5—173·5	65	$C_{20}H_{17}O_2Cl_2P$	8·0	18·4	7·9	18·1

* Crystallisation from alcohol-free chloroform plus light petroleum (b. p. 60—80°), except for the first compound for which acetone was used.

Triarylmethylphosphonic Acids.—The general method of preparation consisted in heating the corresponding phosphonyl dichloride with 6 mols. of sodium ethoxide in alcohol according to Hatt's method (*loc. cit.*, 1929). Where the yield of phosphonic acid was not much influenced by the concentration of alkali a dilute (1·5N) reagent was used to avoid intermediate formation of the less easily hydrolysed diethyl phosphonate. Much stronger alkali (2·5 —3·0N)was used for the more easily hydrolysed phosphonyl dichlorides, in order to increase the yield of phosphonic acid. The reaction time was usually 4 hours in order to convert all intermediate phosphorus compounds into the ethyl hydrogen triarylmethylphosphonate. After the reaction, water was added in excess, the alcohol boiled off, and, when the mixture had cooled sufficiently for the insoluble by-product to coalesce, the liquid was filtered and strongly acidified with hydrochloric acid. If a quantitative estimation of the yield was required, this precipitate was collected and analysed by Hatt's method (*loc. cit.*). By careful control of conditions the yield could easily be replicated to ±1·0%.

Usually the monoethyl ester was not purified, but after drying at 100° was converted into the phosphonic acid by 1 hour's refluxing with 6 parts of 2 : 1 acetic acid–hydriodic acid (*d* 1·7). After cooling and addition of water, the precipitated phosphonic acid was filtered off, washed successively with dilute sulphurous acid, dilute hydrochloric acid, and water, dried, and crystallised.

In the preparation of 9-*phenyl*-9-*fluorenylphosphonic* acid there was no phosphorus-free by-product, but if the action of alcoholic alkali was not allowed to continue for some hours considerable amounts of diethyl 9-phenyl-9-fluorenylphosphonate were produced. In all other cases the by-product was the triarylmethyl ether if sodium ethoxide was used in absolute alcohol. The presence of water in the alcohol led to the production of triarylmethanol together with its ether, in an amount which varied considerably with the nature of the phosphonyl dichloride.

9-Phenyl-9-fluorenylphosphonic acid was prepared more conveniently by refluxing the phosphonyl dichloride for 1 hour with water (1 part) and pyridine (9 parts). Dilution with much water and acidification precipitated the phosphonic acid (90%). The method is not suitable for preparations from the more easily hydrolysed phosphonyl dichlorides.

9-*Phenyl*-9-*fluorenylphosphonic acid.* This acid crystallised from glacial acetic acid as an acetic acid *addition compound*, colourless prisms, losing acetic acid at 120° (Found : C, 66·1; H, 5·0; P, 8·1. $C_{19}H_{15}O_3P,C_2H_4O_2$ requires C, 65·9; H, 5·0; P, 8·1%). The solvent-free *acid* melts at 268° (Found : C, 70·7; H, 4·9; P, 9·5. $C_{19}H_{15}O_3P$ requires C, 70·8; H, 4·7; P, 9·6%).

The *dipotassium* salt crystallised in pearly leaflets from a solution in hot concentrated aqueous potassium hydroxide. It was collected, washed with alcohol, and dried (Found: P, 6·4; K, 16·9. $C_{19}H_{13}O_3PK_2,3H_2O$ requires P, 6·6; K, 16·6%).

Diethyl 9-*phenyl*-9-*fluorenylphosphonate* was formed as a neutral by-product in the hydrolysis of the phosphonyl dichloride with alcoholic alkali. After the action of 1·8N-alcoholic alkali had continued for 1 hour it formed 28% of the product. It crystallised from light petroleum in flat rhombs, m. p. 126° (Found: C, 73·4; H, 5·9; OEt, 23·7. $C_{23}H_{23}O_3P$ requires C, 73·0; H, 6·0; OEt, 23·2%).

