

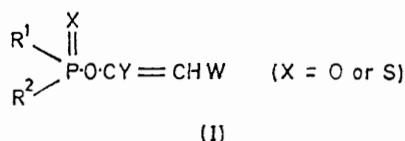
## Determination of Stereochemistry of Vinyl Phosphates from Proton Nuclear Magnetic Resonance Chemical Shifts

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Studies of a wide range of structures  $R^1R^2P(X)\cdot O\cdot CY=CHW$  ( $Y = H, Me, \text{ or } Ph$ ) indicate that in any pair of isomers the proton *cis* to the phosphoryl group resonates to low field of the corresponding *trans*-proton. Reinterpretation of published data suggests that boron trifluoride-ether complex causes a preferential deshielding of the proton *trans* to the phosphoryl group in such compounds. In the absence of knowledge of the signs of the coupling constants,  $J_{PH}$  values cannot be used to determine stereochemistry.

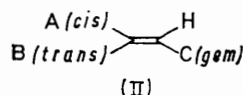
WE are currently investigating the factors which control the stereochemical course of reactions in which the vinyl phosphates (I), particularly where  $Y = Ph$ , are formed



either by elimination of hydrogen chloride from chloroalkyl phosphates<sup>1</sup> or in the abnormal Michaelis-Becker reaction.<sup>2</sup> It is therefore necessary to have a reliable technique for defining the stereochemistry of such compounds. When  $Y = H$  the usual n.m.r. method which relies upon the fact that  $|J_{HH \text{ trans}}| > |J_{HH \text{ cis}}|$  is satisfactory, but despite several attempts<sup>3-8</sup> there is still no general n.m.r. method for dealing with the situation where  $Y \neq H$ .

Borowitz *et al.*,<sup>5</sup> who have considered the most comprehensive range of compounds within this class, observed that with a pair of isomers (all  $X = O$ ) complexation with boron trifluoride-ether generally led to a greater deshielding of the proton which they assigned as *cis* to the phosphoryl group. However, they found several exceptions, *e.g.* when  $Y = H$  and  $W = Cl$ , and when  $Y = Me$  and  $W = H$ . They also concluded that for five pairs of isomers to which they assigned structures,  $|J_{PH \text{ trans}}| > |J_{PH \text{ cis}}|$ , but this was not true for  $Y = Me$  and  $W = CO_2Me$ . The additive substituent chemical shift (S.C.S.) approach<sup>9-11</sup> was used to provide corroborative evidence for the assignments of stereochemistry. In this treatment the chemical shift of a vinylic proton (from  $Me_4Si$  internal reference; positive shift to high field) is calculated from the empirical relationship (i). In this

$$\delta(\text{p.p.m.}) = -5.27 + \sigma_{A \text{ cis}} + \sigma_{B \text{ trans}} + \sigma_{C \text{ gem}} \quad (i)$$



equation,  $-5.27$  p.p.m. is the chemical shift of ethylene,

<sup>1</sup> F. W. Lichtenthaler, *Chem. Rev.*, 1961, **61**, 607.

<sup>2</sup> A. Meisters and J. M. Swann, *Austral. J. Chem.*, 1965, **18**, 168.

<sup>3</sup> A. R. Stiles, C. A. Reilly, G. R. Pollard, C. H. Tieman, L. F. Ward, jun., D. D. Phillips, S. B. Soloway, and R. R. Whetstone, *J. Org. Chem.*, 1961, **26**, 3960.

<sup>4</sup> B. Miller, H. Margulies, T. Drabb, jun., and R. Wayne, *Tetrahedron Letters*, 1970, 3801.

and  $\sigma_A$ ,  $\sigma_B$ , and  $\sigma_C$  are the S.C.S. of the substituent groups (with respect to H) in their appropriate location. Tobey<sup>9</sup> emphasises that the method holds well for small substituent groups of symmetry greater than or equal to  $C_{3v}$  (especially for single atoms) but must be expected to fall down for large substituents of lower symmetry because of long-range interactions which may depend upon conformational properties of the substituents.

With vinyl phosphates in general [II; A or B =  $(RO)_2P(O)\cdot O$ ] and 1-phenylvinyl phosphates in particular [II; A or B =  $(RO)_2P(O)\cdot O$ , B or A = Ph] the additivity relationship might be expected to break down, a fact which Borowitz *et al.* apparently overlooked.<sup>5</sup> We therefore decided to re-examine the situation, in particular for 1-phenyl-substituted compounds, making use of the model compound approach advocated by Tobey<sup>9</sup> as a more reliable method of structural assignment in such circumstances.

