

371. *The Mechanism of Hydrolysis of Phosphonochloridates and Related Compounds. Part I. The Effect of Substituents.*

By R. F. HUDSON and L. KEAY.

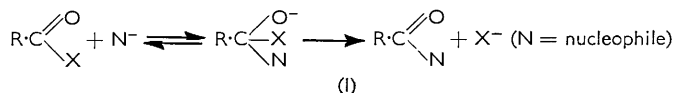
The rates of hydrolysis of diethylphosphinyl chloride, Et_2POCl , methyl ethylphosphonochloridate, $\text{MeO}\cdot\text{PEtOCl}$, and dimethyl phosphorochloridate, $(\text{MeO})_2\text{POCl}$, are discussed in terms of the electronic structures, with the assumption that steric hindrance is similar for these compounds. Ethyl phenylphosphonochloridate, $\text{EtO}\cdot\text{PPhOCl}$, is slightly more reactive than ethyl ethylphosphonochloridate, $\text{EtO}\cdot\text{PEtOCl}$, whereas acetyl chloride is much more reactive than benzoyl chloride. This difference and the relatively small deactivation produced by alkoxy-groups are attributed to the smaller conjugation energies of phosphoryl compounds than of carbonyl compounds.

INVESTIGATION of the preparation and reactions of organophosphorus compounds has been greatly stimulated in recent years by the biological importance of phosphorylation.¹ Much qualitative information on the reactivity of phosphoric acid derivatives has accumulated,² and a few attempts have been made to relate these data to the chemical structures involved. Several kinetic studies have been reported recently, and the formal similarity between phosphorylation * (and phosphonylation) and acylation has been discussed in terms of the basic concepts of physical-organic theory.³

Second-row elements have available d - as well as s - and p -orbitals with the same principal quantum number (3), but first-row elements have $2s$ - and $2p$ -orbitals only. Differences in the effect of structural changes on the reactivity of carbon and phosphorus compounds are therefore to be expected, but principally as follows: (1) The greater polarisability of the phosphorus atom than of the carbon atom may lead to larger inductive effects in phosphorus compounds. (2) The different stereochemistry leads to greater steric effects for phosphorus compounds than for their carbon analogues,⁴ though this effect is reduced by the greater radius of phosphorus. (3) The energies of π -bonds formed by second-row elements are usually less than those for first-row elements;⁵ the use of $3d$ -orbitals for π -bonding in phosphorus compounds leads to multiple bonding of a different kind from the π -bonds of carbonyl compounds.⁶

It follows that conjugation will play a much smaller part in determining the reactivity of a phosphorus compound, and differentiation between σ (inductive) and π (conjugative) bond effects will be particularly difficult.

Moreover, the transition-state structures in acylation and phosphorylation will be completely different. There is now strong evidence that the transition state of a bimole-



cular acylation is similar to the sp^3 hybridised intermediate (I), which has been detected⁷ by ^{18}O exchange. The effect of substituents on the reactivity therefore follows the

* There appears to be no collective term for phosphorylation, phosphonylation, and phosphinylation. At the suggestion of the Editor, we use the term "phosphylation" to cover these reactions.

¹ Sartori, *Chem. Rev.*, 1951, **48**; Nachmansohn and Wilson, *Adv. Enzymology*, 1951, **12**, 259.

² "Phosphoric Acid Esters and Related Compounds," Chem. Soc. Special Publ. No. 8, 1958; Topley, *Chem. and Ind.*, 1950, 859.

³ (a) Dostrovsky and Halmann, *J.*, 1953, 503; (b) Halmann, *J.*, 1959, 305; (c) Heath, *J.*, 1956, 3796, 3804; (d) Green, Sainsbury, Saville, and Stansfield, *J.*, 1958, 1583.

⁴ Hudson and Keay, *J.*, 1956, 2463.

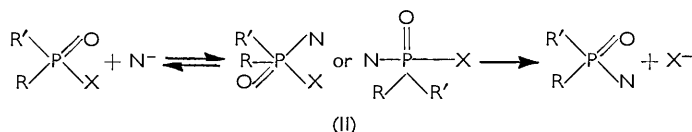
⁵ Hunter, Phillips, and Sutton, *J.*, 1945, 146.

⁶ Koch and Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7; Jaffee, *J. Phys. Chem.*, 1954, **58**, 185.

