The Alkaline Hydrolysis of Some Cyclic Phosphonium Salts: Ring-opening and Ring-expansion Reactions

By **David W. Allen*** and **Ian T. Millar,** Department of Chemistry, The University, Keele, Staffordshire

The alkaline hydrolysis of some five- and six-membered cyclic phosphonium salts has been examined, and the results have been related to current views on the structure and stereochemistry of the phosphorane intermediates of such reactions.

Hydrolysis of the iodomethyl salts (IV; R = Me or Ph, X = I, Y = I⁻) of the 9-substituted 9-phosphafluorenes occurs with ring-expansion to give 9-substituted 9,10-dihydro-9-phosphaphenanthrene 9-oxides (V; R = Me or Ph), whereas hydrolysis of the corresponding salts (XVI; R = Me or Ph) of the 10-substituted phenoxaphosphines occurs with loss of the iodomethyl group and retention of the six-membered ring to give the 10-substituted phenoxaphosphine 10-oxides (XVII; R = Me or Ph). Hydrolysis of the methiodide (XV; R = Ph) of 10-phenylphenoxaphosphine proceeds with fission of the six-membered ring.

The conformation of the phenoxaphosphine ring system is discussed. Variable temperature ^{1}H n.m.r. studies indicate that the energy barrier to conformational inversion in this system is very small.

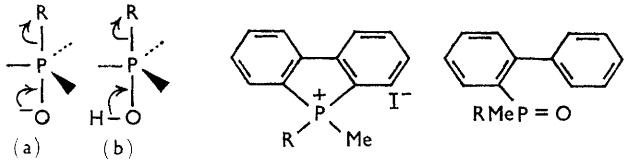
The alkaline hydrolysis of cyclic phosphonium salts has recently received much attention; considerable interest is centred on the nature and sterochemistry of the intermediates in such reactions. In general, the alkaline hydrolysis of phosphonium salts gives mainly phosphine oxides and hydrocarbons, and investigations of the kinetics and mechanism of such reactions have established that in most cases, the rate is proportional to [phosphonium salt][OH^-] [2] although in some cases a second-order process (rate $\propto$ [phosphonium salt][OH^-]) is observed. During the reaction the configuration at phosphorus is inverted, and the group lost as hydrocarbon is that which is most stable as an anion.[1] These findings are usually accommodated in a mechanism which

[1] R. F. Hudson, 'Structure and Mechanism in Organophosphorus Chemistry,' Academic Press, New York, 1965.

[2] S. E. Fishwick, J. Flint, W. Hawes, and S. Trippett, *Chem. Comm.*, 1967, 1113.

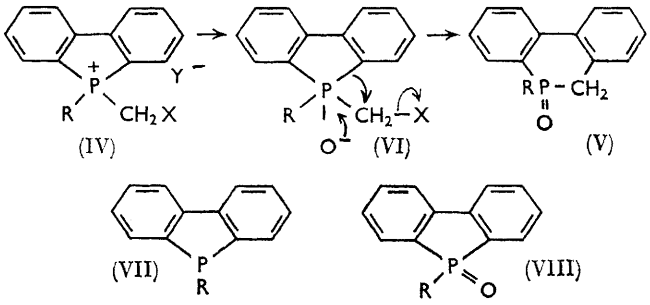
involves the rate-determining collapse of an intermediate trigonal bipyramidal phosphorane [formulated as (Ia) or (Ib), depending on the kinetics], which loses the group most stable as the anion from an apical position. Trippett *et al.*[2,3] have pointed out that if the phosphorus atom is present in a small strained ring system, then the difference in bond angles between apical and equatorial (90°) and diequatorial (120°) positions could lead to constraints on the conformation of the intermediate (I), such that the ring system spans an apical–equatorial position, leading eventually to ring opening or ring expansion, depending upon the nature of the other substituents attached to phosphorus. The behaviour of a number of phosphetanium salts on alkaline hydrolysis supports the above views.[2-4] We now report studies of the alkaline hydrolysis of some five- and six-membered cyclic phosphonium salts.

Alkaline hydrolysis of methiodides (II; R = Ph or Me) of 9-substituted 9-phosphafluorenes proceeds exclusively with opening of the heterocyclic ring to give the biphenyl-2-ylphosphine oxides (III; R = Ph or Me).[5] An analogous ring-opening reaction occurs on alkaline hydrolysis of the methiodides of 1,2,5-triphenyl- and 1,2,3,4,5-pentaphenyl-phosphole.[6] The latter reactions showed second order kinetics, which indicated a phosphorane intermediate of type (Ib), and had an energy of activation considerably smaller than that for hydrolysis, in which a phenyl carbanion is the leaving group. Preliminary investigations of the kinetics of hydrolysis of the quaternary salts (II) of the 9-substituted 9-phosphafluorenes indicate that a third-order rate law is followed; this suggests the rate-determining collapse of phosphorane intermediates of type (Ia). Kinetic studies on the cyclic phosphonium salts discussed in this paper will be reported separately.