Diethyl 1-phenylvinyl phosphate provides a particularly convenient model compound for calculating the effect of a 1-phenyl substituent *gem* to a phosphoryl group, since fortuitously both vinylic protons have the same chemical shift<sup>5</sup> ( $-5.21$  p.p.m. from  $Me_4Si$ ) so there is no problem of assignment; by using the available data for diethyl vinyl phosphate<sup>12</sup> the values  $\sigma'_{Ph \text{ cis}} = -0.7$  p.p.m. and  $\sigma'_{Ph \text{ trans}} = -0.41$  p.p.m. can be deduced.

In the case of 2-substituted vinyl phosphates (I;  $X = O$ ,  $Y = H$ ) the spectra for both isomers can be readily assigned by making use of the fact that  $|J_{HH \text{ trans}}| > |J_{HH \text{ cis}}|$ . By using the foregoing values for  $\sigma'_{Ph \text{ cis}}$  and  $\sigma'_{Ph \text{ trans}}$  the expected chemical shift of the vinylic proton in both the *Z*- and *E*-isomers of the related compounds in which the proton, Y, is replaced by phenyl can be calculated. A series of diethyl 2-substituted vinyl phosphates (I;  $R^1 = R^2 = EtO$ ,  $X = O$ ,  $Y = H$ ,  $W = Ph, Me, Br, \text{ or } Cl$ ) was made by the Perkow reaction (ii),

<sup>5</sup> I. J. Borowitz, S. Firstenberg, E. W. R. Casper, and R. K. Crouch, *J. Org. Chem.*, 1971, **36**, 3282.

<sup>6</sup> M. Cohn, J. E. Pearson, E. L. O'Connell, and I. A. Rose, *J. Amer. Chem. Soc.*, 1970, **92**, 4095.

<sup>7</sup> J. A. Stubbe and G. L. Kenyon, *Biochemistry*, 1971, **10**, 2669.

<sup>8</sup> E. M. Gaydou, *Tetrahedron Letters*, 1972, 4469, 4473.

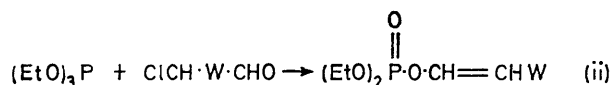
<sup>9</sup> S. W. Tobey, *J. Org. Chem.*, 1969, **34**, 1281.

<sup>10</sup> C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, 1966, **49**, 164.

<sup>11</sup> U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, 1969, **25**, 691, 2023.

<sup>12</sup> R. C. de Selms and Tan-Wan Lin, *J. Org. Chem.*, 1967, **32**, 2033.

the substituent W being selected so that assignments made for the 1-phenyl analogues could be directly compared with those made by Borowitz *et al.*<sup>5</sup> Except for



cases when W = Ph, a mixture of both isomers was obtained from which all the required n.m.r. parameters were measured directly. When W = Ph, only the *E*-isomer

$J_{\text{PH}}(\text{cis})$ , but when Y = Ph the opposite is the case. In the absence of knowledge of the signs of the coupling constants,  $J_{\text{PH}}$  values cannot be used reliably to determine stereochemistry. However, for both groups of vinyl phosphates [*i.e.* (I; Y = H or Ph)] the signal for the vinylic proton *cis* to the phosphoryl group always occurs to low field of that of the corresponding *trans* proton in each of the eight pairs of isomers. This appears to be true irrespective of the nature of the substituents in the phosphoryl group, as evidenced by

TABLE 1  
N.m.r. parameters of diethyl vinyl phosphates

A	B	$\delta$ (in p.p.m. rel. to $\text{Me}_4\text{Si}$ ) <sup>a</sup>			$J/\text{Hz}$					
		$\delta\text{H}$	$\delta\text{A}$	$\delta\text{B}$	HP	AP	BP	HA	HB	AB
H	Br	6.79	6.00		7.50	1.40		11.40		
Br	H	7.02		5.52	5.50		2.20		4.10	
H	Cl	6.76	6.08		7.45	1.5		11.05		
Cl	H	6.80		5.52	5.6		1.9		4.1	
H	Me	6.33	5.28		5.80	1.30	1.50	11.75	1.70	6.90
Me	H	<i>b</i>		4.75			2.20		6.00	6.90
H	Ph	7.00	6.25		6.40	1.20		12.40		
Ph	H	6.52		5.50	5.30		2.80		6.55	
H <sup>c</sup>	H	6.55	4.80	4.51	6.8	1.2	2.7	13.6	6.0	1.7