⁷ Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626; Bunton, Lewis, and Llewellyn, *Chem. and Ind.*, 1954, 1154.

corresponding changes in the bond-forming energies.⁸ In phosphorylation, on the other hand, bonds are converted into weaker sp^3d bonds⁹ in the transition state (II), so that bond-breaking becomes more important. No evidence has been found for opening of the P=O bond during the hydrolysis of phosphorochloridates¹⁰ or phosphorofluoridates.¹¹ These reactions may therefore be satisfactorily represented as direct displacements, as in the S_N2 mechanism of substitution at the saturated carbon atom.

In the present work on the hydrolysis of phosphonochloridates, we have attempted to differentiate between steric and electronic effects by comparing the reactivities of compounds of similar configuration (so-called "homomorphs"¹²), in particular, the



compounds Et_2POCl , $\text{MeO}\cdot\text{PEtOCl}$, and $(\text{MeO})_2\text{POCl}$. The methoxy-group and the ethyl group are assumed to exert similar steric hindrance towards the attacking water molecule (this is supported by the approximately constant PZ values given in Table 2). When such comparisons cannot be made, we have taken the change in the non-exponential factor (PZ) of the Arrhenius equation as a measure of the change in steric hindrance.

The Effect of Alkoxy-groups.—An alkoxy-group may produce two electronic effects: (a) The inductive displacement of the σ -electrons which increases the positive charge on the phosphorus atom as shown by the decrease in pK_a of the corresponding acid.¹³ This assists the approach of the nucleophilic reagent, but also increases the bond energies, as shown, for example, by increases in the corresponding infrared frequencies.¹⁴ (b) p_π - d_π -Conjugation, which stabilises the ground state.

In the hydrolyses so far reported, replacement of alkyl groups by alkoxy-groups reduces the reactivity significantly (Table 1). These decreases in reactivity have been attributed

TABLE 1.

Compound	Conditions	Temp.	k
Me_2POCl	Solvolysis in EtOH	-8.5°	$60 \pm 10 \cdot 10^{-4} \text{ sec.}^{-1}$
$(\text{MeO})_2\text{POCl}$	" "	-8.5	$0.35 \cdot 10^{-4} \text{ sec.}^{-1}$
Et_2POF	OH^- in water	25	$50,000 \text{ l. min.}^{-1} \text{ hr.}^{-1}$
$\text{EtO}\cdot\text{PEtOF}$	" "	25	1,200 " "
$(\text{EtO})_2\text{POF}$	" "	25	110 " "
$\text{EtO}\cdot\text{PPr}^i(\text{O})\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{-}p$	OH^- in water, pH 8.5	37.5	$4.17 \cdot 10^{-4} \text{ min.}^{-1} \dagger$
$(\text{EtO})_2\text{P}(\text{O})\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{-}p$	" "	37.5	6.14 " " \dagger
$\text{Et}_2\text{PO}\cdot\text{OMe}$	OH^- in water	80	5.9*
$(\text{MeO})_2\text{PEtO}$	" "	80	4.2*
$(\text{MeO})_3\text{PO}$	" "	80	1.0*
$(\text{Pr}^i\text{O})_2\text{POF}$	Solvolysis in water	25	$1.2 \cdot 10^{-4} \text{ sec.}^{-1}$
$(\text{Pr}^i\text{NH})_2\text{POF}$	" "	25	$2.3 \cdot 10^{-6} \text{ sec.}^{-1}$

* Relative reactivity per OMe group. \dagger Pseudounimolecular constants.

by Dostrovsky and Halmann^{3a} and by Heath^{3c} to an electromeric effect in the ground state, similar to that observed for carbonyl compounds.⁸ No allowance was made, however, for differences in steric hindrance, so that these rate comparisons have little quantitative significance. In order to keep steric differences at a minimum we have compared the reactivities of the compounds Et_2POCl , $\text{MeO}\cdot\text{PEtOCl}$, and $(\text{MeO})_2\text{POCl}$ in aqueous acetone (Table 2).

⁸ Baker, *Trans. Faraday Soc.*, 1941, **37**, 632; Hughes, *ibid.*, p. 603.

⁹ Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, **332**.

¹⁰ Dostrovsky and Halmann, *J.*, 1956, **1004**.

¹¹ Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

¹² Brown, *Science*, 1946, **103**, 385.

¹³ Jaffee, Freedman, and Doak, *J. Amer. Chem. Soc.*, 1953, **75**, 2209.

