# The Phosphorus Trichloride–Oxygen–Olefin Reaction : Scope and Mechanism

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The principal products of the reaction of phosphorus trichloride and oxygen with a variety of olefins are the corresponding 2-chloroethyl phosphorodichloridate and 2-chloroethylphosphonic dichloride. A linear relationship between $\Sigma\sigma_{para}$ (Hammett) values for the olefinic substituents and the molar ratios of phosphoric and phosphonic dichlorides is discussed in terms of a free-radical scheme that accounts for all the products.

HOMOLYTIC addition of phosphorus trihalides to olefins gives low yields of dihalogenophosphines.[1-4] When the reaction is carried out in the presence of oxygen, it is reported that the related phosphonic dihalides are formed from a variety of olefins, e.g. but-1-ene,[5] but-2-ene,[5] cyclohexene,[5,6] 1,2-dichloroethylene,[7] 1-chloro-2-fluoroethylene,[7] vinyl chloride,[8,9] vinyl fluoride,[7] vinyl bromide,[7] ethylene,[10] propene,[11] acrylonitrile,[12] and methyl acrylate.[12]

$$PX_3 + RCH{=}CHR \longrightarrow X_2P{\cdot}CHR{\cdot}CHRX$$

$$PX_3 + RCH{=}CHR \xrightarrow{O_2} X_2P(O){\cdot}CHR{\cdot}CHRX$$
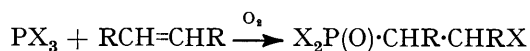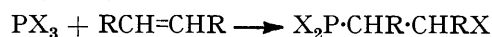
However there is now good evidence that ethylene,[13] 1,2-difluoroethylene,[14] and vinyl chloride [15] give signicant amounts of the phosphoric dichloride in addition to the expected phosphonic dichloride, whereas 1,2-dichloroethylene [16] and 1-chloro-2-fluoroethylene [14] give

[1] M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.,* 1945, **67,** 1864.

[2] B. Fontal and H. Goldwhite, *Chem. Comm.,* 1965, 111.

[3] J. R. Little and P. F. Hartman, *J. Amer. Chem. Soc.,* 1966, **88,** 96.

[4] B. Fontal and H. Goldwhite, *J. Org. Chem.,* 1966, **31,** 3804.

[5] Yu. M. Zinov'ev and L. Z. Soborovskii, *J. Gen. Chem.* *(U.S.S.R.),* 1959, **29,** 611.

[6] K. Chikamune, Y. Okamoto, and H. Sakurai, *Kogyo Kagaku Zasshi,* 1971, **74,** 132 *(Chem. Abs.,* 1971, **75,** 6024).

[7] L. Z. Soborovskii, Yu. M. Zinov'ev, and J. G. Spiridonova, *J. Gen. Chem. (U.S.S.R.),* 1959, **29,** 1110.

[8] W. M. Daniewski, M. Gordon, and C. E. Griffin, *J. Org. Chem.,* 1966, **31,** 2083.

[9] L. Z. Soborovskii, Yu. M. Zinov'ev, and L. I. Muler, *J. Gen. Chem. (U.S.S.R.),* 1959, **29,** 3907.

[10] F. Rochlitz and H. Vilcsek, *Angew. Chem. Internat. Edn.,* 1962, **1,** 652.

[11] Yu. M. Zinov'ev and L. Z. Soborovskii, *J. Gen. Chem. (U.S.S.R.),* 1959, **29,** 3913.

[12] A. Ia. Iakubovich, L. Z. Soborovskii, L. I. Muler, and V. S. Faermark, *J. Gen. Chem. (U.S.S.R.),* 1958, **28,** 313.

[13] L. Maier, *Helv. Chim. Acta,* 1969, **52,** 1337.

[14] C. B. C. Boyce, S. B. Webb, L. Phillips, and I. R. Ager, preceding paper.

[15] C. B. C. Boyce and S. B. Webb, *J. Chem. Soc. (C),* 1971, 3987.

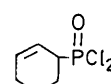[16] C. B. C. Boyce and S. B. Webb, *J. Chem. Soc. (C),* 1971, 1613.

mainly the phosphoric dichloride and little of the expected products.

We now report reinvestigations of the reactions of propene, cyclohexene, 1,2-dibromoethylene, 1,1,2-trichloroethylene, methyl acrylate, and acrylonitrile with phosphorus trichloride and oxygen. These show that by comparison with authentic samples and/or dehydrochlorination experiments.

The formation of phosphonic dichlorides in the phosphorus trichloride–oxygen–olefin reaction can be envisaged as resulting from pathways directly analogous to those proposed [2,4] for the free-radical addition of
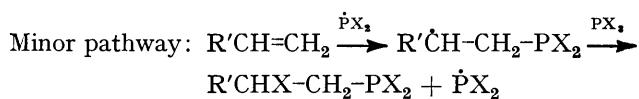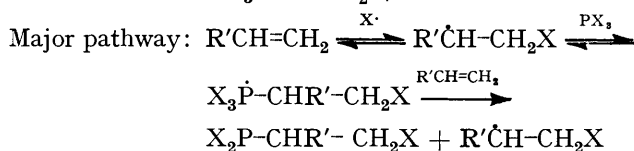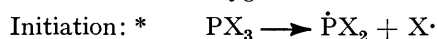
Distribution of products [a] from the reaction of olefins with phosphorus trichloride and oxygen

R'/R" (olefin)		Proportions of products [b] (total = 100)					Approx. total yield (% based on olefin)	Other products isolated/detected (% yield based on olefin)
		$Cl_2P(O) \cdot OCHR'\text{-}CHR''Cl$	$Cl_2P(O) \cdot CHR'\text{-}CHR''Cl$	$Cl_2P(O) \cdot CHR''\text{-}CHR'Cl$	$Cl_2P(O) \cdot CHR''Cl$	$Cl_2P(O) \cdot OCHR''Cl$		
Cl / Cl	c,g	88·8	3·7	6·5	1		41	
Cl / H	c,h	45	39	8·5	7·5		55	
Me / H	c	8	77	15			12	$\{Cl_2P(O)\text{-}CH_2\text{-}CH=CH_2$ / $Cl_2P(O)O\text{-}CH_2\text{-}CH=CH_2\}$ trace
Cl / F	d,j	69	9	13	9	<1	30	
H / H	k	17	83				40	
F / F	e,j	21	70	9			35	
CN / H	c	95·5 f		4·5			44	$\{Cl_2P(O)\text{-}N=C(Cl)\text{-}CH=CH_2$ (5·5) / $ClCH_2\text{-}CHCl(CN)$ (16)$\}$
MeO·C(O) / H	c	71	4	25			66	
Cl / Cl (Cl)	c				85	15	2	$Cl_2CH\text{-}COCl$ (45)
Br / Br								$Cl_2P(O)O\text{-}CHCl\text{-}CHCl_2$ (2)
cyclohexene	c,l		100				47	cyclohexyl-PCl_2 (=O) (4·7)

[a] Except for vinyl chloride, acrylonitrile, and 1,2-dichoroethylene these results are based on single runs. [b] Only trace amounts (g.l.c.) of the isomeric phosphate, $Cl_2P(O)O\text{-}CHR''\text{-}CHR'Cl$, formed in all cases. [c] Proportions obtained from ^1H n.m.r. spectrum of mixed phosphonic–phosphoric dichlorides. [d] Proportions obtained from ^{31}P n.m.r. spectrum of mixed phosphonic–phosphoric dichlorides. [e] Proportions obtained from ^{19}F n.m.r. spectrum of mixed phosphonic–phosphoric dichlorides. [f] Includes corresponding vinyl compound resulting from loss of HCl during distillation. [g] See ref. 16. [h] See ref. 15. [j] See ref. 14. [k] See ref. 13. [l] See ref. 6.