<sup>a</sup> Positive shifts to low field. <sup>b</sup> Buried under H resonance of *E*-isomer. <sup>c</sup> Ref. 11.

was formed, but this was readily photoisomerised to the *Z*-isomer. The observed chemical shifts and coupling constants are given in Table 1. The calculated chemical shifts for the vinylic protons in both isomers of the 1-phenylvinyl phosphates (I; R<sup>1</sup> = R<sup>2</sup> = EtO, X = O, Y = Ph, W = Ph, Me, Br, or Cl) are given in Table 2 together with the experimental values determined by Borowitz *et al.*<sup>5</sup>

This procedure leads to a clear differentiation between the *E*- and *Z*-isomers of each vinyl phosphate and to assignments which are opposite to those proposed by Borowitz *et al.*<sup>5\*</sup> These reassignments of structure for 1-phenylvinyl phosphates (I; Y = Ph) resolve the anomalies apparent in the chemical shift changes induced by boron trifluoride-ether complex observed by Borowitz *et al.*<sup>5</sup> which were attributed to the vicinal shielding effect of various substituents geminal to the phosphoryl group (*i.e.* Y = H, Me, or Ph). It now appears that the proton *cis* to phosphoryl experiences a *smaller* deshielding effect than the *trans*-proton in the presence of boron trifluoride-ether in *all* compounds studied by Borowitz *et al.*<sup>5</sup>

Tables 1 and 2 show that in the series of compounds (I) where Y = H,  $J_{\text{PH}}(\text{trans})$  is numerically greater than

\* *Added in proof:* Borowitz *et al.* (I. J. Borowitz, K. C. Yee, and R. K. Crouch, *J. Org. Chem.*, 1973, **38**, 1713) have recently concluded on the basis of lanthanide shift reagent  $[\text{Eu}(\text{dpm})_3]$  and nuclear Overhauser effects that their original assignments of stereochemistry to diallyl 1-phenylvinyl phosphates should be reversed.

the <sup>1</sup>H n.m.r. data given in Table 3 for a series of 2-chlorovinyl phosphates (I; Y = H, W = Cl) where the geometry can be unambiguously inferred from the magnitude of the vicinal  $J_{\text{HH}}$ . Again the inconsistency of the  $J_{\text{PH}}$  values is obvious.

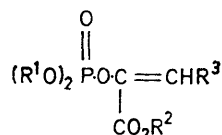
TABLE 2  
Calculated and observed n.m.r. parameters for the diethyl 1-phenylvinyl phosphates

A	B	$\delta\text{A}$ (p.p.m.) (calc.) <sup>a</sup>	$\delta\text{B}$ (p.p.m.) (calc.) <sup>a</sup>	$\delta$ (p.p.m.) (obs.) <sup>a,b</sup>	$J_{\text{PH}}$ (obs)/Hz
H	Br	6.41		6.49	2.8
Br	H		6.22	6.14	1.6
H	Cl	6.49		6.45	2.8
Cl	H		6.22	6.13	2.3
H	Me	5.69		5.77	2.8
Me	H		5.45	5.60	2.5
H	Ph	6.66		6.69	2.5
Ph	H		6.20	6.33	1.0

<sup>a</sup> Relative to  $\text{Me}_4\text{Si}$ ; positive shifts to low field. <sup>b</sup> These values reported by Borowitz *et al.*<sup>5</sup> were all independently confirmed.

