Nucleophilic Reactivity of Organophosphorus Compounds. Part 3.[1] Kinetics and Mechanism of the Reaction of Phosphorus Acids with Keten *OO*-Acetals in Aprotic Medium

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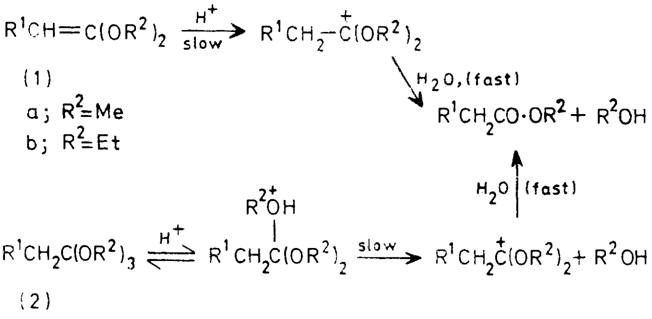
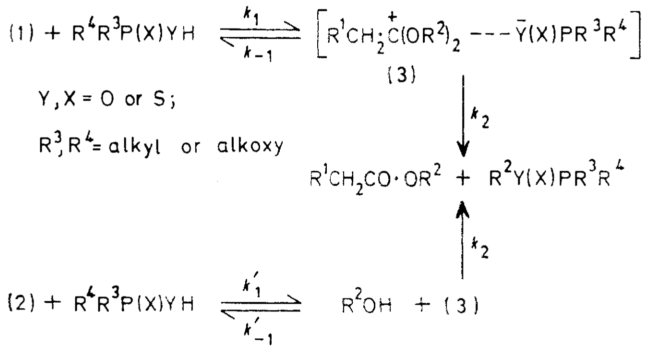
The kinetics of the reactions of *OO*-diethyl *S*-hydrogen phosphorodithioate and *O*-ethyl *S*-hydrogen methylphosphonodithioate with *p*-nitrophenylketen dialkyl acetals in di-n-butyl ether as solvent are reported and discussed in terms of a mechanism which involves a highly reversible protonation (probably to an ion-pair) followed by nucleophilic attack by the phosphorus anion on the intermediate carbonium ion of the ion-pair.

THE mechanistic details of the hydrolysis of keten acetals (1) [3,4] and orthoesters (2) [5,6] are now well established. The former is a general acid-catalysed reaction involving rate determining protonation of the keten acetal [4] and the latter involves rate-determining formation of a carbonium ion derived from dissociation of the protonated substrate [5,6] (Scheme 1).



SCHEME 1

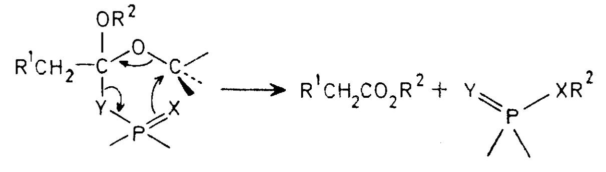
In an aprotic medium (*e.g.* benzene or CCl_4) keten acetals and orthoesters both alkylate phosphorus acids.[1] This is also a two step reaction and use of an optically active keten acetal (or orthoester) strongly suggests that both reactions proceed *via* ion-pairs † [(3), Scheme 2].[2]



SCHEME 2

The alternative mechanism involving intramolecular rearrangement of an addition intermediate (4) to products is a six-electron process and in order to achieve an allowed (Dewar) transition state [7] would appear to require front-side displacement on carbon, a process which does not occur even under the most favourable circumstances [8] and which would lead to retention at the chiral centre in R^2. This latter result is not observed to any extent, at least with the mono- and dithio-acids.[2]