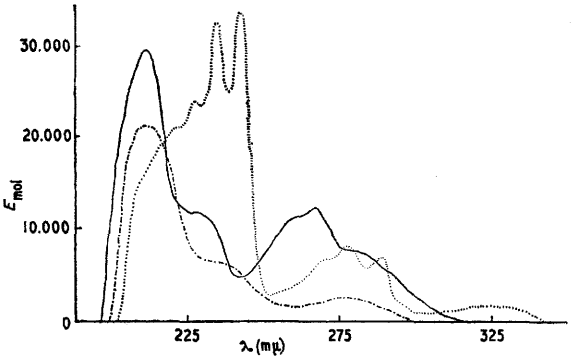
(I) (II) (III)

Intramolecular 1,2-migration of an aryl group from phosphorus to carbon occurs in the alkaline hydrolysis of bromomethyltriphenylphosphonium bromide to give benzyldiphenylphosphine oxide.[7] We have investigated the alkaline hydrolysis of halogenomethyl quaternary salts (IV) of the 9-phosphafluorenes in the anticipation that preferential migration of one of the ring C–P bonds would occur to give the ring-expanded product, a 9-substituted 9,10-dihydro-9-phosphaphenanthrene 9-oxide (V) *via* an intermediate of the type (VI). (An aryl migration in the reaction of arylphosphines with terminal acetylenes in the presence of water [8] has been used to achieve a comparable ring-expansion.[9]) Reaction of 9-methyl-9-phosphafluorene (VII; R = Me)



with chloromethyl methyl ether gave the salt (IV; R = Me, X = OMe, Y = Cl^-). Attempts to convert this salt into the corresponding bromomethyl salt (IV; R = Me, X = Br, Y = Br^-) by heating under reflux with constant-boiling hydrobromic acid gave only the hydroxymethyl salt (IV; R = Me, X = OH, Y = Br^-). The iodomethyl salts (IV; R = Me or Ph, X = I, Y = I^-) were obtained directly in high yield from the phosphines (VII; R = Me or Ph) by heating with an excess of di-iodomethane in benzene.

Alkaline hydrolysis of the salt (IV; R = Me, X = OMe, Y = Cl^-) proceeded exclusively with ring-opening to furnish biphenyl-2-yl(methoxymethyl)methylphosphine oxide (III; R = $MeO{\cdot}CH_2$); ring expansion does not occur, presumably because the methoxide ion is a poor leaving group. The structure of the oxide (III; R = $MeO{\cdot}CH_2$) was proved by (*a*) analytical data, (*b*) the i.r. spectrum [$\nu_{max.}$ 1178s (P=O) and 1110s (C–O) $cm.^{-1}$], (*c*) the u.v. spectrum (Figure), which is typical of a hindered biphenyl system, and (*d*) the ^1H n.m.r. spectrum of a solution in deuteriochloroform [τ 1·85 (1H, m, aromatic), 2·45br (8H, s, aromatic), 6·41 (2H, d, *J* 5·3 c./sec., $P{\cdot}CH_2{\cdot}O$), 6·66 (3H, s, OMe), and 8·55 (3H, d, *J* 13·4 c./sec., PMe)].



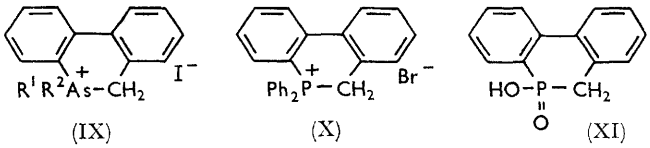
U.v. spectra of compounds (V; R = Me) (——), (III; R = $MeO{\cdot}CH_2$) (— · — · —), and (VIII; R = Me) (· · · ·)

Alkaline hydrolysis of the salt (IV; R = Me, X = OH, Y = Br^-) gave mainly 9-methyl-9-phosphafluorene, by

[3] W. Hawes and S. Trippett, *Chem. Comm.*, 1968, 295.
[4] S. E. Fishwick and J. Flint, *Chem. Comm.*, 1968, 182.
[5] D. W. Allen, F. G. Mann, and I. T. Millar, *J. Chem. Soc.* (*C*), 1967, 1869.
[6] K. Bergeson, *Acta Chem. Scand.*, 1966, **20**, 899.
[7] H. Hellmann and J. Bader, *Tetrahedron Letters*, 1961, 724; M. Schlosser, *Angew. Chem.*, 1962, **74**, 291.
[8] D. W. Allen and J. C. Tebby, *Tetrahedron*, 1967, **23**, 2795.
[9] E. M. Richards and J. C. Tebby, *Chem. Comm.*, 1967, 957.

the established mode of decomposition of a hydroxymethylphosphonium salt.[10]

Alkaline hydrolysis of the salt (IV; R = Me, X = I, Y = I^-) proceeded readily to give the ring-expanded product (V; R = Me), in high yield. The structure of the oxide (V; R = Me) was proved by (*a*) analysis, (*b*) its i.r. spectrum, $\nu_{max.}$ 1150—1200s $cm.^{-1}$ (P=O), (*c*) its characteristic u.v. spectrum (Figure), which is very different from that of the ring-opened product (III; R = $MeO{\cdot}CH_2$) and that of 9-methyl-9-phosphafluorene oxide (VIII; R = Me) but is very similar to those of the structurally similar salts (IX) [11] and (X) [12] and the cyclic phosphinic acid (XI),[13] and (*d*) ^1H n.m.r. spectra (see below).



(IX) (X) (XI)

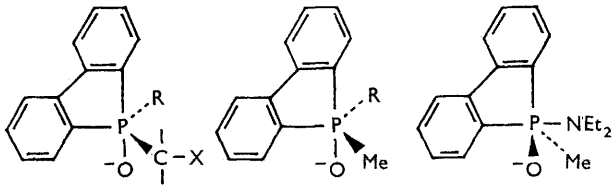
It has been pointed out that in the arsonium salts (IX), owing to the tetrahedral disposition of the central atoms of the bridging group, the two benzene rings of the biphenyl system cannot become coplanar, and such a molecule must therefore possess molecular dissymmetry. In addition, such a molecule with two dissimilar groups (R^1 and R^2) attached to the arsenic atom would have an asymmetric arsenic atom, and should therefore be capable of existing in two distinct racemic forms.[11] A similar situation prevails in the ring-expanded product (V; R = Me). The general asymmetry of the molecule was revealed by the ^1H n.m.r. spectrum, in which the two magnetically non-equivalent benzylic protons (H_A and H_B) appeared as an ABX multiplet centered at τ 6·5 (J_{AB} 16·3 c./sec.) for a solution in deuteriochloroform. The spectrum also included a multiplet centered at τ 2·2, due to the eight aromatic protons, and a doublet centered at τ 8·53 (J_{PCH} 13·5 c./sec.) due to the P(O)Me group.