With these revised assignments the proton *cis* to the phosphoryl group resonates to low field of the corresponding *trans*-proton in all vinyl phosphates defined by the general structure (I) where R<sup>1</sup> and R<sup>2</sup> are alkoxy, alkylthio, alkylamino, dialkylamino, or chloro; X = O

or S; Y = H, Me, or Ph; and W = H, Cl, Br, Me, Ph, or CO<sub>2</sub>Me. However, in the case of phosphoenolpyruvate and butyrate esters (III) the opposite is the case,<sup>7</sup> if we



(III) R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H or Me

assume that the assignments made on the basis of  $J_{\text{CH}}$  values determined from <sup>13</sup>C n.m.r. measurements are

## EXPERIMENTAL

N.m.r. spectra were determined for 0.3–0.5M-solutions in carbon tetrachloride (Me<sub>4</sub>Si internal reference) at a probe temperature of 27 °C (Varian HA 100 spectrometer). Line positions were measured by using a frequency counter. Solvents were dried prior to use; reactions were conducted in an atmosphere of dry nitrogen. Vacuum distillations were carried out with a nitrogen bleed. Isomer ratios were determined by integration of the vinyl region of the <sup>1</sup>H n.m.r. spectra.

**2-Bromovinyl Diethyl Phosphate.**—Dibromoacetaldehyde (5.0 g, 0.025 mol) was added dropwise to a stirred solution of triethyl phosphite (4.15 g, 0.025 mol) in ether (10 ml) at

TABLE 3

N.m.r. parameters of 2-chlorovinyl phosphates

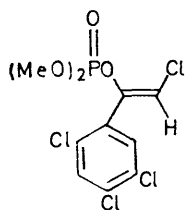
R <sup>1</sup>	R <sup>2</sup>	X	Structure 1					Structure 2				
			$\delta\text{H}_{\alpha}^a$ (p.p.m.)	$\delta\text{H}_{\beta}^a$ (p.p.m.)	$J_{\text{H}_{\alpha}\text{P}}$ /Hz	$J_{\text{H}_{\beta}\text{P}}$ /Hz	$J_{\text{H}_{\alpha}\text{H}_{\beta}}$ /Hz	$\delta\text{H}_{\alpha}^a$ (p.p.m.)	$\delta\text{H}_{\beta}^a$ (p.p.m.)	$J_{\text{H}_{\alpha}\text{P}}$ /Hz	$J_{\text{H}_{\beta}\text{P}}$ /Hz	$J_{\text{H}_{\alpha}\text{H}_{\beta}}$ /Hz
EtO	EtO	O	6.76	6.08	7.45	1.5	11.05	6.8	5.52	5.6	1.9	4.1
MeO	MeO	O	6.78	6.16	7.2	1.5	11.15	6.84	5.61	5.4	1.8	4.1
MeO	MeO	S	6.81	6.05	7.8	2.1	11.1	6.83	5.54	7.6	1.0	4.2
EtO	Et <sub>2</sub> N	O	6.74	5.99	7.8	1.6	11.0	6.78	5.47	6.3	1.5	4.1
EtO	EtO	S	6.82	6.04	7.9	2.1	11.1	ca. 6.8	5.54		1.3	4.1
Cl	Cl	O	6.87	6.46	8.0	3.4	11.1	6.93	5.97	6.9	0.5	4.2
Pr <sup>n</sup> S	Pr <sup>n</sup> S	O	6.83	6.15	9.0	2.4	11.1	6.90	5.65	8.3	ca. 0	4.2
EtO	Bu <sup>n</sup> NH	O	6.75	6.02	7.9	1.5	11.0	ca. 6.79	5.45	ca. 6.5	1.4	4.0
EtO	Cl	O	6.81	6.29	7.9	2.4	11.1	6.81	5.79	6.3	1.4	4.1
EtO	Pr <sup>n</sup> S	O	6.78	6.11	8.1	2.0	11.2	6.84	5.59	7.2	1.2	4.1
Pr <sup>n</sup> S	Pr <sup>n</sup> S	O	6.83	6.13	9.0	2.4	11.2	6.89	5.63	8.5	ca. 0.5	4.1

<sup>a</sup> Relative to Me<sub>4</sub>Si; positive shifts to low field.

correct. Since the use of  $J_{\text{OCCH}}$  values has not yet been established as a reliable technique for deciding olefin geometry, the assignments are still open to question, and it remains to be seen whether the proton *cis* to phosphoryl resonates to low field of the *trans*-proton in an even wider range of vinyl phosphates than defined above.

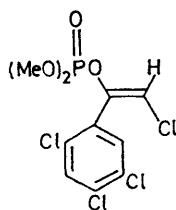
The insecticide Gardona® (IV) falls within the scope of vinyl phosphates defined by (I) and on the basis of the results presented here we conclude that the isomer in which the vinylic proton resonates at 6.0 p.p.m. to low field of Me<sub>4</sub>Si is the *Z*-isomer (IVa).