The identity of the rate-determining step and the possible reversibility of the initial step were, therefore, the outstanding mechanistic problems. Both were resolved by a study of the reactions of (1) and (2) with excess (>20 mol) of deuteriated phosphorus acids in benzene or CCl_4 as solvent. In each case the resultant carboxylic ester was fully deuteriated in the α-position.[9] Furthermore, when *p*-nitrophenylketen dimethyl acetal (1a; $R^1 = p\text{-}NO_2C_6H_4$) (1 mol) was reacted with *S*-deuterio *OO*-diethyl phosphorodithioic acid (0.5 mol) in benzene, unchanged keten acetal was shown by n.m.r. spectroscopy to contain *ca.* 30% deuterium in place of the vinylic hydrogen. Under hydrolytic conditions (D_2O–D^+) each keten acetal molecule incorporated one atom of deuterium into the product carboxylic ester as required by the accepted mechanism of rate-determining proton addition. Likewise, the carboxylic esters obtained from the acid-catalysed hydrolysis of orthoesters in deuterium oxide contained no deuterium. The results in aprotic medium left no doubt, therefore, that formation of the ion-pair was highly reversible and hence in Scheme 2 for keten acetals, $k_{-1} \gg k_2$ and for orthoesters, $k_{-1}' \gg k_2$. The proposal of a common intermediate (3) for the keten acetals, $k_{-1} \gg k_2$ and for orthoesters $k_{-1}' \gg k_2$. The proposal of a common intermediate (3) for the keten acetal and orthoester reactions was substantiated by the observation that with an optically active keten acetal or



(4)

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† The aprotic media would certainly not encourage dissociation of ion-pairs to separate, solvated ions.

[1] Part 2, R. L. Dyer, P. G. Le Gras, P. J. Clifford, and C. D. Hall, *J.C.S. Perkin II*, 1973, 2064.

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[9] R. L. Dyer and C. D. Hall, *Chem. and Ind.*, 1973, 1109.

orthoester the reactions with diethyl phosphate proceeded with the same degree of inversion (88%) in each case.[1]

Hence the rate-determining step of the reaction is nucleophilic attack of the phosphorus acid anion on an intermediate carbonium ion, probably within an ion-pair. The differential rate equation for the reaction with keten acetals is given by equation (1).

$$-\mathrm{d}[(1)]/\mathrm{d}t = K_1k_2[(1)][\mathrm{R^4R^3P(X)YH}]/1 + K_1[\mathrm{R^4R^3P(X)YH}] \qquad (1)$$

Assuming K_1[acid] $\ll 1$, this simplifies to equation (2) which requires that the reaction should be first order in both acid and keten acetal.

$$-\mathrm{d}[(1)]/\mathrm{d}t = K_1k_2[(1)][\mathrm{R^4R^3P(X)YH}] \qquad (2)$$

A kinetic study was undertaken to confirm this rate law and to establish the relative importance of the equilibrium step (governed by K_1) and the dealkylation step (governed by k_2) on the overall rate of reaction for a variety of keten acetals and phosphorus acids.

RESULTS

The two keten acetals used (1a and b; $\mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}$) were chosen because they both possessed long wavelength chromophores, $\lambda_{\mathrm{max.}}$ ($\mathrm{Bu^n{}_2O}$) 364 nm (ε 18 100) for (1a; $\mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}$) and 374 nm (ε 17 400) for (1b; $\mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}$), which were quite distinct from the electronic spectra of the product esters (6), (7), and (9). Hence the reactions were easily followed by monitoring the disappearance of the absorption at λ 364 or 374 nm for (1a and b; $\mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}$) respectively. The aprotic solvent chosen for the kinetic studies was di-n-butyl ether because it could be rigorously dried and because it offered reasonable reaction rates (half-lives of the order of 0.5—5 min). With benzene, carbon tetrachloride, or acetonitrile, the half lives were too short (<5 s) to permit the acquisition of precise kinetic data without the use of fast reaction techniques. Presumably, hydrogen bonding of the phosphorus acids with di-n-butyl ether decreases the reactivity of the acids towards the keten acetals. The phosphorodithioate (5) and phosphonodithioate (8) were used because it was possible to demonstrate by g.l.c. that at kinetic concentrations (*ca.* 10^{-4}M) of (1a and b; $\mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}$), quantitative yields of *S*-alkyl *OO*-diethyl phosphorodithioate (6) or *S*-alkyl *O*-ethyl methylphosphonodithioate (9) were obtained.

