

The Phosphorus Trichloride–Oxygen–Olefin Reaction: Conformation and Elimination Studies on Products derived from 1-Chloro-2-fluoro- and 1,2-Difluoro-ethylene

By Clive B. C. Boyce* and Shirley B. Webb, Shell Research Limited, Woodstock Laboratories, Sittingbourne, Kent

Lawrence Phillips and Ian R. Ager, Organic Chemistry Department, Imperial College of Science and Technology, South Kensington, London SW7

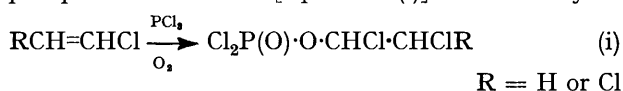
The reaction of phosphorus trichloride and oxygen with fluoro-olefins gives mixtures containing phosphoric and phosphonic dichlorides together with C–C cleavage products. In a wide range of compounds of the type $(\text{RO})_2\text{P}(\text{O})\cdot\text{CHX}\cdot\text{CHYCl}$, including products derived from these reactions, elimination of HCl occurs stereospecifically or stereoselectively, and in the case of pairs of diastereoisomers stereoconvergently, to give the olefins $(\text{RO})_2\text{P}(\text{O})\text{-CX}=\text{CHY}$ with X and Y *cis*. Suggestions are made concerning correlation of ground state conformational properties determined by ^1H and ^{19}F n.m.r. studies, with observed mode of HCl elimination.

RECENT investigations into the reaction of phosphorus trichloride and oxygen with 1,2-dichloroethylene¹ and

vinyl chloride² have shown that the major product is a phosphoric dichloride [equation (i)]. With ethylene³

¹ C. B. C. Boyce and S. B. Webb, *J. Chem. Soc. (C)*, 1971, 1613.
² C. B. C. Boyce and S. B. Webb, *J. Chem. Soc. (C)*, 1971, 3987.

³ L. Maier, *Helv. Chim. Acta*, 1969, **52**, 1337.



however, there is good evidence that 2-chloroethylphosphonic dichloride is the major product and only a small amount of the phosphoric dichloride is formed. We now report results of the reaction of phosphorus trichloride and oxygen with 1-chloro-2-fluoro- and 1,2-difluoro-ethylene.

The products formed in these two reactions are listed in Table 1, together with estimates of their relative abundance, including the ratios of diastereoisomers where relevant. As with the chloro-olefins,^{1,2} the major product from 1-chloro-2-fluoroethylene is a phosphoric and not a phosphonic dichloride as previously claimed,^{4,5}

The relative configurations of the two chiral centres in the pairs of diastereoisomeric phosphonic derivatives (IV) and (VII) can be deduced from n.m.r. data (Table 2) on the basis of the expected ranges of vicinal coupling constants: ^{6,7} $J_{F,H}(trans)$ 25 ± 3 , $J_{F,H}(gauche)$ 7 ± 3 , $J_{H,H}(trans)$ 11–15, and $J_{H,H}(gauche)$ 1–5 Hz. The more abundant diastereoisomers, (IVa) and (VIIa), probably exist predominantly in single conformations whereas the minor diastereoisomers, (IVb) and (VIIb), probably occur as mixtures (weighted average) of two conformers (Scheme). The pairs of diastereoisomers corresponding to the phosphonate (I), and the phosphoric

TABLE 1

Composition (%) of products ^a derived from the reaction of phosphorus trichloride and oxygen, with FCH=CHX					
X	Cl ₂ P(O)·O·CHX·CHFCI	Cl ₂ P(O)·O·CHF·CHCl ₂	Cl ₂ P(O)·CHX·CHFCI	Cl ₂ P(O)·CHF·CHCl ₂	Cl ₂ P(O)·CHFCI
Cl ^b	62 (1.2 : 1)	Trace	13 (2 : 1)	11.5	11.5
F ^c	21 (1.5 : 1)		70 (1.7 : 1)		9

^a Figures in parentheses show the ratios of the diastereoisomers formed. ^b Proportions of products obtained from ³¹P n.m.r. spectrum of mixed phosphoric and phosphonic dichlorides; diastereoisomer ratios obtained from ¹⁹F n.m.r. spectrum of mixed phosphate and phosphonate esters. ^c Proportions of products and diastereoisomer ratios obtained from ¹⁹F n.m.r. spectrum of mixed phosphoric and phosphonic dichlorides.

TABLE 2

N.m.r. parameters of compounds derived from the reaction of phosphorus trichloride and oxygen with FCH=CHX (X = Cl or F)

Compound *	Chemical shifts				J/Hz §									
	F β †	F α †	H β ‡	H α ‡	H β F β	H α F α	H β H α	F β F α	F β H α	F α H β	F β P	F α P	H β P	H α P
(EtO) ₂ P(O)·CHCl·CHFCI (Ia)		23.15	4.20	6.59		48.0	2.8			25.0		3.5		2.8
(Ib)		31.88	4.20	6.44		48.0	3.0			7.8		21.3		4.5
(EtO) ₂ P(O)·CHF·CHCl ₂ (II)	-41.15		4.77	6.01	44.3		5.4		14.3		71.3		6.5	3.8
(EtO) ₂ P(O)·O·CHCl·CHFCI (IIIa)		20.92	6.21	6.17		48.0	4.0			6.0		0		4.0
(IIIb)		16.21	6.21	6.11		48.0	3.6			8.0		0		3.6
Cl ₂ P(O)·CHF·CHFCI (IVa)	-42.81	15.05			46.0	46.0		15.0	17.0	22.0	92		8.0	
(IVb)	-35.77	19.48			45.0	48.0		26.0	11.0	10.0	92		18.0	
Cl ₂ P(O)·O·CHF·CHFCI (Va)	27.72	8.40				49.0		16.0		4.0 ca.	1.5		0	
(Vb)	27.18	7.39				48.0		19.3		6.0 ca.	1.5		0	
(EtO) ₂ P(O)·O·CHF·CHFCI (VIa)	29.87	9.96 ca.	5.75 ca.	6.72	50.0	48.5		15.5	5.0	4.5	2.0 ca.		1	
(VIb)	27.92	8.79 ca.	5.75 ca.	6.72	51.0	48.5		19.0	5.0	5.5	2.0		0	
(EtO) ₂ P(O)·CHF·CHFCI (VIIa)	-54.28	16.95	4.78	6.47	44.5	49.0	3.5	15.0	15.5	23.5	68.0	11.0	8.3	1.4
(VIIb)	-51.93	20.20	4.84	6.42	46.0	47.0	4.8	26.5	11.5	9.3	69.0	19.0	7.0	4.0