Professor F. Korte (Technisches Universität, München) has kindly informed us, prior to publication, of the result of an X-ray analysis of (IVa) which has confirmed this assignment.



(IVa)

$\delta$  6.0 p.p.m.  
( $J_{\text{PH}}$  0.7 Hz)



(IVb)

$\delta$  6.56 p.p.m.  
( $J_{\text{PH}}$  2.5 Hz)

0–5°. The solution was stirred for 24 h at room temperature. Ether was removed *in vacuo* and the residue was distilled. **2-Bromovinyl diethyl phosphate** was isolated (4.3 g, 66%) as a liquid, b.p. 90–95° at 0.3 mmHg (Found: C, 27.8; H, 4.5; Br, 29.1; P, 11.8. C<sub>6</sub>H<sub>12</sub>BrO<sub>4</sub>P requires C, 27.8; H, 4.7; Br, 30.85; P, 11.9%); isomer ratio (*E* : *Z*) ca. 9 : 1.

**Diethyl 2-methylvinyl phosphate** was similarly prepared (70% yield) from 2-chloropropionaldehyde and triethyl phosphite, as a liquid, b.p. 50–54° at 0.15 mmHg (Found: C, 43.5; H, 7.7; P, 15.6. C<sub>7</sub>H<sub>15</sub>O<sub>4</sub>P requires C, 43.3; H, 7.8; P, 15.95%); isomer ratio (*E* : *Z*) ca. 6 : 1.

**Diethyl 2-phenylvinyl phosphate (E-isomer)**, similarly prepared from phenylchloroacetaldehyde and triethylphosphite (55% yield) had b.p. 145–146° at 0.3 mmHg (Found: C, 56.3; H, 6.6; P, 12.4. C<sub>12</sub>H<sub>17</sub>O<sub>4</sub>P requires C, 56.25; H, 6.7; P, 12.1%).

**Diethyl 2-Phenylvinyl Phosphate (Z-Isomer).**—A solution of the *E*-isomer (200 mg) in benzene (150 ml) was irradiated (benzophenone as triplet sensitiser) through Pyrex with a medium-pressure mercury lamp for 2 h. The product, isolated by preparative t.l.c. (silica gel; eluted with ethyl acetate–benzene), was predominantly (*Z*)-diethyl 2-phenylvinyl phosphate; isomer ratio (*E* : *Z*) ca. 1 : 3.

2-Chlorovinyl diethyl phosphate<sup>13</sup> and 2-chlorovinyl dimethyl phosphate<sup>3</sup> were donated by Shell Development Company.

<sup>13</sup> U.S.P. 3,116,201/1963 (to Shell Oil Co. Ltd.).

*2-Chlorovinyl Phosphorodichloridate*.—A mixture of 2-chlorovinyl diethyl phosphate (53.6 g, 0.25 mol), thionyl chloride (119 g, 1 mol), and dimethylformamide (4.2 g, 0.0575 mol) was stirred and heated under reflux for 16 h. During this time the temperature of the mixture rose from 60 to ca. 90°. After cooling to 10° in an ice-bath, water (1.04 g, 0.0575 mol) was added. The mixture was stored overnight at 0°, and was then fractionally distilled. The product (50 g, 51%) had b.p. 50° at 2.5 mmHg and was identified by i.r. and <sup>1</sup>H n.m.r. data (Found: C, 12.1; H, 1.3; P, 15.6. C<sub>2</sub>H<sub>2</sub>Cl<sub>3</sub>O<sub>2</sub>P requires C, 12.3; H, 1.0; P, 15.9%), δ 5.97 (dd) and 6.46 (dd) (total 1H), and 6.87 (dd) and 6.93 (dd) (total 1H) p.p.m.; isomer ratio (*E* : *Z*) ca. 7 : 1.

*O-2-Chlorovinyl OO-Dimethyl Phosphorothioate*.—A mixture of 2-chlorovinyl phosphorodichloridate (32.75 g, 0.1675 mol) and phosphorus pentasulphide (12.75 g, 0.0575 mol) was stirred under nitrogen and heated to an internal temperature of 119°. After 1 h the mixture was cooled and diluted with dry ether. Solids were removed by filtration, solvent was evaporated from the filtrate *in vacuo*, and the residue was distilled. The distillate, b.p. 64–69° at 8 mmHg, shown by i.r. to be 2-chlorovinyl phosphorodichloridothioate (16.5 g, 47%) was used without further purification.