$$\underset{(5)}{(\mathrm{EtO})_2\mathrm{P(S)SH}} + (1;\ \mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}) \longrightarrow \underset{(6)}{(\mathrm{EtO})_2\mathrm{P(S)SR^2}} + \underset{(7)}{p\text{-}\mathrm{NO_2C_6H_4CH_2CO_2R^2}}$$

$$\underset{(8)}{(\mathrm{EtO})\mathrm{MeP(S)SH}} + (1;\ \mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}) \longrightarrow \underset{(9)}{(\mathrm{EtO})\mathrm{MeP(S)SR^2}} + (7)$$

When phosphoromonothioate or phosphonomonothioate was used a substantial (>80%)proportion of the reaction under kinetic conditions was, in fact, hydrolysis of the keten acetal. With phosphoric or phosphonic acid, even with the most scrupulously dried solvents, only hydrolysis was observed and no phosphate or phosphonate esters were produced. The hydrolyses were ascribed to adventitious water competing successfully with the phosphorus anions as a nucleophile towards the intermediate dialkoxycarbonium ion.

The kinetic experiments were carried out using 1×10^{-4}M solutions of the acetals in $\mathrm{Bu^n{}_2O}$ with an excess (>10 mol) of the organophosphorus acid (5) or (8) so that in every case, disappearance of the absorbance due to the acetals followed a pseudo-first-order rate law. In each case, plots of $\ln(A_t - A_\infty)$ *versus* time (A_t = absorbance at time t) gave straight lines and the pseudo-first-order rate constants (k_{obs}) were calculated from the slopes of these lines.

Values of k_{obs} for the reactions of the acetals with various concentrations of acids (5) and (8) and their deuterio-analogues (5_{D}) and (8_{D}) are shown in Tables 1—3.

TABLE 1

Values of k_{obs} for the reactions of (1a; $\mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}$) with (5) and ($5_{\mathrm{D}}$) in $\mathrm{Bu^n{}_2O}$ solvent at 27.5 °C

$10^3[(\mathrm{EtO})_2\mathrm{PSSH}]$/ M	10^3k_{obs}/ $\mathrm{s^{-1}}$	$10^3[(\mathrm{EtO})_2\mathrm{PSSD}]$ *,†/ M	10^3k_{obs}/ $\mathrm{s^{-1}}$
5.21	81.7	4.41	42.9
4.13	63.0	3.28	33.1
3.27	51.3	2.15	20.8
2.40	39.1	1.02	9.6
1.43	21.4		

* Concentrations corrected for an impurity (probably an olefin) in $\mathrm{Bu^n{}_2O}$ solvent which reacts rapidly with the phosphorus acids. † 94 ± 1.5% deuteriation, by n.m.r.

TABLE 2

Values of k_{obs} for the reactions of (1a; $\mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}$) with (8) and ($8_{\mathrm{D}}$) in $\mathrm{Bu^n{}_2O}$ solvent at 27.5 °C

$10^3[(\mathrm{EtO})\mathrm{MePSSH}]$ */ M	10^3k_{obs}/ $\mathrm{s^{-1}}$	$10^3[\mathrm{EtOMePSSD}]$ *,†/ M	10^3k_{obs}/ $\mathrm{s^{-1}}$
6.26	17.0	5.9	14.0
4.73	13.4	4.35	10.2
3.20	9.4	2.80	6.9
1.67	4.3	1.26	2.6
0.91	2.5		

* Concentrations corrected for an impurity (probably an olefin) in $\mathrm{Bu^n{}_2O}$ solvent which reacts rapidly with the phosphorus acids. † 92 ± 1.5% deuteriation, by n.m.r.