The ^1H n.m.r. spectrum of the cyclic salt (X) in deuteriochloroform solution [12] is of interest in that the benzylic protons appear as a simple doublet and not as an ABX multiplet. The appearance of the simple doublet of an A_2X spectrum must indicate rapid conformational inversion in this compound, resulting in the 'time-averaged' equivalence of the benzylic protons. Such equivalence cannot occur in the ring-expanded product (V; R = Me) owing to the presence of the asymmetric phosphorus atom, the stability of which to inversion of configuration is to be expected to be considerable, in view of the fact that a number of tertiary phosphine oxides are optically resolvable.[14]

In the case of the salt (IV; R = Ph, X = I, Y = I^-), there was the possibility that on hydrolysis, migration of the phenyl group to the adjacent methylene to give 9-benzyl-9-phosphafluorene 9-oxide (VIII; R = $PhCH_2$) might compete with the ring-expansion reaction. However this reaction gave the ring-expanded product (V; R = Ph) in high yield, with traces of 9-phenyl-9-phosphafluorene (VII; R = Ph) and 9-phenyl-9-phosphafluorene 9-oxide (VIII; R = Ph). The last two products may be accounted for on the basis of (i) competitive attack by OH^- on the CH_2I group to give a hydroxymethylphosphonium salt which rapidly loses formaldehyde to give the free phosphafluorene, and (ii) loss of the CH_2I fragment (as methyl iodide) from the intermediate (VI). 9-Benzyl-9-phosphafluorene oxide was not detected; this again indicates the preferred cleavage of the ring C–P bond. The structure of (V; R = Ph) was deduced like that of the corresponding methyl compound (V; R = Me); the ^1H n.m.r. spectrum (deuteriochloroform) again showed an ABX multiplet for the benzylic protons centered at τ 6·3 (J_{AB} 16·3 c./sec.).

Trippett *et al.*[3] have suggested that the course of the above reactions, involving ring-fission or ring-expansion on alkaline hydrolysis of the quaternary salts of the 9-phosphafluorenes, may be understood in terms of the general thesis that the presence of a small ring imposes a steric constraint on the conformation of the intermediate phosphorane (XII), in which the ring system occupies an apical–equatorial position, resulting eventually in cleavage of the apical P–C bond on decomposition of the phosphorane.

However, fission of a ring carbon–phosphorus bond on hydrolysis does not occur with all quaternary salts of the 9-phosphafluorenes. Hydrolysis of the salts (II; R = NEt_2 or $PhCH_2$) gave 9-methyl-9-phosphafluorene 9-oxide (VIII; R = Me) with retention of the five-membered ring. The course of these reactions, as opposed to the ring-opening and ring-expansion reactions of the other salts discussed above, must be dictated by the relative stabilities of the diethylamino and benzyl anions. On the assumption that the ring system must occupy an apical–equatorial position in the intermediate phosphorane (XII), with the remaining apical position occupied by the electronegative oxygen atom, loss of the exocyclic leaving group must occur from an equatorial position, unless the intermediate phosphorane undergoes pseudorotation to a second configuration (XIII) where the oxygen is equatorial and the



(XII) (XIII)

[10] L. Horner, H. Hoffmann, H. G. Wippel, and G. Hassel, *Chem. Ber.*, 1958, **91**, 52; H. Hellmann, J. Bader, H. Birkner, and O. Schumacher, *Annalen*, 1962, **659**, 49.

[11] G. H. Cookson and F. G. Mann, *J. Chem. Soc.*, 1949, 2888.

[12] E. A. Cookson and P. C. Crofts, *J. Chem. Soc.* (*C*), 1966, 2003, and personal communication.

[13] E. R. Lynch, *J. Chem. Soc.*, 1962, 3729; E. M. Richards and J. C. Tebby, personal communication.

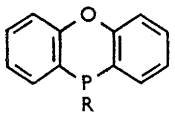
[14] See, *e.g.*, G. Kamai and G. M. Usacheva, *Russ. Chem. Rev.*, 1966, **35**, 601.

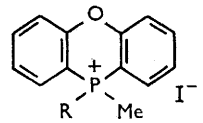
exocyclic leaving group (Et_2N or $PhCH_2$) is apical. A similar situation prevails in the alkaline hydrolysis of a benzylphosphetanium salt, which proceeds with loss of the benzyl group; the ring system and the absolute configuration of the phosphorus atom are retained.[3]

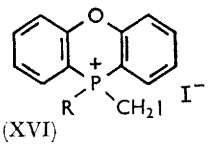
The aminophosphafluorene (VII; R = NEt_2) was prepared by the reaction of diethylaminophosphonous dichloride with 2,2′-dilithiobiphenyl in ether, at −10° in order to reduce attack by the organolithium reagent on the P–N bond. With methyl iodide, the phosphine gave the salt (II; R = NEt_2), the ^1H n.m.r. spectrum and subsequent mode of hydrolysis of which confirmed that quaternisation had occurred at phosphorus, as is usual for aminophosphonium salts.[1]