Dry nitrogen was bubbled through the stirred crude phosphorodichloridothioate, which was cooled at –5 to 0° in an ice-salt bath. Dry methanol (75 ml) was added dropwise during 1 h, and the mixture was stirred at 0–5° for a further 2 h, then at room temperature overnight. After removal of the excess of methanol *in vacuo*, the product was isolated from the residue by column chromatography (silica gel–benzene), followed by distillation. The pure 2-chlorovinyl dimethyl phosphorothioate (4.7 g, 30%) had b.p. 66–67.5° at 1.6 mmHg, *n*<sub>D</sub><sup>20.5</sup> 1.4879, and was shown by <sup>1</sup>H n.m.r. data to be a mixture of *E*- and *Z*-isomers in the ratio 4 : 1 (Found: C, 23.6; H, 3.9; Cl, 17.3; P, 15.3. C<sub>4</sub>H<sub>8</sub>ClO<sub>3</sub>PS requires C, 23.7; H, 4.0; Cl, 17.5; P, 15.3%), δ 3.79 (d) and 3.80 (d) (total 3H), and 5.54 (dd), 6.05 (dd), 6.81 (dd), and 6.83 (dd) (total 2H) p.p.m.

*O-2-Chlorovinyl OO-diethyl phosphorothioate*, similarly prepared, had b.p. 80–81° at 1.5 mmHg, *n*<sub>D</sub><sup>21</sup> 1.4759 (Found: C, 31.3; H, 5.1; Cl, 15.3; P, 13.6. C<sub>6</sub>H<sub>12</sub>ClO<sub>3</sub>PS requires C, 31.2; H, 5.2; Cl, 15.4; P, 13.4%), δ 1.38 (6H, dt), 4.14 (4H, m), and 5.54 (dd), 6.04 (dd), and 6.82 (dd) (total 2H), p.p.m.; isomer ratio (*E* : *Z*) ca. 19 : 1.

*2-Chlorovinyl Ethyl Phosphorochloridate*.—Dry nitrogen was bubbled through a stirred solution of 2-chlorovinyl phosphorodichloridate (19.55 g, 0.1 mol) in dry ether (60 ml), which was cooled at 0–5° in an ice-bath. A solution of dry ethanol (4.6 g, 0.1 mol) in dry ether (30 ml) was added dropwise during 1 h. The mixture was stirred at 0–5° for a further 2 h, then at room temperature overnight. Solvent was removed *in vacuo*, and the residue was distilled. 2-Chlorovinyl ethyl phosphorochloridate was isolated as a liquid (16.4 g, 80%), b.p. 92–94° at 1 mmHg (Found: C, 23.1; H, 3.4; P, 15.2. C<sub>4</sub>H<sub>7</sub>Cl<sub>2</sub>O<sub>3</sub>P requires C, 23.4; H, 3.4; P, 15.1%), δ 1.45 (3H, m), 4.34 (2H, m); and 5.79 (dd), 6.29 (dd), 6.81 (dd), and 6.87 (dd) (total 2H) p.p.m.; isomer ratio (*E* : *Z*) ca. 4 : 1.

*O-2-Chlorovinyl SS-Dipropyl Phosphorodithioate*.—2-Chlorovinyl phosphorodichloridate (9.8 g, 0.05 mol) was added at room temperature to a stirred solution of propane-1-thiol (7.6 g, 0.1 mol) in dry benzene (100 ml). Triethyl-

amine (10.1 g, 0.1 mol) was then added dropwise at 20–25°. The mixture was stirred at room temperature overnight, then filtered, and solvent was removed *in vacuo*. Column chromatography (silica gel–methylene chloride) of the residue led to isolation of the phosphorodithioate (2.7 g, 20%) (Found: C, 34.8; H, 5.8; P, 11.4. C<sub>8</sub>H<sub>16</sub>ClO<sub>2</sub>PS<sub>2</sub> requires C, 35.0; H, 5.9; P, 11.3%), δ 1.06 (6H, t), 1.78 (4H, m), 2.93 (4H, m), and 5.65 (d), 6.15 (dd), 6.83 (dd), and 6.90 (dd) (total 2H) p.p.m.; isomer ratio (*E* : *Z*) ca. 6 : 1.