* In all cases compound a was formed in higher yield than compound b. † In p.p.m. from C₆F₆ (internal); positive shifts to low field (CCl₄ solution). ‡ δ Values (Me₄Si internal standard; CCl₄ solution). § Obtained from approximate first-order analyses only.

TABLE 3

N.m.r. parameters * of compounds (VIII) and (IX)

Compound	δ Values †			J/Hz							
	H _a	H _b	H	H _a H _b	H _a H	H _b H	H _a P	H _b P	HP	H _a Me	H _b Me
(EtO) ₂ P(O)·CH _a H _b ·CH(Me)Cl (VIII)	2.28	2.03	4.33	15.4	5.1	8.9	19.3	18.2	8.5	ca. 0.25	<0.1
(MeO) ₂ P(O)·CH _a H _b ·CH(CO ₂ Me)Cl (IX)	2.28	2.64	4.44	15.4	5.5	9.1	19.3	17.4	9.1		

* Obtained by iterative analysis using the LACOON III program. † Internal Me₄Si standard; CCl₄ solution.

and 1,2-difluoroethylene, like ethylene,³ gives mainly a phosphonic dichloride. Possible pathways to the products together with factors controlling the regioselectivity of the reaction and the ratio of P–O–C to P–C bond formation are discussed in the following paper. This paper is concerned with the conformational properties and elimination reactions of these and related compounds.

⁴ L. Z. Soborovskii, Yu. M. Zinov'ev, and T. G. Spiridonova, *J. Gen. Chem. (U.S.S.R.)*, 1959, **29**, 1110.

⁵ Yu. M. Zinov'ev and L. Z. Soborovskii, *J. Gen. Chem. (U.S.S.R.)*, 1959, **29**, 3913.

derivatives (III), (V), and (VI) all appear to exist predominantly in single conformations (Scheme) but in these cases it is not possible to deduce the relative configurations of the chiral centres.

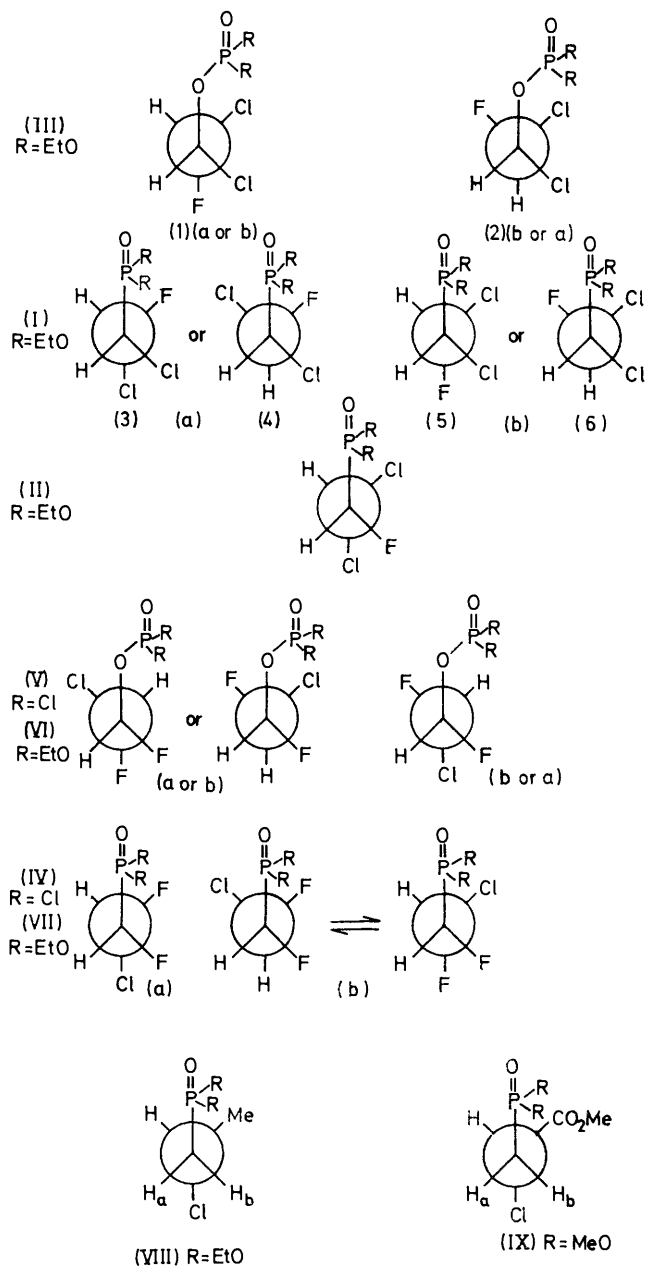
N.m.r. data (Table 3) for diethyl 2-chloropropylphosphonate ⁸ (VIII) and dimethyl 2-chloro-2-methoxycarbonylethylphosphonate ⁸ (IX) suggest, on the basis

⁶ L. Phillips and V. Wray, *Progr. N.M.R. Spectrometry*, in the press.