P–O–C bond formation is relatively common. Only in the case of cyclohexene [5,6] were literature reports fully confirmed. Propene [11] gave three hitherto unobserved products (a phosphoric dichloride and two allylic compounds) in addition to those reported. Acrylonitrile [12] and methyl acrylate [12] both gave the phosphoric dichloride and not the phosphonic dichloride as main products. 1,1,2-Trichloroethylene [7] gave a 45% yield of dichloroacetyl chloride, contrary to reports that it does not react. A summary of products obtained and their proportions, together with data reported previously for ethylene,[13] vinyl chloride,[15] 1,2-difluoroethylene,[14] 1-chloro-2-fluoroethylene,[14] and 1,2-dichloroethylene,[16] is given in the Table. Products were characterised by ^1H and ^{31}P n.m.r. and i.r. spectroscopy and combined g.l.c.–mass spectrometry. In several instances corroborative evidence was obtained
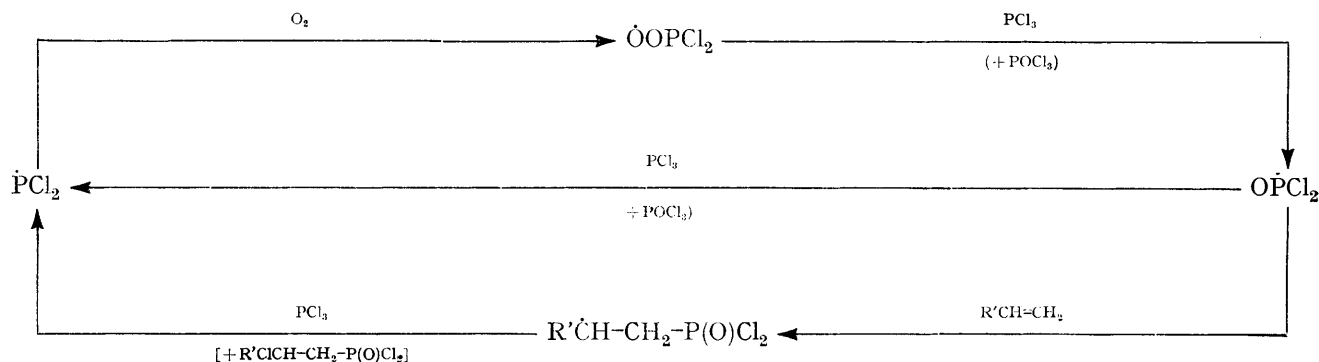
phosphorus trihalides (PX_3; X = Br or Cl) to olefins in the absence of oxygen:

Initiation: * $PX_3 \longrightarrow \dot{P}X_2 + X\cdot$

Major pathway: $R'CH=CH_2 \underset{X\cdot}{\overset{}{\rightleftharpoons}} R'\dot{C}H\text{-}CH_2X \overset{PX_3}{\rightleftharpoons}$

$X_3\dot{P}\text{-}CHR'\text{-}CH_2X \overset{R'CH=CH_2}{\longrightarrow}$

$X_2P\text{-}CHR'\text{-} CH_2X + R'\dot{C}H\text{-}CH_2X$

Minor pathway: $R'CH=CH_2 \overset{\dot{P}X_2}{\longrightarrow} R'\dot{C}H\text{-}CH_2\text{-}PX_2 \overset{PX_3}{\longrightarrow}$

$R'CHX\text{-}CH_2\text{-}PX_2 + \dot{P}X_2$

* Recent work has established the generation of the $\cdot PCl_2$ radical from phosphorus trichloride, and $\cdot PCl_2$ has been the subject of both i.r. and e.s.r. studies.[17]

[17] W. G. Bentrude, ' Free Radicals,' vol. II, ed. J. K. Kochi, Wiley, New York, 1973, ch. 22.

In the presence of oxygen the intermediate phosphoranyl radical $(X_3\dot{P}\text{-}CHR'\text{-}CH_2X)$ is expected [18] to react rapidly and irreversibly with oxygen to form the related oxidised product $[X_2P(O)\text{-}CHR'\text{-}CH_2X]$. Formation of the isomeric adduct could result from direct oxidation of the product of the minor pathway $(R'CHX\text{-}CH_2\text{-}PX_2)$. Alternatively the $\cdot PX_2$ radical $(X = Cl)$ may itself be directly oxidised to give the $\cdot P(O)Cl_2$ radical [17] $[\cdot P(O)Cl_2 \longleftrightarrow \cdot OPCl_2]$, which could add to the olefin:

phosphoric dichlorides produced in the reaction between alkanes and phosphorus trichloride in the presence of oxygen result from an ionic reaction between an alcohol (produced by hydrogen abstraction with an alkoxyl radical) and phosphoric trichloride. We rule out this possibility because the reaction of alkoxyl radicals with trivalent phosphorus is extremely fast and much faster than hydrogen abstraction,[24,25] and HCl in an amount equivalent to the phosphoric dichloride formed is not

The $\cdot P(O)Cl_2$ radical is presumably involved in the free radical (benzoyl peroxide initiated) addition of phosphoric trichloride to olefins.[19] An alternative mode of formation of the isomeric adduct via Markovnikov addition of a chlorine atom is improbable in the case of propene and vinyl chloride [20] but cannot be ruled out for some of the other unsymmetrical olefins, especially 1-chloro-2-fluoroethylene, as there is evidence that radical addition can occur at either end of the double bond in fluoro-olefins.[20,21]

The mode of formation of the phosphoric dichlorides and the C–C cleavage products is less obvious. The high orientational selectivity in the formation of the phosphoric dichlorides, together with the fact that for each olefin at least 75% of the total yield of phosphonic and phosphoric dichlorides can be accounted for by anti-Markovnikov addition of a chlorine atom, suggests that chlorine atoms compete favourably with $\cdot PCl_2$ [or $\cdot P(O)Cl_2$] for the olefin to give a preponderance of the X-substituted 2-chloroethyl radical as a first step.

Oxygen can compete with phosphorus trichloride for alkyl radicals,[18,22] and moreover, the resulting alkylperoxyl radicals are known to react with trivalent phosphorus compounds to form alkylperoxyphosphoranyl radicals.[23] These are expected to fragment exclusively by β-scission to give alkoxyl radicals, the driving force being the low strength of the O–O bond,[23] and presumably formation of the P=O bond.

Mayo et al.[18] have postulated that small amounts of

produced in the reaction with olefins. However the phosphoranyl radicals derived from reaction between alkoxyl radicals and trivalent phosphorus compounds can undergo scission, the mode of which depends on the substituents and reaction conditions: [23]

α-scission: $RO\dot{P}Cl_3 \longrightarrow ROPCl_2 + Cl\cdot$

β-scission: $RO\dot{P}Cl_3 \longrightarrow R\cdot + POCl_3$
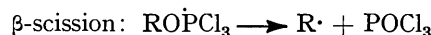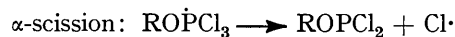
Oxidation of the product of α-scission will give the phosphoric dichloride with the same substitution pattern as observed for the major isomer formed (i.e. $R\cdot = R'\dot{C}H\text{-}CH_2Cl$). If β-scission occurs it will give rise to the chloroalkyl radical $(R'\dot{C}H\text{-}CH_2Cl)$ which can undergo recycling. In the presence of oxygen however the phosphoranyl radical may be trapped before scission can occur,[26] providing an alternative pathway to the same phosphoric dichloride:

$$RO\dot{P}Cl_3 \xrightarrow{O_2} ROP(OO\cdot)Cl_3 \xrightarrow{PCl_3}$$
$$ROP(O)Cl_2 + POCl_3 + Cl\cdot$$
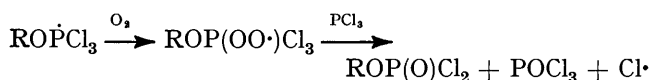
It is unlikely that the phosphoric dichlorides are formed by combination–termination reactions, e.g. between $\cdot P(O)Cl_2$ or $\cdot OOPCl_2$ and alkoxyl or alkyl radicals, since they are major products in many cases.