*Reaction of 2-Chlorovinyl Ethyl Phosphorochloridate with Propane-2-thiol and Triethylamine*.—The phosphorochloridate (15 g, 0.075 mol) was added at room temperature to a stirred solution of propane-2-thiol (5.7 g, 0.075 mol) in dry benzene (60 ml). Triethylamine (7.5 g, 0.075 mol) in dry benzene (10 ml) was then added dropwise at 20° during 0.5 h. The mixture was stirred at room temperature overnight, then filtered, and solvent was removed *in vacuo*. Column chromatography (silica gel–methylene chloride) of the residue yielded two materials. The faster eluted material (5.8 g, 28%) was *O-2-chlorovinyl SS-di-isopropyl phosphorodithioate* (Found: C, 34.6; H, 5.6; P, 11.0. C<sub>8</sub>H<sub>16</sub>ClO<sub>2</sub>PS<sub>2</sub> requires C, 35.0; H, 5.9; P, 11.3%), δ 1.48 (12H, m), 3.55 (2H, m), and 5.63 (dd), 6.13 (dd), 6.83 (dd), and 6.89 (dd) (total 2H) p.p.m.; isomer ratio (*E* : *Z*) ca. 10 : 1.

The slower eluted material, purified by column chromatography (silica gel–ether), was *O-2-chlorovinyl O-ethyl S-isopropyl phosphorothioate* (1.75 g, 10%) (Found: C, 34.7; H, 5.9; P, 12.4. C<sub>7</sub>H<sub>14</sub>ClO<sub>3</sub>PS requires C, 34.4; H, 5.8; P, 12.7%), δ 1.39 (9H, m), 3.50 (1H, m), 4.20 (2H, m), and 5.59 (dd), 6.11 (dd), 6.78 (dd), and 6.84 (dd) (total 2H) p.p.m.; isomer ratio (*E* : *Z*) ca. 10 : 1.

*2-Chlorovinyl Ethyl N-n-Butylphosphoramidate*.—A solution of *n*-butylamine (7.3 g, 0.1 mol) in dry ether (50 ml) was added dropwise during 0.5 h to a stirred solution of 2-chlorovinyl ethyl phosphorochloridate (10.25 g, 0.05 mol) in dry ether (100 ml) at –10 to 0°. The mixture was stirred at 0–5° for a further 2 h, then filtered. Solvent was removed *in vacuo*. Column chromatography of the product yielded the phosphoramidate (7.2 g, 60%) (Found: C, 39.9; H, 7.2; N, 5.6. C<sub>8</sub>H<sub>17</sub>ClNO<sub>3</sub>P requires C, 39.8; H, 7.1; N, 5.8%), δ 0.92 (3H, m), 1.34 (7H, m), 2.80 (2H, m), 4.06 (2H, m), 4.99 (1H, m), 5.45 (dd) and 6.02 (dd) (total 1H), and 6.75 (dd) and ca. 6.79 (dd) (total 1H) p.p.m.; isomer ratio (*E* : *Z*) ca. 7 : 1.

*2-Chlorovinyl Ethyl NN-Diethylphosphoramidate*.—A solution of diethyl *NN*-diethylphosphoramidite (48.3 g, 0.25 mol) in dry toluene (25 ml) was added dropwise during 1 h to a stirred solution of freshly distilled dichloroacetaldehyde (28.5 g, 0.25 mol) in dry toluene (75 ml) at 20–25°. The mixture was stirred at 60° for 1.5 h, then cooled and filtered. Solvent was removed *in vacuo* and the residue was taken up in ether. The solution was washed with cold water (× 4), dried (MgSO<sub>4</sub>), and evaporated and the residue was fractionally distilled to give the diethylphosphoramidate (65%) as a liquid, b.p. 69–71° at 0.04 mmHg (Found: C, 39.6; H, 7.1; N, 5.7; P, 12.8. C<sub>8</sub>H<sub>17</sub>ClNO<sub>3</sub>P requires C, 39.8; H, 7.1; N, 5.8; P, 12.8%), δ 1.07 (6H, dt), 1.31 (3H, dt), 3.05 (4H, m), 4.02 (2H, m), 5.47 (dd) and 5.99 (dd) (total 1H), and 6.74 (dd) and 6.78 (dd) (total 1H) p.p.m.; isomer ratio (*E* : *Z*) ca. 5 : 1.

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