Phenyl-p-*tolylmethylphosphonic acid.* This acid separated as an acetone *addition compound* from acetone and light petroleum (b. p. 60—80°), which readily lost the acetone at 100° (Found: loss at 100°, 13·2. $C_{21}H_{21}O_3P,C_3H_6O$ requires C_3H_6O, 14·2%). The solvent-free *acid* melted at 262—264° (Found: C, 71·4; H, 6·3; P, 8·8. $C_{21}H_{21}O_3P$ requires C, 71·6; H, 6·0; P, 8·8%). The *dipotassium* salt separated from a solution of the acid in concentrated aqueous potassium hydroxide on cooling and was obtained in small colourless needles by crystallisation from ethanol (Found: P, 5·6; K, 13·8; H_2O, 22·5: $C_{21}H_{19}O_3PK_2,7H_2O$ requires P, 5·6; K, 14·1; H_2O, 22·7%).

Tri-p-*tolylmethylphosphonic acid* separated in colourless crystals [from carbon tetrachloride and light petroleum (60—80°)], m. p. 272—273° (Found: C, 71·7; H, 6·8; P, 8·4. $C_{22}H_{23}O_3P$ requires C, 72·1; H, 6·3; P, 8·4%). Its *disodium* salt separated from a solution of the acid in concentrated aqueous sodium hydroxide and crystallised from aqueous alcohol in colourless small plates (Found: P, 5·4; Na, 8·0; H_2O, 28·2. $C_{22}H_{21}O_3PNa_2,9H_2O$ requires: P, 5·4; Na, 8·0; H_2O, 28·3%).

Diphenyl-o-*tolylmethylphosphonic acid* separated from acetone as an *addition compound* which readily lost its acetone at 110° (Found: loss, 14·7. $C_{20}H_{19}O_3P,C_3H_6O$ requires C_3H_6O, 14·7%). The solvent-free material melted at 264° (Found: C, 71·4; H, 6·1; P, 9·2. $C_{20}H_{19}O_3P$ requires C, 71·0; H, 5·7; P, 9·3%).

o-*Methoxytriphenylmethylphosphonic acid.* The crude monoethyl ester obtained from the phosphonyl dichloride and alcoholic alkali was not converted into the *phosphonic acid.* The latter was obtained in 10% yield as a by-product in the preparation of the phosphonyl dichloride (cf. Boyd and Smith, 1926, *loc. cit.*), being precipitated on acidification of the ammoniacal wash-liquors. It formed colourless crystals (from glacial acetic acid), m. p. 239—240° (Found: P, 9·0. $C_{20}H_{19}O_4P$ requires P, 9·0%).

Among the ethers obtained as by-products in the formation of phosphonic acids, *ethyl* o-*methoxytriphenylmethyl ether* appears to be new. As the Table indicates, it was the chief product from the reaction between the corresponding triarylmethylphosphonyl dichloride and alcoholic alkali. It formed colourless parallelepipeds (from ethanol), m. p. 81° (corr) (Found: C, 83·0; H, 7·0; total alkoxyl, as MeO, 19·4. $C_{22}H_{22}O_2$ requires C, 83·0; H, 7·0; total alkoxyl, as MeO, 19·5%). The same compound was prepared from the reaction between the triarylchloromethane and alcoholic sodium ethoxide. It could not be prepared from the alcohol and alcoholic mineral acid, for even with very small concentrations of acid there was considerable reduction to the triarylmethane. A 3 : 1 mixture of sulphuric and acetic acids at 40° converted this ether into the carbonium sulphate, which was hydrolysed by water to the alcohol.