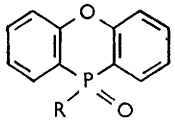
The ^1H n.m.r. spectra of phosphonium salts of type (IV) where the methylene group attached to phosphorus bears an electronegative atom or group, are of interest in that the geminal PCH coupling constants for the methylene protons are significantly smaller than those of the α-protons of unsubstituted alkyl- or benzylphosphonium salts, and a relationship has been established between the magnitude of J_{PCH} and the electronegativity of the substituent X. The data have been interpreted on the basis of the electronegative substituent X causing some rehybridisation of the carbon atom bonding orbitals, the *s* character of which is increased, resulting in a positive contribution to a negative coupling constant, and thus reducing the magnitude of J_{PCH}.[15] The effect is most marked in the hydroxymethylphosphonium salts where the $\overset{+}{P}$–CH_2–OH signal occurs as a singlet at 60 Mc./sec. in deuteriochloroform. For a solution in trifluoroacetic acid, resolution into a doublet is observed, with J 1·1 c./sec., *cf.* J 11—16 c./sec. for the α-protons of unsubstituted alkylphosphonium salts.[16]

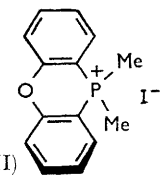
We have also investigated the alkaline hydrolysis of some quaternary salts of the six-membered cyclic phosphines, 10-methyl- and 10-phenyl-phenoxaphosphine (XIV; R = Me or Ph), prepared from 2,2′-dilithiodiphenyl ether and the appropriate organophosphonous dichloride in petroleum–benzene.[17]

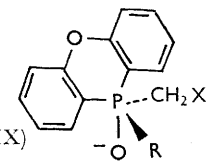

(XIV)


(XV)

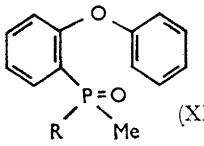

(XVI)

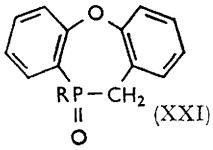

(XVII)


(XVIII)


(XIX)

The conformation of a 10-substituted phenoxaphosphine such as (XIV) is at present uncertain. It has been suggested[17] that if the usual intervalence angles at phosphorus and oxygen are retained in the phenoxaphosphine ring system, then the molecule may be folded about the O–P axis, thus raising the possibility of the existence of isomeric forms of compounds of type (XIV). Dreiding models support this idea for both the tertiary phosphines (XIV), the quaternary derivatives (XV) and (XVI), and (XVII). A direct consequence of any such folding of the molecule is that the exocyclic substituents on the phosphorus atom would be in different magnetic environments, owing to their different spatial relationship with the two benzenoid rings. Thus in the salt (XVIII) the two methyl groups would be magnetically non-equivalent and would be expected to give rise to two distinct signals in the ^1H n.m.r. spectrum, if the ring system is conformationally stable. However, the ^1H n.m.r. spectrum of the salt (XVIII) at room temperature in deuteriochloroform shows only a simple doublet for the methyl groups attached to phosphorus, and no broadening of the signal is observed when the solution is cooled to −55°. This indicates the magnetic equivalence of the methyl groups and the effective planarity of the ring system, and suggests that the energy barrier to conformational inversion is small.


(XX)


(XXI)

Examination of a Dreiding model also indicates that the six-membered phenoxaphosphine ring would preferentially occupy an apical–equatorial position in the intermediate phosphorane (XIX), and thus on the basis of earlier arguments[3] the alkaline hydrolysis of quaternary salts of the phenoxaphosphines would be expected to resemble those of the phosphoniafluorene salts discussed above in undergoing ring-fission or ring-expansion.

Alkaline hydrolysis of the salt (XV; R = Ph) gave the ring-opened phosphine oxide (XX; R = Ph); this indicates cleavage of the apical ring-phosphorus bond in the phosphorane intermediate (XIX; R = Ph, X = H). However, alkaline hydrolysis of the iodomethyl salts (XVI; R = Me or Ph) gave the corresponding 10-substituted phenoxaphosphine 10-oxides (XVII; R = Me or Ph); ring-expansion to the seven-membered cyclic phosphine oxides (XXI) does not occur. Retention of the six-membered phenoxaphosphine ring system on hydrolysis of the salts (XVI; R = Me or Ph) indicates preferential loss of CH_2I from the phosphorane (XIX; X = I). The possibility of effecting ring-expansion reactions by alkaline hydrolysis of the easily available iodomethyl salts of cyclic tertiary phosphines therefore seems to be confined to the four- and five-membered ring systems. The structure of the above products of hydrolysis of the phenoxaphosphonium salts was determined by analysis, their characteristic i.r., u.v., and

[15] D. W. Allen, I. T. Millar, and J. C. Tebby, *Tetrahedron Letters*, 1968, 745.

[16] C. E. Griffin and M. Gordon, *J. Organometallic Chem.*, 1965, **3**, 414.

[17] F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 1953, 3746.

^{1}H n.m.r. spectra, and comparison with authentic compounds where possible.

EXPERIMENTAL

Operations involving phosphines were performed under nitrogen. M.p.s were determined with a Kofler hot-stage apparatus. ^{1}H N.m.r. spectra were recorded with a Perkin-Elmer 60 Mc./sec. instrument equipped with a variable temperature probe, with tetramethylsilane as internal standard. Coupling constants were determined from spectra expanded to 1 c./sec./unit. U.v. spectra were determined for solutions in 95% ethanol with a Unicam SP 800 spectrophotometer. Microanalyses were carried out by Mr. J. F. Boulton, Department of Chemistry, University of Keele.