¹⁴ Bell, Heisler, Tannenbaum, and Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185.

TABLE 2. *The effect of methoxy-groups on the rate of hydrolysis in 5% aqueous acetone (v/v).*

	Et ₂ POCl	MeO·PEtOCl	(MeO) ₂ POCl
10 ³ k ₁ (sec. ⁻¹) at 0°	1500 *	98	1.75
E (kcal./mole ⁻¹)	7.3	8.4	10.6
log ₁₀ PZ	5.9	5.7	5.7

* Extrapolated.

The importance of multiple bonding in phosphorus compounds is in some doubt,¹⁵ so that it is necessary first to see if the observed rate changes can be explained consistently in terms of inductive effects only. For example, the rate decreases produced by the introduction of alkoxy-groups at the phosphorus atom (Table 2) could be explained by assuming that the P-Cl bond energy is increased more than the energy of the H₂O-P bond in the transition state. This explanation is unlikely for the following reasons: (1) The few results available at present show that electron-withdrawing substituents increase the rate of hydrolysis.¹⁶ (2) Alkyl-amino-groups normally decrease reactivity more than alkoxy-groups do (Table 1), although nitrogen is less electronegative than oxygen. The observed order is in agreement with the formation of stronger multiple bonds with nitrogen. There is some evidence that bond-breaking becomes increasingly important in the hydrolysis of phosphorochloridamides,¹⁷ owing to this conjugation. (3) If the rate changes are produced by induction only, successive substitution would be expected to produce decreasing effects. The reverse effect is observed in the solvolysis of the chlorides (Table 2), which is explained by postulating opposing inductive and conjugative effects (see below).

For these reasons we assume that the decreases in rate shown in Table 2 are due to π -bonding between the phosphorus and oxygen atoms, which is considerably weaker than in carbonyl compounds. This difference is reflected in the greater changes in reactivity observed in the hydrolysis of acid chlorides. Thus acetyl chloride¹⁸ is hydrolysed *ca.* 10⁴ times more rapidly than ethyl chloroformate,¹⁹ with a decrease of 9 kcal. mole⁻¹ in the activation energy.²⁰ This change in activation energy is of the same order of magnitude as the conjugation energy between an oxygen atom and a carbonyl group in an ester, estimated²¹ at 10–15 kcal. mole⁻¹.

An approximate value for the π -bond energy of the P=O group may be estimated from recent thermochemical results. Neale and Williams²² have obtained a value of 102–103 kcal. mole⁻¹ for the P-O single-bond energy in the quinquevalent state of phosphorus, and values ranging from 121 to 140 kcal. mole⁻¹ for the P=O bond energy. These lead to values ranging from 18 to 38 kcal. mole⁻¹ for the additional stabilisation energy of the P=O bond. These increases in energy may be produced by increases in bond polarity²³ and by rehybridisation,²⁴ in addition to π -bonding, so that it is preferable to take the lowest value for the π -bonding energy. This value agrees with an assignment²⁵ for the P=O bond energy in P₄O₁₀, and is approximately one-quarter of the corresponding value for the C=O bond²⁶ (70–80 kcal. mole⁻¹).

If similar bonding is assumed to occur in the P-O bonds (by alternative 3*d*-orbitals), this would produce an activation energy increase of *ca.* 2.25 kcal. mole⁻¹ (one-quarter of

¹⁵ Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140; Wells, *J.*, 1949, 55.¹⁶ (a) Larsson, *Acta Chem. Scand.*, 1957, **11**, 1138; (b) Fukuto and Metcalf, *J. Amer. Chem. Soc.*, 1959, **81**, 372.¹⁷ Hall, *J. Org. Chem.*, 1956, **21**, 248.¹⁸ Zimmerman and Yuan, *J. Amer. Chem. Soc.*, 1955, **77**, 332.¹⁹ Bohme and Schurhoff, *Chem. Ber.*, 1951, **84**, 28.²⁰ Saville, Ph.D. Thesis, London, 1954.²¹ Dewar, "Electronic Theory of Organic Reactions," Oxford, 1949, p. 117.²² Neale and Williams, *J.*, 1955, 2485.²³ Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1940, p. 47; Cottrell and Sutton, *Quart. Rev.*, 1948, **2**, 263.²⁴ Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166; Brown, *Trans. Faraday Soc.*, 1959, **55**, 694.²⁵ Koerner and Daniels, *J. Chem. Phys.*, 1952, **20**, 113.²⁶ Syrkin and Dyatkina, "Structure of Molecules," Butterworths, London, 1950, p. 240.

the difference in the activation energies for the hydrolysis of ethyl chloroformate and acetyl chloride). This is regarded as a maximum value, because the P=O bond should involve the $3d$ -orbital most favourably orientated for π -bonding.⁶ The increases in the experimental activation energy (Table 2) are observed to be somewhat less than this estimated value, in agreement with this explanation.