TABLE 3

Values of k_{obs} for the reactions of (1b; $\mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}$) and (5) or (8) in $\mathrm{Bu^n{}_2O}$ solvent at 27.5 °C

$10^3[(\mathrm{EtO})_2\mathrm{PSSH}]$ */ M	10^3k_{obs}/ $\mathrm{s^{-1}}$	$10^3[(\mathrm{EtO})\mathrm{MePSSH}]$/ M	10^3k_{obs}/ $\mathrm{s^{-1}}$
4.64	60.8	6.26	31.5
3.50	38.0	4.70	23.3
2.37	30.4	3.13	15.6
1.23	18.8	1.57	8.1
0.66	7.9	0.79	3.9

* Concentrations corrected for an impurity (probably an olefin) in $\mathrm{Bu^n{}_2O}$ solvent which reacts rapidly with the phosphorus acids.

Plots of k_{obs} *versus* acid concentrations also gave straight lines which passed through the origin and from the slopes of these lines values of k_2' (= k_{obs}/[acid]) were calculated. These are shown in Table 4 together with the deuterium isotope effects for the reactions of (1a; $\mathrm{R^1} = p\text{-}\mathrm{NO_2C_6H_4}$) with (5) and (8).

DISCUSSION

The results recorded in Tables 1—4 show that each reaction is first-order in keten acetal and phosphorus acid. Furthermore, the deuterium isotope effects of

TABLE 4

Values of k_2' (= k_{obs}/[acid]) for the reactions of (5), (5_D), (8), and (8_D) with (1; $R^1 = p\text{-}NO_2C_6H_4$) in Bu^n_2O at 27.5 °C

Keten acetal	Acid	k_2'/ l mol^{-1} s^{-1} *	$k_2'^D$ (corr) †/l mol^{-1} s^{-1}	$k_2'^H/k_2'^D$
$p\text{-}NO_2C_6H_4CH{=}C(OMe)_2$	$(EtO)_2PSSH$	15.6 ± 0.5		1.65 ± 0.1
$p\text{-}NO_2C_6H_4CH{=}C(OMe)_2$	$(EtO)_2PSSD$	9.8 ± 0.2	9.5 ± 0.2	
$p\text{-}NO_2C_6H_4CH{=}C(OMe)_2$	(EtO)MePSSH	2.8 ± 0.1		1.2 ± 0.1
$p\text{-}NO_2C_6H_4CH{=}C(OMe)_2$	(EtO)MePSSD	2.4 ± 0.1	2.3 ± 0.1	
$p\text{-}NO_2C_6H_4CH{=}C(OEt)_2$	$(EtO)_2PSSH$	12.2 ± 1.3		
$p\text{-}NO_2C_6H_4CH{=}C(OEt)_2$	(EtO)MePSSH	5.0 ± 0.1		

* Obtained by linear regression analysis on the data from Tables 1—3; errors are from standard deviation of slopes. † The corrected values of $k_2'^D$ were calculated from the equation $k_2'^D$ (corr) $= 100[k_2'^D(obs) - (100 - X)k_2'^H/100]/X$ where X = % deuterioacid in the sample used.

Table 4 [1.65 for (5) and 1.2 for (8)] confirm that proton transfer is not involved in the rate-determining step. By contrast, the carboxylic acid catalysed *hydrolysis* of cyanoketen dimethyl acetal shows a primary deuterium isotope effect of 5.3.[4] The deuterium exchange studies establish that $k_{-1} \gg k_2$ and since the intermediate ion pair (3) or the equivalent covalent addition intermediate (4) is never detected one may assume $k_{-1} > k_1$, *i.e.* $K_1 < 1$. This assumption is justified further by the fact that the absorbance *versus* time curves for the disappearance of the acetals are not S shaped, *i.e.* show no evidence for the build-up of an intermediate.[10] Hence the kinetic results substantiate the proposed mechanism of a pre-equilibrium to (3) or a kinetically equivalent addition species, followed by nucleophilic attack of the phosphorus anion on the dialkoxycarbonium ion of (3).