Preparation of Phosphines, Phosphine Oxides, and Phosphonium Salts.—9-Phenyl-9-phosphafluorene (VII; R = Ph) was prepared by the procedure of Wittig and Maercker,[18] and had m.p. 92—93° (from ethanol) (lit.,[18] 92—94°) (Found: C, 82·7; H, 5·3. Calc. for $C_{18}H_{13}P$: C, 83·05; H, 5·05%). A sample of the phosphine, when treated with a solution of hydrogen peroxide (100 vols.) in acetone and set aside overnight gave the corresponding oxide (VIII; R = Ph), m.p. 163—164° (from aqueous ethanol) (lit.,[19] 162—164·5°) (Found: C, 78·7; H, 4·0. Calc. for $C_{18}H_{13}OP$: C, 78·25; H, 4·6%). 9-Methyl-9-phosphafluorene (VII; R = Me) was prepared as previously described.[5] Treatment of a sample of the phosphine in acetone with hydrogen peroxide (100 vols.) gave *9-methyl-9-phosphafluorene 9-oxide* (VII; R = Me), m.p. 149—150° [from light petroleum (b.p. 80—100°)–benzene] (Found: C, 73·2; H, 5·05. $C_{13}H_{11}OP$ requires C, 72·9; H, 5·15%), $\nu_{max.}$ (mull) 1190s cm.$^{-1}$ (P=O), $\lambda_{max.}$ 229 (ε 23,890), 235 (31,800), 243 (32,800), 278 (8093), 289 (7065), and 323 (1850) mμ, τ ($CDCl_3$) 2·2 (8H, m) and 8·08 (3H, d, J_{PCH} 13·7 c./sec.).

9-Hydroxymethyl-9-methyl-9-phosphoniafluorene Chloride (IV; R = Me, X = OH, Y = Cl$^-$).—9-Methyl-9-phosphafluorene (0·5 g.), formaldehyde (37% aq. soln.; 0·35 ml.), and concentrated hydrochloric acid (0·4 ml.) were shaken together for 15 min.; the mixture solidified to a crystalline mass. The supernatant liquid was decanted and the residue triturated several times with dry ether to give the *salt* (IV; R = Me, X = OH, Y = Cl$^-$), m.p. 151—152° (decomp.) (from propan-2-ol) (Found: C, 63·3; H, 5·2. $C_{14}H_{14}ClOP$ requires C, 63·5; H, 5·35%), τ (CF_3CO_2H) 2·0 (8H, m), 4·91 (2H, d, J_{PCH} 1·1 c./sec.), and 7·52 (3H, d, J_{PCH} 15·0 c./sec.).

9-Chloromethyl-9-methyl-9-phosphoniafluorene Chloride.—The hydroxymethyl salt (IV; R = Me, X = OH, Y = Cl$^-$) was dissolved in an excess of thionyl chloride and the solution was heated under reflux for 1 hr. The excess of reagent was then removed and the residue was triturated with dry ether to give the hygroscopic phosphonium chloride (IV; R = Me, X = Cl, Y = Cl$^-$), τ ($CDCl_3$) 0·9 (2H, m), 2·0 (6H, m), 4·07 (2H, d, J_{PCH} 8·0 c./sec.), and 6·81 (3H, d, J_{PCH} 15·6 c./sec.), τ (CF_3CO_2H) 1·95 (8H, m), 5·44 (2H, d, J_{PCH} 7·4 c./sec.), and 7·41 (3H, d, J_{PCH} 14·9 c./sec.). Satisfactory analytical values could not be obtained for the salt (IV; R = Me, X = Cl, Y = Cl$^-$); for characterization it was converted into the corresponding yellow *picrate*, m.p. 214° (from ethanol) (Found: C, 50·5; H, 3·05; N, 8·8. $C_{20}H_{15}ClN_3O_7P$ requires C, 50·5; H, 3·2; N, 8·85%).

9-Methoxymethyl-9-methyl-9-phosphoniafluorene Chloride (IV; R = Me, X = OMe, Y = Cl$^-$).—9-Methyl-9-phosphafluorene (0·5 g.) in chloromethyl methyl ether (5 ml.) was heated on a steam-bath for 1 hr. The solvents were evaporated off and the residue triturated with dry ether to yield the *salt* (IV; R = Me, X = OMe, Y = Cl$^-$) (0·63 g., 90%), m.p. 167—168° (Found: C, 63·9; H, 6·0. $C_{15}H_{16}ClOP$ requires C, 64·6; H, 5·7%), τ ($CDCl_3$) 1·0 (2H, m), 2·0 (6H, m), 4·40 (2H, d, J_{PCH} 4·4 c./sec.), 6·44 (3H, s), and 7·05 (3H, d, J_{PCH} 15·6 c./sec.), τ (CF_3CO_2H), 1·95 (8H, m), 5·31 (2H, d, J_{PCH} 4·8 c./sec.), and 7·57 (3H, d, J_{PCH} 15·0 c./sec.).

9-Hydroxymethyl-9-methyl-9-phosphoniafluorene Bromide (IV; R = Me, X = OH, Y = Br$^-$).—The salt (IV; R = Me, X = OMe, Y = Cl$^-$) (0·26 g.) in hydrobromic acid (50% aq. soln.; 10 ml.) was heated under reflux for 1 hr., and set aside overnight. The excess of acid was distilled off under reduced pressure to give a glassy solid, precipitated from chloroform solution with ethyl acetate to yield the *salt* (IV; R = Me, X = OH, Y = Br$^-$), m.p. 170—173° (Found: C, 54·3; H, 4·45. $C_{14}H_{14}BrOP$ requires C, 54·4; H, 4·55%), τ ($CDCl_3$) 1·3 (2H, m), 2·1 (6H, m), 4·74 (2H, s), and 7·15 (3H, d, J_{PCH} 15·4 c./sec.), τ (CF_3CO_2H) 1·95 (8H, m), 4·82 (2H, d, J_{PCH} 1·1 c./sec.), and 7·50 (3H, d, J_{PCH} 15·0 c./sec.).