⁷ R. J. Abraham and G. Gatti, *J. Chem. Soc. (B)*, 1969, 961.

⁸ C. B. C. Boyce, S. B. Webb, and L. Phillips, following paper.

of the vicinal $J_{H,H}$ values,⁹ and in the case of the phosphonate (VIII) the long-range coupling observed between the methyl group and the proton assigned as *trans* to



SCHEME Probable relative configurations and conformations of compounds (I)—(IX)

it,¹⁰ that they exist predominantly in the single conformations shown in the Scheme. Thus with the

* This notation is used throughout in line with the accepted convention for elimination reactions.

⁹ L. Phillips and V. Wray, *J.C.S. Perkin II*, 1972, 536.

¹⁰ M. Barfield and B. Chakrabarti, *Chem. Rev.*, 1969, **69**, 757.

¹¹ R. J. Abraham and K. Parry, *J. Chem. Soc. (B)*, 1970, 539; E. Elkik and C. Francesch, *Bull. Soc. chim. France*, 1973, 1277; L. H. L. Chia, E. Huang, and H.-H. Huang, *J.C.S. Perkin II*, 1973, 766; A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, 1962, **84**, 743; R. J. Abraham and J. R. Monasterios, *J.C.S. Perkin I*, 1973, 1446.

exception of the 1,2-difluoroethylphosphoric dichloride (V) and the corresponding diethyl ester (VI), the 1,1,2,2-tetrasubstituted ethanes have preferred conformations in which the two hydrogens have a *gauche* relationship, which is in accord with data on other 1,1,2,2-tetrasubstituted ethanes.¹¹ The observation that the 1,2,2-trisubstituted ethanes (VIII) and (IX) prefer to exist in conformations in which there is one *trans* and one *gauche* relationship between hydrogen atoms is also in agreement with previous studies.¹¹

Treatment of the diastereoisomeric mixture of 1,2-dichloro-2-fluoroethyl diethyl phosphates (III) (1-2a : 1b), with potassium *t*-butoxide in *t*-butyl alcohol at 0 °C gave a mixture of two vinyl phosphates in the ratio *ca.* 1 : 1.3. ¹⁹F N.m.r. data confirmed that these were the isomers of 1-chloro-2-fluorovinyl diethyl phosphate, (X) and (XI). The method of Phillips and Wray¹² for estimating the difference in ¹⁹F chemical shift between the *Z*- and *E*-isomers of a fluoro-olefin suggests that the *Z*-isomer (XI) is the more abundant. This is supported by the fact that the vinylic proton in (XI) which is *cis* to the

phosphoryl group resonates at lower field than the corresponding *trans*-proton¹³ in (X). If the more abundant vinyl phosphate (XI) is formed from the more abundant diastereoisomeric phosphate (IIIa) by an *anti*-elimination, the relative configurations and preferred conformations of (IIIa) and (IIIb) can be assigned as (1) and (2) respectively (Scheme).

2-Chloro-1,2-difluoroethyl diethyl phosphate (VIa and b) was not dehydrochlorinated by treatment with potassium *t*-butoxide in *t*-butyl alcohol. The lack of reactivity parallels that of 2-chloroethyl phosphate esters.¹⁴ Clearly the β -proton (*i.e.* that *gem* to phosphorus) * in these phosphoric derivatives is not very acidic. However the situation is very different in the corresponding phosphonic derivatives since the phosphoryl group can stabilize the conjugate base (*i.e.* the carbanion) through conjugative and inductive effects.¹⁵ Although such carbanions are well known and have been widely exploited synthetically¹⁶ the effect of a β -phosphonyl substituent in 1,2-eliminations of HX has not been explored, which is surprising in view of the interest there has been in the effect of analogous β -

¹² L. Phillips and V. Wray, *J.C.S. Perkin II*, 1972, 223.

¹³ C. B. C. Boyce, L. Phillips, S. B. Webb, and P. A. Worthington, *J.C.S. Perkin I*, 1973, 2881.

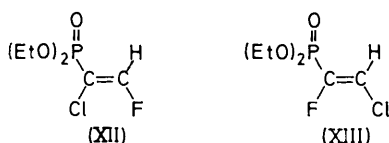
¹⁴ J. F. Allen, S. K. Reed, O. H. Johnson, and N. J. Brunsvold, *J. Amer. Chem. Soc.*, 1956, **78**, 3715.

¹⁵ D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York and London, 1965.

¹⁶ For leading references see Chemical Society Specialist Periodical Reports, 'Organophosphorus Chemistry,' Vols. I—III, chapters, 8, pp. 205, 183, and 180, respectively.

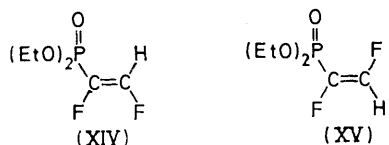
substituents in olefin-forming eliminations where *E1cb* or *E1cb*-like mechanisms are thought to operate.¹⁷⁻²⁰

Treatment of the diastereoisomeric mixture of diethyl 1,2-dichloro-2-fluoroethylphosphonates (I) (2a : 1b) with triethylamine (ether; 24 h; 20°) resulted in stereoconvergent¹⁹ elimination of HCl: *only* the *Z*-isomer of diethyl 1-chloro-2-fluorovinylphosphonate (XII) was formed.