An interesting feature of the rate data of Table 2 is the increased effect of progressive substitution, which we attribute to opposing electronic changes. We shall assume that the rate is increased by an increase in the formal charge, δ , on the phosphorus atom (inductive effect). Detailed calculations^{27,9} have shown that the overlap integral of a $d_{\pi}-p_{\pi}$ bond formed by phosphorus is very sensitive to the charge, δ , since the $3d$ -orbital energy of the free atom is too high for effective hybridisation with $2s$ - and $2p$ -orbitals. It follows that the conjugation energy of a P-O bond (which leads to a decrease in reactivity) increases considerably with increases in δ . The increase in activation energy on introduction of an alkoxy-group, producing a charge increase δ_1 , may be represented in a general way as follows:

$$\Delta E_1 = f_c(\Delta + \delta_1) - f_i(\delta_1)$$

where Δ is the charge on the phosphorus atom before introduction of the alkoxy-group.

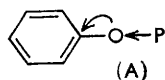
On the introduction of a second alkoxy-group which produces a charge increase δ_2 , the increase in activation energy is given by:

$$\Delta E_2 = 2f_c(\Delta + \delta_1 + \delta_2) - f_c(\Delta + \delta_1) - f_i(\delta_2)$$

Since alkoxy-groups normally produce deactivation it follows that $f_c(\Delta + \delta_1) > f_i(\delta_1)$. If the charge on the phosphorus atom is such that the overlap increases rapidly with δ , then ΔE_2 may be greater than ΔE_1 , as observed for the solvolysis of the chlorides (Table 2). The rates of the alkaline hydrolyses of the esters²⁸ given in Table 1 may be explained in a similar way, the smaller differences arising from the increased electrostatic attraction between the reactants.

In the hydrolysis of the corresponding fluorides, however, the second alkoxy-group causes less deactivation than the first (Table 1). Here the phosphorus atom carries a greater charge owing to the powerful inductive effect of the fluorine atom, and further increases may eventually lead to decreases in overlap, because of the contraction of the $3d$ -orbital beyond the optimum value for $d_{\pi}-p_{\pi}$ bonding (see Fig. 5 of ref. 9). This qualitative interpretation, although tentative, illustrates the difficulty of differentiating between inductive and conjugative effects in these reactions, and emphasises the difference between conjugation effects in phosphoryl and carbonyl compounds.

The Effect of Phenyl Groups.—Replacement of an ethoxy- by a phenoxy-group increases the reactivity slightly (Table 4), as in the solvolysis of phosphorochloridates.^{3a} This increase, and the small decrease in activation energy, may be due to the withdrawal of electrons from the phosphorus atom by the electronic change (A). This explanation of the rate increase is supported by the increase in the rate of alkaline hydrolysis of ethyl methylphosphonofluoridate^{16a} on introduction of a β -bromine atom, and by the effect of introduction of a γ -chlorine atom on the rate of hydrolysis of ethyl *p*-nitrophenyl propylphosphonate.^{16b}



Introduction of a phenyl group on the phosphorus atom may produce a small rate increase and a significant decrease in the activation energy (Table 3). This contrasts with the large rate decreases for hydrolysis of the corresponding organic acid chlorides and esters, normally attributed to conjugation between the carbonyl group and the aromatic group.²¹

²⁷ Jaffee, *J. Chem. Phys.*, 1953, **21**, 258.

²⁸ Harper and Hudson, *J.*, 1958, 1356.

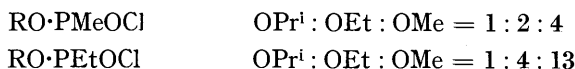
TABLE 3.