Trichloroethylene reacts atypically, giving mainly the autoxidation product, dichloroacetyl chloride (45% yield), together with ca. 2% of the C–C cleavage products, $Cl_2P(O)\text{-}CHCl_2$ and $Cl_2P(O)\text{-}O\text{-}CHCl_2$ (6 : 1); no other

[18] F. R. Mayo, L. J. Durham, and K. S. Griggs, J. Amer. Chem. Soc., 1963, 85, 3156.
[19] G.P. 2,032,136/1969.
[20] J. M. Tedder, J. C. Walton, and K. D. R. Winton, J.C.S. Faraday I, 1972, 1866.
[21] J. M. Tedder, J. C. Walton, and K. D. R. Winton, J.C.S. Faraday I, 1972, 160.
[22] R. L. Flurry and C. E. Boozer, J. Org. Chem., 1966, 31, 2076.

[23] K. U. Ingold and B. P. Roberts, ' Free Radical Substitution Reactions,' Wiley-Interscience, New York, 1971.
[24] C. Walling and M. S. Pearson, J. Amer. Chem. Soc., 1964, 86, 2262.
[25] W. H. Starnes and N. P. Neureiter, J. Org. Chem., 1967, 32, 333.
[26] G. B. Watts and K. U. Ingold, J. Amer. Chem. Soc., 1972, 94, 2528.

products are observed. The autoxidation of highly halogenated olefins,[27] initiated by chlorine atoms, is believed to involve polychloroethoxyl radicals and this indicates that the intermediate alkoxyl radical, if suitably substituted, can undergo α-scission of a C–Cl bond, rather than interaction with PCl_3 to form a phosphoranyl radical:

$$Cl_2C(O\cdot)\text{--}CRCl_2 \longrightarrow ClC(O)\text{--}CRCl_2 + Cl\cdot \quad (R = H \text{ or } Cl)$$
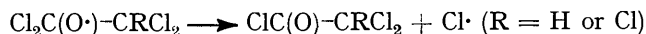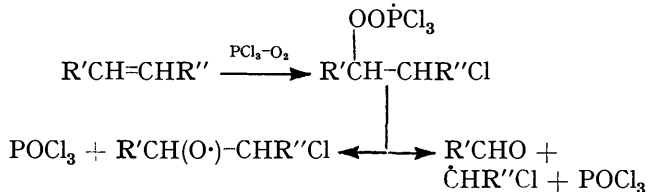
Dichloroacetyl chloride, like acetyl chloride,[28] does not react with phosphorus trichloride and oxygen, but dichloroacetaldehyde does react to give ca. 6% of the same cleavage products as trichloroethylene in approximately the same ratio (10 : 1). In this case hydrogen abstraction by chlorine atoms, followed by fragmentation,[29] can give the dichloromethyl radical:

$$Cl_2CH\cdot CHO + Cl\cdot \longrightarrow Cl_2CH\dot{C}{=}O + HCl$$
$$Cl_2CH\dot{C}{=}O \longrightarrow Cl_2\dot{C}H + CO$$
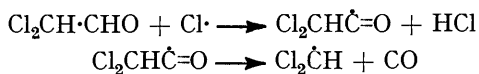
We envisage that this radical will react by similar pathways to those already proposed to give the observed products.

Substituted chloromethyl radicals could be produced in the reaction of olefins with phosphorus trichloride and oxygen by a competitive fragmentation of the chloroethylperoxyphosphoranyl radical, since homolysis of a peroxide bond is often accompanied by cleavage of an adjacent C–C bond: [30]

$$R'CH{=}CHR'' \xrightarrow{PCl_3\text{--}O_2} \underset{\displaystyle R'CH\text{--}CHR''Cl}{\overset{\displaystyle OO\dot{P}Cl_3}{|}}$$

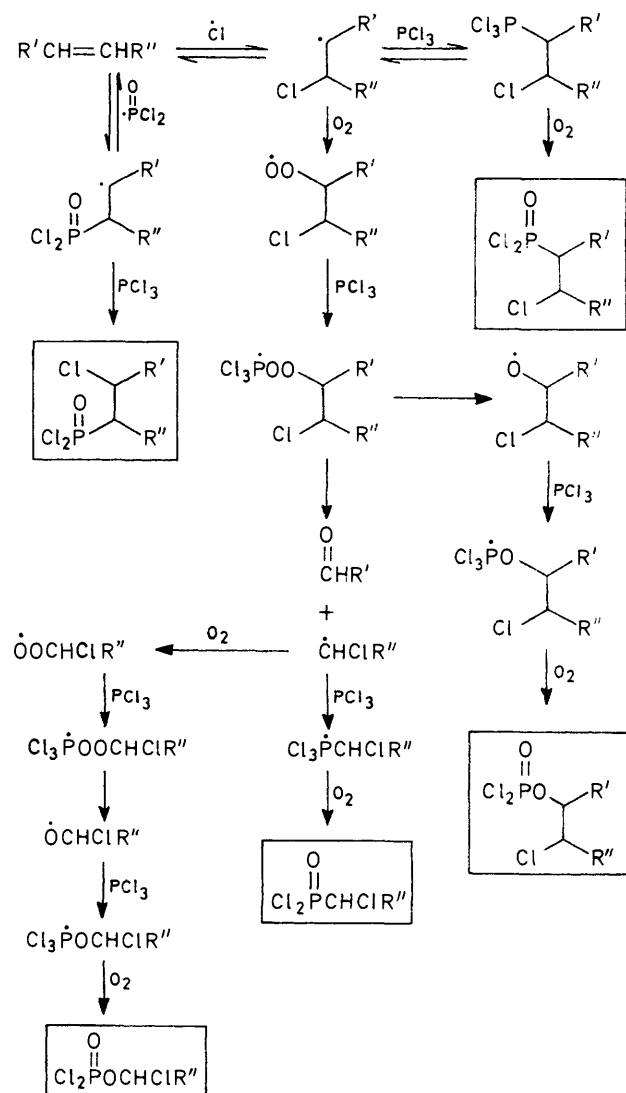$$POCl_3 + R'CH(O\cdot)\text{--}CHR''Cl \longleftrightarrow R'CHO + \dot{C}HR''Cl + POCl_3$$

Accordingly, vinyl chloride will give the chloromethyl radical, 1,2-difluoroethylene and 1-chloro-2-fluoroethylene the chlorofluoromethyl radical, and 1,2-dichloroethylene and trichloroethylene a dichloromethyl radical. With each of these olefins the corresponding phosphonic dichloride is formed, and represents 5—10% of the phosphorus-containing products. The equivalent phosphoric dichlorides are formed only from 1,2-dichloroethylene and trichloroethylene. The fact that the ratio of dichloromethylphosphonic dichloride to dichloromethyl phosphorodichloridate is approximately the same from both these olefins and from dichloroacetaldehyde supports the involvement of the dichloromethyl radical.