The experimentally derived second-order rate constants, k'_2 (= k_{obs}/[HA]) are however, a combination of an equilibrium constant, K_1, and a second-order rate constant, k_2 [equation (3)] and both these factors must influence the overall rate of each reaction.

$$k_2' = K_1k_2 \qquad (3)$$

Comparisons of the rate of reaction of the acetals with (5) and (8) are shown in Table 5. Since a combination of K_1 and k_2 governs the overall rate, the relative rates with different substrates and acids may be understood in terms of a balance between these two constants. However, changes in K_1 and k_2 from one system to another tend to cancel each other and hence the combined effect on rate is small. For example, in the reaction with (1a; $R^1 = p\text{-}NO_2C_6H_4$), changing from (5) to (8) causes an almost six-fold decrease in the rate although the anion of the phosphonodithioate acid is more nucleophilic than the phosphorodithioate anion. This behaviour must be due to the higher acidity of (5) exerting a larger influence on K_1 than does the greater nucleophilicity of the phosphonodithioate anion on k_2. A similar explanation applies to the reactions of (1b; $R^1 = p\text{-}NO_2C_6H_4$) where a change from (5) to (8) caused a decrease in the rate of reaction of *ca.* 2.5.

TABLE 5

Comparative rates between (1; $R^1 = p\text{-}NO_2C_6H_4$) and phosphorus acids (5) and (8)

Keten acetal	k_2' [for (5)]/ k'_2 [for (8)]	Phosphorus acid	k_2' [for (1a)]/ k_2' [for (1b)]
$p\text{-}NO_2C_6H_4CH{=}C(OMe)_2$	5.6 ± 0.4	$(EtO)_2PSSH$	1.3 ± 0.2
$p\text{-}NO_2C_6H_5CH{=}C(OEt)_2$	2.4 ± 0.3	(EtO)MePSSH	0.55 ± 0.03

These results are not surprising since in a reaction such as that described by Scheme 2, the effect of substituents R^3 and R^4 on the stability of $R^3R^4PS_2^-$ governs changes in K_1 and this effect would be expected to be greater than the effect of R^3 and R^4 on k_2, a step in which the charge on S is reduced.

In the reactions of phosphorodithioate (5) with the acetals, the keten dimethyl acetal reacted faster than the diethyl acetal whereas with the phosphonodithioate (8) the reverse was true. Therefore, in the reaction involving *OO*-diethyl *S*-hydrogen phosphorodithioate, the nucleophilicity of the anion towards methyl as opposed to ethyl groups (*i.e.* a factor which influences k_2) appears to be the major influence on the rate but with the phosphonodithioate (8) the relative basicity of the keten acetals (a factor which influences K_1) seems to be the dominant feature.

These results are also reasonable since the stronger phosphorodithioate would give a weaker, but more selective nucleophile whereas the weaker phosphonodithioate would give rise to a more selective protonation but a more powerful, less discriminating nucleophile.

The idea that the nucleophilicity of the acid anion may have a significant influence on the rate of these reactions is borne out by relative rate studies at preparative concentrations in benzene or di-n-butyl ether. Equimolar mixtures of two phosphorus acids were allowed to compete for one mole of methylketen diethyl acetal and the relative amounts of phosphorus ester formed were estimated by g.l.c. Hence relative rates were established in benzene (Table 6) and di-n-butyl

TABLE 6

Relative rates for the reactions of $CH_3CH{=}C(OEt)_2$ with a variety of phosphorus acids in benzene at 25 °C

Acid	pK_a *	k_{rel}
$(EtO)_2PSSH$	2.56	100
$(MeO)_2PSSH$	2.64	86.6
$(EtO)_2P(S)OH$	2.84	49.0
$(Pr^nO)_2P(S)OH$	2.93	31.6
$(EtO)_2POOH$	3.15	21.5
(EtO)MePSSH	2.60	170
(EtO)MeP(S)OH	3.51	32.0
(EtO)EtP(S)OH	3.72	37.7
$(EtO)Pr^nP(S)OH$	3.81	43.7

* In 80% ethanol–20% water.[11]

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[10] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1961, 2nd edn., p. 166.

ether (Table 7) with *OO*-diethyl *S*-hydrogen phosphorodithioate (5) being assigned an arbitrary value of $k_{rel} = 100$.