	Relative reactivity *	Activation energy	
		R = Ph	R = Me
† EtO·PROCl	1 : 1.4	7.7	8.5
† R·COCl	1 : 100	11.7	7.6
‡ R·PO(OEt) ₂	1.8 : 1	12.9	14.0
‡ R·CO·OEt	1 : 15	14.1	11.5

* Ratio of the rate constants for the aromatic and the aliphatic compound. † In 5% aqueous acetone (v/v) at 0°. ‡ Alkaline hydrolysis.

Measurements of the ultraviolet²⁹ and infrared¹⁴ spectra of phosphonic acids and their derivatives show negligible conjugation between the phenyl group and the phosphorus atom. It appears that the inductive effect of the phenyl group predominates in phosphorus compounds, leading to small increases in reactivity (Table 3). Similar increases have been observed in the alkaline hydrolysis of the corresponding esters⁴ (Table 3). These observations support the conclusion reached in the previous section that conjugation exerts a much smaller influence on the reactivity of phosphorus compounds than on the reactivity of their organic analogues.

The Effect of Alkyl Groups.—Introduction of alkyl groups in both the ester group OR' and the alkyl group R of a phosphonochloridate, R'O·PROCl, reduces the reactivity (Table 4), as in the hydrolysis and alcoholysis of phosphorochloridates.^{3a} The rate reductions may be due to electron-release to the phosphorus atom, *viz.*, $R \longrightarrow CH_2 \longrightarrow P$ and $R \longrightarrow O^+=P^-$, in view of the small, but significant, increases in the activation energy. Part of the rate changes are almost certainly produced by steric hindrance, as indicated by the decreases in the *PZ* factor with substitution. This is also supported by the following observations, which show that the rate changes depend markedly on the size of the group directly bonded to the phosphorus atom:



Much greater reductions in rate have been observed on introduction of highly branched alkyl groups.⁴

Although it is impossible to separate the rate changes into steric and electronic effects (similar difficulties are experienced in interpreting reactions at the saturated carbon atom³⁰), both effects in the present instance show the reaction to be bimolecular, as assumed throughout the paper. This is supported by studies of the solvent effect and the effect of added reagents on the rate (Part 2, following paper).

TABLE 4.

R	Me	Me	Me	Me	Et	Et
R'	Me	Et	Pr ¹	Ph	Me	Et
10 ³ <i>k</i> (min. ⁻¹)	176	87.6	41.2	131	98.5	29.7
<i>E</i> (kcal. mole ⁻¹)	8.3	8.5	8.7	8.1	8.4	8.9
log ₁₀ <i>PZ</i>	5.9	5.8	5.4	5.6	5.7	5.6

EXPERIMENTAL

Preparation of Materials.—The phosphonochloridates were prepared in most cases from the alkylphosphonic dichloride and the alcohol in the presence of triethylamine³¹ in ether at 0–5°. After removal of the base hydrochloride by filtration, the product was isolated by fractional distillation under reduced pressure. The following compounds were prepared by this method. Ethyl methylphosphonochloridate⁴ (yield 55%), b. p. 40–41°/1 mm. (lit., b. p. 40°/1 mm.).

²⁹ Jaffee, *J. Chem. Phys.*, 1954, **22**, 1430.

³⁰ Evans, *Trans. Faraday Soc.*, 1946, **42**, 719.

³¹ McCombie, Saunders, and Stacey, *J.*, 1945, 380.

Methyl methylphosphonochloridate (55%), b. p. 38°/0.4 mm. (Found: C, 18.0; H, 4.7; Cl, 27.3%; equiv., 128.1. $C_2H_5O_2ClP$ requires C, 18.7; H, 4.7; Cl, 27.6%; equiv., 128.6).

Ethyl ethylphosphonochloridate (72%), b. p. 52°/2 mm. (lit.,³² b. p. 55°/2.4 mm.) (Found: C, 31.1; H, 6.3; P, 20.5%; equiv., 155.4. Calc. for $C_3H_8O_2ClP$: C, 30.7; H, 6.4; P, 19.9%; equiv., 156.6).

Methyl ethylphosphonochloridate (74%), b. p. 38—40°/0.2 mm. (Found: C, 25.2; H, 5.8; P, 21.3; Cl, 25.2%; equiv., 140.6. $C_3H_8O_2ClP$ requires C, 25.3; H, 5.6; P, 21.8; Cl, 24.9%; equiv., 142.6).

Phenyl methylphosphonochloridate (67%), b. p. 80°/0.5 mm. (Found: C, 44.1; H, 4.4; P, 15.8%; equiv., 192.0. $C_8H_9O_2ClP$ requires C, 44.2; H, 4.2; P, 16.3%; equiv., 190.6).