The small amount of 1,2,2-trichloroethyl phosphorodichloridate formed as the only product when 1,2-dibromoethylene was treated with phosphorus trichloride and oxygen could not be attributed to traces of chloro-olefins in the dibromoethylene. It presumably arises by halogen exchange, and subsequent reaction of the re-

sulting 1,2-dichloroethylene with phosphorus trichloride and oxygen.

A summary of the likely radical pathways leading to the phosphorus-containing products observed in the reaction of phosphorus trichloride and oxygen with olefins is given in the Scheme.

$$
\begin{array}{c}
R'CH{=}CHR'' \underset{\overset{\dot{C}l}{\displaystyle \rightleftharpoons}}{} \underset{Cl}{\overset{R'}{\diagdown}}\!\!\dot{C}\!\!\underset{R''}{\diagup} \underset{\overset{PCl_3}{\displaystyle \rightleftharpoons}}{} \underset{Cl}{\overset{Cl_3P \diagdown \diagup R'}{\diagdown}}\!\!\underset{R''}{\diagup}
\end{array}
$$

It is apparent from the Table that the relative amounts of phosphoric and phosphonic products vary with the polarity of the olefinic substituents. With propene and cyclohexene there is little or no phosphoric product but a high proportion of phosphonic derivative is formed; with olefins bearing electron-withdrawing substituents, such as acrylonitrile or 1,2-dichloroethylene, the opposite result is obtained.

The quantitative influence of polar substituents upon the course of free radical processes has been discussed

[27] C. Schott and H. J. Schumacker, Z. phys. Chem. (Frankfurt), 1941, B49, 107.

[28] A. F. Isbell and F. T. Wadsworth, J. Amer. Chem. Soc., 1956, 78, 6042.

[29] C. Walling, ' Free Radicals in Solution.' Wiley, New York, 1957.

[30] J. E. Leffler, Chem. Rev., 1949, 45, 385.

by Bamford *et al.*[31] and by Jenkins.[32] For the addition of radicals R· and R'· to a common substrate, S, the rate constants k_R and $k_{R'}$ are related by the equation:

$$\log(k_R/k_{R'}) = \log(k_T/k_{T'}) + (P_{R·} - P_{R'·})$$

where k_T and $k_{T'}$ are reference rate constants for the transfer of these radicals to toluene, and $P_{R·}$ and $P_{R'·}$ are polarity parameters for the radicals R· and R'·, respectively. For any two radicals, $k_T/k_{T'}$ is constant, as is $P_{R·}-P_{R'·}$; in the absence of any side reactions and the presence of a sufficient excess of substrate to ensure pseudo-unimolecular conditions, $k_R/k_{R'}$ will be given by the product ratios. This suggests that the relative amounts of products formed by reactions of two
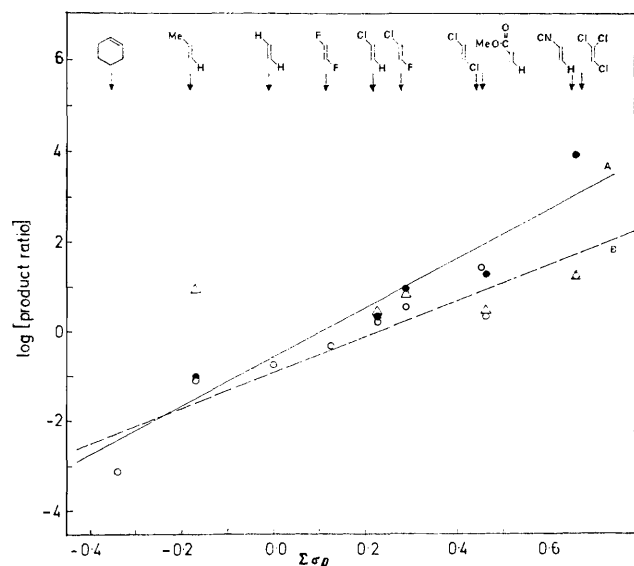
A ● log [product ratio] $= \log\left(\dfrac{a + b + c}{d}\right)$

B ○ log [product ratio] $= \log\left(\dfrac{a + b + c}{d + e}\right)$

△ log [product ratio] $= \log\left(\dfrac{a + b + c + d}{e}\right)$

where a = [Cl$_2$P(O)·O·CHR'·CHR''Cl]; b = [Cl$_2$P(O)·CHR''Cl]; c = [Cl$_2$P(O)·O·CHR''Cl]; d = [Cl$_2$P(O)·CHR'·CHR''Cl]; e = [Cl$_2$P(O)·CHR''·CHR'Cl]

Correlation of product ratios with $\Sigma\sigma_p$ for the reaction of olefins with phosphorus trichloride and oxygen

different radicals with a given substrate will depend on the polar properties of the radicals but not on those of the substrates. This is an oversimplification and the substrate may play some part. Bamford *et al.* suggest that an ' intrinsic polarity ' (or tendency of the substrate to give rise to polar transition states) is a useful measure of this, but it is apparent from the data given by these workers that the intrinsic polarity does remain essentially constant for olefins with widely varying substituents.

In the Scheme it is suggested that Cl· and ·P(O)Cl$_2$ compete for the olefin. Since reaction with ·P(O)Cl$_2$

[31] C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, 1959, **55**, 418.

leads directly to the product Cl$_2$P(O)–CHR''–CHR'Cl, the amount formed should be more or less independent of the polar nature of the substituents R' and R''. This is confirmed to some extent since it only varies from 5 to 25% and there is no obvious relationship with substituent polarity (Figure). Some of the variations undoubtedly arise from the limitations of our estimation techniques (especially of compounds present in very small amount), and are probably not far outside experimental error. The high proportion of this product from methyl acrylate is notable.

Bamford *et al.* show that if a radical R· is derived from an olefin, the polarity parameter $P_{R·}$ may be simply related to the sum of the Hammett (*para*) substituent parameters, σ_p,[33] of the substituents present on the radical. For reaction of such a radical with two different substrates S and S':

$$\log(k_S/k_{S'}) = (\alpha - \alpha')\Sigma\sigma_p + (\beta - \beta')$$

where k_S and $k_{S'}$ are the rate constants for the two different reactions, and α, α', β, and β' are constants depending on the particular substrates. If the substrates react competitively for the radical and are present in sufficient excess to give pseudo-unimolecular conditions, then the ratio of the relevant products is given by $\log(k_S/k_{S'})$.

In the Scheme it is suggested that R''CH(Cl)–ĊHR' reacts competitively with oxygen and PCl$_3$, from which it follows that:

$$\log\left(\frac{[Cl_2P(O)\text{–CHClR''} + Cl_2P(O)\text{–O–CHR'–CHClR'']}}{[Cl_2P(O)\text{–CHR'–CHClR'']}}\right)$$
$$= (\alpha - \alpha')\Sigma\sigma_p + (\beta - \beta')$$

This holds for all the unsymmetrical olefins with the exception of trichloroethylene, where the relevant phosphorus compounds were not observed (Figure, A). The correlation coefficient, r, is 0·94, with $(\alpha - \alpha') = 5·4$ and $(\beta - \beta') = -0·53$.