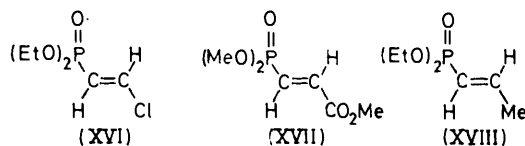
Dehydrochlorination of the isomeric diethyl 2,2-dichloro-1-fluoroethylphosphonate (II) with triethylamine (ether; 7 days; 36°) resulted in a stereospecific elimination to give the vinylphosphonate (XIII).

When the mixture of diastereoisomers of diethyl 2-chloro-1,2-difluoroethylphosphonate (VII) (1·7a : 1b), was heated with triethylamine in ether under reflux for 9 days, the major diastereoisomer (VIIa) did not react and only the *E*-isomer (XIV) of diethyl 1,2-difluorovinylphosphonate was formed (as indicated by ¹H n.m.r.). Dehydrochlorination of the major diastereoisomer (which was recovered in almost quantitative yield) under more forcing conditions (heating with triethylamine in toluene for 24 h at reflux, or treatment with potassium *t*-butoxide in *t*-butyl alcohol at 0 °C) also gave the *E*-isomer (XIV), together with about 10%



of the *Z*-isomer (XV) of diethyl 1,2-difluorovinylphosphonate. Since the configurational assignments of (VIIa and b) are unambiguous the minor diastereoisomer must undergo *anti*-elimination of HCl whereas the major diastereoisomer suffers mainly *syn*-elimination.

Diethyl 2,2-dichloroethylphosphonate² and dimethyl 2-chloro-2-methoxycarbonyl ethylphosphonate⁸ (IX) undergo stereospecific elimination of HCl, and diethyl 2-chloropropylphosphonate⁸ (VIII) undergoes a similar but stereoselective (80%) elimination. The products are the *E*-vinylphosphonates (XVI)–(XVIII), respectively.

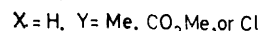
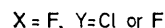
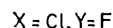
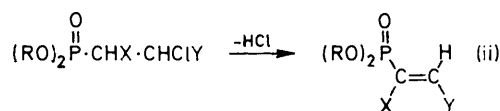


With a wide variety of substituents, therefore, elimination of HCl from 2-chloroalkylphosphonates occurs

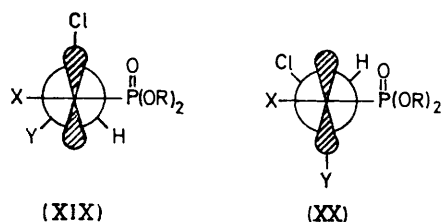
¹⁷ D. V. Banthorpe, 'Elimination Reactions,' Elsevier, Amsterdam, London, and New York, 1963.

¹⁸ J. Sicher, *Angew. Chem. Internat. Edn.*, 1972, **11**, 200.

stereospecifically and always in the same sense [equation (ii)]. Moreover in the five cases where the conformational properties of the substrate in solution (CCl₄) have been deduced [(II), (VIIa), (VIIb), (VIII), and (IX)], the geometry of the product is that which most resembles the preferred conformation of the substrate irrespective of whether a formal *syn*- or *anti*-elimination is involved (*i.e.* the elimination appears to have occurred from the lowest-energy conformation of the substrate). This correlation may be fortuitous since the relative rates of formation of the *Z*- and *E*-olefins are generally expected to be determined solely by the differences in the standard potentials of the respective transition states, and will be independent of the relative energies of the ground-state



conformations of the substrate.²¹ If, however, the transition states leading to *syn*- and *anti*-elimination resemble carbanions (*i.e.* an *E1cb* mechanism is involved which, for reasons already given, is likely) the energy difference between them may indeed be similar to, or less than the ground state conformational energy differences between the substrates. If we assume that the acidity of the β-hydrogen atoms in a pair of diastereoisomeric substrates is governed mainly by the nature of the α- and β-substituents rather than by their spatial arrangement, the rates of formation of the two carbanions will be largely decided by the populations of the ground-state conformations. Since carbanions stabilized by substituents capable of delocalizing the electron pair onto more electronegative elements are expected to approach *sp*² hybridization (which maximizes overlap between the *p*-orbital of the carbon atom and those of the substituent, and allows negative charge to reside



largely on the heteroatom),¹⁵ the carbanions initially formed from the preferred conformations of the pairs of diastereoisomers are expected to be of types (XIX) or (XX).

anti-Elimination of chloride ion from the carbanion (XIX) is expected to be favoured compared with elimination from (XX), since there is already maximum

¹⁹ D. J. McLennan, *Quart. Rev.*, 1967, **21**, 490.

²⁰ J. F. Bunnett, *Angew. Chem. Internat. Edn.*, 1962, **1**, 225.

²¹ D. Y. Curtin, *Rec. Chem. Progr.*, 1954, **15**, 111.

overlap between the non-bonding orbital on the carbon atom bearing the negative charge and the C-Cl bond. However, *syn*-elimination of chloride ion is expected to predominate from the carbanion (XX) since this minimizes eclipsing interactions on the reaction pathway.

In the case of the 2-chloro-1,2-difluoroethylphosphonate (VIIa), in which the preferred conformation has H and Cl in a *gauche* relationship, the product is formally that of 9:1 *syn*:*anti*-elimination, and, as expected, the reaction is slower than elimination from the other diastereoisomer, in which H and Cl are *anti*. Application of this rationale to the diastereoisomeric 1,2-dichloro-2-fluoroethylphosphonates (Ia and b) suggests that the preferred conformations are (3) and (5) respectively (Scheme), and that the product (XII) is formed by *syn*-elimination from (Ia) and by *anti*-elimination from (Ib). Similarly consideration of the relationship between the preferred conformations of the 2-methyl- (VIII) and 2-methoxycarbonyl-ethylphosphonates (IX) and the observed products of elimination suggests that in each case a stereoselective *syn*-elimination of H_aCl occurs. Selective removal of H_a is expected on the grounds that it is less sterically hindered than H_b , which is *gauche* to two large substituents (Scheme). However the diastereotopic protons H_a and H_b may have intrinsically different reactivity, even in the absence of conformational effects, and we recognize the possibility that the observed elimination products from (VIII) and (IX) may arise by a stereoselective *anti*-elimination of H_bCl .