Ethyl phenylphosphonochloridate (88%), b. p. 103°/0.3 mm. (Found: C, 46.7; H, 4.6; Cl, 17.2%; equiv., 202.8. $C_8H_{10}O_2ClP$ requires C, 46.9; H, 4.9; Cl, 17.3%; equiv., 204.6).

The isopropyl phosphonochloridates were prepared by the reaction of the di-isopropyl ester at 0—10° with carbonyl chloride.³³ After being kept overnight at room temperature, the product was isolated by distillation under reduced pressure.

Isopropyl methylphosphonochloridate (88%), b. p. 47°/3 mm. (Found: C, 30.2; H, 6.3; P, 20.2; Cl, 23.0%; equiv., 157.5. Calc. for $C_4H_{10}O_2ClP$: C, 30.7; H, 6.4; P, 19.8; Cl, 22.7%; equiv., 156.5).

Isopropyl ethylphosphonochloridate (85%), b. p. 55°/2 mm. (Found: C, 35.9; H, 7.2; P, 18.5%; equiv., 170.6. Calc. for $C_5H_{12}O_2ClP$: C, 35.2; H, 7.0; P, 18.2%; equiv., 170.5).

Dimethyl phosphorochloridate, prepared by the chlorination of dimethyl phosphite³¹ (yield 76%), had b. p. 80°/25 mm. (lit., b. p. 75—80°/20—25 mm.).

Diethylphosphinic chloride was kindly provided by Dr. A. F. Childs.

Acetone was purified as described previously, and the water content, determined by titration with Karl Fischer reagent, varied between 0.05 and 0.10%.

Rate Measurements.—A large well-insulated Dewar vessel, containing water or aqueous acetone cooled with solid carbon dioxide, was used as thermostat. The temperature was maintained within $\pm 0.1^\circ$ for ~ 0.5 hr. Reaction was initiated by introducing a weighed quantity of the phosphonochloridate from a weight pipette into 50 ml. of a solution of 5% of water in acetone made up by volume, contained in a stoppered flask in the thermostat. The flask was shaken for a few seconds. Portions (5 ml.) were removed at suitable times and added to 40 ml. of anhydrous acetone at *ca.* -20° , to retard the reaction. The liberated hydrogen chloride was titrated with 0.05N-triethylamine in toluene with lacmoid as the indicator.

R	R'	Initial concn. (M)	Temp.	10^3k_1 (min. ⁻¹)	R	R'	Initial concn. (M)	Temp.	10^3k_1 (min. ⁻¹)		
Me	OMe	0.049	-35.0°	9.67	Et	OEt	0.039	0.0°	29.7		
		0.050	-21.0	37.0			0.067	12.0	60.0		
		0.051	0.0	176			0.044	26.0	124.7		
Me	OEt	0.054	-24.0	19.8	Et	OPr ⁱ	0.017	20.0	25.2		
		0.049	-10.5	47.7			Ph	OEt	0.052	-24.0	15.4
		0.051	0.0	87.6					0.052	-14.5	29.1
Me	OPr ⁱ	0.023	-16.0	16.8	OMe	OMe	0.053	0.0	59.4		
		0.023	-8.5	23.8			0.047	0.0	1.75		
		0.024	0.0	41.2			0.051	16.0	5.16		
		0.024	26.1	163			0.039	24.5	8.43		
Me	OPh	0.039	-30.0	20.7	Et	Et	0.052	25.0	9.21		
		0.053	0.0	131			0.026	-65.0	18.4		
Et	OMe	0.048	-32.5	13.5			0.025	-41.0	117		
		0.049	-10.0	53.2			0.047	-23.0	356		
		0.066	0.0	98.5							

The rates of solvolysis are tabulated. Duplicate experiments were carried out in each case. The reproducibility was 2—3%.

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QUEEN MARY COLLEGE, (UNIVERSITY OF LONDON),
MILE END ROAD, LONDON, E.1.

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³² Hoffmann, Simmons, and Glunz, *J. Amer. Chem. Soc.*, 1957, **79**, 3570; Razumov *et al.*, *Khim. i Primevenie Fosfororgen Soedinanii Akad. Nauk S.S.S.P. Trudy I-oi Konferents*, 1955, 194.

³³ Charlton, personal communication.