Since the amount of Cl$_2$P(O)–CHR''–CHR'Cl formed should be more or less independent of the substituents R' and R'', a similar relationship should be observed with all olefins when the total amount of phosphonic dichloride is considered. This appears to be the case [Figure, B, $r = 0·93$, $(\alpha - \alpha') = 4·0$, $(\beta - \beta') = -0·93$] when trichloroethylene and 1,2-dibromoethylene, where the relevant phosphorus compounds were not detected, are excluded. The substituent polarity approach does not predict the lack of reactivity of 1,2-dibromoethylene, but the observed products from trichloroethylene are not inconsistent with this concept. From the $\Sigma\sigma_p$ value of the three chloro-substituents (0·681), large amounts of phosphoric dichloride and/or cleavage products, derived from Cl$_2$C(OȮ)–CHCl$_2$, would be expected. In fact the major observed product, dichloroacetyl chloride, is expected to originate from the same radical.[29]

The overall results indicate that the reaction of olefins

[32] A. D. Jenkins, *Adv. Free Radical Chem.*, 1967, vol. 2.
[33] P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

with phosphorus trichloride in the presence of oxygen is more complex than originally suggested.[5,7,9,11,12,34] The previously unrecognised phosphoric dichlorides are major products from several olefins, and with halogeno-olefins significant amounts of C–C cleavage products are also formed. The Scheme accounts for the formation of all the products observed through a series of radical reactions, each of which has a precedent. The use of the Bamford polarity parameter (or σ_p) provides a useful means of predicting the proportions of P–O–C and P–C bond formation.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 grating spectrometer. N.m.r. spectra were recorded with a Varian HA-100 spectrometer operating at 100 MHz for ^{1}H, and at 40·5 MHz for ^{31}P. Column chromatography was carried out with a silica gel stationary phase (Crosfield Sorbsil brand), and was monitored by g.l.c. (Perkin-Elmer F11 instrument, 2 m column packed with 10% QF1 on Chromosorb W, at 130 °C) and/or t.l.c. (Merck pre-coated plates; silica gel F_{254}). Combined g.l.c.–mass spectrometry was carried out on a Perkin-Elmer 452 gas chromatograph connected via a Biemann separator to a Quad 250 mass analyser.

The phosphorus trichloride–oxygen–olefin reactions were conducted as far as possible under standardised conditions. All reactions were carried out between -5 and $-30°$, with no solvent, and with a constant oxygen flow rate leading to a constant proportion of oxygen to phosphorus trichloride.[18] A large excess of phosphorus trichloride over olefin was used (ca. 10 : 1 molar ratio); however, the initial concentration was not standardised. Gaseous olefins were introduced into the reaction mixture over several hours; liquid olefins were added all at once. All vacuum distillations were carried out under nitrogen.

Reaction of Propene with Phosphorus Trichloride and Oxygen.[11]—The reaction of propene (150 g, 3·58 mol) with phosphorus trichloride (700 ml, 1102 g, 8·0 mol) and oxygen was carried out as previously described.[15,16] The product (84·3 g, ca. 12%) had b.p. 54—55° at 0·4 mmHg; $\nu_{max.}$ 2990w, 2960w, 2940w, 2905w, 2880w, 1455m, 1440w, 1385m, 1270s, 1230w, 1190w, 1100w, 1065w, 995m, 905w, 870w, 855w, 830w, 755m, 730w, 715w, and 645m cm^{-1}; ^{31}P δ 4·58 (d), 42·1 (m), and 51·6 (unresolved) p.p.m. to low field of external H_3PO_4. Analysis of the ^{1}H n.m.r. spectrum and comparison with an authentic sample showed that 2-chloropropylphosphonic dichloride[35–37] was present (15%) [δ 1·76 (3H, d), 3·11 (2H, m), and 4·48 (1H, m)]. The major product (77%) was 2-chloro-1-methylethylphosphonic dichloride [δ 1·46 (1·5H, d), 1·73 (1·5H, d), 2·95 (1H, m), 3·6 (1H, m), and 4·07 (1H, m)], and 2-chloro-1-methylethyl phosphorodichloridate [δ 1·61 (3H, d), 3·67 (2H, dd), and 5·02 (1H, m)], a hitherto unexpected product, was also present (8%).

Ethanolysis of the Product of the Foregoing Reaction.— The product (80 g) was treated with ethanol as described

previously.[15,16] The excess of ethanol was removed in vacuo. G.l.c. analysis of the residue suggested that several compounds were present; g.l.c.–mass spectrometry (2 m column containing 10% QF1 on 100—120 mesh Chromosorb W at 160 °C) indicated that the major component was a phosphonate [m/e 214 (M^+) and 178 ($M - \mathrm{HCl}$)$^+$]; the presence of a second phosphonate (m/e 214) and a phosphate (m/e 230), both in small amount, was also demonstrated, together with traces of allylic phosphate (m/e 194) and phosphonate (m/e 178).

Fractional distillation of the residue afforded the major component, b.p. 80·5—81° at 1·5 mmHg, n_D^{22} 1·4386, which was identified by ^{1}H n.m.r. as diethyl 2-chloro-1-methylethylphosphonate (lit.,[38] b.p. 84—85° at 10 mmHg, n_D^{20} 1·4355) (Found: C, 39·2; H, 7·7; Cl, 16·2; P, 14·3. Calc. for $C_7H_{16}ClO_3P$: C, 39·2; H, 7·5; Cl, 16·6; P, 14·45%); δ_H 1·34 (t), 1·2 (d), and 1·65 (d) (total 9H), 2·13 (1H, m), 3·4 (1H, m), and 3·98 (5H, m).

A fraction, b.p. 135—138° at 0·6 mmHg (0·42 g), was shown by g.l.c. and ^{1}H n.m.r. comparison with an authentic sample[39] [δ_H 1·37 (9H, m), 3·59 (2H, d, J 5·0 Hz), 4·06 (4H, m), and 4·56 (1H, m)] to contain 70—80% 2-chloro-1-methylethyl diethyl phosphate.

Treatment of Diethyl 2-Chloro-1-methylethylphosphonate with Triethylamine.—A mixture of the phosphonate (0·05 mol) and triethylamine (0·1 mol) in dry toluene (30 ml) was stirred and heated under reflux for 5 days. After cooling, solids were removed by filtration, and solvent was removed in vacuo. Distillation of the residue gave a liquid (52%), b.p. 75—76° at 2 mmHg, $n_D^{20·5}$ 1·4309, identified by ^{1}H n.m.r. as diethyl isopropenylphosphonate (lit.,[40] b.p. 86° at 12 mmHg, n_D^{20} 1·4308) (Found: C, 46·5; H, 8·8; P, 17·0. Calc. for $C_7H_{15}O_3P$: C, 47·2; H, 8·4; P, 17·4%); δ_H 1·32 (6H, t), 1·89 (3H, dt), 4·02 (4H, m), and 5·7 (2H, m).

Treatment of Diethyl 2-Chloropropylphosphonate with Triethylamine.—A mixture of the phosphonate[38] (5·5 g, 0·0257 mol; prepared by ethanolysis of 2-chloropropylphosphonic dichloride[36,37]) and triethylamine (5 g, 0·05 mol) in dry toluene (30 ml) was stirred and heated under reflux for 4 days. After cooling, solids were removed by filtration, and solvent was removed in vacuo. Distillation gave a crude product (58%), b.p. 89—90·5° at 3·5 mmHg, which was further purified by column chromatography (silica gel; ether) and redistillation. (*E*)-Diethyl prop-1-enylphosphonate[38,41] was obtained as a liquid, b.p. 78—79° at 2 mmHg, $n_D^{19·5}$ 1·4389 (lit.,[38] b.p. 93—95° at 8 mmHg, n_D^{20} 1·4370) (Found: C, 46·8; H, 8·7; P, 16·8. Calc. for $C_7H_{15}O_3P$: C, 47·2; H, 8·4; P, 17·4%); δ_H 1·28 (6H, t), 1·91 (3H, m), 3·96 (4H, m), 5·55 (1H, m), and 6·70 (1H, m).