Banthorpe¹⁷ has pointed out the difficulty of predicting the mode of elimination in any particular *ELcb* reaction, and has suggested that this will vary among substrates depending on the size and type of substituents and the carbanion stability. We suggest that with the diethyl 2-chloroethylphosphonates under consideration the major product is derived by elimination from the most highly populated conformation of the substrate, irrespective of whether a formal *syn* or *anti* process is involved. It may be more than coincidental that examples of stereoconvergent²² and stereospecific²³ eliminations from tetrasubstituted ethanes in which one of the substituents is a sulphonyl group, $ArSO_2\cdot CHX\cdot CHYZ$ ($Ar = p\text{-MeC}_6\text{H}_4$, $X = Y = Ph$, $Z = Cl$; ²² $Ar = Ph$, $X = D$, $Y = SPh$, $Z = F$ ²³), also give olefins in which the α -proton is in a *cis*-relationship to the activating group; and the most likely conformations of these substituted ethanes, predicted on the basis of the results of Abraham and Parry,¹¹ are those which lead to the observed products.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 grating spectrometer and n.m.r. spectra with a Varian HA-100 spectrometer, operating at 100 MHz for ¹H, 94.1 MHz for ¹⁹F, and 40.5 MHz for ³¹P; for ¹⁹F spectra field-frequency lock and extended lock operation with fully automatic phase correction were used.²⁴ Column chromatography, which was carried out with silica gel as stationary phase (Crosfield Sorbsil brand) and ether as

eluant, was monitored by g.l.c. (Perkin-Elmer F11, 2 m column packed with 10% QF1 on Chromosorb W, at 130°) and/or by t.l.c. (Merck pre-coated silica gel F₂₅₄ plates). Combined g.l.c.-mass spectrometry was carried out on a Perkin-Elmer 452 gas chromatograph fitted with a 2 m column containing 10% QF1 on 100-120 mesh Chromosorb W, at 155°, connected *via* a Biemann separator to a Quad 250 mass analyser. Mass spectra were recorded with an A.E.I. MS9 instrument. Vacuum distillations were carried out under nitrogen.

Reaction of 1-Chloro-2-fluoroethylene with Phosphorus Trichloride and Oxygen.^{4,5}—1-Chloro-2-fluoroethylene (100 g, 1.24 mol), phosphorus trichloride (1 l, 1574 g, 11.45 mol), and oxygen were treated as previously described.^{1,2} The product (90.7 g, *ca.* 30% based on olefin) had b.p. 60-84° at 3.5 mmHg, n_D^{20} 1.4718, ν_{max} 3000w, 2930w, 1295s, 1215w, 1125m, 1085s, 1010s (P-O-C), 980m, 950m, 885w, 865w, 810m, 765m, 725w, and 680w cm^{-1} ; ³¹P δ 12.3 (m) and 36.4 (m) p.p.m. to low field of external H₃PO₄ attributable to the phosphoric and the phosphonic dichloride, respectively (65:35).

Ethanolysis of the Product of the Foregoing Reaction.—The product (80 g) was treated with absolute ethanol as described previously.^{1,2} The excess of ethanol was removed *in vacuo*, and the residue distilled to give a product (82.65 g) b.p. 98-116° at 2.5 mmHg, n_D^{20} 1.4334. T.l.c. and g.l.c. indicated that this contained at least five components. G.l.c.-mass spectrometry showed the presence of the expected phosphonates (I) and (II), two isomeric phosphates (one in very small amount), and a small amount of a vinylphosphonate, subsequently identified as (*Z*)-diethyl 1-chloro-2-fluorovinylphosphonate. ¹H N.m.r. studies revealed, in addition, the presence of *ca.* 2% of diethyl dichloromethylphosphonate.¹ Fractional distillation gave two fractions. The lower boiling fraction, b.p. 94-104° at 2.5 mmHg (6.4 g), after column chromatography and subsequent distillation yielded pure *diethyl chlorofluoromethylphosphonate*, b.p. 76-77° at 2.2 mmHg, n_D^{23} 1.4213 (Found: C, 29.0; H, 5.2; Cl, 17.2; P, 14.7. C₆H₁₁ClFO₃P requires C, 29.35; H, 5.4; Cl, 17.3; P, 15.15%); δ_H 1.40 (6H, t), 4.26 (4H, m), 6.19 (1H, dd, $J_{H,P}$ 9.7, $J_{H,F}$ 46.7 Hz); ¹⁹F δ 2.83 (dd) p.p.m. to low field of C₆F₆ ($J_{F,H}$ 46.3; $J_{F,P}$ 77.0 Hz).