Action of Methyl Salicylate on Triphenylmethylphosphonyl Dichloride.—Triphenylmethylphosphonyl dichloride (10 g.) and pure dry methyl salicylate (20 g.) were heated at 150—160°. When the vigorous evolution of hydrogen chloride slackened, the mixture was heated for a few minutes at 200° and then cooled. Aqueous sodium carbonate was added and the unchanged methyl salicylate removed in steam. The residues were dissolved in benzene and extracted with aqueous sodium hydroxide. Acidification of the sodium hydroxide and carbonate extracts precipitated *o*-carboxyphenyl hydrogen triphenylmethylphosphonate. Evaporation of the benzene liquors and addition of ether and light petroleum gave crystals of *o*-carbomethoxyphenyl triphenylmethylchlorophosphinate. The mother-liquors from this crystallisation on evaporation left a light yellow resin which behaved as if it consisted chiefly of bis-*o*-carbomethoxyphenyl triphenylmethylphosphonate. The proportions in which these three phosphorus compounds were isolated varied considerably with small changes in the reaction conditions.

o-*Carbomethoxyphenyl triphenylmethylchlorophosphinate* separated from benzene or ethyl acetate in colourless crystals, m. p. 157° (Found: P, 6·7; Cl, 7·2. $C_{27}H_{22}O_4ClP$ requires P, 6·5; Cl, 7·4%). It is difficultly soluble in ether and in light petroleum, but readily soluble in benzene. It was unaffected by prolonged boiling of its solutions in alcohol and in acetic acid. Sulphuric acid dissolved it and subsequent dilution of the solution with water precipitated triphenylmethanol. Refluxing (1 hour) with an excess of N-alcoholic sodium hydroxide gave a 96% yield of the *o*-carboxyphenyl hydrogen triphenylmethylphosphonate, isolated by the method used for ethyl hydrogen triphenylmethylphosphonate. When *o*-carbomethoxyphenyl triphenylmethylchlorophosphinate (3 g.) was boiled (1 hour) with constant-boiling hydriodic acid (1·5 ml.) and acetic acid (20 ml.) it was converted in part into triphenylmethane and in part into *o*-carboxyphenyl hydrogen triphenylmethylphosphonate, which were easily separated. Salicylic acid was also formed.

o-*Carboxyphenyl hydrogen triphenylmethylphosphonate* was also obtained by hydrolysis of *o*-carbomethoxyphenyl triphenylmethylchlorophosphinate or the crude bis-*o*-carbomethoxyphenyl triphenylmethylphosphonate. By all methods, after crystallisation from alcohol it was obtained as colourless crystals, m. p. 217° (Found : C, 70·0; H, 4·9; P, 7·0. $C_{26}H_{21}O_5P$ requires C, 70·3; H, 4·8; P, 7·0%). Boiling hydriodic–acetic acid slowly hydrolyses it to triphenylmethylphosphonic acid. It is dibasic and readily forms salts which crystallise well.

The *dipotassium* salt crystallised when a hot solution of the acid (1 g.) in potassium hydroxide (1·5 g.) and 80% alcohol (50 ml.) was allowed to cool. Recrystallised from 80% alcohol and air-dried, it formed colourless prisms (Found : P, 5·2; K, 13·4; H_2O, 12·2. $C_{26}H_{19}O_5PK_2,4H_2O$ requires P, 5·2; K, 13·2; H_2O, 12·2%). By double decomposition, the *barium* salt was obtained as a white precipitate, which was dried to constant weight under reduced pressure (Found : Ba, 19·9. $C_{26}H_{19}O_5PBa,6H_2O$ requires Ba, 19·9%).

The resinous material described above as probably bis-*o*-carbomethoxyphenyl triphenylmethylphosphonate (Found : P, 5·5. Calc. for $C_{35}H_{29}O_7P$: P, 5·2%) was assigned this structure because hydrolysis with potassium hydroxide in alcohol and subsequent acidification gave a theoretical yield of *o*-carboxyphenyl hydrogen triphenylmethylphosphonate together with salicylic acid. Reaction with sulphuric acid and subsequent addition of water gave triphenylmethanol. Hydriodic–acetic acid reduced it to triphenylmethane.

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