Reaction of Cyclohexene with Phosphorus Trichloride and Oxygen.[5,6]—Cyclohexene (82 g, 1·0 mol), phosphorus trichloride (872 ml, 10·0 mol), and oxygen reacted under the usual conditions. The product (110 g, ca. 47%) had b.p. 35—130° at 2 mmHg; $\nu_{max.}$ 2945m, 2870w, 1450m, 1360w, 1340w, 1325w, 1270s, 1240w, 1200w, 1145w, 1115w, 1090w, 1030w, 990w, 940w, 910w, 875w, 870w,

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[40] G.P. 1,159,443/1963.

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850w, 835w, 815w, 805w, 765w, 735w, 720w, 705w, 695w, and 655w cm^{-1} (no evidence of a P–O–C stretching band); δ_H 1·9 (part resolved m), 2·83 (m), 4·48 (m), and 5·75 (part resolved m), ^{31}P δ 36·2 (d, $J_{P,H}$ 25 Hz) and 47·7 (unresolved) p.p.m. to low field of external H$_3$PO$_4$.

Methanolysis of the Product of the Foregoing Reaction.— The product (47·15 g, 0·2 mol) was treated with methanol in the usual way. G.l.c. showed the presence of two compounds, the more abundant having t_R 7·0 min, and the less abundant 4·2 min. A combination of fractional distillation and column chromatography (silica gel; ether–acetone) gave pure samples of both. The more abundant compound was a liquid, b.p. 107—108° at 0·6 mmHg, $n_D^{20·5}$ 1·4812, identified by ^{1}H n.m.r. as *dimethyl 2-chloro-cyclohexylphosphonate* (Found: C, 42·0; H, 7·0; Cl, 15·9; P, 13·5%. C$_8$H$_{16}$ClO$_3$P requires C, 42·4; H, 7·1; Cl, 15·7; P, 13·7%); δ_H 1·2—2·4 (9H, part resolved m), 3·72 (6H, 2d), and 4·26 (1H, m).

The less abundant compound had b.p. 78—79° at 0·5 mmHg, $n_D^{20·5}$ 1·4743, and was identified by ^{1}H n.m.r. as dimethyl cyclohex-2-enylphosphonate (lit.,[42] b.p. 92·5— 93·5° at 1·5 mmHg, n_D^{20} 1·4728) (Found: C, 50·0; H, 7·7; P, 16·3. Calc. for C$_8$H$_{15}$O$_3$P: C, 50·45; H, 7·9; P, 16·3%); δ_H 1·3—2·65 (7H, part resolved m), 3·68 (6H, d), and 5·75 (2H, m). These results are in accord with recent work.[6]

Treatment of Dimethyl 2-Chlorocyclohexylphosphonate with Potassium t-Butoxide.—The phosphonate (6·3 g, 0·0278 mol) was treated with potassium t-butoxide under conditions described previously.[15,16] After work-up and column chromatography (silica gel; ether–acetone) the product (2·0 g, 38%), b.p. 77—78° at 0·25 mmHg, $n_D^{20·5}$ 1·4750, was identified by ^{1}H n.m.r. as dimethyl cyclohex-1-enyl-phosphonate[43] (Found: C, 49·9; H, 7·8; P, 16·1. Calc. for C$_8$H$_{15}$O$_3$P: C, 50·45; H, 7·9; P, 16·3%); δ_H 1·35 (4H, part resolved m), 2·14 (4H, part resolved m), 3·65 (6H, d), and 6·64 (1H, dm). Dimethyl cyclohex-2-enylphosphonate was not detected (^{1}H n.m.r.).

Reaction of 1,2-Dibromoethylene with Phosphorus Tri-chloride and Oxygen.—1,2-Dibromoethylene (135 g, 0·725 mol), phosphorus trichloride (700 ml, 8·0 mol), and oxygen reacted under the usual conditions. The semi-crystalline mass was allowed to reach ambient temperature, and was then distilled at atmospheric pressure. The distillate (1328 g in all) was fractionated over the boiling range 88—110 °C; i.r. examination showed that all fractions were mixtures of phosphoric trichloride and unchanged 1,2-dibromoethylene. No carbonyl frequencies were observed. The residue was vacuum distilled, giving a nearly colourless liquid (3 g, 1·5%), b.p. 66—78° at 1·3 mmHg, $\nu_{max.}$ 1310s (P=O) and 980s (P–O–C) cm^{-1}, δ_H 5·88 (1H, dd) and 6·44 (1H, dd). To facilitate identification this material was subjected to ethanolysis under the usual conditions and after purification by column chromatography (silica gel; ether) the product was identfied by i.r., g.l.c., and ^{1}H n.m.r. as 1,2,2-trichloroethyl diethyl phosphate.[16]

Reaction of Trichloroethylene with Phosphorus Trichloride and Oxygen.[7]—Trichloroethylene (65·75 g, 0·5 mol), phosphorus trichloride (436 ml, 5·0 mol), and oxygen reacted under the usual conditions. The reaction mixture was distilled at atmospheric pressure. The distillate (total

806 g) was fractionated over the boiling range 80—110 °C; i.r. examination showed that all fractions were mixtures of phosphoric trichloride together with varying amounts of unchanged trichloroethylene and/or dichloroacetyl chloride. The fractions were bulked, and a sample was analysed by ^{1}H n.m.r. for trichloroethylene and dichloro-acetyl chloride. Of the original trichloroethylene, 22% was recovered unchanged, and 45% converted into di-chloroacetyl chloride.

The distillation residue was vacuum distilled yielding material (2·35 g, ca. 2%), b.p. 76—92° at 10 mmHg, $\nu_{max.}$ 1290s (P=O) and 1000s (P–O–C) cm^{-1}. This was subjected to methanolysis under the usual conditions and after purification by column chromatography (silica gel; ether) gave a liquid, b.p. 64—65° at 0·3 mmHg. This was identified by ^{1}H n.m.r. as a mixture of dimethyl dichloro-methylphosphonate (85%), [δ_H 5·75 (CH, d, $J_{P,H}$ 2 Hz)] and dichloromethyl dimethyl phosphate (15%) [δ 7·52 (CH, d, $J_{P,H}$ 7·5 Hz)].

Reaction of Methyl Acrylate with Phosphorus Trichloride and Oxygen.[12]—Freshly distilled methyl acrylate (86 g, 1·0 mol), phosphorus trichloride (872 ml. 10·0 mol), and oxygen reacted under the usual conditions. The product (168·5 g, ca. 66%) had b.p. 108—112° at 1 mmHg; $\nu_{max.}$ 3030w, 2950m, 2850w, 1770s, 1750s, 1440s, 1355m, 1290s, 1230s, 1195m, 1180m, 1155w, 1070s, 1030s (P–O–C), 995m, 945w, 905w, 845w, 810w, 790w, 765w, 715w, and 690w cm^{-1}; δ_H 3·30 (m), 3·90 (m), 4·75 (dt), and 5·41 (dt); ^{31}P δ 7·9 (d) (phosphoric dichloride) and 36·3 (m) and 42·0 (part resolved m) (phosphonic dichloride) p.p.m. to low field of external H$_3$PO$_4$ (ratios ca. 100 : 15 : 8).