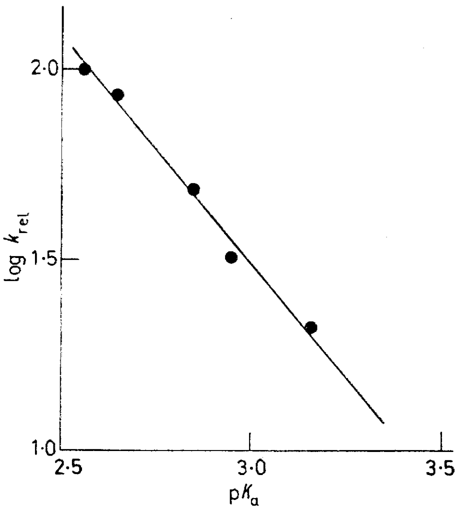
Three significant points emerge from these results. In the first place, in both solvents, a plot of log k_{rel} *versus* pK_a for the *phosphoro*-acids gives a straight line (Figure, for benzene only) showing that the reaction rate increases linearly with acidity in this series. This also indicates that any thiolo–thiono-tautomerism in the monothioic acids has no major influence on the rates since such an effect should be felt most keenly in the phosphoro-series where the tautomeric equilibrium constants may be close to unity, even in benzene as solvent.[11] Secondly, however, the rates for the *phosphono*-acids are all significantly higher than predicted by their pK_a values when compared to the phosphoro-series. This suggests that the enhanced nucleophilicity of phosphonate over phosphate anions influences the rate. Finally for a series of phosphonomonothioic acids, (EtO)RP(S)OH, in benzene, the rates increase in the order, R = Me < Et < Pr. Since the pK_a values *increase* in the same order and all three acids would be almost exclusively in the thiono-form, the results suggest, yet again, that the nucleophilicity of the anion can dominate the rate of each reaction.

TABLE 7

Relative rates for the reactions of $CH_3CH=C(OEt)_2$ with a variety of phosphorus acids in $Bu^n{}_2O$ at 25 °C

Acid	pK_a *	k_{rel}
$(EtO)_2PSSH$	2.56	100
$(EtO)_2P(S)OH$	2.84	21.0
$(Pr^nO)_2P(S)OH$	2.93	20.9
$(EtO)_2POOH$	3.15	1.7
(EtO)MeP(S)OH	3.51	11.7

* In 80% ethanol–20% water.[11]



Plot of log k_{rel} *versus* pK_a for reactions of $CH_2CH=C(OEt)_2$ with phosphoro-acids in benzene

The system provides another illustration of the dangers inherent in assuming that a mechanism established in protic medium may be extrapolated to similar reactions in aprotic media. In this, as in many other systems,[12-14] a change in solvent serves to bring about a dramatic change in the mechanistic picture.

EXPERIMENTAL

Methylketen diethyl acetal and the *p*-nitrophenylketen dialkyl acetals (1) were prepared as described previously;[1,2] the dimethyl acetal had m.p. 76—77°, $\delta(CCl_4)$ 3.77 and 3.82 (each 3 H, 2 × s, OCH_3), 4.55 (1 H, s, $-CH=$), and 7.66 (4 H, m, C_6H_4) (Found: C, 57.2; H, 5.35; N, 6.85. Calc. for $C_{10}H_{11}NO_4$: C, 57.4; H, 5.5; N, 6.7%).