9-Iodomethyl-9-methyl-9-phosphoniafluorene Iodide (IV; R = Me, X = I, Y = I$^-$).—9-Methyl-9-phosphafluorene (0·5 g.) in benzene (10 ml.) and di-iodomethane (6 ml.) was heated on a steam-bath for 1 hr. The solution was then cooled, and the crystals of the crude salt were filtered off. Evaporation of the mother-liquor gave more crystals, which were combined with the initial crop and heated with absolute ethanol (5 ml.) for 5 min. to remove soluble impurities and give the *salt* (IV; R = Me, X = I, Y = I$^-$) (0·98 g., 83%), m.p. 235—236° (from ethanol) (Found: C, 37·4; H, 3·1. $C_{14}H_{13}I_2P$ requires C, 37·7; H, 2·95%), τ (CF_3CO_2H) 1·85 (8H, m), 5·94 (2H, d, J_{PCH} 8·4 c./sec.), and 7·32 (3H, d, J_{PCH} 14·8 c./sec.).

9-Iodomethyl-9-phenyl-9-phosphoniafluorene Iodide (IV; R = Ph, X = I, Y = I$^-$).—9-Phenyl-9-phosphafluorene (0·2 g.) in benzene (5 ml.) and di-iodomethane (4 ml.) was heated on a steam-bath for 1 hr. The solvents were then distilled off under reduced pressure, and the residue was triturated with absolute ethanol to give the *salt* (IV; R = Ph, X = I, Y = I$^-$) (0·306 g., 75%), m.p. 219—220° (from ethanol) (Found: C, 43·2; H, 2·70. $C_{19}H_{15}I_2P$ requires C, 43·2; H, 2·85%), τ (CF_3CO_2H) 1·9 (13H, m,) and 5·54 (2H, d, J_{PCH} 8·1 c./sec.).

9-Diethylamino-9-phosphafluorene (VII; R = NEt_2).—2,2′-Dilithiobiphenyl solution [from 2,2′-dibromobiphenyl (11·03 g.) and lithium foil (0·98 g.) in ether (150 ml.)] was added dropwise during 1 hr. to diethylaminophosphonous dichloride [20] (5·8 g., 0·95 mol.) in dry ether (50 ml.) at −10° with vigorous stirring. The solution was then allowed to warm to room temperature and heated under reflux for 45 min. It was then cooled, filtered, and evaporated to yield a viscous residue which on distillation under reduced pressure gave the *aminophosphine* (VII; R = NEt_2) (2·05 g., 23%), b.p. 130°/0·1 mm. (Found: C, 75·5; H, 7·05; N, 5·3. $C_{16}H_{18}NP$ requires C, 75·3; H, 7·05; N, 5·5%).

9-Diethylamino-9-methyl-9-phosphoniafluorene Iodide (II; R = NEt_2).—The aminophosphine (0·14 g.) was set aside at room temperature with an excess of methyl iodide for

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[19] G. Wittig and G. Geissler, *Annalen*, 1953, **580**, 44.
[20] K. Issleib and W. Seidel, *Chem. Ber.*, 1959, **92**, 2681.

3 hr. The excess of methyl iodide was then evaporated off and the residue was triturated with dry ether to give a hygroscopic solid, which resisted crystallisation from a variety of solvents; τ ($CDCl_3$) 1·90 (8H, m), 6·0—7·18 (7H, m, including a sharp doublet centred at τ 7·03, J_{PCH} 12 c./sec., PMe) and 8·78 (6H, m). Treatment of an aqueous solution of the salt (II; R = NEt_2) with a cold, saturated aqueous solution of sodium picrate gave the corresponding *picrate* as yellow crystals, m.p. 115° (from aqueous ethanol) (Found: C, 55·8; H, 4·25; N, 10·8. $C_{23}H_{23}N_4O_7P$ requires C, 55·4; H, 4·6; N, 11·2%). An aqueous solution of the salt rapidly became cloudy owing to hydrolysis.

9-*Benzyl*-9-*methyl*-9-*phosphoniafluorene Bromide* (II; R = $PhCH_2$).—Reaction of 9-methyl-9-phosphafluorene with benzyl bromide in warm benzene gave the *salt*, m.p. 246—247° (Found: C, 64·9; H, 4·55. $C_{20}H_{18}BrP$ requires C, 65·05; H, 4·9%).

10-*Phenylphenoxaphosphine* (XIV; R = Ph), prepared as described by Mann and Millar,[17] had m.p. 94—95° (lit.,[17] 94·5—95°). Oxidation with aqueous hydrogen peroxide in acetone gave the oxide (XVII; R = Ph), m.p. 177—178° (lit.,[17] 173—174°). Treatment with methyl iodide gave the methiodide (XV; R = Ph), m.p. 244—245° (lit.,[17] 236—237°). When heated with an excess of di-iodomethane in benzene, the phosphine gave 10-*iodomethyl*-10-*phenyl*-10-*phenoxaphosphonium iodide* (XV; R = Ph), m.p. 218° (from ethanol) (Found: C, 41·8; H, 2·6. $C_{19}H_{15}I_2OP$ requires C, 41·95; H, 2·8%), τ (CF_3CO_2H–$CDCl_3$) 2·0 (13H, m) and 5·6 (2H, d, J_{PCH} 7·3 c./sec.).