Methanolysis of the Product of the Foregoing Reaction.— The product (50·0 g) was treated with methanol under the usual conditions. The excess of methanol was removed *in vacuo* and the residue distilled yielding a liquid (42 g), b.p. 108—115° at 0·5 mmHg. G.l.c. showed this to be a mixture; the major component had t_R 7·3 min and the minor components 3·7 and 5·4 min. G.l.c.–mass spectro-metry (2 m column containing 3% OV-225 on 100—120 mesh GasChrom Q at 170 °C) indicated that the major component was a phosphate [m/e 247 $(M + 1)^+$ and 211 $(M - Cl)^+$]. Of the two minor components, the slower eluted was probably a phosphonate [m/e 231 $(M + 1)^+$ and 195 $(M - Cl)^+$] and the faster appeared to be a mixture of a vinylphosphonate and a vinyl phosphate.

Column chromatography on silica gel [elution with ether containing increasing proportions of acetone (0—50%)] allowed almost complete separation of the major phos-phate (eluted first) from the two phosphonates. After redistillation it had b.p. 104° at 0·2 mmHg, $n_D^{18·5}$ 1·4419, and was identified by ^{1}H n.m.r. as *2-chloro-1-methoxycar-bonylethyl dimethyl phosphate* (Found: C, 28·9; H, 4·8; Cl, 14·0; P, 12·9. C$_6$H$_{12}$ClO$_6$P requires C, 29·25; H, 4·9; Cl, 14·4; P, 12·6%); δ_H 3·81 (11H, m) and 5·04 (1H, dt, $J_{H,H}$ 4·3, $J_{H,P}$ 8·8 Hz). Addition of the shift reagent Eu(fod)$_3$ separated the multiplet at δ 3·81 into a singlet (3H), two doublets (6H), and two doublets of doublets (2H).

Careful repeated fractionation of the slower-eluted material enabled the two phosphonates to be separated and identified. The lower boiling material (g.l.c. t_R 3·7 min) was identified by ^{1}H n.m.r. as *dimethyl 1-methoxycarbonyl-vinylphosphonate*, b.p. 88—89° at 0·7 mmHg, $n_D^{19·5}$ 1·4478

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(Found: C, 36·8; H, 5·8; P, 16·0. $C_6H_{11}O_5P$ requires C, 37·1; H, 5·7; P, 16·0%), δ_H 3·81 (6H, d, $J_{H,P}$ 11·0 Hz), 3·84 (3H, s), 6·77 (1H, dd, $J_{H,H}$ 1·6 $J_{H,P\text{-}cis}$ 20·8 Hz), 7·03 (1H. dd, $J_{H,H}$ 1·6, $J_{H,P\text{-}trans}$ 42·2 Hz). The higher boiling material (g.l.c. t_R 5·4 min) was identified by ^1H n.m.r. as dimethyl 2-chloro-2-methoxycarbonylethylphosphonate, b.p. 98—100° at 0·65 mmHg, $n_D{}^{19\cdot0}$ 1·4515 (Found: C, 31·1; H, 5·1; Cl, 14·9; P, 13·7. $C_6H_{12}ClO_5P$ requires C, 31·2; H, 5·2; Cl, 15·4; P, 13·45%); δ_H 2·57 (2H, m), 3·76 (6H, d, $J_{H,P}$ 11 Hz), 3·82 (3H, s), and 4·55 (1H, dq, $J_{H,H}$ 6·2, $J_{H,H}$ 8·4, $J_{H,P}$ 9·8 Hz), and was identical (i.r., ^1H n.m.r.) with the product obtained in 46·5% overall yield from the reaction of trimethyl phosphite with methyl 2,3-dichloropropionate at 100 °C (erroneously identified by previous workers as dimethyl 2-chloro-1-methoxy-carbonylethylphosphonate [44,45]).

Dehydrochlorination of Dimethyl 2-Chloro-2-methoxycarbonylethylphosphonate.—A stirred solution of the phosphonate (2·85 g, 0·0124 mol) in dry ether (50 ml) was treated with triethylamine (5·0 g) in dry ether (10 ml). The mixture was heated under reflux for 0·5 h, then stirred at room temperature overnight. After filtration, solvent was removed *in vacuo* and the residue was chromatographed on silica gel (elution with ether). After distillation the product (1·3 g, 54%) had b.p. 77·5—78° at 0·1 mmHg, $n_D{}^{19}$ 1·4547, and was identified by ^1H n.m.r. as (E)-dimethyl 2-methoxycarbonylvinylphosphonate [46,47] (Found: C, 36·6; H, 5·7; P, 15·8. Calc. for $C_6H_{11}O_5P$: C, 37·1; H, 5·7; P, 16·0%); δ_H 3·78 (6H, d, $J_{H,P}$ 11 Hz), 3·82 (3H, s), 6·69 (1H, dd, $J_{H,H}$ 17·3, $J_{H,P}$ 20·4 Hz), and 6·90 (1H, dd, $J_{H,H}$ 17·3, $J_{H,P}$ 18·9 Hz), identical (i.r. ^1H n.m.r.) with the product obtained from the reaction of trimethyl phosphite with methyl 2-chloroacrylate [48] or (Z)-methyl 3-chloroacrylate [46].

Treatment of 2-Chloro-1-methoxycarbonylethyl Dimethyl Phosphate with Triethylamine.—The phosphate (4·75 g, 0·0193 mol) was similarly treated with triethylamine in ether. After chromatography (silica gel; ether) and distillation, the product (2·5 g, 62%) had b.p. 87·5—88° at 0·25 mmHg, $n_D{}^{18\cdot5}$ 1·4360, and was identified by ^1H n.m.r. as 1-methoxycarbonylvinyl dimethyl phosphate (Found: C, 34·3; H, 5·2; P, 15·0. $C_6H_{11}O_6P$ requires C, 34·3; H, 5·2; P, 14·8%); δ_H 3·81 (3H, s), 3·82 (6H, d, $J_{H,P}$ 11 Hz), 5·57 (1H, t, $J_{H,H}$ 2·2, $J_{H,P}$ 2·2 Hz), and 5·87 (1H, t, $J_{H,H}$ 2·2, $J_{H,P}$ 2·2 Hz), identical (i.r., ^1H n.m.r.) with that obtained in 65% yield from the reaction of methyl bromopyruvate with trimethyl phosphite in ether at 0—5 °C.

Reaction of Acrylonitrile with Phosphorus Trichloride and Oxygen.[12]—Acrylonitrile (53 g, 1·0 mol), phosphorus trichloride (872 ml, 10·0 mol), and oxygen reacted under the usual conditions. Phosphoric trichloride and other very volatile materials were removed by distillation at *ca.* 12 mmHg (bath temperature below 70 °C). The residue was distilled at 1—2·5 mmHg (bath temperature below 130 °C), to yield a product (91 g, *ca.* 44%) of b.p. up to 115 °C. The i.r. spectrum showed, in addition to a band at 1020 cm^{-1} attributable to P–O–C and weak C≡N absorptions at 2240 and 2260 cm^{-1}, bands at 3135, 1650, 1635,

1605, and 1550 cm^{-1} suggesting the presence of C=C and C=N bonds. The ^1H n.m.r. spectrum showed δ 3·89 (d), 3·94 (dd), 4·79 (dd), 5·65 (m), and 6·03 (m) and the ^{31}P n.m.r. spectrum indicated the presence of four phosphorus-containing materials [δ 3·22 (s), 4·56 (unresolved), 7·64 (d), and 32·2 (s) p.p.m. to low field of external H_3PO_4] in the ratio of *ca.* 22 : 9 : 53 : 16.