Chromatography of the higher boiling fraction, b.p. 109-111° at 2.9 mmHg (60.55 g), gave two sub-fractions. The faster eluted material (40 g) was distilled to yield a pure product (36.5 g), b.p. 144° at 2 mmHg, $n_D^{21.5}$ 1.4299, identified by ¹H and ¹⁹F n.m.r. (Table 2) and mass spectrometry as a mixture of diastereoisomers of 1,2-dichloro-2-fluoroethyl diethyl phosphate (III) (Found: C, 27.1; H, 4.7; Cl, 25.9; P, 11.4. C₆H₁₂Cl₂FO₄P requires C, 26.8; H, 4.5; Cl, 26.4; P, 11.5%); m/e 267 [(*M* - 1)⁺], 241, 233, 213, 205, 201 [(*M* - CHFCl)⁺], 177, 173, 137, 109, 81, and 67 [(CHFCl)⁺]. The slower eluted material (14 g) was distilled and the product (10.5 g), b.p. 109° at 2 mmHg, n_D^{20} 1.4478, identified by ¹H and ¹⁹F n.m.r. (Table 2) as a 1:1 mixture of the diastereoisomers of diethyl 1,2-dichloro-2-fluoroethylphosphonate (I) and diethyl 2,2-dichloro-1-fluoroethylphosphonate (II) (Found: C, 28.6; H, 4.8; Cl, 27.5; P, 12.3. Calc. for C₆H₁₂Cl₂FO₃P: C, 28.5; H, 4.8; Cl, 28.0; P, 12.25%).

²² S. J. Cristol and P. Pappas, *J. Org. Chem.*, 1963, **28**, 2066.

²³ V. Fiandanese, G. Marchese, and F. Naso, *J.C.S. Chem. Comm.*, 1972, 250.

²⁴ P. N. Jenkins and L. Phillips, *J. Phys. (E)*, 1971, **4**, 530.

Reaction of 1,2-Difluoroethylene with Phosphorus Trichloride and Oxygen.—1,2-Difluoroethylene (100 g, 1.565 mol), phosphorus trichloride (1365 ml, 2150 g, 15.65 mol), and oxygen were treated as described previously.^{1,2} The product (76 g, ca. 35% based on olefin) had b.p. 45–82° at 7–8 mmHg; ν_{\max} 3000w, 2930w, 1285s, 1230w, 1200w, 1145w, 1125m, 1085m, 1050m, 990w, 970w, 920m, 825w, 815w, 795w, 765w, 735w, and 720w cm^{-1} ; δ_{H} 4.96–7.16 (complex); ^{31}P δ 7.04 (unresolved; attributable to the phosphoric dichloride), and 30.1 and 32.59 p.p.m. (partially resolved; attributable to the phosphonic dichloride) to low field of external H_3PO_4 ; ^{19}F δ -42.81 (m), -35.77 (m), 7.39 (m), 8.40 (m), 10.6 (dd), 15.05 (m), 19.48 (m), and 27.45 (m) p.p.m. to low field of internal C_6F_6 .

Ethanolysis of the Product of the Foregoing Reaction.—The product (33 g) was treated with ethanol as described previously.^{1,2} Distillation gave material (34.1 g; b.p. 68–83° at 0.4–0.3 mmHg; resolved by g.l.c. into three components, t_{R} 2.5, 3.0, and 3.3 min) which was separated into two fractions by column chromatography.

The faster eluted fraction yielded a pure liquid, b.p. 64° at 0.3 mmHg (6.6 g), n_{D}^{22} 1.4015, t_{R} 3.0 min, identified by ^1H and ^{19}F n.m.r. (Table 2) as a mixture of diastereoisomers of 2-chloro-1,2-difluoroethyl diethyl phosphate (VI) (Found: C, 27.8; H, 4.9; Cl, 13.8; P, 12.1. $\text{C}_6\text{H}_{12}\text{ClF}_2\text{O}_4\text{P}$ requires C, 28.5; H, 4.8; Cl, 14.0; P, 12.3%).

The slower eluted fraction yielded a liquid, b.p. 86.5–87.5° at 0.8 mmHg, n_{D}^{22} 1.4191, consisting of two materials, t_{R} 2.5 and 3.3 min in the ratio ca. 1:10. The minor component was identified (^1H and ^{19}F n.m.r.) as diethyl chlorofluoromethylphosphonate (see before); and the major component was shown, also by ^1H and ^{19}F n.m.r. (Table 2), to be a mixture of diastereoisomers of diethyl 2-chloro-1,2-difluoroethylphosphonate (VII) (Found: C, 30.7; H, 5.3; Cl, 14.7; P, 12.9. $\text{C}_6\text{H}_{12}\text{ClF}_2\text{O}_3\text{P}$ requires C, 30.5; H, 5.1; Cl, 15.0; P, 13.1%).

Dehydrochlorination of 1,2-Dichloro-2-fluoroethyl Diethyl Phosphate (III) (1.2:1b).—The phosphate (III) (26.9 g, 0.1 mol) was treated with potassium *t*-butoxide at 0 °C as described previously.^{1,2} After work-up, the product (13.8 g, 59%), b.p. 83.5–87° at 2 mmHg, was shown by g.l.c. to be a mixture of two compounds, t_{R} 3.2 and 3.7 min (ca. 1:3:1). Repeated column chromatography provided pure samples of both. The faster eluted material (t_{R} 3.7 min) was identified by i.r. and ^1H and ^{19}F n.m.r. spectra as (*E*)-1-chloro-2-fluorovinyl diethyl phosphate (X), b.p. 84.5–85.5° at 2 mmHg, n_{D}^{22} 1.4212 (Found: C, 30.6; H, 5.0; Cl, 14.9; P, 13.2. $\text{C}_6\text{H}_{11}\text{ClFO}_4\text{P}$ requires C, 31.0; H, 4.8; Cl, 15.25; P, 13.3%), ν_{\max} 1695m cm^{-1} (C=C); δ_{H} 1.39 (6H, t), 4.21 (4H, m), 6.62 (1H, dd, $J_{\text{H,P}}$ 2.9, $J_{\text{H,F}}$ 75 Hz); ^{19}F δ 19.19 (dd) p.p.m. to low field of C_6F_6 ($J_{\text{F,H}}$ 75, $J_{\text{F,P}}$ 8 Hz).