10-*Methylphenoxaphosphine* (XIV; R = Me).—A solution of n-butyl-lithium in petroleum (b.p. 40—60°) (1·265N; 87·5 ml.) was added to 2,2′-dibromodiphenyl ether (16·4 g.) in benzene–petroleum (b.p. 40—60°) (200 ml.) and the resulting solution was boiled under reflux for 4 hr., then cooled. Methylphosphonous dichloride (5·85 g.) in benzene (50 ml.) was then added slowly to the solution of the organolithium reagent, and the resulting solution was heated under reflux for 45 min., cooled, and hydrolysed with cold air-free water. The organic layer was separated and dried (Na_2SO_4), and the solvents were evaporated off. The residue was distilled under reduced pressure to give 10-*methylphenoxaphosphine* (XIV; R = Me) (3·2 g., 30%), b.p. 95°/0·05 mm. (Found: C, 73·25; H, 4·9. $C_{13}H_{11}OP$ requires C, 72·9; H, 5·15%). Treatment of the phosphine with methyl iodide gave 10,10-*dimethylphenoxaphosphonium iodide* (XV; R = Me), m.p. 298—301° (from ethanol) (Found: C, 47·5; H, 3·75. $C_{14}H_{14}IOP$ requires C, 47·2; H, 3·95%), τ (CF_3CO_2H) 2·0 (8H, m) and 7·42 (6H, d, J_{PCH} 14·5 c./sec.), τ ($CDCl_3$) 0·9 (2H, m), 2·2 (6H, m), and 6·92 (6H, d, J_{PCH} 15·1 c./sec.). No significant change in the PMe doublet occurred when the sample was cooled to −55°. Oxidation of the phosphine with hydrogen peroxide in aqueous acetone gave 10-*methylphenoxaphosphine* 10-*oxide*, m.p. 32—33° (sublimation) (Found: C, 67·3; H, 5·4. $C_{13}H_{11}O_2P$ requires C, 67·8; H, 4·8%), $\lambda_{max.}$ ε 225 (ε 17,725), 242 (12,429), 277 (3242), 289 (4539), and 297 (5079) mμ, $\nu_{max.}$ (film) 1320s, 1275s, and 1222s $cm.^{-1}$.

When heated with an excess of di-iodomethane in benzene, the phosphine gave 10-*iodomethyl*-10-*methylphenoxaphosphonium iodide* (XVI; R = Me), m.p. 241° (Found: C, 34·6; H, 2·7. $C_{14}H_{13}I_2OP$ requires C, 34·9; H, 2·7%), τ (CF_3CO_2H) 1·95 (8H, m), 5·85 (2H, d, J_{PCH} 6·8 c./sec.), and 7·1 (3H, d, J_{PCH} 13·6 c./sec.).

Alkaline Hydrolysis of Phosphonium Salts.—(a) 9-*Hydroxymethyl*-9-*methyl*-9-*phosphoniafluorene bromide* (IV; R = Me, X = OH, Y = Br^-). The salt (0·167 g.) was dissolved in aqueous acetone (50%; 10 ml.) containing potassium hydroxide solution (30% aq.; 0·15 ml.), and the mixture was heated under reflux for 2 hr. The acetone was then distilled off and the residual solution was neutralised and extracted with chloroform (2 × 10 ml.). The extract was dried (Na_2SO_4) and evaporated to give an oil (0·135 g.) containing two components (t.l.c. on silica gel in ethyl acetate), which were separated by column chromatography on silica gel (6 g.). Elution with ethyl acetate gave 9-methyl-9-phosphafluorene (VII; R = Me) (0·060 g.), characterised by conversion into the methiodide (m.p. and mixed m.p. 280°) and methopicrate (m.p. and mixed m.p. 218°). Elution with absolute ethanol then gave 9-methyl-9-phosphafluorene 9-oxide (VIII; R = Me) (0·020 g.), identical with authentic material obtained by oxidation of 9-methyl-9-phosphafluorene with hydrogen peroxide in aqueous acetone.

(b) 9-*Methoxymethyl*-9-*methyl*-9-*phosphoniafluorene chloride* (IV; R = Me, X = OMe, Y = Cl^-). The salt (0·250 g.) was hydrolysed and the product extracted with chloroform as described above. Evaporation of the dried chloroform extract gave an oil which crystallised to give *biphenyl*-2-*ylmethoxymethylmethylphosphine oxide* (III; R = $MeO{\cdot}CH_2$) (0·230 g.), m.p. 84—85° (Found: C, 69·4; H, 6·55. $C_{15}H_{17}O_2P$ requires C, 69·25; H, 6·55%), $\nu_{max.}$ (film) 1178s (P=O) and 1110s (C–O) $cm.^{-1}$, $\lambda_{max.}$ 213 (ε 21,410), 240sh (6661), and 277 (2379) mμ, τ ($CDCl_3$) 1·8 (1H, m), 2·46 (8H, m), 6·4 (2H, d, J_{PCH} 5·3 c./sec.), 6·62 (3H, s), and 8·55 (3H, d, J_{PCH} 13·4 c./sec.).