Repeated fractional distillation of this mixture yielded, in addition to fractions of lower purity, the fractions (a)—(d). Fraction (a) was 2,3-dichloropropionitrile, b.p. 53—54° at 6 mmHg (lit.,[49,50] b.p. 58—59° at 7—8 mmHg, λ_{max} 13·6s μm) (Found: C, 28·8; H, 2·4; Cl, 57·3; N, 11·3. Calc. for $C_3H_3Cl_2N$: C, 29·0; H, 2·4; Cl, 57·3; N, 11·3%), ν_{max} 730s cm^{-1}; δ_H 3·89 (2H, d, $J_{H,H}$ 6·9 Hz) and 4·79 (1H, dd, $J_{H,H}$ 6·9 Hz). Fraction (b) was 1-cyano-vinyl phosphorodichloridate, b.p. 59—66° at 3 mmHg (lit.,[51] b.p. 52° at 0·001 mmHg, $n_D{}^{20}$ 1·4670, ν_{max} 1640, 2250, 1010, and 1310 cm^{-1}, ^{31}P δ 2 p.p.m. to low field of H_3PO_4); ν_{max} 2250w, 1640s, 1310s, and 1010s cm^{-1}; δ_H 5·93 (1H, dd, $J_{H,P}$ 3·4, $J_{H,H}$ 3·9 Hz) and 6·03 (1H, t, $J_{H,P}$ 3·9, $J_{H,H}$ 3·9 Hz); ^{31}P δ 2·59 (s) p.p.m. to low field of external H_3PO_4; this was slightly contaminated with 2,3-dichloropropionitrile.

Methanolysis of this material in the presence of triethylamine gave after work-up, the expected 1-cyanovinyl dimethyl phosphate (29%), b.p. 79° at 1 mmHg (g.l.c. t_R 4·6 min), $n_D{}^{19\cdot5}$ 1·4272 (Found: C, 33·1; H, 4·5; N, 7·9; P, 17·1. $C_5H_8NO_4P$ requires C, 33·9; H, 4·5; N, 7·9; P, 17·5%); δ_H 3·86 (6H, d), 5·62 (1H, dd, $J_{H,P}$ 1·75, $J_{H,H}$ 3·2 Hz), and 5·78 (1H, dd, $J_{H,P}$ 2·15, $J_{H,H}$ 3·1 Hz). Fraction (c), b.p. 71—82° at 0·8 mmHg, was not positively identified but was probably N-(1-chloroprop-2-enylidene)-phosphoramidic dichloride, ν_{max} 3140w, 3050w, 3010w, 1655w, 1653w, 1610w, 1550s, 1430w, 1380w, 1315s, 1360w, 1220w, 1085w, 1050s, 1020w, 955s, 920w, 835m, 770w, 700w, and 680w cm^{-1}; δ_H 5·66 (complex m); ^{31}P δ 31·2 (s) p.p.m. to low field of external H_3PO_4 (concentrated solution in dry ethyl methyl ketone). This material solidified and rapidly darkened. Fraction (d), b.p. 97—100° at 0·9 mmHg, was 2-chloro-1-cyanoethyl phosphorodichloridate (Found: C, 16·7; H, 1·8; N, 6·4; P, 13·7. $C_3H_3Cl_3NO_2P$ requires C, 16·2; H, 1·35; N, 6·3; P, 13·9%); ν_{max} 3030w, 2960w, 2260w, 1430w, 1290s, 1200w, 1050s, 1020s, 985w, 960m, 880w, 815w, 770w, 730w, and 700w cm^{-1}; δ_H 3·94 (2H, dd, $J_{H,P}$ 1·0, $J_{H,H}$ 5·4 Hz) and 5·58 (1H, dt, $J_{H,P}$ 11·7, $J_{H,H}$ 5·4 Hz); ^{31}P δ 8·42 (d, $J_{P,H}$ 11·7 Hz) p.p.m. to low field of external H_3PO_4.

Ethanolysis of this material in the presence of triethyl-amine gave, after work-up, a product which was identified (i.r. and ^1H n.m.r.) as 1-cyanovinyl diethyl phosphate (33%) (lit.,[51] b.p. 66° at 0·001 mmHg, $n_D{}^{20}$ 1·4260), b.p. 78° at 0·3 mmHg, $n_D{}^{20}$ 1·4268, g.l.c. t_R 6·4 min (Found: C, 40·9; H, 6·0; N, 6·8; P, 14·7. Calc. for $C_7H_{12}NO_4P$: C, 41·0; H, 5·85; N, 6·8; P, 15·1%); δ_H 1·39 (6H, dt), 4·20 (4H, m), 5·58 (1H, dd, $J_{H,P}$ 1·85, $J_{H,H}$ 3·0 Hz), and 5·75 (1H, dd, $J_{H,P}$ 2·2, $J_{H,H}$ 3·0 Hz).

However, ethanolysis in the presence of acrylonitrile

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gave a mixture of two compounds (g.l.c. t_R *ca.* 6 and 18 min) which were separated by fractional distillation. The more volatile compound (10%), b.p. 88—110° at 0·4 mmHg (t_R 6·4 min) was identical (i.r. and ^{1}H n.m.r.) with the 1-cyanovinyl diethyl phosphate already described. The second compound (21%), b.p. 113·5—115° at 0·4 mmHg (t_R 18·4 min) (21% yield) was identified by i.r. and ^{1}H n.m.r. as 2-*chloro*-1-*cyanoethyl diethyl phosphate*, n_D^{20} 1·4365 (Found: C, 35·1; H, 5·6; N, 6·1; P, 13·0. $C_7H_{13}ClNO_4P$ requires C, 34·8; H, 5·4; N, 5·8; P, 12·8%); δ_H 1·39 (6H, 4t), 3·86 (2H, d, $J_{H.H}$ 2·7, $J_{H.P}$ 0 Hz), 4·16 (4H, m), and 5·32 (1H, dt, $J_{H.H}$ 2·7, $J_{H.P}$ 4·3 Hz).

Reaction of Dichloroacetaldehyde with Phosphorus Trichloride and Oxygen.—Oxygen gas was bubbled for 24 h into a stirred mixture of phosphorus trichloride (5·0 mol, 436·5 ml) and freshly prepared dichloroacetaldehyde [52] (0·5 mol, 56·5 g) cooled in a bath at −30 °C, so that the temperature of the mixture was kept below 0 °C. The mixture was allowed to come to ambient temperature, and was then distilled at atmospheric pressure. The distillate (777 g) boiled at 105—108 °C and was shown by ^{1}H n.m.r. to contain unchanged dichloroacetaldehyde (35 g, 62%) [δ 5·9 (1H, d) and 9·0 (1H, d)]. The residue was distilled at 0·5 mmHg to give a liquid (5·8 g, 5·8%),

b.p. 50—56°, shown by ^{1}H n.m.r. to be a mixture of dichloromethyl phosphorodichloridate [δ 7·5 ($J_{H.P}$ 9·8 Hz)] and dichloromethylphosphonic dichloride [δ 6·0 ($J_{H.P}$ 7·4 Hz)] in a ratio *ca.* 1 : 10.

To facilitate separation, the mixture was converted into the corresponding dimethyl esters by treatment with absolute methanol (35 ml) under the usual conditions. After removal of solvent, the residue was chromatographed (silica gel; ether). The faster eluted material (300 mg) was dichloromethyl dimethyl phosphate [δ 3·8 (6H, d) and 7·5 (1H, d, $J_{H.P}$ 7·5 Hz)]. The slower eluted material (3·2 g) had b.p. 54·5° at 0·15 mmHg, and was dimethyl dichloromethylphosphonate (Found: C, 18·9; H, 3·7; Cl, 36·3; P, 16·2. Calc. for $C_3H_7Cl_2O_3P$: C, 18·7; H, 3·6; Cl, 36·8; P, 16·05%), δ_H 3·9 (6H, d) and 5·75 (1H, d, $J_{H.P}$ 2 Hz).

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