The slower eluted material (t_{R} 3.2 min) was identified by i.r. and ^1H and ^{19}F n.m.r. spectra as (*Z*)-1-chloro-2-fluorovinyl diethyl phosphate (XI), b.p. 84.5–85.5° at 2 mmHg, n_{D}^{22} 1.4192 (Found: C, 31.0; H, 5.1; Cl, 15.0; P, 13.6. $\text{C}_6\text{H}_{11}\text{ClFO}_4\text{P}$ requires C, 31.0; H, 4.8; Cl, 15.25; P, 13.3%), ν_{\max} 1695vw cm^{-1} (C=C); δ_{H} 1.39 (6H, t), 4.18 (4H, m), and 7.22 (1H, dd, $J_{\text{H,P}}$ 3.9, $J_{\text{H,F}}$ 75.5 Hz); ^{19}F δ 8.54 (dd) p.p.m. to low field of C_6F_6 ($J_{\text{F,H}}$ 75.5; $J_{\text{F,P}}$ 9 Hz).

Treatment of the Mixture of Diethyl Dichlorofluoroethylphosphonates (Ia and b) and (II) with Triethylamine.—The mixture (6.7 g) was treated with triethylamine (5.5 g) in dry ether (50 ml) at room temperature for 24 h. Work-up and chromatography gave a mixture of unchanged phos-

phonate and vinylphosphonate (6.0 g), separated by careful fractionation. The more volatile material, b.p. 71–76° at 2 mmHg (2 g), after further chromatography and distillation was shown by g.l.c. and ^1H and ^{19}F n.m.r. to be a single geometric isomer of diethyl 1-chloro-2-fluorovinylphosphonate (XII), b.p. 68–69° at 2 mmHg, $n_{\text{D}}^{19.5}$ 1.4332 (lit.,⁵ b.p. 80–82° at 3 mmHg, n_{D}^{20} 1.4090) (Found: C, 33.3; H, 5.2; Cl, 16.4; P, 13.8. Calc. for $\text{C}_6\text{H}_{11}\text{ClFO}_3\text{P}$: C, 33.3; H, 5.1; Cl, 16.4; P, 14.3%), ν_{\max} 1640s cm^{-1} (C=C); δ_{H} 1.38 (6H, t), 4.10 (4H, m), and 7.52 (1H, dd, $J_{\text{H,P}}$ 4.1, $J_{\text{H,F}}$ 78.0 Hz); ^{19}F δ 58.89 (dd) p.p.m. to low field of C_6F_6 ($J_{\text{F,H}}$ 77.5, $J_{\text{F,P}}$ 33 Hz). The small $J_{\text{H,P}}$ value²⁵ (4.1 Hz) suggests that this is the *Z*-isomer.

The less volatile material (3.0 g), b.p. 100–101° at 2 mmHg, was identified by ^1H and ^{19}F n.m.r. (Table 2) as unchanged diethyl 2,2-dichloro-1-fluoroethylphosphonate (II) (Found: C, 28.7; H, 5.0; Cl, 28.1; P, 12.1. $\text{C}_6\text{H}_{12}\text{Cl}_2\text{FO}_3\text{P}$ requires C, 28.5; H, 4.8; Cl, 28.0; P, 12.25%).

Neither the *E*-isomer of diethyl 1-chloro-2-fluorovinylphosphonate nor the *E*- or *Z*-isomers of diethyl 2-chloro-2-fluorovinylphosphonate were detected.

Treatment of Diethyl 2,2-Dichloro-1-fluoroethylphosphonate (II) with Triethylamine.—The phosphonate (II) (2.4 g), triethylamine (5 g), and dry ether (40 ml) were heated under reflux for 7 days. After work-up and chromatography, the product (1.8 g) was identified by g.l.c. and ^1H and ^{19}F n.m.r. as (*E*)-diethyl 2-chloro-1-fluorovinylphosphonate (XIII), b.p. 69.5–70° at 1.9 mmHg, n_{D}^{20} 1.4372 (Found: C, 33.6; H, 5.2; Cl, 16.5; P, 13.8. $\text{C}_6\text{H}_{11}\text{ClFO}_3\text{P}$ requires C, 33.3; H, 5.1; Cl, 16.4; P, 14.3%), ν_{\max} 1630w cm^{-1} (C=C); δ_{H} 1.40 (6H, t), 4.15 (4H, m), 6.55 (1H, dd, $J_{\text{H,P}}$ 4.5, $J_{\text{H,F}}$ 24.5 Hz); ^{19}F δ 37.41 (dd) p.p.m. to low field of C_6F_6 ($J_{\text{F,H}}$ 24.5, $J_{\text{F,P}}$ 83 Hz).

*Treatment of 2-Chloro-1,2-difluoroethyl Diethyl Phosphate (VI) with Potassium *t*-Butoxide.*—The phosphate (VI) (1.65 g, 0.006 mol) was treated with potassium *t*-butoxide (0.006 mol) in *t*-butyl alcohol as described previously. No reaction was detected after 0.5 h by g.l.c.