(c) 9-*Iodomethyl*-9-*methyl*-9-*phosphoniafluorene iodide* (IV; R = Me, X = I, Y = I^-). The salt (0·7 g.) was hydrolysed and the products were extracted with chloroform as described above. T.l.c. of the dried chloroform extract (silica gel in ethyl acetate) showed it to contain one major and several minor components. Column chromatography on silica gel (10 g.) gave, on elution with ethyl acetate–ethanol (7 : 3), 9-*methyl*-9,10-*dihydro*-9-*phosphaphenanthrene* 9-*oxide* (V; R = Me) (0·24 g., 71%), as a viscous gum which resisted crystallisation from a variety of solvents. It was purified further by preparative-scale t.l.c. (Kieselgel P.F. 254; 1·5 mm. thick; ethyl acetate × 6) to give the oxide V; R = Me) as a hygroscopic gum (Found: C, 73·2; H, 5·7. $C_{14}H_{13}OP$ requires C, 73·7; H, 5·7%), $\nu_{max.}$ (film) 1190s $cm.^{-1}$ (P=O), $\lambda_{max.}$ 215 (ε 28,950), 228sh (11,990), 267 (11,980), and 281sh (7236) mμ, τ ($CDCl_3$) 2·2 (8H, m), 6·5 (2H, m, J_{AB} 16·3 c./sec.), and 8·53 (3H, d, J_{PCH} 13·5 c./sec.).

(d) 9-*Iodomethyl*-9-*phenyl*-9-*phosphoniafluorene iodide* (IV; R = Ph, X = I, Y = I^-). The iodide (0·28 g.) was hydrolysed and the product extracted with chloroform as described above. T.l.c. of the dried extract (silica gel in ethyl acetate) showed it to contain several components. Polar and non-polar products were initially separated by column chromatography on silica gel (7 g.). Elution with ethyl acetate gave 9-phenyl-9-phosphafluorene (VII; R = Ph) (0·027 g.). Elution with ethyl acetate–ethanol (8 : 2) gave a viscous gum (0·130 g.), shown by t.l.c. to contain one major and one minor component. Preparative scale t.l.c. (Kieselgel P.F. 254; 1·5 mm.; ethyl acetate × 4) gave 9-phenyl-9-phosphafluorene 9-oxide (VIII; R = Ph) (0·010 g.), identical with authentic material, and 9-*phenyl*-9,10-*dihydro*-9-*phosphaphenanthrene* 9-*oxide* (V; R = Ph) (0·089 g., 58%), m.p. 127—130° (Found: C, 78·6; H, 5·15. $C_{19}H_{15}OP$ requires C, 78·65; H, 5·15%), $\nu_{max.}$ (film) 1197s

cm.$^{-1}$ (P=O), $\lambda_{max.}$ 213 (ε 34,580), 271 (11,600), and 286 (6960) mμ, τ ($CDCl_3$) 2·3 (13H, m) and 6·3 (2H, m, J_{AB} 16·3 c./sec.).

(e) *9-Diethylamino-9-methyl-9-phosphoniafluorene iodide* (II; R = NEt_2). The iodide (0·40 g.) was hydrolysed and the product extracted with chloroform as described above. Column chromatography of the dried chloroform extract on silica gel gave, on elution with ethanol, 9-methyl-9-phosphafluorene 9-oxide (VIII; R = Me) (0·10 g.) which on recrystallisation from petroleum (b.p. 100—120°)–benzene gave crystals, m.p. 148—150°, not depressed in admixture with authentic material obtained by direct oxidation of 9-methyl-9-phosphafluorene.

(f) *9-Benzyl-9-methyl-9-phosphoniafluorene bromide* (as II; R = $PhCH_2$). The salt (0·035 g.) was hydrolysed and the product extracted with chloroform as described above. Evaporation of the dried extract gave 9-methyl-9-phosphafluorene 9-oxide (VIII; R = Me) (0·020 g.), ^{1}H n.m.r., i.r., and u.v. spectra identical with those of an authentic specimen.

(g) *10-Methyl-10-phenyl-10-phenoxaphosphonium iodide* (XV; R = Ph). The iodide (0·10 g.) was hydrolysed and the product extracted with chloroform as described above. T.l.c. of the dried extract (silica gel in ethyl acetate) indicated the presence of one major component. Evaporation of the extract gave *methyl-(2-phenoxyphenyl)phenylphosphine oxide* (XX; R = Ph) (0·068 g.) as a hygroscopic gum, which resisted crystallisation from a variety of solvents (Found: C, 73·6; H, 5·6. $C_{19}H_{17}O_2P$ requires C, 74·0; H, 5·55%), $\nu_{max.}$ (film) 1230s and 1180s cm.$^{-1}$; bands at 1330—1320, 1277—1268, and 1223—1215 cm.$^{-1}$, reported to be characteristic of quaternary derivatives of the phenoxaphosphine ring system,[21] were absent from the spectrum, indicating the cleavage of the ring system on hydrolysis; $\lambda_{max.}$ 223 (ε 17,567) and 280 (3846) mμ, τ ($CDCl_3$) 2·4 (14H, m) and 7·8 (3H, d, J_{PCH} 14 c./sec.).

(h) *10-Iodomethyl-10-phenyl-10-phenoxaphosphonium iodide* (XVI; R = Ph). The iodide (0·130 g.) was hydrolysed and the product extracted with chloroform as described above. Evaporation of the extract gave 10-phenyl-10-phenoxaphosphine oxide, m.p. and mixed m.p. with authentic material 178°, i.r. spectrum identical with that of authentic material.

(i) *10-Iodomethyl-10-methyl-10-phenoxaphosphonium iodide* (XVI; R = Me). The iodide (0·250 g.) was hydrolysed and the product extracted with chloroform as described above. Evaporation of the extract gave 10-methyl-10-phenoxaphosphine oxide (0·10 g.), i.r.; and u.v. spectra were identical with those of authentic material.

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[21] J. B. Levy, L. D. Freedman, and G. O. Doak, *J. Org. Chem.*, 1968, **33**, 474.