The phosphorus acids were also prepared by established literature procedures.[15-17] *OO'*-Diethyl *S*-[^{2}H]hydrogen phosphorodithioate (5_D) was prepared from phosphorus pentasulphide and ethan[^{2}H]ol using the method described by Norman *et al.* for the protic acid[18] and *O*-ethyl *S*-[^{2}H]hydrogen methylphosphonodithioate was prepared from the protio-acid by repeated (× 3) exchange with D_2O. After evaporation of water, traces of D_2O remaining in the acid were removed as follows. The deuterio-acid was dissolved in carbon tetrachloride which had previously been washed with D_2O to exchange any water present in the solvent and the solution was then dried over anhydrous calcium sulphate which had previously been baked for three days at 400 °C and 0.01 mmHg. The solution was then filtered in a dry box and the solvent was evaporated off to leave the acid as an oil of >95% isotopic purity in deuterium.

For the kinetic experiments and relative rate studies di-n-butyl ether was dried and purified by heating under reflux with sodium for several hours, distilling through a 40 cm Vigreux column, repeating the process twice more, and finally storing the solvent over molecular sieves (type 4A). Benzene was dried over sodium and distilled.

Analyses of reaction mixtures by g.l.c. were carried out as described previously[1] except that a phosphorus–halogen detector was added to the F11 analytical g.l.c. system to facilitate the detection and quantitative estimation of the phosphorus ester products. A typical procedure for the relative rate studies (Tables 6 and 7) was as follows.

A mixture of (5) (0.45 g, 2.4×10^{-3} mol) and diethyl phosphate (0.37 g, 2.4×10^{-3} mol) in benzene (2.0 g) was added over 30 s to a solution of methylketen diethyl acetal (0.29 g, 2.24×10^{-3} mol) in benzene (5.0 g) maintained at 25 °C in a thermostatted bath. On completion of the reaction (usually overnight) the mixtures were analysed using a Perkin-Elmer F11 analytical g.l.c. fitted with a 2 m QF 1 column maintained between 100 and 130 °C.

Kinetic data were obtained at 27.5 ± 0.1 °C using a Pye–Unicam SP 800 u.v. spectrophotometer fitted with an SP 825 series 2 programme controller, a Smiths Servoscribe

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[11] M. I. Kabachnik, T. A. Mastryakova, A. E. Shipov, and T. A. Melent'eva, *Tetrahedron*, 1960, **9**, 10.

[12] M. R. J. Dack, *Chem. in Britain*, 1970, **6**, 347.

[13] J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1956.

[14] For a recent example of the influence of solvent on mechanism see S. Schnell and J. C. Tebby, *J.C.S. Chem. Comm.*, 1975, 134.

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external chart recorder and a Digico analogue–digital (A–D) converter. The paper tape outputs from the A–D converter were fed to a Digiac computer programmed to carry out a least-mean-squares analysis of the data and hence to give the rate constants (k_{obs}) of the pseudo-first-order reactions.

A typical kinetic procedure was as follows. A solution (3 ml) of the appropriate phosphorus acid of known concentration in dry di-n-butyl ether was pipetted into a spectrophotometer cell (10 mm path length), the cell stoppered, and the solution allowed to attain thermal equilibrium in the thermostatted cell holder of the u.v. instrument. A concentrated solution of the keten acetal in dry di-n-butyl ether (*ca.* 3 µl of a 0.1M solution) was then injected into the solution of the acid using a Hamilton syringe so that the initial concentration of the keten acetal was *ca.* 1×10^{-4}M. The cell was stoppered, shaken vigorously for a few seconds, replaced in the spectrophotometer and the absorbance followed as a function of time using the external recorder and the A–D converter. Four kinetic runs were carried out at each acid concentration and the data of Tables 1—3 represents an average value of k_{obs} in each case.

All pipettes, cells, and volumetric flasks were washed several times with distilled water, dried in an oven at 150 °C, and stored in a desiccator over silica gel.

[5/1949 *Received, 6th October,* 1975]