Treatment of Diethyl 2-Chloro-1,2-difluoroethylphosphonates (VIIa and b) with Triethylamine.—(i) *In ether.* The mixture of diastereoisomeric phosphonates (VIIa and b) (2:1; containing 10% diethyl chlorofluoromethylphosphonate) (5.5 g, 0.0233 mol), triethylamine (5.05 g, 0.05 mol), and dry ether (40 ml) were heated under reflux. After 9 days (when g.l.c. showed no further reaction) the mixture was worked up. ^1H N.m.r. showed that only one vinylphosphonate was formed [$\text{CH}=\text{}$ signal at δ 6.97 (ddd)], and that the major diastereoisomer (VIIa) [δ_{H} 4.78 (dddd, H_a) and 6.47 (dddd, H_b)] had not reacted. Column chromatography followed by fractional distillation led to almost complete separation of the two compounds. (*E*)-Diethyl 1,2-difluorovinylphosphonate (XIV) (1.6 g, 34%) was isolated as a liquid, b.p. 57–59° at 2 mmHg, n_{D}^{22} 1.4015 (Found: C, 35.7; H, 5.8; P, 15.1. $\text{C}_6\text{H}_{11}\text{F}_2\text{O}_3\text{P}$ requires C, 36.0; H, 5.5; P, 15.5%); δ_{H} 1.37 (6H, t), 4.12 (4H, m), and 6.97 (1H, ddd, $J_{\text{H,F-gem}}$ 72.4, $J_{\text{H,F}}$ 17.2, $J_{\text{H,P}}$ 1.6 Hz); ^{19}F δ 4.51 (dt, $J_{\text{F,P}}$ 70.5, $J_{\text{F,F}}$ 17, $J_{\text{F,H}}$ 17 Hz) and 23.33 (ddd, $J_{\text{F,P}}$ 27, $J_{\text{F,F}}$ 17, $J_{\text{F,H}}$ 72.5 Hz) p.p.m. to low field of C_6F_6 . Diethyl 2-chloro-1,2-difluoroethylphosphonate (VIIa) [contaminated with 10% of diethyl chlorofluoromethylphosphonate and a little diethyl 1,2-difluorovinylphosphonate] (2.55 g, 46%), b.p. 83–89° at 2 mmHg, was recovered. (*Z*)-Diethyl 1,2-difluorovinylphosphonate was not detected.

²⁵ G. Mavel, *Progr. N.M.R. Spectrometry*, 1966, **1**, 251.

To confirm that the dehydrohalogenation of (VIIb) is stereospecific, and that some *Z*-isomer is not formed and subsequently isomerized to the *E*-isomer, a mixture of the (*Z*)- (see later) and (*E*)-diethyl 1,2-difluorovinylphosphonate and diethyl chlorofluoromethylphosphonate (1 : 2.4 : 1; 1.0 g) was heated under reflux for 9 days with triethylamine hydrochloride (1.0 g) and triethylamine (0.5 g), in ether (12 ml). After removal of the solvent, examination of the vinyl region of the ^1H n.m.r. spectrum (δ 5.5–8.5) showed that no change had occurred in the proportions of (*Z*)- and (*E*)-diethyl 1,2-difluorovinylphosphonate.

(ii) *In* [$^2\text{H}_4$]methanol. Mixtures of the phosphonates (VIIa and b) containing 20% diethyl chlorofluoromethylphosphonate (100 mg) and triethylamine (100 mg) in [$^2\text{H}_4$]methanol (1 ml) were kept (*a*) at 50 °C for 5 h, and (*b*) at ambient temperature (20 °C) for 48 h. In both cases periodic examination (^1H and ^{19}F n.m.r.) showed that there was no incorporation of deuterium into the starting material, and the ratio of (*E*)- and (*Z*)-diethyl 1,2-difluorovinylphosphonate formed was *ca.* 9 : 1.

A similar experiment under conditions (*b*) carried out on the major diastereoisomer (VIIa) of diethyl 1,2-difluoro-2-chloroethylphosphonate showed, additionally, no evidence of any inversion to the minor diastereoisomer.

Reactions of Diethyl 2-Chloro-1,2-difluoroethylphosphonate (VIIa).—(i) *With potassium *t*-butoxide.* The recovered diastereoisomer (VIIa) of diethyl 2-chloro-1,2-difluoroethyl-

phosphonate (2.1 g, 0.0085 mol) was treated with potassium *t*-butoxide as described previously.^{1,2} After work-up, the ^1H n.m.r. spectrum of the product showed, in addition to the resonance centred at δ 6.97 attributable to the vinyl proton of (*E*)-diethyl 1,2-difluorovinylphosphonate (XIV), a resonance centred at δ 7.52 (ddd, J 7.4, 2.3, and 7.7 Hz) attributable to the vinyl proton of the (*Z*)-vinylphosphonate (XV). Integration indicated that this represented about 10% of the product formed. The ^{19}F n.m.r. data support this assignment: δ -14.75 (ddd, $J_{\text{F,H}}$ 8.0, $J_{\text{F,F}}$ 136, $J_{\text{F,P}}$ 84 Hz) and 4.46 (ddd, $J_{\text{F,H}}$ 7.3, $J_{\text{F,F}}$ 136, $J_{\text{F,P}}$ 9 Hz) p.p.m. to low field of C_6F_6 .

(ii) *With triethylamine in toluene.* A mixture of the phosphonate (VIIa) (2.37 g, 0.01 mol) and triethylamine (2.5 g, 0.0248 mol) in dry toluene (30 ml) was stirred and heated under reflux for 24 h. After work-up, ^1H n.m.r. showed that both (*E*)- and (*Z*)-diethyl 1,2-difluorovinylphosphonate were present, in the ratio *ca.* 9 : 1.

We thank Messrs. P. N. Jenkins and R. A. G. Carrington for n.m.r. spectra, Mr. V. Williams for mass spectra, and Mr. M. A. Pinnegar for the g.l.c.-mass spectrometry measurements. Mr. M. H. Pendlebury helped with the analysis of the n.m.r. spectra using the LACOON program. We also thank the S.R.C. for a maintenance grant (to I. R. A.).

[3/2042 Received, 4th October, 1973]